
International Conference on Materials for Advanced Technologies 2009

AND

International Union of Materials Research Societies-International Conference in Asia 2009

28 June - 3 July 2009, Singapore
Suntec Singapore International Convention & Exhibition Centre

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Institute of Materials Research and Engineering

Nanyang Technological University
Symposium F


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Scope of Symposium

This symposium will provide an excellent opportunity to bring together experts in the area of energy conversion and storage. Nanomaterials have shown unusual and exciting performances in the area of electrochemical energy systems due to enhanced surface to volume ratio and reduced transport length for the charge carriers, ions and electrons. Number of novel mechanisms has been introduced recently for the energy conversion and storage due to nanocrystallinity. Members belonging to materials community will be highly benefited as this symposium is expected to provide an excellent exposure for them to exploit the usage of nanostructured materials in various electrochemical systems such as fuel cells, lithium batteries and supercapacitors.

Symposium Topics

• Fundamentals, theory and modeling of energy conversion and storage
• Lithium batteries: cathode materials - insertion reaction
• Lithium batteries: Anode Materials - insertion, alloy and conversion reactions
• Fuel cells: low temperature fuel cells
• Fuel cells: high temperature fuel cells
• Supercapacitors
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A-Reum HAN; Seok KIM; Soo-Jin PARK

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A02542-04431 Effect of Processing Parameters on Pore Structure And Thickness ofAnodic Alumina Membranes
MohammadAHMADI DARIKAFKARI; Mohsen SEIFI; Hadi TABAIAN; Hossein KAZEMI

A02553-04366 New Materials for PEM Fuel Cells
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A02574-04397 The Catalytic Performance of Ni-based on Al2O3 Support for Steam Reforming of Biogas
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Chung-Kiaik POH; Zaiping GUO; Xuebin YU; Zhenguo HUANG; Hua-Kun LIU

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A02642-04481 kW SOFC System And Related Development At Huazhong University of Science And Technology
Jian LI; Jian PU; Bo CHI; Xi LI

A02651-04545 Novel Composite Membrane Based on Pore-Filling Electrolyte for Direct Methanol Fuel Cells
Tien Hoa NGUYEN; Xin WANG

A02725-04549 Doped Cobaltite Nanofibres for Energy Conversion Applications
Adrian LOWE; Khairunnadim Ahmad SEKAK; Tai Hou (Lennie) TENG; Jose RAJAN

A02725-04691 Electrical Characterization of Zirconia Based sol Gel Electrospun Fibres
Adrian LOWE; Yan FENG; Li LU

A02766-04731 Structural And Electrochemical Properties of Nanocrystalline LiCoPO$_4$ having Olivine Structure
Namrata SHUKLA; Awalendra K. THAKUR

A02767-04911 Power Generating Property of Direct CH$_4$ Fueled SOFC using LaGaO$_3$ Electrolyte
Sakai TAKAAKI; Hao ZHONG; Hiroshige MATSUMOTO; Tatsumi ISHIHARA

A02779-04749 Reality Check on Using NaAlH$_4$ As A Hydrogen Storage Material
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Gayathri VENKATACHARI; Devi NEELAMEGAM RAJAN

A02868-04906 Comparative Study of Lithium Transport Kinetics in Olivine Cathodes for Li-Ion Batteries
Nonglak MEETHONG; Yu-Hua KAO; Yet-Ming CHIANG

A02876-04918 Phase Stability of Nanostructured Storage Materials during Electrochemical Cycling
Yet-Ming CHIANG; Ming TANG; Nonglak MEETHONG; Yu-Hua KAO

A02954-05060 To Study the Effect of Dopant AgI in Transport of Silver Ions in the Superionic Glass System
x AgI – (55-x) [2Ag$_2$O – B$_2$O$_3$] – 5TeO$_2$ where x = 40, 45, …65
D. K. KANCHAN; Dharmesh H. KOTHARI

A02955-05059 Development of Nanoporous Pt supported Electrocatalysts As Anode Component for DirectAlcohol Fuel Cell
Sujoy DAS; J. DATTA; N. R. BANDYOPADHYAY

A02956-05061 Nonaqueous Electrolyte Containing Boron Based Anion Receptors (BBAR)
L. F. LI; B. XIE; G. X. FENG; H. S. LEE; X. Q. YANG; H. LI; L. Q. CHEN; X. J. HUANG

A02957-05062 Nanometal Oxides for Electrochemical Li-Ion Capacitors And Batteries: Effects of Porosity And Particle Size
S. R. S. PRABAHARAN; B. RAMBABU

A02958-05063 Neutron Scattering Study of Diffusion And Disorder in Cu-Se Superionic Conductor
S.A. DANILEKIN; C. LING; R. MACQUART; M. RUSSINA; Z. IZAOLA; T. SAKUMA

A02959-05064 A Group of New Polyonion Materials Li$_x$M$_y$(MoO$_4$)$_z$ [0 ≤ x<3] [M=Co, Ni] for Lithium Batteries: Findings And Issues
K. M. BEGAM; M. S. MICHAEL; S. R. S. PRABAHARAN

A03019-05157 CuO-Polyacrylic Acid Hybrid Films for Supercapacitor Application
J. S. SHAIKH; R. C. PAWAR; S. S. PISAL; C. E. PATIL; P. S. PATIL

A03027-05158 Li Intercalation/Deintercalation in V2O5 Nanowires Supported by Ni MicrotubesArrays
MansourAL HOSHAN; William H. SMYRL
Advanced Si-Based Electrolyte for Lithium Ion Battery
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Polysiloxanes, due to their highly flexible skeleton, good thermal stability and largely amorphous compositions, are promising candidates for polymer-based electrolytes. Our recent research showed that conductivity gradually increases with decreasing Si-O repeating unit of the polysiloxane backbone. The story originated from the evaluation of a polymeric siloxane material. It was found that conductivity gradually increases with decreasing Si-O repeat unit of the polysiloxane backbone, which leads us to a new class of electrolytes based on tetra-, tri-, and disiloxanes and monomeric silanes containing oligo(ethylene glycol) substituents, as shown in Scheme 1. Synthesis, conductivity and electrochemical cell performance of Si-based electrolyte are presented in this talk. Their viscosity, cyclic voltammetry and thermal properties are also described. These properties and the results of electrochemical testing in lithium ion battery indicate that these oligomeric siloxane electrolytes are ideal alternatives to conventional organic carbonate-based electrolytes.

To fully evaluate the feasibility of Si-based electrolyte in Li-ion chemistry, extensive characterizations have recently been conducted, in the aspects concerning its fundamental ionics as non-aqueous solutions, stability on anode and cathode surfaces, safety concern, as well as its cycle life performance. This presentation will summarize our recent work on this new electrolyte by using both electrochemical and spectroscopic analyses.

Soft Matter as a Versatile Source for Generation of Novel Lithium Battery Electrolytes
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Soft matter ion conductors comprise a distinct class of electrolytes under the field of solid state ionics. Superior ambient temperature ionic conductivity, mechanical and electrochemical properties make them potential candidates over liquid and solid crystalline electrolytes for application in electrochemical devices such as lithium battery. These electrolytes become an ideal choice in the context of worldwide efforts to develop all solid state electrochemical devices using nanostructured electrodes. Soft matter exhibit several complex as well as unique intrinsic physicochemical features (e.g. solvent dynamics, ion solvation) which have been observed to heavily influence electrolyte macroscopic properties. Insight into ion conduction mechanism and material property optimizations must necessarily account the system specific complexities. This presentation will focus on soft matter solid composite electrolytes which were obtained from liquid or semi-liquid electrolytes as starting materials. This concept of solid electrolyte synthesis from liquid is significantly different from the prevalent approaches. We discuss the correlation of structure with ion transport and application of the soft matter electrolytes with nanostructured materials in rechargeable lithium batteries.

Electrodics of Methanol Oxidation on Platinum doped Multiwalled Carbon Nanotubes (MWCNTs)
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The metal composites of carbon nanotubes (CNTs) are of immense interest currently owing to potential application in the field of catalysis, sensors, and fuel cells. In the present work we report the electrodics of methanol oxidation on the composite of Pt with -COOH functionalized multiwalled carbon nanotubes (f-MWCNTs). f-MWCNTs were subjected to γ-radiolysis in presence of K₂PtCl₆ and 2- propanol. Based on Raman, XRD, EDAX and SEM analyses of the product, f-MWCNTs loaded with 5.4 at.wt.% Pt is inferred. Cyclic voltammograms (CVs) recorded on Pt-f-MWCNTs/indium tin oxide (ITO) in
methanol and H₂SO₄ gave two characteristic anodic peaks, which were shifted to more positive potential by ca. 0.2 V than one observed on polycrystalline Pt. This is attributed to the shift in the Pt work function towards more positive potential due to the MWCNT contact. An increase in the anodic current with repetition of cycles was observed, from which the facile oxidation of CO, assisted by the oxy groups on MWCNTs is inferred. Electrodes of the reaction at various temperatures was studied with the help of linear sweep voltammetry (LSV) on Pt-f-MWCNTs modified rotating disc gold electrode. From the Koutecky-Levich plots, the standard rate constant (k0) was found to be of the order of 10⁶ cm²s⁻¹, which is about 10 times higher than the one recorded on polycrystalline Pt under the identical conditions. Using Arrhenius plot, the activation energy was determined to be ca. 27 kJ mol⁻¹, which is almost half the value reported for Pt/carbon system.

**Synthesis and characterization of carbon coated LiNi₁/₃Co₁/₃Mn₂/₃O₂ cathode material for Li-ion batteries**

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Intensive investigations are underway to improve the electrochemical characteristics of Li-ion battery materials. Among various cathode materials studied for positive electrodes in rechargeable Li-ion batteries, the mixed transition metal oxide, namely LiNi₁/₃Co₁/₃Mn₂/₃O₂, is consider one of the most important compounds because of its high discharge capacity, and safety. However, its rate capability is rather poor for its application in high power Li-ion batteries. Generally, coating of particles with conductive carbon layers is known to improve the electrochemical properties of semiconducting oxides such as LiNi₁/₃Co₁/₃Mn₂/₃O₂. In the present research, synthesis of LiNi₁/₃Co₁/₃Mn₂/₃O₂ as well as coating of carbon layers on sub-micron size particles are achieved in one-pot novel procedure, namely, inverse microemulsion route. The synthesized products are subjected to physiochemical and electrochemical studies. The carbon coated mixed transition metal oxides are found to provide higher specific capacity with greater satiability on repeated charge-discharge cycling than the uncoated samples. The electrodes were also subjected to charge-discharge cycling at several rates between C/7 and C/0.8 rates. The carbon coated samples are found to provide discharge capacities with a marginal decrease on increasing the cycling rate. However, there is a substantial decrease in capacity of uncoated samples on increasing charge-discharge rate. The electrochemical impedance studies support that samples are superior to uncoated samples with respect to charge-transfer resistance. Results of these studies will be presented in the conference.

**Nanostructured Composite Anode Materials for Lithium-Ion Batteries**

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Lithium-ion batteries are the most promising devices for electrochemical energy storage due to their high energy density and cycle life. The more popular active material for negative electrode is usually flake graphite due to its excellent cycle life (up to 1000 cycles). The main disadvantage of graphite is a relatively low specific capacity, because even the theoretical value of capacity is $Q_{\text{C}} = 372 \text{ mAh/g}$.

Si, Sn, Al, hard carbons and some other materials are actively investigated as an alternate to graphite materials for lithium-ion batteries. However, they have not received a practical application, since a huge theoretical capacity (for example $Q_{\text{Si}} = 4,200 \text{ mAh/g}$ for Si, $Q_{\text{Sn}} = 994 \text{ mAh/g}$ for Sn) is accompanied by sharp drop of capacity (during the few cycles), high irreversible capacity (up to 50% and more), non-horizontal shape of charge–discharge curves. The main reason of sharp capacity degradation is considerable (in 2-4 times) volume changes of these materials during intercalation-deintercalation of lithium ions in the structure of above mentioned active materials (AMs).

We have formulated the following principles of practical usage of above-mentioned materials for development of advanced composite anode materials for lithium-ion batteries:

1) Anodes has to contain a composite of graphite with high-dispersed (as ideal – nano-dispersed) particles of AMs (like Si, Sn) as active additives;

2) Particles of AMs have to be surrounded by a quite elastic porous electro-conductive matrix (ECM), like amorphous carbon, Al, etc. This ECM has to compensate the considerable volumetric changes of AMs particles during the cycling. It creates the possibilities to prevent a destruction of AM particles and to reach relatively stable cyclization of electrodes.

3) A concentration of AMs particles has to not be very high (not more than 10%).

We made some experimental investigations in our laboratory, as well as in collaboration with Superior Graphite Co. (USA) and have developed SiC/graphite based composite nanostructured anode materials for lithium-ion batteries with high level of specific capacity (up to 550-600 mA-h/g), quite stable cyclization (during
the hundred cycles), minimal irreversible capacity (ca 8%), horizontal shape of charge–discharge curves.

The similar results we have achieved also with Sn C/ graphite based composite nanostructured anodes (up to 400 mA·h/g).

Both these nanostructured composites give possibility to exceed noticeably the maximal achieved capacity of graphite anodes (ca 350-370 mA·h/g).

**Acknowledgments:**
Authors would like to acknowledge Superior Graphite Co., Chicago, IL, USA for submission of advanced graphite samples for this investigation, IPP Program and Science and Technology Center in Ukraine (project P-154) for financial support.

**Nanostructured Non-noble Catalysts for Oxygen Electrodes**

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Oxygen (air) electrodes with non-noble catalysts are critical for development of fuel cells and air-metal batteries for a wide practical application. It is well known, that usually such noble metals like platinum and silver play a dominating role as effective electrocatalysts for the oxygen reduction. However, a high cost of such metals and their high sensitivity toward different admixtures (even toward nitrogen content in an air) are very serious limitations for their commercial application.

Our team was among the first who has founded the effect of catalytic activity of some film of conducting polymers /polyaniline (PANI) polypyrrole (PPy), polypthiophen (PTh), poly(3-methyl)thiophen (PMeT), etc. / formed at such carbon supports like thermally-exfoliated graphite, graphitized carbon black (so called Pureblack) and other nanostructured materials.

Our electron-optical investigations show that combination of two quite different types of nanostructures during the chemical precipitation of composite catalysts (fibril or globular films of conducting polymers with large-scale porous structure of carbon supports) creates an excellent bi-porous structure of gas-diffusion electrode, which are necessary for the effective reduction of oxygen.

Recently quite good results were achieved by using above-mentioned nanostructured carbon supports in combination with conducting polymers and some compounds of transition metals (like Co, Mn and Ni). Some components of such nanostructured composites demonstrate a synergetic effect toward the oxygen reduction and give possibility to ensure a 4-electron reduction of oxygen to H$_2$O.

The important peculiarity of such nanostructured composites is their capability for reduction of oxygen directly from an air due to the good stability for the inert admixtures.

We have created the porous gas-diffusion electrodes with above-mentioned types of nanostructured catalysts, as well as active models of air-metal batteries (Air-Zn and Air-Mg electrochemical systems) with the specific energy of 140-200 W·h/kg.

We hope that above-mentioned non-noble types of nanostructured composites could find a practical application for development of air-metal batteries and fuel cells.

**Acknowledgments:**
Authors would like to acknowledge Superior Graphite Co., Chicago, IL, USA for submission of advanced graphite samples for this investigation

**Fabrication of 10%Gd doped ceria (GDC)/ NiO-GDC half-cell for low or intermediate temperature solid oxide fuel cells using spray pyrolysis**

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Solid Oxide Fuel Cells (SOFCs) with comparably low operating temperature plays a critical role in its commercialization and reliability by allowing low cost fabrication and a promised longer life. However, intermediate or low temperature (IT or LT) SOFCs require an electrolyte either prepared from alternate material than conventional (i.e. Yttria Stabilized Zirconia, YSZ) with a higher ionic conductivity at lower temperatures or having thickness in the range of 10-20µm. Recently, 10%Gd doped ceria (GDC) has revealed its importance as solid electrolytes for IT-SOFCs. Further literature cleared that if GDC is prepared in thin film form; it shows rather higher ionic conductivity at further lower temperatures and thereby allows its use in LT-SOFCs.

In the present investigation, the preparative parameters of spray pyrolysis technique (SPT) were optimized to deposit dense and adherent films of GDC on ceramic substrate. NiO-GDC was used as ceramic substrate, which also acts as a precursor composite anode for GDC based SOFCs.
NiO-GDC substrates were prepared using conventional ceramic route. Prepared half cells (GDC/NiO-GDC) were characterized using XRD, SEM and electrochemical impedance spectroscopy. The surface and fractal SEM observations of post heat treated (at 1000°C) GDC/NiO-GDC system revealed that GDC films were uniform in thickness and morphology along with improved adherence to substrate. The relative density of post heat treated films was of the order of 96%, which was attributed to presence of nano-granules in the thin films. Maximum thickness of GDC film prepared with optimized preparative parameters (in single run) was of the order of 13μm. Fractal SEM of post heat treated GDC/NiO-GDC system showed homogenous interface, which was further analyzed by electrochemical impedance spectra and found that it does not affect electrical properties of structure significantly. Activation energy of GDC/NiO-GDC system for grain interior conduction (Ea_int) was 1.02 eV while for grain boundary conduction (Ea_gb), it was 0.93 eV. The contradiction in the estimation of activation energies (i.e. Ea_int < Ea_gb) for GDC/ NiO-GDC structure was attributed to the fact that the NiO phase resides along the grain boundaries of substrates and thereby leads easier path for electrical conduction.

A00195-00428

Effect of Ionic Conductivity and Light Intensity on the Performance of a Solid State TiO2 Photoelectrochemical Cell
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A photoelectrochemical cell of ITO/TiO2/PAN-PC-LiClO4/graphite has been fabricated and its performance has been tested in dark and under illumination of 100 mWcm⁻² light. The nanostructured TiO2 film was deposited ontoITO-covered glass substrate by controlled hydrolysis technique. A solid electrolyte of PAN-LiClO4 with propylene carbonate plasticizer (PC) prepared by solution casting technique was used as a redox couple medium. A graphite electrode was prepared onto a glass slide by electron beam evaporation technique. The device shows the rectification property in dark and shows the photovoltaic effect under illumination. The short-circuit current density, Jsc, and open-circuit voltage, Voc, increases with ionic conductivity of the electrolyte and light intensity. The highest Jsc of 2.0 μA/cm² and Voc of 0.64 V were obtained at the intensity of 100 mWcm⁻².

A00206-00477

Nanostructure and Electrochemical Property of Hydrothermally Prepared One-dimensional Manganese Dioxide
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One-dimensional manganese dioxide used in electrochemical capacitor was synthesized via the hydrothermal route. The characterization of X-ray diffraction (XRD), scanning electron microscopy (SEM) and N₂ adsorption (BET) reveal that the nanostructures of the prepared powders varied with the hydrothermal temperature. The synthesized manganese dioxide was coated on titanium foil to analyse the electrochemical properties using cyclic voltammetry (CV). The electrochemical properties of the prepared materials directly depended on the temperature of hydrothermal conditions. The manganese dioxide particles prepared via the hydrothermal route showed high specific capacitance and high electrochemical reversibility. These results indicate that the specific capacitance and the cycleability of manganese dioxide electrodes can be adjusted via the hydrothermal process.

A00209-02367

Isolation of Solid Solution Phases in Size-Controlled LixFePO4 at Room Temperature
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The pervasive trends in research into LixFePO4 basically fall into understanding the mechanism of charge transport and the phase diagram. An incomplete miscibility gap at α < x < 1-β at room temperature has been confirmed by several groups with solid-solution compositional domains at 0 < x < α and 1-β < x < 1. Meethong et al. have recently suggested that the miscibility gap systematically shrinks with decreasing particle size down to ca. 40 nm. However, it should be noted that the surface potion of the particle abruptly increases when the size is smaller than 100 nm. In the nanoscale regime, there is an increasing possibility to observe simultaneous effects both from the bulk crystal and the particle surface, which may lead to some confusion. In addition, the side reaction under ambient exposure is known to be pronounced for smaller particles, which leads to spontaneous lithium extraction and surface oxidation. More importantly, the surface redox potential was calculated to be dependent on the crystallographic
plane and displayed a wide dispersion over the range of 2.95–3.84 V. Both the surface impurities and the redox potential on the specific crystallographic facet plane would be important as perturbations that could cause parasitic capacity below/above the bulk two-phase equilibrium potential in the voltage curve. The capacity outside the two-phase region for LiFePO4 has been used as an indicator of the solubility limit and therefore may require careful reinvestigation. Herein, the important subject that should be addressed is the separation of bulk and surface effects in the nanoscale regime. To this end, highly crystalline pure LiFePO4 powders with various particle sizes (200 nm, 80 nm, and 40 nm) were carefully prepared. The samples were treated in inert atmosphere during all processes of synthesis and characterization. The lithium content was adjusted both chemically and electrochemically, followed by high-resolution synchrotron X-ray diffraction (XRD) analysis to address further evidence in order to facilitate a more comprehensive understanding of the phase transitions of LixFePO4. In this work, we have succeeded in isolating an intermediate solid solution phases close to x = 0 and x = 1 at room temperature using both chemical and electrochemical routes. Size-dependent modification of the phase diagram, as well as systematic variation of lattice parameters inside the solid-solution compositional domain closely related to the electrochemical redox potential, are demonstrated. These experimental results reveal that the bulk miscibility dominates electrochemical behavior of LiFePO4, at least for particle sizes larger than 40 nm, even though the geometric surface portion becomes evident when particles are smaller than 100 nm. The capacity observed below/above the two-phase equilibrium potential in the present study is not caused by impurities or the potential distribution dependence on the equilibrium potential in the voltage curve. The capacity outside the two-phase region for LiFePO4 samples was prepared by sintering at 1073 K and high-resolution synchrotron XRD (HR-XRD) experiments were performed at the High Energy Accelerator Research Institute (KEK) Photon Factory (PF) BL-4B2, Japan7, coupled with selected area electron diffraction experiment. In both experiments, extra reflections are observed in addition to the fundamental reflections assigned to the previous structural model. According to the observed reflections and systematic extinction, 2 types of unit cell configuration and 3 space groups were considered as candidates; primitive monoclinic lattice with P21 or P21/m symmetry (asuper=(−a+b), bsuper=c, csuper=(a+b)), and C-centered orthorhombic lattice with C2221 symmetry (asuper=2a, bsuper=2b, csuper=c). P21 symmetry with a monoclinic supercell a=8.22898(18) Å, b=5.02002(4) Å, c=8.23335(18) Å, β=99.2027(5)°, was adopted as the P21/m symmetry did not allow the construction of a reasonable structural model, and the C2221 based model gave rather large value of the reliability factor of integrated intensities RI (>8%). A Rietveld refinement for HR-XRD data with P21 supercell model gave good reliability with Rwp=9.67%, Rp=9.79%, χ2=0.871, RI=3.14% RF=0.83%. The intensities of the supercell reflection were successfully explained by considering the modified cation arrangement in the new set of monoclinic unit cell. The structural modulation to form the supercell originates from the availability of vacant tetrahedral sites in the pseudo-hexagonal packing of oxygen atoms. This leads to a variation in the orientation of trigonal pyramids, particularly those in the corner shared one-dimensional FeO4–SiO4 chains along the [101]super direction. Overall phase relationship in the Li2MSiO4 system will be given in the poster.
The reverse micelles procedure is a convenient route for the preparation of nanomaterials. Chemical reactions in aqueous media, such as precipitation or reduction, are carried out within a restricted volume, limited by the array of surfactant molecules. The coalescence and aggregation of nanoparticles is avoided by the surfactant hydrophobic chains. In addition, the shape of the resulting nanoparticles can be tailored by selecting a particular surfactant (an cosurfactant) molecules and changing the oil:water:surfactant ratios. Three types of processes can be used to promote the reaction inside the micellar volume: coalescence of micelles having different reagents in the aqueous phase, diffusion of reagents through the oil phase and the micellar walls, or thermal or photochemical promotion of the reaction in previously formed micelles. The versatility of this technique allows its use in the preparation of different electrode materials for lithium-ion batteries. Concerning cathode materials, a suitable technique is the thermal decomposition of the micelles, which can be achieved by putting the emulsion in contact with a hot organic solvent such as kerosene. Thus, it was possible to obtain \( \text{LiCoO}_2 \), using TRITON X-10 surfactant, n-hexanol co-surfactants and cyclohexane as the oil phase, and \( \text{LiMn}_2\text{O}_4 \) and \( \text{LiNi}_0.5\text{Mn}_1.5\text{O}_4 \) using SPAN80 surfactant and kerosene oil. On the other hand, for conversion oxide electrodes, it was possible to prepare \( \text{Co}_x\text{O}_y \) materials with controlled particle size and microstructure, by mixing two emulsions that contained reverse micelles formed in hexane or octadecene oils. The precipitation reaction took place by the coalescence of two different reverse micelles containing 1 M aqueous solutions of NaOH and cobalt chloride, respectively. After sintering, single-phase submicrometric particles that interconnect into larger, spherical aggregates can be obtained with spherical shape and no porosity. The electrochemical response found in lithium cells was excellent after annealing at 600°C, with capacities of up to ca. 800 mAh/g and good capacity retention. Recently, we have studied several examples of oxysalts which partially behave as conversion oxide electrodes. Among them, iron and cobalt anhydrous oxalates in the form of nanoribbons, and submicrometric rhombic particles of manganese carbonate can be prepared by the reverse micelles method, by mixing separate emulsions containing the cation and the anion. The electrochemical reaction with lithium of these new oxysalt materials takes place by a different conversion reaction than the corresponding oxide. Thus XANES data unequivocally showed that cobalt is reduced to the metallic state during cell discharge while it is reoxidized during charge. In contrast, after reduction to Fe metal, iron is converted to an intermediate 0+3 oxidation state.
1H, 7Li and 19F Transverse Nuclear Magnetic Relaxation Studies of the (PEO)9LiCF3SO3-Al2O3 Nanocomposite Polymer Electrolyte

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1H, 7Li and 19F transverse nuclear magnetic relaxation was investigated by recording the Hahn-echo decay in the composite polymer electrolyte (PEO)9LiCF3SO3+Al2O3 incorporating alumina filler grains of two different sizes, 10 µm and 104 µm (pore size 5.8 nm) with different specific surface areas, 0.17 m2/g and 150 m2/g, respectively.

In a previous work (MAKL Dissanayake et al, Journal of Power Sources, 119-121, 2003, 409-414) the same system was characterized by using AC impedance spectroscopy and revealed that 15 wt% Al2O3 content in the case of the grains having the size of pores of 5.8 nm and 10 wt% Al2O3 content in the case of the grains of size 10 µm show maximum conductivities.

In the former system, 1H Hahn-echo decay was the slowest for the 15 wt% Al2O3 containing electrolyte and the Hahn-echo decays of 7Li and 19F showed their slowest for the electrolyte containing 0 wt% Al2O3 and fastest for the 20 wt% Al2O3 containing electrolyte.

In the latter system (i.e. the system containing alumina grain size of 10 µm), all the 1H, 7Li and 19F Hahn-echo decays showed their slowest for the electrolyte containing 10 wt% Al2O3.

By considering the AC impedance data and the NMR Hahn-echo decay results it can be concluded that the dynamics of the host polymer chains assist strongly to the ionic conductivity of this type of solid polymer electrolytes.

We acknowledge PARD Jayathilaka for the sample preparation.

A Solid Polymer Electrolyte Containing Ionic Liquid for Photo-Electro-Chemical Solar Cells

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Polymer electrolytes have many applications, mainly in the fields of energy conversion, for example in photo-electrochemical solar cells. Various iodide ion conducting polymer electrolytes have been studied as candidate materials for fabricating photo-electro chemical solar cells. In the present study we focus on iodide ion conducting polymer electrolytes for solar cell applications using an ionic liquid.

In this study enhanced ionic conductivity values were observed for the ionic liquid tetrahexylammonium iodide containing polyethylene oxide (PEO) based plasticized electrolytes. The analysis of thermal properties revealed the existence of two phases in the electrolyte and the conductivity measurements showed a marked conductivity enhancement during the melting of the plasticizer rich phase of the electrolyte. Annealed electrolyte samples showed higher conductivity than non annealed samples revealing the existence of hysteresis in electrolytes. The optimum conductivity was observed for the electrolytes with PEO : Salt =100 : 15 mass ratio and this sample exhibited the minimum glass transition temperature of 72.2 °C. At optimum PEO : Salt ratio, the conductivity of non-annealed electrolyte was 4.36×10-4 S cm-1 whereas that of annealed sample was 4.55×10-4 S cm-1 at 30° C.

Photo-electrochemical solar cells were fabricated with the configuration FTO/TiO2/Dye/Electrolyte/Pt/FTO using optimum conducting electrolyte. The cells exhibited good stability, although the efficiencies were low compared to gel or liquid electrolytes due to resistive losses.

Research support from IRQUE project Faculty of Applied Sciences, Rajarata University of Sri Lanka and IPPS, VR/SIDA Sweden is gratefully acknowledged.
Enhancement of Electrochemical Properties by Doping of PEG into the MoO₃ Nanobelts for Lithium Battery Application

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MoO₃ have attracted considerable attention due to their typical two dimensional layered structure consisting of double layers of edge-and vertex-sharing MoO₆ octahedral being weakly held together by Vander walls bonds. Theses MoO₃ nanostructures and their polymer composites are current drawn interest for the application of Li batteries, super capacitors and other electrochemical as well as electrochromic display devices. In this paper we report the synthesis of MoO₃ nanobelts and PEG doped such as 0.25, 0.5, 1 mol% nanobelts by using hydrothermal method. Structure and morphology of the samples were investigated by XRD, FTIR SEM and TEM. MoO₃ nanobelt composite shows the initial specific capacity 275 mAh/g, whereas PEG doped MoO₃ shows 307 mAh/g. It was found that PEG doped MoO₃ nonmaterial’s shows not only high initial specific capacity but also showed better cyclic performance compared to the other pure MoO₃ nanobelts. The role of the polymeric component of the composite material seems to be the stabilization and improvement of the capacity due to probable homogeneous distribution of the induced stress during cycling.

Ag/Pt Hexagonal Nanoplates as Electro catalysts for Oxygen Reduction

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Hexagonal Ag/Pt nanoplates were prepared by using a hexagonal Ag nanoplate as the displacement template and by introducing Pt ions. The prepared Ag/Pt nanoplates played the role of an electrocatalyst in an oxygen reduction process. Compared to spherical Pt and Ag/Pt nanoparticles, the hexagonal Ag/Pt nanoplates showed better activity for oxygen electroreduction.

Towards Fuel Cell Commercialization – NRC’s Focused R&D Program

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National Research Council of Canada’s Institute for Fuel Cell Innovation (NRC-IFCI) in Vancouver collaborates closely with world leading Canadian fuel cell companies to help with their commercialization efforts. NRC-IFCI focuses on R&D efforts to significantly reduce cost, improve durability and operational flexibility for Proton Exchange Membrane (PEMFC) and Solid Oxide Fuel Cells(SOFC). The Institute also has research activities in hydrogen generation and storage. NRC-IFCI’s R&D spectrum varies from fundamental long-term research done in collaboration with universities and research institutes in Canada and abroad, to medium term research done as pre-competitive consortium with multiple companies, and, to short term research done in collaboration with individual companies. Two PEMFC based pre-consortiums have been set up - 1) to develop novel high performance low cost durable membrane electrode assembly (MEA), and 2) to study effect of fuel, air and stack component contaminations on performance degradation. In SOFC area, the consortium aims to reduce stack and BOP degradation at high temperatures. Institute runs a number of fuel cell and hydrogen demonstration projects, such as, building integrated SOFC, hydrogen fuelling station, solar hydrogen generation, etc., and is part of the Vancouver Fuel Cell Vehicle Program. This paper will describe the fuel cell and hydrogen R&D&D progress achieved at the Institute.

Impedance Spectroscopy Studies on Plasticized Polymer Electrolyte System [PEO- LiCF₃SO₃–DBP]

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Progress in lithium battery technology may be achieved by passing from a conventional liquid electrolyte structure to a solid-state, polymer configuration. Solid polymer electrolyte was chosen to be studied because it has some advantages such as, it can prevent leakage, easy to handle and fabricated. A polymer electrolyte based on PEO complexed with lithium salt (LiCF₃SO₃) has been prepared by a solution-cast technique. The amounts of LiCF₃SO₃ were varied from 2% to 14% and the conductivity (σ) measurements were carried out using HIOKI 3531 LCR at room and elevated temperature. The highest σ obtained is 9.48x10⁻⁷ Scm⁻¹ for 14% of salt at room temperature.
A plasticizer that is dibutyl phthalate (DBP) was added to the salted polymer electrolyte for the conductivity improvement. The ionic conductivity achieved was $9.4718 \times 10^{-6}$ S cm$^{-1}$. X-Ray Diffraction (XRD) measurement was carried out to investigate the crystalline/amorphous profile of the solid polymer electrolyte. At the highest conductivity, the structure tends to be more amorphous. This is in good agreement with ionic conductivity theory. Differential Scanning Calorimetry (DSC) measurement was also carried out and glass transition temperature was determined.

Very few literature is available with Co-precipitation method and also with wide stiochiometric compound of Cerium Zirconium Oxide. As the Co-precipitation method is cheaper method which yield more uniform particle size distribution, an attempt is made in this work to synthesize nanostructured $\text{Ce}_x \text{Zr}_2 \text{O}_2$ ($x=0.8$ to 0.2). The structural and morphological characterizations are carried out by XRD, SEM and the results are presented here. The nanoparticle size is observed and is in good agreement with the literature. The variation of composition vs particle size ; composition vs size distribution are discussed. Impedance analysis of the $\text{Ce}_x \text{Zr}_2 \text{O}_2$ ($x=0.8$ to 0.2) is also presented here. A comparison between the nanoscaled and microscaled $\text{Ce}_x \text{Zr}_2 \text{O}_2$ ($x=0.8$ to 0.2) is made in the paper.

**Morphological Studies on $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ Solid Solutions**

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The advantages of lowering the operation temperature of SOFCs have attracted great interest worldwide. Reduced operation temperature, however requires increased electrolyte ionic conductivity and enhanced electrode reaction activity.

Enormous amounts of efforts can be found in the literature on improvement of ionic conductivity for the oxide electrolyte materials, including zirconia-based oxides, ceria-based oxides, lanthanum gallate-based oxides and bismuth-based oxides. However, at lower temperatures, the ionic conductivity of Yttria-Stabilised-Zirconia (YSZ) is much lower than that of ceria-based electrolytes. Rare earth oxide doped ceria ($\text{Y}_2\text{O}_3$-$\text{CeO}_2$, $\text{Gd}_2\text{O}_3$-$\text{CeO}_2$, $\text{Sm}_2\text{O}_3$-$\text{CeO}_2$) is considered to be a candidate for electrolyte due to its superior ionic conductivity.

Very few literature is available for $\text{Ce}_x \text{Zr}_2 \text{O}_2$ electrolyte targeting SOFC. Horita et.al., have reported ceria-zirconia-ceria sandwich structured composite film electrolytes to possess high ionic conductivity compared to YSZ and have reported two order of magnitude increase as a thin film from bulk.

On the other hand, the cycling performance of nanosized alloy is expected to improve by forming composite of alloy and carbon, since carbon could act as a barrier to prevent the aggregation between the alloy particles and provides a void space where the alloy particles experience a volume change. Zhong et al. reported that the amorphous carbon coated SnSb electrode has great potential as a material for improving the energy density of lithium battery and it showed excellent initial capacity of 634mAh/g and reversible capacity over 500mAh/g after 20 cycles.

Wide range of studies show that tin based alloys and composites can be considered as an anode in lithium ion battery due to their superior lithium storage capacity of 900mAh/g. Multiphase composite structures and small particle alloy systems are reported to decrease volume change to a greater extent during charge-discharge processes. Fei Wang have synthesized the nanosized SnSb alloy by reductive co-precipitation method which revealed a reversible capacity of 400mAh/g within 20 cycles along with an excellent cycling performance. Sn/SnSb composite electrode material exhibited capacities exceeding 500mAh/g for more than 30 cycles. Zhong et al. reported that SnSb ultra fine particle, size in the range of 100-300nm, exhibited a high reversible lithium-ion storage capacity of 701mAh/g in the initial cycle, which has remained at 81% (i.e., 566mAh/g) of its original capacity after 20 cycles.

At this juncture, nanosized electroceramic particles are expected to improve ionic conductivity to make the system suitable for electrolyte with better thermal matching with the available electrodes. V.Grover et.al., have prepared nanocrystalline ceria-doped-zirconia powder ($\text{Zr}_{0.80}\text{Ce}_{0.20}\text{O}_2$) by combustion technique. A maximum of 18-23µm of agglomeration were patent however 7-10nm of sizing is expected which could not be ensured. H.S.Potdar et.al., have prepared nanosized $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ porous powders via an auto ignition process. The as-prepared powders were nanosized (20-35nm), having a spherical shape.
In this work, the alloy SnSb with the CNT and without CNT are synthesized by two methods of preparation namely rapid mixing and slow titration process. The different concentration of alloy with CNT is studied and the results are presented in this paper. All the samples were prepared in the nanoscale and the morphological studies such as XRD, SEM and TEM have been characterised, particle size of 50nm has been confirmed. Incorporation of CNT is confirmed through UV-Vis-NIR spectrograph. The influence of SnSb alloy on CNT absorption peaks are brought to light through this study. PL Mapping of the SnSb with CNT is made and is also compared. The preparation methodology vs scaling of particle size has been discussed in this. Also size distribution vs preparation methodology is presented here.

**A Deflagration Method to Synthesize LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 Cathode Materials for Li-ion Batteries**

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A deflagration method to synthesize LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 cathode materials from sol-gel precursor was proposed. Phase-pure material was produced when precursors were deflagrated and calcined at 900°C for 8h. This material and its layered structure were confirmed from X-ray diffraction analysis. The particle size distribution was quite uniform from the SEM images, which was about 300-400 nm. The first discharge specific capacity of 170mAh/g was obtained at 0.05C in the potential between 2.8-4.3V at room temperature and the specific capacity of 225mAh/g between 2.8-4.6V.

**Effect of High-energy Ball-milling on Electrical Properties of Li_{1/3}Al_{0.3}Ti_{1.7}(PO_4)_{2.9}(VO_4)_{0.1} Material**

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Lithium ion conducting materials are of growing interest because of their potential application in solid–state batteries. NASICON (Na SuperIonic CONductor) type, A,B,(PO_4)_x, materials have been extensively studied because of their high ionic conductivity at room temperature. In the present study, electrical properties of conventionally prepared microcrystalline Li_{1/3}Al_{0.3}Ti_{1.7}(PO_4)_{2.9}(VO_4)_{0.1} [LATPV] material are compared to that of smaller crystallites of LATPV prepared by ball-milling. Structural studies are carried out exploiting XRD, FTIR and SEM. Impedance, modulus and permittivity representations are used for electrical characterization.

High-energy milling increases lattice parameters and X-ray diffraction pattern gradually broadens out with milling time. The pattern broadening occurs due to simultaneous size and strain effects. High-energy ball milling introduces considerable strain in the compound; hence strain contribution to line broadening is not negligible. One way to separate these two effects has been developed by Williamson and Hall and is known as Williamson-Hall plot. The Williamson-Hall equation is, Bcosθ=Kλ/D+4εsinθ, where, B is full width at half maximum of XRD peaks, K is Scherrer constant, D crystallite size, λ is wavelength of X-ray, ε is lattice strain and θ is Bragg angle. In this method Bcosθ is plotted against 4sinθ. Using a linear extrapolation to this plot, intercept gives particle size D/λ and slope gives micro strain (ε). Si sample is taken as standard reference for strain calculation.

The impedance plots are obvious indication of blocking effect at grain-boundaries and at electrode sample interface. Impedance plot of 55h ball-milled material points out overlapped semicircles and high frequency arc can be attributed to grain-interior contributions. Grain–boundary conductivity of prepared microcrystalline material is lower than the reported value due to poor densification of pellet. The 55h ball-milled material shows around two order of increase in total conductivity (σ_{pl55x}=1.48x10^4Scm⁻¹) in comparison to microcrystalline counterpart. As milling time increases activation energy for dc conduction decreases, shows that grain-boundary introduced by milling is an easier path for conduction. Observed conductivity of 55h ball-milled material is comparable to that of spark plasma sintered material. Hence long hours of ball-milling can be considered as effective method for increasing conductivity like spark plasma sintering.

Permittivity and modulus representation corroborates results of impedance representation. Permittivity loss of 55h ball-milled material shows one order increase compared to microcrystalline counterpart. The augmented permittivity loss may be due to easy diffusion through the grain-boundary; which reflects in total conductivity hike of 55h ball-milled material. Non-Debye behavior of conductivity relaxation reflects in broad maximum of M*(ω) spectroscopic plot. Since grain-interior and grain-boundary capacitive contributions differ only by one order, two modulus maxima are observed in 55h ball-milled material. The modulus and permittivity representation support constriction effect at grain–boundary as shown by impedance representation.

**Symposium F - Nanostructured Materials for Electrochemical Energy Systems:**

Lithium Batteries, Supercapacitors and Fuel Cells
A00535-01081

Study of Nano-dispersed Polymer Electrolyte Thin Films and its Electrical and Dielectric Properties

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Electrical conductivity and dielectric properties of solid polymer electrolyte of PVA-LiBr, dispersed with nano particle of Al2O3 (average size 50 nm) have been studied. Enhancement in ionic conductivity in four different compositions is observed due to enhanced surface to volume ratio and reduced transport length for the charge carriers. Dispersion of different weight ratio of nano - fillers to the polymer electrolyte having composition of 15 wt. % Al2O3 gives the maximum conductivity at room temperature as determined by impedance method using sample holder with brass electrodes. The interaction between the PVA backbone and the Al2O3 filler has affected the dynamics of the host polymer. The addition of Al2O3 modifies the conductivity and viscosity behaviour of polymer electrolyte due to increased amount of amorphous phase present in the electrolyte system (XRD pattern). A possible explanation based on the presence of pores/voids (SEM studies) in the sample and creation of hopping sites and favorable conducting pathways for migrating ionic species is suggested. Results obtained from dielectric relaxation spectroscopy agree with the characteristics consideration that the increased mobility is largely responsible for the conductivity enhancement caused by the nano-dispersed particles.

A00591-02843

Synthesis and the Effect of Nanosized ZrO2 Filler in the Ionic Conductivity of P(ECH -co- EO) Based Polymer Electrolyte

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The development of a new polymeric system to be used as an electrolyte in advanced batteries and fuel cell is critical for commercial success of these types of power systems. Among many materials much attention has been focused on an elastomeric solid polymer electrolyte, because suitably elastic material can give a flat, thin and flexible solid electrolyte for application in electrochemical devices. The halogenated polyethers, the copolymer poly(epichlorohydrin co ethyleneoxide) an elastomeric material, combines the amorphous property of PECH and the solvating behavior of PEO. This strongly suggests that they could be used as solid polymeric electrolyte. Consistent research have been focused to increase the ionic conductivity and to lower the operating temperature of the polymer electrolyte to near ambient temperature. Among the various methods to increase the ionic conductivity, the addition of inert particles into polymer electrolyte has attracted considerable attention due to its improved mechanical stability, enhanced ionic conductivity, transference number, electrolyte-electrode interfacial stability etc. Hence in the present study nanosized ZrO2 filler have been synthesized by polyacrylamide gel method and have been used for the preparation of Nano Composite Polymer Electrolyte Membrane (NCPEM) by simple solution casting technique. Various composition of synthesized nanosized ZrO2 have been incorporated to P(ECH - co- EO) : LiClO4 system to understand the role of nano filler. NCPEM have been characterized by X- ray diffraction, SEM, and complex AC impedance studies. The XRD pattern for the synthesized ZrO2 nanoparticles reveal the highly nanocrystalline phase for the product calcined at 500°C for 6hr. The diffractogram patterns of P(ECH co EO) based NCPEM reveals a broad peak which confirms the polymer- salt- nanoparticle complexation. The amorphous nature of NCPEM produces greater ionic diffusivity leading to high ionic conductivity. The SEM photograph of NCPEM confirms that the ZrO2 nanoparticles are distributed uniformly in the polymer matrix. The presence of nano filler has substantially increased the ionic conductivity. This may be due to the availability of large amount of hopping sites for the migrating ionic species at the ZrO2 surface.

A00612-01114

Preparation of Nano-sized LiMnPO4 Modified by Carbon Coating

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Preparation of Nano-sized LiMnPO4 Modified by Carbon Coating Some of phosphate materials (LiMPO4, M= Fe, Mn, Ni, Co) have been investigated as new generation of cathode materials with high thermal stability. LiFePO4 has been already applied to lithium ion batteries for power tools and other power applications. However, its electrode potential is 3.5 V vs. Li/Li+, leading to lower energy density compared with transition metal oxides, such as LiCoO2 and LiMn2O4. Therefore, LiMPO4 with higher electrode potential has been investigated. For example, LiMnPO4 has 4 V vs. Li/Li+. Many research groups...
extensively studied on this cathode material, in order to obtain higher energy density of lithium ion batteries. However, the electrochemical performance is not adequate for practical use. In this study, LiMnPO₄ was prepared by hydrothermal process, which generally provided well-crystallized fine particles. Simultaneously, carbon coating was conducted in this hydrothermal process by using carbon sources, such as CMC, PEO, and ascorbic acid. The obtained particles were small secondary particles with less than 1 mm diameter. The primary particle was about 100 nm. The carbon-coating layer was successfully obtained and its thickness was less than 5 nm. The conductivity of LiMnPO₄ particles was not so high due to extremely low crystallinity of carbon layer. This problem was solved by heat treatment at 700 °C under inert atmosphere. The discharge and charge characteristics of LiMnPO₄ were tested by galvanostatic method by using 2032 coin type cell. The discharge capacity of prepared LiMnPO₄ covered with non-heat treated carbon coating layer was 6 mA h g⁻¹. This capacity was smaller than that of the theoretical capacity of LiMnPO₄, 170 mA h g⁻¹. On the other hand, LiMnPO₄ with heat-treated carbon coating layer exhibited higher discharge capacity, 30 mA h g⁻¹. The conductivity measurement on both samples showed an improvement of particle conductivity, which was adequate as positive porous electrode for rechargeable lithium ion batteries. This means that the low discharge and charge capacity is not due to electronic property of electrode, but may be caused by crystal or particle nature of LiMnPO₄ prepared by hydrothermal process. The X-ray diffraction pattern and Raman spectra for LiMnPO₄ prepared in this study showed a formation of single phase of olivine structure and no impurity. More detail analyses on LiMnPO₄ were conducted to clarify the reason why the LiMnPO₄ exhibited a lower capacity than the theoretical one. The lattice constant of LiMnPO₄ increased with increasing of defects in its crystal structure. Simultaneously, the discharge and charge capacity decreased. Therefore, more fine and careful synthesis of LiMnPO₄ is a key factor. For example, the replacement of Li⁺ ion and Mn²⁺ ion should be suppressed (should be zero) by selecting proper conditions. Moreover, small size cation, such as Mg²⁺ or Fe²⁺, may doped in LiMnPO₄ to reduce the lattice constant of LiMnPO₄.

For the preparation of the glass-ceramic sealants, analytical grade SiO₂, Al₂O₃, TiO₂, H₃BO₃, Na₂CO₃ etc., were mixed and then the mixtures were heated to be melted. The melting glasses were poured into cooled water and the obtained glass frits were further ground as sealant precursors. A dilatometer was used to observe the sintering behaviors of the precursor with a designed cylinder. The sealants were placed between the alpha-alumina and beta-alumina and heated to a proper temperature according to a certain sealing process.

The thermal expansion coefficients (TECs) of the glass-ceramics were carefully modified, since an effective sealant should seal different components of the batteries with fewer mismatches between sealant and interconnect. The TECs of the glass-ceramic sealants were found to be 6-7×10⁻⁶ K⁻¹. And the glass ceramic sealants well matched with alpha-alumina and beta-alumina, the two parts to be sealed in the NAS battery.

Three sealing method, namely directive sealing, pulsing sealing and sustaining sealing, were developed and compared. The thermal shock revisiting of the sealants were satisfactory. No micro-crack was observed after 100 times thermal shock between room temperature and the working temperature of sodium sulphur battery. The chemical stability of the sealants was fine and no obvious diffusion of the elements was found at the alpha-alumina/glass-ceramic sealant / beta-alumina interfaces after holding at 350°C for long period.

This work was financially supported by NSFC (project No 50730001, Ministry of Science and Technology of China (No.2007CB209700 and 2007BA07B001) and Science and Technology Commission of Shanghai Municipality (No. 06DZ12213-07DZ12004).
**A Nonaqueous Gel-Casting Process for the Preparation of Na-beta-Al<sub>2</sub>O<sub>3</sub> Green Bodies**

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The Gel-casting process, which is a combination of polymer chemistry, colloidal chemistry and ceramic technology, has drawn worldwide attentions for the past decades. In such a process, stable and flowable slurry is first prepared by dispersing ceramic powders into a premixed monomer solution. After mixing for several hours, an initiator is added and the slurry is casted into a mould. The monomer and crosslinker copolymerize in situ at a certain temperature and the ceramic green parts are therefore obtained. Compared to the conventional ceramic forming techniques such as dry pressing, slip-casting and injection molding, gel-casting is a new ceramic forming technique with several distinctive advantages: near-net-shape forming, homogeneous green parts and machinability of the green because of high strengths.

Na-beta-Al<sub>2</sub>O<sub>3</sub> is a well-known excellent sodium ion conductor. It exhibits a conductivity over 1×10<sup>-2</sup> S/cm at room temperature, making it the best solid electrolyte material for the sodium-sulfur battery. This kind of battery has been recognized as a potential candidate for the energy storage applications, because of its various significant advantages such as high power and energy density, low material cost and low rate of self-discharge. The Na-beta-Al<sub>2</sub>O<sub>3</sub> electrolyte is the central part of the sodium-sulfur battery, and plays a particularly important role in the battery. For such an application, specifically shaped Na-beta-Al<sub>2</sub>O<sub>3</sub> ceramics need to be prepared through the ceramic forming processes. In this study, we try to prepare the Na-beta-Al<sub>2</sub>O<sub>3</sub> green bodies with the nonaqueous gel-casting technique.

Ethanol and n-butanol were used as the solvents for the forming process, methacrylamide (MAM) was used as a monomer, and N,N’-methylenebisacylamide (MBAM) as a crosslinker. The precursor powder of Na-beta-Al<sub>2</sub>O<sub>3</sub> with an appropriate mean particle size and a specific area was prepared via solid state reaction. The effects of dispersant content and solid loading on the rheological properties of the ceramic slurries were studied systematically. It was found that most of the slurries exhibited a shear thinning behavior at low shear rates and a shear thickening behavior at high shear rates. Only the slurries with solid loadings no more than 35 vol% displayed a shear thinning behavior over the entire measuring shear rate range. Microstructure of the green bodies was investigated using scanning electron microscopy. The green parts with n-butanol as the precursor solvent showed a compact microstructure with few agglomerates and pores.

This work was financially supported by NSFC (project No 50730001, Ministry of Science and Technology of China (No.2007CB209700 and 2007BA07B001) and Science and Technology Commission of Shanghai Municipality (No. 06DZ12213/07DZ12004).

**Structure and Electrochemical Performance of Nanostructured Sn-Co Alloy/Carbon Nanotube Composites as Anodes for Lithium Ion Batteries**

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Since Idota et al. discovered amorphous Sn-based oxides as a novel anode material for lithium ion batteries (LIB), Sn-based anode materials have attracted much attention due to the high specific capacity, which is about twice that of graphite, and considered as the best candidate for LIB anode material. However, this material usually exhibits very poor long-term cyclability and a huge irreversible capacity during the first cycle. To overcome this problem, two strategies have been adopted. One is to use Intermetallic compounds or active/inactive composite alloy materials. The other way is to use nanosized active materials. These materials show better cyclability compared with bulk materials, because of their large surface area and short ion diffusion length. However, superfine materials always aggregate severely and merge into large particles during lithium insertion and extraction. The aggregation leads to significant volume change in the electrode and a gradual decline of the electrochemical capacity. The nanocomposites of Sn-based alloy / carbonaceous materials such as SnNi/CNTs, Sn-Sb/CNTs, SnSb/MCMB and Sn-Co-C nanocomposites have recently attracted much attention because of synergistic effect between carbonaceous materials and Sn, which improved cycling performance of Sn-based alloys. Although these nanocomposites are promising, they all have problems related to either capacity or cyclability, which prevents their practical use as anodes in commercial systems. There is still a need for improving the concept of CNT supported nanocomposites further. Up to now, we did not find any report about the synthesis and lithium storage performance of nanostructured Sn-Co alloy/carbon nanotube composites. In this study, nanoparticles of Sn-Co alloy were deposited on the surface of multi-walled carbon nanotubes (CNTs) by reductive precipitation of solution of chelating metals within a CNTs suspension. The chelating agents were used to reduce difference of deposition potential between Sn and Co. Thereinto, we obtained nanosized particles of Sn-Co alloy but not merely mixture of the two metals. The Sn-Co/CNTs nanocomposite revealed a high reversible capacity of 424 mAh g<sup>-1</sup> and stable cyclic retention at 30th cycle. The improvement of reversible capacity and cyclic performance of the Sn-Co/CNTs composite is attributed...
to the nanoscale dimension of the Sn-Co alloy particles (<20 nm) and the framework of CNTs. Inactive Co as glue matrix of Sn prevents the possible pulverization of nanosized alloy particles. The CNTs could be pinning the Sn-Co alloy particles on their surfaces so as to hinder the agglomeration of Sn-Co alloy particles, while maintaining electronic conduction as well as accommodating drastic volume variation during Li insertion and extraction reactions. So the electrode of nanocomposites of Sn-Co alloy / CNTs exhibited a relatively high capacity and excellent cycleability.

Acknowledgements:
This work was financially supported by NSFC (grant no. 20773102, 20833005), the “973” program (grant no. 2009CB220102).

A00640-01228

Methanol-to-Hydrogen Decomposition and Electrochemical Hydrogen Absorption in Carbon Nanostructured Materials

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One of the main problems of hydrogen power engineering is the development of high efficient materials for hydrogen storage and conversion. Hydrogen is now considered as the general-purpose energy carrier which in combination with electric energy can make available transition to ecologically pure, sustainable power engineering. In direct methanol fuel cell the catalytic reforming of methanol to hydrogen and oxidation of hydrogen simultaneously takes place. It goes through the formation of intermediate reaction products, such as formaldehyde (CH₂O), carbon oxide (CO) and hydrogen. In situ μSR and NMR methods are applied to study methanol-to-hydrogen decomposition and hydrogenation of multiwall carbon nanotubes. Carbon nanotubes were grown by CVD method on specially treated Ni plates using granular polyethylene as a precursor. Obtained in a such way the composite structure consisting of Ni plate with carbon nanotubes grown at plate surface is used as the electrode. Hydrogenation of carbon nanotubes is carried out by electrochemical method in alkaline and acid aqueous solutions at various current densities. The results obtained allow us for the first time to estimate in situ the contribution of chemical decomposition reaction process with rate constant of 5 µs for the formaldehyde - carbon oxide - hydrogen conversion on Pt-Ru/Vulcan XC-72 catalytic material. The process of carbon nanotube growth develops in atmosphere which contains carbon-hydrogen vapour and it is important to know the state of surface before to explore their adsorption properties. ¹H NMR spectra as-prepared multiwall carbon nanotubes demonstrate broad resonance line with chemical shift 3.81 ppm. NMR spectra of multiwall carbon nanotubes loaded with hydrogen after purification by heating at 800°C in vacuum display the resonance line at the same chemical shift, but with width three times larger of as-prepared samples. Most experiments on carbon nanotube hydrogenation is performed by means of high pressure technique. Electrochemical method as applied to carbon nanotubes gives rise to extremely strong electric field near the tips of nanoscaled tubes even with moderate electric potentials. Such electric field can initiate the penetration of hydrogen between graphene planes in multiwall carbon nanotubes and give the additional contribution to the hydrogen storage capacity. The comparison of results obtained with NMR investigations of high-pressure hydrogen loaded single- and multiwalled carbon nanotubes is carried out and peculiarities connected with the introduction of protons (H⁺) in carbon nanotubes during electrochemical hydrogenation is discussed.

Acknowledgment:
This work was supported by the Ministry of Education and Science of the Russian Federation through the project adtp № 2.1.1/4982

A00648-02275

Preparation and Characterization of Nanosized Li₄V₃O₈ Electrode Material by AC Impedance Spectroscopy

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Lithium ion batteries have become attractive for portable electronic devices due to their higher cell voltage and energy density compared to the other rechargeable systems. The commercially available lithium ion batteries use LiCoO₂ as the cathode material which suffers from major drawbacks like structural and chemical instability. Also it is found to be highly expensive and toxic. So today research is focused on alternative cathode materials which could overcome these drawbacks. Lithium trivanadate (Li₄V₃O₈) is considered as an attractive alternative cathode material for rechargeable lithium batteries due to
Preparation, Structural and Impedance Studies of Nanosized LiNiVO₄ Electrode Material

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Lithium ion batteries have been attracting considerable interest worldwide in the past few years in the field of rechargeable batteries because they possess high energy density, long cycle life, good safety, steady discharging properties, and a wide range of working temperatures. Currently, the possible candidates for cathode materials used in lithium ion batteries are LiCoO₂, LiNiO₂, and LiMnO₂. Besides the above materials, LiNiVO₄ is the first material with the inverse spinel structure that has been patented as a potential cathode material for rechargeable lithium cells. It possesses a very high voltage value of 4.8 V versus lithium and is found to be an attractive cathode material. But LiNiVO₄ is a poor electrical conductor, which will strongly affect its rate capability. The electrical conductivity of this material could be improved by preparing the material with a particle size in the nanometre range, since with the decrease in particle size, the diffusion path for the charge carriers could be decreased. A few reports are already made on the electrical conductivity of micron-sized LiNiVO₄, whereas the electrical study of nanosized material is found to be very scarce. In this work, preparation of the nanosized material has been made through a simple, less time consuming polymer pyrolysis route using non-toxic and inexpensive raw materials. The samples were prepared at a low calcination temperature of 723 K for 12 hr. The as prepared powder samples were characterized by X-ray diffraction, FTIR spectroscopy and Scanning electron microscopic techniques. The XRD analysis confirms the highly nanocrystalline structure with a crystallite size of 34 nm. SEM analysis also reveals the nanosized particles in the range of 50-60 nm. The samples are subjected to AC impedance spectroscopic studies in the frequency range of 42 Hz to 1 MHz over the temperature range of 573 K to 673 K. The impedance spectra show a decrease in overall resistance of the compound with the increase in temperature. The conductivity spectra obey the Johnshers power law and indicate a low repulsion between the lithium ions. The dielectric spectra show the presence of electrode polarization at low frequencies. The modulus spectra show a non-Debye nature of the compound indicating a distribution of relaxation time.
compared with initial ionic salts. Summing qualitative conceptions about mechanism of the reported phenomena we can point to the following set of causes:

Generation of great number of defects on the interfaces of nano-composites that stipulated by mechano-activation treatment;

Order-disorder (disordering) transition and amorphization of ionic salts;

Formation and stabilization on the interfaces of nano-composite of uncommon phases which unstable in the bulk;

Total mass of electrolyte exists in the form of nano-films covering the surface of oxide particles;

Realization of the new “joint jumps” [(j-j) ionic conductivity’s mechanism on the “ionic salt-oxide” interfaces.

We used the methods of molecular dynamics, percolation theory and quantum-chemistry calculations to carry out the evaluations of specific contributions of the causes pointed above and to explain the improvement of ionic conductivity. The potentials of interaction required for the method of molecular dynamic were calculated by the means of quantum chemistry code. The results show that on the “ionic salt-oxide” interfaces may occur the loosening of structures that resulting in the considerable reduction of activation energy of ionic diffusion.

Characterization of PVA Based Proton Conducting Polymer Electrolyte Membrane

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PVA based proton conducting polymer electrolytes with different concentration of NH4NO3 have been prepared using solution casting technique. The XRD pattern reveals the increase in amorphous nature of the film with the addition of salt. FTIR measurements carried out on the prepared polymer electrolytes reveal the complexation between the host polymer matrix and the guest salt. The glass transition temperature of PVA has been found to be reduced with the addition of salt up to 20mol% beyond which it decreases. The band broadening in Raman spectroscopy proves to be an additional tool to confirm the amorphous nature of the polymer films. Using Raman spectroscopy the fraction of free ion, ion-pair and higher order ion aggregates have been calculated indirectly from the peak area of the deconvoluted peaks of NO3− anion. Raman analysis also confirms that free ion concentration is maximum for 80 PVA: 20NH4NO3 polymer electrolyte. The temperature dependent 1H NMR study reveals the increase in mobility of NH4+ ion with temperature in all the prepared polymer electrolyte films. The presence of residual solvent DMSO has been confirmed from FTIR, Raman and 1H NMR studies. The ac conductivity value for all the prepared polymer electrolytes has been evaluated using impedance spectroscopic analysis at different temperatures. The highest ionic conductivity has found to be 7.5x10−4 Scm−1 at 303K for 80PVA: 20NH4NO3. The residual solvent, DMSO acts as an additional enhancer of the conductivity other than the salt. The activation energy obtained from conductivity data decreases with increasing ionic conductivity and vice versa. The dielectric loss spectra analysis shows the existence of β-relaxation in the prepared polymer electrolyte samples. The ionic transference number measurement shows that the charge transport in the prepared electrolyte films is predominantly due to ions.

The optimized polymer electrolyte, 80PVA: 20NH4NO3 possess the high amorphous nature (as confirmed from XRD), low activation energy (temperature dependent conductivity results), more free ion concentration (Raman results), low glass transition temperature (DSC results). Temperature dependent 1H NMR results confirms that proton is responsible for conduction at all temperatures. The above results reveal that 80PVA: 20NH4NO3 polymer electrolyte is well suited for its electrochemical device applications such as fuel cells and proton batteries etc.

A00676-01217

Acknowledgement:
One of the authors M.Hema acknowledges the Council of Scientific and Industrial Research (CSIR), Government of India, for the award of Senior Research Fellowship (SRF).

Investigation of Nd0.5Ce0.5CuO4 (x = 0.05, 0.1, 0.2, 0.25) Prepared by Acetate Pyrolysis Method

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In recent past, the fuel cell technology has been developed rapidly and several types of fuel cells have investigated depending on the intended applications. Development of novel cathode materials with adequate mixed, ionic and electronic, conductivity (MIEC) has been needed to make the intermediate temperature SOFC technology successful. In more recent past, research efforts have been focused on materials aspects and/or synthesis techniques that can
provide electrode with high oxygen-permeation rate.

Perovskite-type MIEC or related oxides have widely been tested as oxidation catalysts and electro-catalysts for SOFC or solid-oxide electrolysis. The materials belonging to Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO) series having layered structure has been studied extensively for super conductivity viewpoint. Practically, the super conductivity has been induced in them due to the partial replacement of Nd$^{3+}$ for Ce$^{4+}$. They have also been exploited as cathode material by using Ni ion in place of Cu ones.

In the present work, various compositions of Nd$_{2-x}$Ce$_x$CuO$_4$ with $x = 0.05, 0.1, 0.2, 0.25$ were prepared following acetate pyrolysis method. The X-ray powder diffraction scans of the prepared samples was recorded with the help of Panalytical X-ray diffractometer for the phase and structure analysis. The size and the shape of grain were examined with the help of scanning electron microscope. The electrical conductivity was measured at various temperatures in the range 300 to 800°C following four-probe DC method. The Vickers hardness tester, HMV Shimadzu, was use to determine the microhardness of all samples.

The XRD results suggest formation of single tetragonal phase. Further, the expected crystallite size determined using Scherer formula reveals formation of nanocrystalline materials. SEM study suggests agglomeration of grains thereby formation of nano-pores. The results on electrical conductivity behavior are discussed in the light of the crystal structure, the composition and the grain size.

A series of La$_{1-x}$Sr$_x$MnO$_3$ with $x = 0, 0.2$ and $0.4$ was prepared by solid state sintering method. The dilatometric study of all the three compositions was carried out by recording XRD scans at various temperatures in the range 25-800°C under vacuum of the order of 10$^{-5}$ Torr using HTK-16, high temperature attachment (Anton Parr, Austria) to Panalytical x-ray diffraction system. The microstructures were observed with the help of scanning electron microscope. The dc conductivity was measured as a parametric function of temperature.

La$_{1-x}$Sr$_x$MnO$_3$ show the change in crystal symmetry from orthorhombic to rhombohedral between compositions La$_{0.8}$Sr$_{0.2}$MnO$_3$ and La$_{0.6}$Sr$_{0.4}$MnO$_3$. The SEM study reveals the submicron size grains. The thermal expansion coefficient of orthorhombic is very small compared to that for rhombohedral phase. Hence, the former may be preferred over the latter for SOFC application. Therefore, Sr substitution should not exceed 20%, if it is desired to maintain orthorhombic phase of cathode material.

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**Structural and Electrical Characteristics of Bi$_4$V$_{2(1-x)}$Ni$_x$O$_{11-3x}$, 0.00 ≤ x ≤ 0.1**

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Bi$_4$V$_{2(1-x)}$Ni$_x$O$_{11-3x}$ ceramics were prepared by a modified mixed-oxide method. The phase formation was studied by XRD analysis. All compositions studied complete solid solutions with perovskite phase having tetragonal symmetry. Impedance spectroscopy is employed to investigate the electrical properties associated with the changes in the crystal structure and with the change in the Ni content. The tetragonality of the samples showed a increasing trend with increase of Ni content. The ionic conductivity of polycrystalline samples of BINIVOX was extracted from Nyquist plots and the ionic conductivity was found to increase with increase in Ni content and temperature for all the composition. The impedance data was analyzed to drive the values of bulk resistance.
Effect of Fabrication Route on the Mechanical and Electrochemical Properties of SOFC’s

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The present paper is focused on the mechanical and electrochemical properties of tubular and micro-tubular solid oxide fuel cells (SOFC) and stacks, for potential use in an APU-system, requiring fast start-up. High volumetric power density and ease of fabrication are the pre-requisites of such a system, and thus we will examine how the processing route (synthesis, fabrication and manufacturing) affects the aforementioned properties of such a system. Attention has been made to the development of a materials’ set for the electrodes and electrolytes that lower the operating temperatures to below 650°C, as well as to the development of manufacturing processes for sub-millimeter tubular SOFC cells for arrangement and integration at the micro level. We will study how the materials’ set can be fabricated into tubes that have superior properties over conventional routes, and how these routes can be up-scaled to potentially make them commercially viable, while keeping their required properties.

The results of a micro-tubular SOFC, and a “cube-type” cell stack module, fabricated and tested to check its applicability for commercialization as an auxiliary power unit (APU) and a stationary small power source system are presented. The micro-tubular SOFCs with high energy efficiency, quick start-up and shut-down performance and low production cost are described in addition to the mechanical properties and fabrication technology data for the SOFC materials operating in the temperature range of 450-650°C.

Reversible and High Capacity Nanostructured Electrode Materials for Li-ion Batteries

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Reversible and high capacity nanostructured electrode materials are at the center of R & D parts of the lithium rechargeable batteries which require high power, high capacity and high safety. The higher capacities and higher rate capabilities for the nanostructured electrode materials than for the bulk counterparts can be attributed to the higher surface area, which reduces the overpotential and allows faster reaction kinetics at the electrode surface. These electrochemical enhancements can lead to versatile potential applications of the batteries, and can provide breakthroughs for currently limited to power suppliers of the mobile electronics. This talk will deliver recent research advances on the nanostructured cathode and anode materials, such as metals, metal oxides, metal phosphides and LiCoO₂, LiNiₓMnO₂ with zero, one, two and three dimensional morphologies.

Feasibility Study of Sago Waste based Activated Carbon as an Electrode Material for Electric Double Layer Capacitor

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Carbon, in all its allotropic forms, is one of the most widely used materials and has countless applications in various industrial processes and technical devices. Among them are those related to the development of advanced energy storage systems with high energy and power density, e.g. electric double layer capacitor (EDLC). The key components of each EDLC are the electrodes made of carbon with high degree of porosity and, correspondingly, with high specific surface area (SSA). The overall performance of the entire EDLC system depends strongly on the parameters of the electrode material. The potentially appropriate material is the activated carbon (AC) since it is characterized by SSA up to 3000 m²/g. The detailed analysis of the experimental data shows that AC with characteristic sizes of the pores less than 2 nm are not appropriate because the ionic motion in such narrow channels is slower and prohibits the percolation of the electrolyte. Similar adverse effects can be caused also by various irregularities of the pores as well as by the absence of connections between them (isolated pores).

In the present study, we report the results of the research focused on both the preparation of AC based on sago waste and on the investigation of their electrochemical properties. We discuss also the importance of the technological parameter such as the potassium hydroxide (KOH) to charcoal (SC) ratio and its influence on the capacitance of EDLC.

The SC was prepared by carbonizing the sago waste at 350°C for one hour. The chemical activation on the SC was done by suspending in a concentrated solution of KOH and four types of samples were prepared by varying the weight ratio of KOH and charcoal. Then the samples were heated at the activation temperature of 800°C for one hour. The SSA values were calculated by applying the Brunauer-Emmett-Teller (BET) model. For preparing an electrode of EDLC, the samples were mixed with 5% of polytetrafluoroethylene powder. In the electrochemical experiments, a two-electrode cell was used to measure the capacitance.
The samples have a microporous structure with a relatively high percentage of small mesopores that depends on the KOH to SC ratio. An increase of the latter leads to the formation of bigger number of small mesopores than the number of micropores and eventually causes an increase of the total SSA. The SSA was in the range from 212 to 1498 m$^2$/g. The specific capacitance increases with increasing of KOH ratio in H$_2$SO$_4$ or LiClO$_4$ electrolyte. It should be noted however that such increase is larger in LiClO$_4$ electrolyte than in H$_2$SO$_4$ electrolyte. This means that the variation of KOH ratio influences significantly the development of small mesopores, because the size of LiClO$_4$ ion is larger than that of H$_2$SO$_4$ ion. The specific capacitance has been found to be in the range from 16 to 64 F/g.

**Enhanced Electrochemical Performance of Ni(OH)$_2$/CNT Composite for Supercapacitor**

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Ni(OH)$_2$/CNT composite as electrode material for supercapacitor was synthesized by chemical precipitation. The morphology and structure of prepared Ni(OH)$_2$/CNT composite were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Electrochemical investigation indicated that Ni(OH)$_2$/CNT composite presented preferable electrochemical performances than Ni(OH)$_2$. In comparison with Ni(OH)$_2$, Ni(OH)$_2$/CNT composite had better capacitive response in cyclic voltammetry and could deliver larger specific capacitance in galvanostatic charge-discharge process. Enhanced conductivity of Ni(OH)$_2$/CNT composite was considered to be responsible for its increased electrochemical performances.

This project was supported by Excellent Youth Foundation of Shanghai Education Commission (EGD-07004).

**Metallic and Transition Metal Oxide Nanoparticles Decorated Carbon Nanotubes for Energy Storage Devices**

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Electrochemical charge storage systems are essential links between energy generation and energy consumption and play an equally critical role in green energy storage, electric vehicles, as well as mobile electronics. Increasing the power and energy densities is recognized as the prime objective towards more efficient and cost effective charge storage solutions.

In this work, carbon nanotubes (CNTs) decorated with metallic and transition metal oxide nanoparticles are demonstrated to be effective means of improved energy and power densities of supercapacitors. Moreover, these materials are also demonstrated to be effective bi-functional charge collectors and electrode materials for energy storage devices, particularly for supercapacitors and batteries. CNTs were decorated with Ag using a room-temperature deposition-precipitation process that yielded excellent control on the Ag nanocluster sizes.
reaction in PEMFC. Catalytic activity and stability for oxygen reduction results indicate that the present catalyst shows good electrode assembly were also prepared and polarization in the presence of methanol. Electrodes and membrane and the results show that the ORR activity was unaffected metal oxide/MWNT modified glassy carbon electrodes. Electrochemical studies were performed using Metal-chemical method and characterized by SEM and TEM. MWNTs (f-MWNT) by acid treatment. Metal-metal chemical vapor deposition technique and functionalized in PEMFC. MWNTs have been prepared by the catalytic (MWNTs) as electrocatalyst for oxygen reduction process. Side and active only towards oxygen reduction reaction activity towards methanol oxidation at the cathode. However, using a better catalyst that cannot show any circulating the solution can minimize this problem. Methanol from anode to cathode poses a serious problem. Methanol is directly supplied at anode, the crossover of voltage plateaus are obtained and a low polarisation leads to a narrow potential window, between 0.1 and 0.45 V. attractive working potential window, between 0.1 and 0.45 V vs. Li+/Li. Moreover, high storage capacities in the order of 1500 mAh.g⁻¹ are achieved and are still available over more than 10 cycles. The increasingly demand on secondary batteries with higher specific energy densities requires new materials for both positive and negative electrodes. Concerning the negative, many researches are carried out in order to replace the actual electrode based on carbonaceous materials. Indeed even if these materials are cheap and present interesting electrochemical properties, the maximal insertion of one lithium ion for six carbon atoms leads to a theoretical capacity limited to 372 mAh g⁻¹. Because of its high theoretical specific capacity, silicon can appear as a good candidate (maximal insertion of 4.4 Li ion for one Si atom that leads to a theoretical capacity of 4200 mAh. g⁻¹). However, the large volume expansion associated with lithium insertion, which can rise to more than 300%, limits its ability to cycle with high efficiency. To solve the problem of cycle life, we propose to use a threedimensional architecture which allows combining the accommodation of the large volume changes expected for lithium insertion in crystalline silicone with a continuous and efficient electrical contact between the Si particles. This architecture consists in a thin film based on Si nanowires (SiNWs). The used substrates, acting as current collector, are stainless steel foils of 50 µm thickness. They are firstly covered by 50 nm of Ti as an adhesive layer, 100 nm of TiN as a conductive diffusion barrier and 10 nm of Au as catalyst layer. Then, SiNWs are synthesized directly at the surface by chemical vapour deposition (CVD) according to the VLS growth mechanism in SiH₄ diluted in H₂, in the temperature range of 500-600°C. To date, such SiNWs have been very little investigated as anodic materials for Li-ion batteries or microbatteries and yet, our first results are very promising. The electrochemical behaviour, studied in a two-electrode cell, has shown an attractive working potential window. Indeed, well defined voltage plateaus are obtained and a low polarisation leads to a narrow potential window, between 0.1 and 0.45 V vs. Li+/Li. Moreover, high storage capacities in the order of 1500 mAh.g⁻¹ are achieved and are still available over more than 10 cycles.

MWNTs Supported Nanocrystalline Metal-metal Oxide as Methanol Tolerant Oxygen Reduction Reaction Electrocatalyst for Proton Exchange Membrane Fuel Cell

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Recently proton exchange membrane fuel cells (PEMFC) have drawn considerable attention as a clean energy conversion device due to its high energy conversion efficiency. In direct methanol fuel cell (DMFC), where methanol is directly supplied at anode, the crossover of methanol from anode to cathode poses a serious problem. Circulating the solution can minimize this problem. However, using a better catalyst that cannot show any activity towards methanol oxidation at the cathode side and active only towards oxygen reduction reaction (ORR) will provide a better solution. In the present work, we report the methanol tolerant nanocrystalline metal-metal oxide supported on multi walled carbon nanotubes (MWNTs) as electrocatalyst for oxygen reduction reaction in PEMFC. MWNTs have been prepared by the catalytic chemical vapor deposition technique and functionalized MWNTs (f-MWNT) by acid treatment. Metal-metal oxide was dispersed on the surface of the f-MWNTs by chemical method and characterized by SEM and TEM. Electrochemical studies were performed using Metal-metal oxide/MWNT modified glassy carbon electrodes and the results show that the ORR activity was unaffected in the presence of methanol. Electrodes and membrane electrode assembly were also prepared and polarization measurements for single cell have been performed. The results indicate that the present catalyst shows good catalytic activity and stability for oxygen reduction reaction in PEMFC.
The lithiation/delithiation mechanisms are currently investigated by different methods (XRD, TEM, microRaman spectroscopy) to understand structural responses of SiNWs vs. Li content, in order to determine which parameters should be modified during the SiNWs growth (temperature, duration, pressure ratio...) to increase both the storage capacity and the cycle life.

Acknowledgments:
The authors thank Dr. C. T. Lin, D. P. Chen, J. Peng for single crystal preparation, G. Götz for powder X-ray measurements, and T. Acartürk and Dr. U. Starke for providing and discussing the SIMS data.

Investigation on the Effect of Addition of Phthalate-based Plasticizers on PVDF-AgCF3SO3 Gel Polymer Electrolytes
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Gel polymer electrolytes comprising poly(vinylidene fluoride) (PVDF), silver triflate (AgCF3SO3) and a series of plasticizers namely dibutyl phthalate (DBP), dioctyl phthalate (DOP) and diphenyl phthalate (DPP) were prepared by solution casting technique using dimethyl formamide (DMF) as the common solvent. The effects of different side chains like aliphatic and aromatic groups of the plasticizers on the conductivity, structure, thermal stability and surface morphology of (PVDF+ 30 wt. % AgCF3SO3) gel have been investigated. A maximum ionic conductivity of 5.3 x 10^{-4} S cm^{-1} at 298 K was registered for the electrolyte (PVDF+ AgCF3SO3) + 20 wt. % DOP suggesting that the addition of aliphatic group substituted phthalate increased the ionic conductivity when compared to that of the aromatic group substituted phthalate. Interestingly, the electrolyte with the longer aliphatic chain possessed the maximum electrical conductivity. The structural characterization, carried out by the Fourier Transform Infrared (FTIR) spectral investigations in the wave number region 4000 – 400 cm^{-1}, revealed that the addition of plasticizers increased the concentration of free ions thereby enhancing the ionic conductivity value. The thermal stability and surface morphology studies, carried out using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) respectively, indicated the decrease in the degree of crystallinity of the gel polymer electrolytes.

Regeneration of Spent-NaBH4 Back to NaBH4 by Using High-energy Ball Milling
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With increasing awareness in outcomes of severe climate changes and global warming arising from excessive emission of greenhouse gases, such as carbon dioxide from excessive usage of fossil fuels, since the Industrial Revolution, urgent measures in developing alternative and renewable energies have been implemented by mankind.
However, the key to realize the hydrogen economics is the successful development of less expensive hydrogen storage materials having enough energy-storage density. Among various hydrogen storage materials, chemical hydrides such as sodium borohydride are of the most promising candidates. Sodium borohydride is liquid and relatively stable at room temperature, and evolves hydrogen of high purity that could be consumed directly by subsequent fuel cell devices. Unfortunately, the cost of using sodium borohydrides based on per unit of energy is still quite expensive than fossil fuels. That is, cost-down of such materials is critical to its successful applications.

High-energy ball milling was employed to regenerate spent-sodium borohydride, i.e., principally the sodium metaborate (NaBO$_3$), back to sodium borohydride (NaBH$_4$) by a reaction with magnesium hydride (MgH$_2$). The samples were characterized by using scanning electron microscopy (SEM), Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy, X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) spectroscopy. In general, as the ball-milling duration increases, the yield of NaBH$_4$ increases accordingly and leads to an extreme value of 76%, when MgH$_2$ in stoichiometric excess by 40% was initially present in ball mills.

The The development of lithium ion batteries is very rapid since its birth in the early 1990s. However, a lot of improvements are still urged due to the drastic development of applications such as electronics and electric vehicles. In order to meet the rapid applications, the traditional methods have limitation to further improve the electrochemical performance of lithium ion batteries. As a result, the new ‘nanotechnology’ or ‘nano engineering’ will play an important role.

In our laboratory, we developed several kinds of nano electrode materials such as core-shell Si/C, Si/SiO$_2$, and TiO$_2$/C, 3D nanoporous TiO$_2$, LiCoO$_2$/C and MoO$_3$ [1-8]. In the case of the core-shell structured nanocomposites, the shells prevent the nano cores from aggregating. In addition, some shells are favorable for the increase of diffusion of lithium ions and electronic conductivity. As to the nanoporous electrode, the nanoporous structure favors rapid movement of lithium ions during charge and discharge process. As to new structured nano electrode materials, the diffusion distance is very short for lithium ions. Consequently, the prepared nanocomposites present better cycling behavior, better kinetics with good rate capability. As to other nano electrode materials, they also present unique performance.

These above results suggest that nanotechnology will greatly promote the development of new electrode materials.

**Acknowledgments:**
Financial support from National Basic Research Program of China (973 Program No: 2007CB209708) is greatly appreciated.

**References:**

**Oleylamine-Mediated Synthesis of Monodisperse Pd-Composite Nanoparticles for Catalytic Formic Acid Oxidation**

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The need to limit Pt usage in fuel cell catalysis, has promoted the search for non-Pt nanoparticle (NP) catalysts with analogous property. Among all nobel metal based catalysts studied thus far, Pd is a promising alternative. We report a facile synthesis of monodisperse Pd NPs by the reduction of Palladium Acetylacetonate with oleylamine and borane tributylamine complex. Oleylamine's versatility is displayed in its role as a solvent, surfactant and reductant. The synthesis' flexibility allows the incorporation of 5nm Pd core-shell NPs. The oleylamine coated Pd-composite Au seeds – leading to a size-controlled synthesis of Au/Pd core-shell NPs. The oleylamine coated Pd-composite NPs are readily “cleaned” by a 99% acetic acid wash and characterized by TEM, HR-TEM, XRD, EDAX and ICP-MS. The Pd-based NPs supported on the Ketjen carbon are catalytically active for formic acid oxidation in HClO$_4$ solution. Along with the activity, we have also attempted to address the stability issue in catalysts for fuel cell reactions, when comparing to commercially available catalysts. Our catalysts show no obvious activity degradation after 1500 cyclic voltammetry cycles under ambient conditions. These Pd-composite NPs hold promise as a highly active non-Pt catalyst for fuel cell applications.

**Nano Electrode Materials for Lithium Ion Batteries**

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The synthesis of monodisperse Pd NPs supported on Ketjen carbon allows for the development of electrochemical performance for formic acid oxidation in HClO$_4$. The Pd-based NPs supported on the Ketjen carbon displayed in its role as a solvent, surfactant and reductant. Oleylamine's versatility is displayed in its role as a solvent, surfactant and reductant. The synthesis' flexibility allows the incorporation of 5nm Pd core-shell NPs. The oleylamine coated Pd-composite Au seeds – leading to a size-controlled synthesis of Au/Pd core-shell NPs. The oleylamine coated Pd-composite NPs are readily “cleaned” by a 99% acetic acid wash and characterized by TEM, HR-TEM, XRD, EDAX and ICP-MS. The Pd-based NPs supported on the Ketjen carbon are catalytically active for formic acid oxidation in HClO$_4$ solution. Along with the activity, we have also attempted to address the stability issue in catalysts for fuel cell reactions, when comparing to commercially available catalysts. Our catalysts show no obvious activity degradation after 1500 cyclic voltammetry cycles under ambient conditions. These Pd-composite NPs hold promise as a highly active non-Pt catalyst for fuel cell applications.

**A00861-01495**

**A00896-01563**

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The need to limit Pt usage in fuel cell catalysis, has promoted the search for non-Pt nanoparticle (NP) catalysts with analogous property. Among all nobel metal based catalysts studied thus far, Pd is a promising alternative. We report a facile synthesis of monodisperse Pd NPs by the reduction of Palladium Acetylacetonate with oleylamine and borane tributylamine complex. Oleylamine’s versatility is displayed in its role as a solvent, surfactant and reductant. The synthesis’ flexibility allows the incorporation of 5nm Au seeds – leading to a size-controlled synthesis of Au/Pd core-shell NPs. The oleylamine coated Pd-composite NPs are readily “cleaned” by a 99% acetic acid wash and characterized by TEM, HR-TEM, XRD, EDAX and ICP-MS. The Pd-based NPs supported on the Ketjen carbon are catalytically active for formic acid oxidation in HClO$_4$ solution. Along with the activity, we have also attempted to address the stability issue in catalysts for fuel cell reactions, when comparing to commercially available catalysts. Our catalysts show no obvious activity degradation after 1500 cyclic voltammetry cycles under ambient conditions. These Pd-composite NPs hold promise as a highly active non-Pt catalyst for fuel cell applications.
In this presentation, we report a novel approach for mass synthesis of V$_2$O$_5$ belt-like nanorods. In this two-step approach, the nanorods are formed in a controlled recrystallization process from nanocrystalline V$_2$O$_5$ produced by ball milling. The nanorods grow along the [010] direction and are dominated by {001} surfaces. Large quantity production of nanorods can be achieved by annealing in a fluidized bed, which suppresses agglomeration. The structure of nanorods provides an improved cycling stability for lithium intercalation.

**A00903-01584**

**Tremella-like Molybdenum Dioxide Consisting of Nanosheets as an Anode Material for Lithium Ion Battery**

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Since the introduction of nanotechnology in the past decade, nanoscale materials with different morphologies have stimulated great interest due to their unique properties in contrast to the bulky counterparts and envisioned/potential applications in various fields. As for lithium ion battery, nanostructured materials as electrodes have drawn much attention for their high capacity and good rate capability because of their large surface area and short diffusion distance for lithium ions. Molybdenum dioxide, with excellent chemical and physical properties, has been widely used in various fields. As an anode material for lithium ion battery, it exhibits higher capacity than commercial carbonaceous materials, and proper morphology, structure and particle size are necessary for MoO$_2$ to be employed as an anode material for lithium ion battery$^2$.

In this paper, through hydrothermal method using ethylenediamine as a reducer and Fe$_2$O$_3$ as an assisting agent, we have successfully synthesized hexagonal MoO$_2$ with tremella-like structure which is assembled with nanosheets (<5nm). Such tremella-like MoO$_2$ was tested as anode for lithium ion battery. It exhibits capacity as high as 600 mAh g$^{-1}$ at 0.5 mA cm$^{-2}$, while under higher current density, 2.5 and 5.0 mA cm$^{-2}$, the charge capacities are around 400 and 300 mAh g$^{-1}$, respectively. The cycleability proves good too: the capacity keeps around 300 mAh g$^{-1}$ after 20 cycles even at the current density of 5 mA cm$^{-2}$. The excellent electrochemical performance of the tremella-like MoO$_2$ is probably due to its nanostructure which facilitates lithium ions diffusion and reversible intercalation into and deintercalation from the active material. The high reversible capacity and good cycleability even under high current density suggest that tremella-like MoO$_2$ a promising anode for lithium ion battery.
**Acknowledgments:**

Financial support from National Basic Research Program of China (973 Program No: 2007CB209708) is greatly appreciated.

**A00913-01938**

**Electro-activity in Natural Gum and its Application Potential**

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In the recent period soft matter occupies leading position in material science research. The most of the soft matters are derived from living matter. Biomaterials especially the biopolymers are playing most crucial role in the soft matter studies. The biopolymers/biomaterials systems are mostly dominated by weak, non-covalent interactions, and fluctuations like Brownian motion are also present in them. In the recent period a good number of biopolymers have been identified as electro-active in nature and hereafter they will be termed as electro-active biopolymer (EABP). EABP are a new class of natural materials having conductivities comparable to that of synthetic high conducting polymers.

The known EABP’s like Starch, Cellulose, Chitosan, Pectin, plant gums etc. are found to exhibit electrical conduction over a wide range of conductivity (between $10^{-9}$ to $10^{-14}$ S/cm). In earlier studies it has been found that the plant gum Acacia Arabica exhibits many interesting features of electro-activity from material science view point. It consists of polysaccharides unit, formed by the polymerization of mono-sacharride with charged groups. These polymers glue together the cellulose micro-fibril to make the composite structure – most plant gums belong to this class. Its electro-activity can be tailored and controlled by complex formation with organic and inorganic compound... In an earlier study a proton conductive gel is developed with Gum Arabica and H$_3$PO$_4$ in sol-gel route, which is found to be a good member for various electro-chemical applications e.g. Cell. The developed gels were found to satisfy requirements as an electrolyte for practical implications of a cell. In a recent work solid specimens of gum Arabica complex are prepared by forming complexes with organic Citric acid at different concentration were formed. The resulting specimens were found to be electro-active and its enhancement of electro-activity was observed with increase in acid concentrations. Gum Arabica, is employed to develop a photosensitive biocomplex with Chromophore matter collected from natural leaves / flower. The photosensitivity and enhancement of electro-activity of the developed complex are examined experimentally. It was found that their electrical property found to enhanced and of fascinating photo electrical behavior. The chromophore molecules are capable of absorbing and/ or emitting light by losing or gaining an electron. In this present study, chromophore/LH molecules are used in the form of small clusters of chlorophyll from Sigma Aldrich (USA) and from leaf of plant Neem are employed to form a complex system with Acacia Arabica as a host electro-active biopolymeric background. The former guest molecules act as the light absorbing group and host material act as external donor or acceptor.

This high potential material may be used in interdisciplinary research and technology. In subsequent studies the eco-friendly application potential of EABP namely Gum Arabica was exploited to develop (i) electric cell (ii) Solar photo voltaic cell (iii) sensors using electroactivity. All the results are found to be good, important and fascinating.

**A00950-01667**

**Studies on Grain Boundary Effects in Spray Deposited BICOVOX.1 Films on Platinum Coated Stainless Steel Substrate**

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The solid electrolytes with oxygen ion conductivity in the intermediate temperature range find applications in verities of fields such as solid oxide fuel cells and oxygen separators,oxygen sensors. The divalent metal substituted $\gamma$-Bi$_4$V$_2$O$_{11}$ (BIMEVOX) compounds are considered as the best oxide ion conductors at moderate temperature, 673–873 K useful for intermediate temperature solid oxide fuel cell. Amongst all, cobalt doped bismuth vanadate (BICOVOX) is most promising oxygen ion conductor with very high ion conductivity in thin film form. The application of these films in SOFC demands the understanding of ionic transport through these polycrystalline systems. The grain boundaries were found to be affecting the ionic transport significantly in solid state ionic thin films. In the present work we report synthesis and electrical characterization of sry deposited BICOVOX.1 ($\text{Bi}_2 \text{Co}_{0.91} \text{V}_{0.9} \text{O}_{3.35}$) thin films. The dielectric relaxation process and grain boundary blocking is probed using bricklayer model to understand the effect of polycrystallinity in these films.

Thin films of Bi$_2$Co$_{0.91}V_{0.9}O_{3.35}$ have been deposited by using spray pyrolysis on platinum coated stainless steel substrate. The films were characterized by XRD, SEM and AFM techniques. Impedance measurements were done in the frequency range 1Hz to 10MHz and in the temperature range 502 K to 720 K revealed two relaxation processes with distinguishable time constants. The first corresponds to the grain interior charge transfer while the second could be due to grain boundary blocking. The change in
polarization seems to be associated with hopping of charge carriers showing Arrhenius behaviour with increase in temperature.

The relaxation frequency of bulk transport for spray deposited BICOVOX0.1 thin film ranges from 96 KHz to 2.59MHz which is comparable to the reports in bulk samples for the same temperature range. The grain thickness estimated using ratio of grain and grain boundary capacitances proves diffusive nature of grain boundaries at higher temperatures above 640K. The blocking factor was found to be increasing with increase in temperature in low temperature region from 502 K to 640 K. At higher temperature above 640 K the diffusive nature of grain boundaries is inferred with the decrease in blocking factor. Same inference is derived by specific grain boundary conductivity calculations, specific grain boundary conductivity decreases in low temperature region while it increases rapidly for higher temperature. These changes are attributed to structural phase transformation, or ordering of vacancies in BICOVOX 0.1 films.

A00955-01676
What Does NMR Tell Us about Lithiation Processes in Nanosized Materials?
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NMR is a local characterization spectroscopic technique that does not require long range order in the materials studied; it is therefore appropriate for nanosized materials, although it suffers a relatively poor signal/noise ratio. It reveals a wide range of interactions experienced by the probed nucleus from its environment. When electron spins or delocalized electrons are present in the materials (as is often the case in active electrode materials for Li-based batteries) the so called hyperfine interactions usually dominate and govern the spectral shape (often making it rather broad) and position. Using magic angle spinning (MAS), it is often possible to determine the isotropic position of such spectra, and to exploit them to understand the lithiation/delithiation processes that occur when these materials operate as electrodes in Li batteries.

We will illustrate the kind of information that can be obtained using several classes of materials that we studied in ICMCB or in cooperation with other research groups in the framework of the ALISTORE European network of excellence.

Surface layers on the active materials can be identified by NMR, even in very small amount, like Li$_2$CO$_3$ on Li(Ni,Co,Al)O$_2$ materials depending on their storage conditions and their operation in batteries. LiF deposits were also observed using $^7$Li and $^19$F NMR on the surface of layered Li(Ni,Mn,Co)O$_2$ in which fluorine substitution was (unsuccessfully) attempted. (ICMCB).

The “interfacial” lithium that had been suggested earlier to appear reversibly after the conversion process in the lithiation of nano RuO$_2$ was observed by $^7$Li NMR. This species is clearly different from Li in Li$_2$O (resulting from the conversion) and from Li in the Solid Electrolyte Interphase that also forms in this system. (Cooperation with Max-Planck Institute, Stuttgart, Germany).

The extended single-phase domain in the lithiation of nano (anatase) TiO$_2$ vs. microcrystalline samples was clearly observed by $^7$Li NMR. (Cooperation with LRCS, Amiens, France).

The insertion and conversion mechanisms during lithiation of transition-metal phosphides were studied using $^{31}$P and $^7$Li NMR. This clearly reveals the presence or absence of Li,P as a result of the conversion. It also shows that the reconstructed materials upon Li extraction are different from the pristine ones. (Cooperation with Institut Gerhardt, Montpellier, France).

Because the MAS NMR studies are so far necessarily ex-situ, we will also address the question of the equilibrium state or stability of the nano-sized materials. It is indeed clear from the NMR studies in many cases that the lithiated materials are rather far from equilibrium (even though the overall kinetics of the reaction appears fast), and sometimes even unstable in the battery medium. This sets limits to the ex-situ characterization of such compounds, but also to the practicability of electrochemical systems based on them.

A01006-01789
Lithium Ion Conductivity at Interfaces of Multi-component Systems
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Composite systems, such as LiI / Al$_2$O$_3$, are well-known examples for exhibiting interfacial effects on the Li$^+$ ionic conductivity. The most likely model for the interfacial effects is that Li$^+$ ions are adsorbed on the Al$_2$O$_3$ surface, which subsequently generates lithium vacancies in the LiI. The composite material then has a strongly increased ionic conductivity compared to pure LiI.

In literature, there are many studies on the ionic conductivity of such composite systems as a function of particle sizes, preparation conditions and temperature. The systematic characterization of such composite materials however is problematic, since there are many more degrees of freedom, with some of these, such as the network arrangement into percolation domains, being purely stochastic due to frozen-in kinetics.
We have therefore decided to study the interfaces, that drive ionic conductivity in these composite systems, in a more systematic approach. By depositing layered structures with thin-film techniques such as rf-sputtering and MBE, we can precisely tune the layer thicknesses and interface spacings in these materials, and extract key parameters that are required to model the ionic conductivity of such systems. We report on recent results not only with regard to Li$^+$ ion conductivity, but also with regard to Li storage behavior, in composite, mesoporous, and thin-film systems.

A01018-01773

Electrochemical Performance of Sm – Doped LiFePO4 Cathode Material for Li – Ion Batteries

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Olivine type Sm – doped LiFePO4 cathode material has been prepared by sol – gel method and detailed structural characterization in terms of characteristic vibration spectral changes has been undertaken by means of X- ray diffraction (XRD), thermal analysis and Fourier transform infrared spectroscopy (FT- IR) respectively. The uniform particle size distribution of as- prepared olivine compound has been confirmed by the scanning electron microscopy (SEM) technique. Impedance measurements were carried out over the frequency range 1 MHz – 20 Hz at various temperatures in the region 298 – 500 K. The observed temperature dependence of electrical conductivity has revealed the applicability of the Arrhenius relationship. The electrical behaviour of modulus and dielectric permittivity over the above said temperature has revealed a non – Debye nature of conductivity relaxation and dielectric relaxations within the material. The addition of trace amount of Sm to the olivine LiFePO4 has indicated an improvement in the rate performance when compared to the undoped system. The results of the electrochemical charge/ discharge characteristics have suggested an improvement in the cycle performance in the case of Li$^+$ ion batteries based on Sm – doped LiFePO4 cathode when compared to that of the undoped LiFePO4 electrode.
suggest that the low Li+ ion conductivity in LiFePO4 is practically two-dimensional within the b-c-plane. Thus it has to be controlled whether a detailed structure model including likely defect scenarios affects the pathway prediction. Of particular importance are Li+/Fe2+ antisite defects. Both Fe•Li and Li•Fe get exactly the matching BV sums, so that an energetic disadvantage of antisite defects arises only from the BV sum mismatch of the surrounding O. Even for a hypothetical complete Li(Fe site exchange the global instability index (GII), i.e. the root mean square average BV sum mismatch would rise to GII = 0.035 to GII = 0.103. The effect of antisite defects on the local pathways is twofold: Fe•Li block the channel || b, but Li•Fe open up new connections between channels ⊥ b.

To achieve a percolating 2D pathway a sufficient number of antisite defects has to be present. From Monte Carlo simulations in a 180 × 180 Li site supercell we estimate the antisite concentration required to create a 2D percolating Li+ pathway in the b-c plane to 4.6% for a random defect distribution. Introducing a significant energetic preference for antisite formation in the vicinity of existing defects however reduces the percolation threshold to ca. 2.2%. While defect concentrations will strongly depend on the thermal history and stoichiometry, estimates from neutron diffraction are typically in the range 1-2 %. TEM visualisations also qualitatively suggest that antisite defects are to some extent clustered. Thus it appears feasible that samples produced under conditions favouring antisite formation exhibit 2D Li+ ion mobility.

Replacing Fe by other transition metal cations affects the antisite pair concentration. Except for Co3+: all the investigated transition metal cations lead to higher BV mismatches and lower antisite pair concentrations. Thus, except for the series LiFe1-xCoxPO4 no other LiMPO4 olivines will exhibit a similarly high tendency for antisite formation. In the intensely investigated LiMnP04 or LiNiPO4 no percolating pathways for Li transport ⊥ b can be formed. More detailed structure models are currently investigated to determine the effect of delithiation, nanosize and aliovalent dopants on the pathway dimensionality.

Effects of Ca Doping on the Electrochemical Properties of LiFePO4 Cathode Material

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Substituting Ca with Fe in LiFePO4 by the high temperature solid-state reaction method using sebacic acid as a carbon source has yielded better electrochemical performance. The Ca-doped LiFe0.99Ca0.01PO4/C composite material achieved a significant improvement in electronic conductivity from 1.3 x10-9 S cm-1 for LiFePO4 to 1.43 x10-4 S cm-1 for LiFe0.99Ca0.01PO4/C. In the galvanostatic charge–discharge, the composite cathode showed an initial specific discharge capacity of 149 mA h/g at a 0.2 C-rate between 2.8 and 4.0 V. The XRD results indicated that the LiFe0.99Ca0.01PO4/C compound resembled LiFePO4 in structure without affecting the lattice structure or enlarging the lattice volume. The Ca-doped composite materials were further characterized by SEM, TEM, EDAX and total organic carbon determination.

Ionic Conduction in a New PEO–AgCF3SO3–ZrO2 Based Nanocomposite Polymer Electrolyte System

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A novel approach has been adopted for developing Ag+ ion conducting nanocomposite polymer electrolyte batteries based on polyethylene oxide (PEO) – silver triflate (AgCF3SO3) complex dispersed with zirconia (ZrO2) nanoparticles that exhibit interesting electrochemical
properties. The observed position of conductivity maximum (1.7 × 10−5 S cm−1 at 295 K) depends on the Lewis acid-base type of interactions between the filler surface centres, ions, and ether oxygen base groups. Ionic conductivity and thermal behavior of PEO50AgCF3SO3 complex have been investigated with different levels of loading of nanosized ZrO2 powder whereas the complexation has been confirmed by X-ray diffraction and Fourier transform infrared spectroscopic analyses. A higher concentration (15 wt%) of strong Lewis-acid ZrO2 nanoparticles has led to suppression of the crystalline kinetics, which would have enhanced both the segmental motion and flexibility of polymer chain. Structural, Thermal and morphology results have also clearly demonstrated the reduction of crystallinity of the composite polymer electrolyte by the addition of fine ZrO2 nanoparticles. The nanocomposite polymer electrolyte while employed in the fabrication of electrochemical power cells has yielded an open-circuit voltage (OCV) of 557 mV and short circuit current (SCC) of 113 µA at 299 K.

A01153-01977

Effect of Vanadate Substitution on Chemical Stability & Bonding Geometry of FeO₆ and PO₄ in LiFePO₄

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In phospha-olivines, LiFe(VO₄)₃(PO₄)₉ₓ in particular, four oxygens are strongly covalent bonded to phosphorus forming the (PO₄)₄⁻ tetrahedral polyion and consequently difficult to extract. The present work focuses on the synthesis of nanoparticles of LiFe(VO₄)₃(PO₄)₉ₓ (x = 0.0 – 0.5) through an acetate-based non-aqueous sol-gel synthesis route and their structural, vibrational and magnetic characterization through XRD, FTIR and Fe-Mössbauer spectroscopy to investigate the chemical stability of the FeO₆ octahedra and PO₄ tetrahedra upon substitution of phosphate by vanadate. It is shown that material retains its orthorhombic structure even after 50% of the PO₄ is substituted by the VO₄. The substitution of vanadate breaks the chains of highly distorted FeO₆ octahedra and results in the valence transformation from ferrous to ferric at the atomic scale, leaving the molecular energy levels of the anion group unchanged. The variation in the bonding geometry at the Fe site has been quantified for the first time.

Acknowledgements:
One of the authors (YS) would like to thank UGC (India) for a JRF under Research fellowships in sciences for meritorious students (RFSMS) scheme.

A01158-02133

Speed of Response of Polypyrrole/Dodecyl Benzene Sulfonate Actuators in Aqueous Alkali Electrolytes

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Even though the Polypyrrole (PPy) polymer film doped with large, immobile dodecyl benzene sulfonate (DBS) anions is a good candidate for a soft actuator, a major limitation to its practical usage is the slow speed of response in aqueous electrolytes at high frequencies. The purpose of this study is to investigate the effect of cycling electrolytes containing different monovalent cations on the speed of response of the actuator. Aqueous solutions of 0.1 M alkali metal chlorides of Li, Na, K, Rb, and Cs were used for this study. The speed of response of the films was investigated using simultaneous cyclic voltammetry (CV) and Electrochemical Quartz Crystal Microbalance (EQCM) measurement, as well as force-displacement (FD) measurements. Free standing PPy/DBS films formed on stainless steel plate and peeled off were used for the FD studies and films formed on gold coated quartz crystal were used for CV and EQCM measurements. The FD studies show that the strain of the film decreases rapidly with increasing actuation frequency in all electrolytes used. However, the films have higher strains in NaCl and LiCl and very low strain in CsCl at all frequencies in the range 0.02 mHz to 0.1 Hz. The EQCM studies confirm that the amount of ionic species, solvated cations and osmotic water molecules that move into the film depends on the type of cations present in the cycling electrolytes. At higher frequencies PPy/DBS actuators show better speed of response if the cycling electrolyte contains highly solvated cations, i.e. Li⁺ and Na⁺.

A01162-01991

Effects of Various Aromatic Compounds on the Performance of LiFePO₄/C Composite Cathode by a Solid State Method

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Electronic conductivity of pristine LiFePO₄ is only 10⁻⁸–10⁻¹⁰ S cm⁻¹, which leads to initial capacity loss and poor rate capability. To improve the electrochemical properties of LiFePO₄ powders, LiFePO₄/C composite powders were prepared with various aromatic compounds by a high
Lithium Antimony Oxide Based New Anode Materials for Lithium Ion Battery

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To keep pace with the demand for high energy density lithium ion batteries, an alternative anode to replace the low performing graphite must be found. In the pursuit, several new materials such as Li$_4$Ti$_5$O$_{12}$, Si, Sn, Sn$_3$O$_4$, Sb, Sb$_2$O$_3$ and intermetallics have shown promises. Particularly, from the safety concern, it has been suggested that using a transition metal oxide host as anode would be much safer. During the course of experiments with Li$_4$Ti$_5$O$_{12}$/Sb composite anodes, we have found a new class of electroactive materials namely, the family of lithium antimonites which shows excellent performance as lithium battery anode. The materials have been synthesized by chemical mixing followed by thermal treatment at 800°C. The crystal structure and morphology of the synthesized lithium antimonites have been investigated by X-ray diffraction, field emission scanning electron microscopy and transmission electron microscopy. 2032 type coin cells versus Li have been fabricated and the electrochemical properties have been investigated by impedance spectroscopy, cyclic voltammetry and galvanostatic charge discharge. The new anodes show very flat charge discharge potentials at 0.3 and 0.45 V respectively. A large capacity of 600 mAhg$^{-1}$ has been obtained at a current density of 0.05 mAce$^{-2}$ which remains nearly constant up to 20 cycles. The detailed results on this new family of anode materials will be presented at the conference.

References

Ionic conductors are of great interest because of their applications in batteries, sensors... Solid ionic conductors have been found to exhibit an ionic conductivity similar to that of the best liquid electrolytes. Since the past ten years several groups have worked on solid ionic conductors and on a promising type: ionic conductor composites. In the early 70's, C.C. Liang has shown that the conductivity of LiI could be increased by several orders of magnitude when it was mixed with an insulating phase Al₂O₃ [1]. Since these pioneering works, various other works have been carried out on composite materials showing an improvement in conductivity correlated with the composition, the host matrix and its porosity. Physical properties of materials embedded in nanoporous solids were more and more studied and the strong influence of the nanoconfinement on the characteristics properties like melting, freezing, phase transition temperatures, diffusion... has been evidenced. Concerning ionic conductors’ field, effects of nanostructuration, as well as confinement, were investigated.

The most studied systems are AgI-based ones because silver iodide exhibits a first order phase transition β/γ↔α that generally occurs at 147°C (420 K). An anomalous behaviour in the form of a hysteresis loop in the electrical conductivity curve has been found for such systems whereas only a step in conductivity is obtained for ‘pure AgI’. The phenomenon can be explained by considering existence of AgI-polytypes [2] or by considering the effect of the nanoconfinement [3].

In a previous work it has been demonstrated that it could be possible to insert an ionic conductor with a weak solubility such as silver iodide using an electric field into bulk Vycor®7930 porous glass (VPG) [4]. Herein, we report the fabrication of AgI-Vycor®7930 composites using the ‘electrocrystallisation’ process and their characterisation by scanning electron microscopy, composition analysis by electron probe for micro analysis and phase identification by X-rays microdiffraction. The shape of the material led us to adapt the classical electrical measurement method and to use instead the here called ‘transverse mode’ method. Results of the electrical characterisation of the composites by complex impedance spectroscopy are reported. Firstly, the conductivity measurements have evidenced a conductivity enhancement of about 1.5 orders of magnitude at room temperature. Secondly, the presence of a shift in the phase transition temperature upon heating (150°C/423K) and cooling (110°C/383K), giving an hysteresis in the “conductivity versus temperature” curve because of the nanoconfinement has been observed.
Rapid charge and discharge reactions are required if Li-ion batteries are to be used for high power applications such as HEV. To enhance the charge and discharge reactions, fast Li-ion transfer at electrode/electrolyte interfaces as well as fast Li-ion transport through the electrodes and electrolyte are essential. Nano-sized active materials serve to shorten the diffusion path of Li-ion through them, and hence apparent rapid Li-ion diffusion through the electrode would be achieved. In addition, nano-sized particles provide a large surface area, and therefore Li-ion transfer resistances at electrode/electrolyte interfaces can be effectively decreased. Thus, nano-sized particles of active materials would affect the performance of Li-ion batteries. A number of studies have been done on the nano-sized materials in Li-ion batteries. However, nano-sized particles generally have a large distribution in particle size, and are agglomerated. Nano-sized particles with a uniform size should be very useful to study the effect of the particle size on the electrochemical properties definitely.

In this work, uniformly nano-sized particles of olivine LiMnPO$_4$ were synthesized in nonaqueous solution at around 280 °C.

Manganese nitrate hexahydrate and lithium hydroxide monohydrate were dissolved in oleic acid, oleylamine, phosphoric acid, and 1-octadecene. The mixture was kept at 280 °C for 3 h under argon atmosphere. After cooling to 70 °C, the solution was poured into ethanol and the resultant mixture was centrifugally separated. The deposits were washed several times in a mixture of hexane and ethanol by centrifugation. The products were characterized by X-ray diffraction (XRD). The LiMnPO$_4$ particles dispersed in hexane were deposited on micro grids to observe their morphology and microstructure by transmission electron microscopy (TEM). Electrochemical properties of the LiMnPO$_4$ particles were studied by charge and discharge measurements using a two-electrode coin cell. A working electrode consisted of the LiMnPO$_4$ particles, acetylene black, and PVdF-binder. A Li foil was used as a counter electrode. An electrolyte used was 1 mol dm$^{-3}$ LiPF$_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate. All experiments were conducted under an argon atmosphere with a dew point below -60 °C.

XRD pattern of the resultant particles indicated that single-phase olivine LiMnPO$_4$ was obtained. TEM images clarified that LiMnPO$_4$ particles had a distinct crystal form, i.e. rectangle, and their size was about 10 nm. The LiMnPO$_4$ particles were not agglomerated but spaced-apart and highly dispersed. FT-IR spectra suggested that oleic acid attached on the LiMnPO$_4$ particles, and hence the particles could be dispersed by the effect of steric hindrance of oleic acid molecules. Since the organic ligands could be replaced by other functional molecules, their effects on the electrochemical properties were investigated.

Polyaniline (PANI) films were deposited on glassy carbon substrates using direct current and cyclic voltammetric electropolymerizations by controlling deposition time, deposition potential and solution concentration. The bonding structure and surface morphology of the films were characterized using X-ray photoelectron spectroscopy (XPS) and scanning-electron microscopy (SEM). An anodic stripping performance of the PANI modified glassy carbon electrodes was investigated in HAc and NaAc buffer solution by detecting single-elements (Cd$^{2+}$ and Pb$^{2+}$) and multiple-elements (Cd$^{2+}$ + Pb$^{2+}$) with square wave anodic stripping voltammetric method. The experimental results were presented in terms of pH value, preconcentration time and potential, and film thickness.

Pd thin film electrodes were successfully prepared by magnetron sputtering method taking Si wafer as substrates. The surface morphology was characterized by scanning electron microscopy. Electron transfer processes of Fe(CN)$_6^{3-}$ and Ru(NH$_3$)$_6^{3+}$ redox probes at the electrodes were studied by cyclic voltammetry and electrochemical impedance spectroscopy. Importantly, Pd thin film electrodes without and with the modification of SCN$^-$ presented excellent electrochemical sensing to nitric oxide and peroxynitrite. And the NO$^-$ and O$_2$-saturated solutions didn’t interfere with electrochemical sensing of peroxynitrite at Pd thin film electrodes.
Vanadium Oxide \((V_2O_5)\) Nanobelts for Supercapacitor Applications

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High yield vanadium oxide \((V_2O_5)\) nanobelts with around 50nm in thickness and 150nm in width were formed through hydrothermal process. Phase transformation from cubic to tetragonal was observed after the annealing with the specific capacitance improved from 116 F/g to 223 F/g. Two additional redox peaks were observed on the annealed sample which corresponded to the phase transition from \(\alpha\) to \(\varepsilon\) phase upon Li intercalation. Cyclic voltammetry study was applied to the nanobelt samples for the scan rate ranging from 5mV/s to 1000mV/s and the current components in the charging process were studied for understanding in Li charge storage. The inserted charges in transition metal oxide supercapacitor were contributed from two main aspects, namely surface dependent capacitance and diffusion controlled capacitance. The ratio of the two capacitances could be extracted from the scan rate studies based on their different degree of scan rate dependent. The annealed sample was found to have the enhancement in both capacitances with a slight increase in surface dependent capacitance proportion from 57% to 66% after the annealing.

A01304-02542

Studies on Dielectric Properties in Polymer-clay Nanocomposite Electrolyte

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Solid polymer electrolytes (SPEs) formed by complexation of macromolecular polymer (polymer must contain a Lewis base) with alkali metal salts are of high technological importance for rechargeable lithium ion batteries. The main obstacle towards the practical realization of all solid state rechargeable Li batteries using such SPEs is their low ionic conductivity at ambient temperature. Furthermore, the mechanism of ionic transport behavior in polymer electrolytes is still not well understood. Hence it becomes important to understand the ion transport behavior (ion polymer, ion-ion interactions) along with polymer segmental relaxation processes, which ultimately govern the conductivity of polymer electrolytes. To understand the ion transport behavior and obtain the information characteristics of ionic and molecular interactions in solid polymer electrolytes, the study of dielectric relaxation properties is an essential tool.

In view of the above, a series of free standing solid polymer electrolyte films based on polyethylene oxide (PEO) and LiAsF₆, where EO/Li ranged from 5 to 100 were prepared using solution-casting method. The electrolyte films (100-150 \(\mu\)m) were characterized by XRD, DSC, and dielectric spectroscopy. The XRD and DSC results revealed the semicrystalline nature of all films. Conductivity values were calculated from impedance measurements using a small a. c. signal (10 mV) across the sample cell with blocking electrodes. The conductivity increased with increasing salt content and showed a maxima at ~ EO/Li = 20, the maximum value of the conductivity at 293 K was ~ \(2 \times 10^{-4}\) S/cm. In order to minimize the contribution of dual ionic motion, the optimized EO/Li ratio (from conductivity point of view) in the electrolyte has been subsequently integrated into organically modified Na montmorillonite clay to form polymer nanocomposite electrolytes (PNCEs). The PNCEs have been prepared by intercalating an appropriate amount of polymer/polymer–salt complex in nanometric channels of inorganic clay. The addition of 2% clay increased the conductivity by more than one order of magnitude at 273 K. The temperature dependence of the conductivity followed VTF behavior suggesting the coupling of conductivity to the polymer segmental relaxations. The coupling of conductivity to the segmental process will be discussed in terms of coupling index.

A01313-02297

Effect of Preparative Method on the Properties of \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}\): The Oxygen Permeable Membranes

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Solid oxide fuel cells (SOFCs) are currently attracting considerable interest as stationary power generators due to the high efficiency and low levels of pollution. Fuel cells have been commonly accepted to be a kind of clean, safe and convenient power source with high energy efficiency, and have been on the verge of revolutionizing the electric power industry by offering better ways to produce electricity and to deliver it to the consumers. To be promising oxygen separating membrane material, it must possess high oxygen permeability as well as stable lattice structure under changes in oxygen partial pressure. The structure of the porous electrodes has been critical for the performance of a SOFC. The \(\text{Ln}_{x}\text{Sr}_{1-x}\text{Co}_{y}\text{Fe}_{1-y}\text{O}_{3-\delta}\) (\(\text{Ln=La,}\)
Pr, Nd, Sm), and Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{y-δ}$ (BSCF) compounds have been also evaluated and achieved excellent results in both dual-chamber and single chamber configurations. The development of innovative processing methods through chemistry permits one to lower the preparation temperature and to improve homogeneity and reproducibility ceramics. Furthermore, it facilitates synthesis of porous, ultrafine and chemically pure powders of mixed metal oxides.

In the present investigation, the perovskite Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{y-δ}$ were prepared using glycine nitrate route, EDTA-citric acid method and solid state sintering in order to tailor apt permeation membrane in terms of crystalline size, grain shape and electrical conductivity. Samples were characterized by x-ray powder diffraction and scanning electron microscopy. The electrical conductivity was measured using the four-point dc technique. The thermal properties were studied with the help of DTA/TG.

The XRD study confirms the formation of solid solution irrespective of preparation technique. Amongst all preparation techniques EDTA-citric acid method yields smallest particle size. SEM study suggests the agglomeration leading to porous material. The conductivity results are understood on the basis of structural characterization.

The present work is focused on the development of anode material for SOFC. The Ce$_{1-x}$Cu$_x$O$_{3-δ}$ anode material with $x = 0.05, 0.1, 0.3, 0.4, 0.5$ and $0.6$ were prepared by combustion method using nitrates as starting materials, and glycine as a fuel. The prepared samples were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM).

The crystal structure of the prepared sample is found to be cubic fluorite. The crystallite size reduces with increase in copper concentration. SEM study reveals the agglomeration of nano size grains leading to sufficient porosity. The combustion method gives nano size material with improved homogeneity.

A01316-02303

All-solid-state Batteries Seen from a Multi-dimensional Perspective

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Micro-batteries are expected to become more and more important in numerous small-sized devices, like medical implants, biosensors, hearing aids and autonomous network devices. Characteristic for these electronic applications is that they have to operate autonomously and reliably. Due to these requirements the thin film power source needs to be rechargeable, mechanically stable for a long period of time and hence reveal an extremely long cycle life. As the average energy consumption of these future devices will be rather small, this opens up the possibility to integrate all-solid-state rechargeable batteries, enabling a high degree of IC integration.

It has been reported that all-solid-state, Li-based, rechargeable batteries can be charged and discharged more than 10,000 times without significant degradation. These thin-film batteries are, however, planar-structured, resulting in a relatively low energy density. By depositing the complete battery stack in a 3D etched substrate, obtained by for example physical or wet-chemical etching of mono-crystalline Silicon-wafers, the effective energy and power density can be tremendously increased. Moreover, utilizing novel battery anode materials with a very high storage capacity comprising of thin films electrodes are highly beneficial.

Silicon wafers are common substrates in semiconductor industry, and also the anisotropic etching of several 3D geometries (e.g. pores, trenches and pillars) using reactive ion etching is a relatively mature technique. The step conformal deposition of battery layers into these structures require non-line of sight techniques which are, on one hand, established in the production of integrated devices but are, on the other hand, still mostly unexplored for the
deposition of battery materials. These methods include Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD).

In this presentation the concept of the 3D-integrated battery will be discussed and the highlights in the experimental investigations will be shown. The focus of this contribution will be on the exploration of CVD and ALD as deposition techniques for thin-film micro-batteries. Moreover, the (electro-)chemical characterization of several active battery layers will be discussed.

A01318-02305

Conductivity and Stability of Particle Networks in Composite Lithium Based Electrolytes
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All solid state electrochemical devices such as lithium ion batteries, electrochromic windows and dye sensitized solar cells require solid, though flexible electrolyte matrices, which allow fast ion transport. Plastic materials, polymers, gels, ionic liquids/zwitterions are relevant examples, some of which in their crystalline or ordered form, exhibit significant but not really sufficient ionic conductivity at room temperature.

We successfully applied the concept of Heterogeneous Doping to composite electrolytes consisting of solid oxide nano-particles e.g. SiO₂ in lithium salt solutions using non-aqueous solvent.

At high oxide-particle content, the investigated systems show enhanced conductivities compared to liquid electrolytes. Furthermore, the insulating oxide particles in the electrolyte matrix provide improved mechanical properties, which are again advantageous for electrochemical devices. The composite conductors were characterized using dc-polarization measurements, ac-impedance spectroscopy, DSC, zeta potential measurements and viscosimetry. Oxide particle size, surface area and volume fraction, as well as solvent molecular weight and viscosity, time and temperature were varied to understand the conduction mechanism together with the percolation behaviour in the system.

To supplement the experimental findings, we employed Monte Carlo Random Walk simulations to model the network formation. The filler particles randomly and dynamically create clusters, and for a certain concentration threshold, a stable cluster is formed which allows percolation of the ions in the cluster. Here we address the question why the network, having reached the percolation threshold, may become unstable and collapses by addition of a little excess of the filler particles. We model the network formations by to an irreversible hit- and stick-mechanism. Once a percolating network is formed, it can coarsen on a long time scale to minimize their surface energy, which then leads to an interruption of the network percolation and the observed decrease in the overall conductivity.

Interfacial Structures of Intercalation Materials during the Electrochemical Process
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Interfacial reactions between the intercalation electrodes and electrolyte have attracted much attention in recent year to achieve high current drain and long-term stability of lithium batteries. A series of reactions takes place at the interface: lithium diffusion in the electrolyte, adsorption of solvated lithium on the electrode surface, de-solvation, surface diffusion, charge-transfer, and intercalation from the surface to the bulk crystal. Electrochemical analyses point to de-solvation as the rate-determining step in battery reactions among the series of electrochemical reactions taking place at the interface. However, in the absence of detailed information on each reaction, the key factors that determine rate capabilities remain unclear. High-resolution insight into the interface during electrochemical reactions is a prerequisite for an atomistic understanding and control of kinetics in lithium battery reactions. In the present study, we tried to design an ideal electrode suitable for investigating interfacial reactions at the two-dimensional electrode surface using epitaxial film electrodes.

The epitaxial films of intercalation materials, LiMnO₄(M=Co,Ni,Mn), LiMn₂O₄, LiFePO₄, and Li₄Ti₅O₁₂, were deposited on SrTiO₃ single crystal substrates (0.5wt%Nb doped) using a pulsed laser deposition (PLD) method. Orientations of the electrode films were successfully controlled by changing substrate lattice planes. The orientations of (110), (104) and (003) were obtained for LiCoO₂, LiNi₀.₅Co₀.₅O₂, and LiNi₀.₅Mn₀.₅O₂ with the layered rocksalt structure, (110) and (111) for LiMn₂O₄, and Li₄Ti₅O₁₂ with the spinel structure, and (100) for LiFePO₄ with the olivine structures. Most of these oxide electrodes have impurity phases in the pristine sample, and these phases disappeared with the contact with the liquid electrolyte. Surface and bulk structural changes were observed during the electrochemical reaction. Changes...
in the surface structure during the electrochemical (de) intercalation reactions were different from those observed for the bulk structures. The surface structural changes are dependent on the materials. Surface of the olivine and the nickel-manganese layered materials are rather stable while the spinels showed various structure changes during the electrochemical reaction. The surface structural changes might be related to the stability of the electrode during the electrochemical reactions. Reaction mechanism of the intercalation electrodes for lithium batteries will be discussed based on new insight into the surface and bulk structural changes using epitaxial model electrodes.

A01356-02369
Phosphorus Poisoning Effects on Nickel/Yttria-stabilized Zirconia Anode of Solid Oxide Fuel Cells
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Coal-derived syngas (CSG) that is fed into the SOFCs in the IGFC systems is a “dirty gas”, which contains various impurities such as phosphorus, arsenic, zinc, sulfur, mercury, selenium and vanadium. This work deals with the phosphorus poisoning effects the Ni/yttria-stabilized zirconia (YSZ) anode of the solid oxide fuel cell in the coal syngas in the temperature range from 750 °C to 900 °C. Electrochemical impedance analysis shows that both the charge transfer resistance and the diffusion resistance increase with time during exposure to the P-containing syngas. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) studies show that the phosphorous impurity reacts with the Ni-YSZ anode to form secondary phases of nickel phosphate and zirconium phosphate phosphates. The P-impurity poisoning leads to the deactivation of the Ni catalyst and to the reduction of the electronic and ionic conductivities of the anode. The impurity poisoning effect on the anode is controlled by three governing factors: the operating temperature, the PH3 concentration and the applied bias.

Micro and Nanostructured Materials for Lithium Battery Applications

With the demand for battery capacity and power exceeding what current materials can deliver, much attention is now being turned to lithium-ion cells incorporating nanotechnology. As battery applications evolve from lighting a flashlight to moving a vehicle to load-leveling a power grid, new technology will be needed to shorten diffusion paths, increase packing densities, and assure safe operation of cells from the bottom up. To this end, researchers at Argonne National Laboratory and the University of Illinois have been collaborating to create and advance the key nanotechnologies needed for tomorrow’s batteries. We have been developing low-cost, low-temperature methods for the formation of aligned arrays of nanowires – ideal structures for next-generation battery electrodes. Unlike techniques described in the literature, our method uses no gold catalysts, no toxic materials, no photolithography, no expensive anodized alumina templates, and no processing temperatures above 200°C. It can grow nanowires on virtually any current-collecting surface. The process can make nanowires of virtually any solid material that can be deposited by physical vapor deposition, so nanowire arrays can be grown for either the positive or negative electrode, as desired.

In this presentation we’ll describe the growth of aligned silicon nanowire electrodes, which were synthesized by a low-temperature, ion-enhanced, reactive Vapor-Liquid-Solid (VLS) method. Synthesis of these randomly-ordered arrays begins with a thin indium film deposited on a Si or SiO2 surface. At the processing temperature of 190°C, the indium film becomes a self-organized seed layer of molten droplets, receiving atomic silicon from a DC magnetron sputtering source rather than from the gaseous precursors used in conventional VLS growth. Simultaneous vigorous ion bombardment aligns the objects vertically and expedites mixing of oxygen and silicon into the indium. Oxide precipitates from each droplet in the form of multiple thin strands having diameters as small as 5 nm. These strands form a single loose bundle growing normal to the surface, eventually consolidating to form one nanowire. The vertical rate of growth can reach 300 nm min⁻¹ in an environment containing argon, hydrogen, and traces of water vapor.
We will discuss the assembly of a custom-designed chamber for nanostucture growth, describe the preparation of silicon nanostructured electrodes, and show cycling and impedance data obtained on these electrodes. Our nanowire Si arrays survive repeated cycling, show excellent electrode impedance levels, and have faster charge-transfer dynamics than conventional graphite-based electrodes. The potential and challenges involved in assembling solid-state cells from these electrodes will be briefly discussed.

Acknowledgements:
The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory (“Argonne”). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. We acknowledge the use of the Center for Microanalysis of Materials (CMM) at the Frederick Seitz Materials Research Laboratory, which is partially supported by the U.S. Department of Energy under grant DEFG02-91ER45439.

Ab Initio Prediction of Nano-scale Platinum Dissolution in Aqueous Environments

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The mechanism behind the observed performance loss of the Pt catalyst in low-temperature fuel cells is not well understood. Using ab initio methods, we predict the dissolution potential of nano-sized Pt in an aqueous environment as a function of pH. We calculate 0.5 – 2 nm diameter Pt nanoparticles with varying degrees of O and OH surface absorbates, optimized by site and particle surface structure, and then equilibrate them in water at a specific pH. Dissolved species are incorporated from experiments. Thus, we are able to predict the thermodynamic stability of nanoparticle Pt in equilibrium with water, as a function of particle size, potential and pH. As a result, the Pourbaix diagram of nanoparticles shows substantially enhanced dissolution for the smaller Pt nanoparticles compared to the larger particles. Furthermore, we conclude that surface passivation effects from O and OH adsorption do not significantly increase the stability of the nano-particle phases in the potential-pH region relevant for fuel cell operating conditions. Thus, we can identify size-dependent dissolution as a mechanism, which will promote the growth of larger particles at the expense of smaller ones and ultimately cause a degradation in the nanoparticle Pt catalyst performance.

First Principles Modeling of Nano and Bulk Materials for Li Batteries

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First principles methods, in which the properties of a material are computed from quantum mechanics have shown to be capable of predicting many materials properties. For Li battery electrodes, they can predict voltage, crystal structure, stability, Li mobility, electron mobility, surface structure, and even thermal decomposition in the charged state. To investigate nanomaterials, first principles methods are particularly useful as they offer full control and specification of the size and chemistry of the system, which is often difficult to achieve experimentally. We have been systematically investigating how the lithiation potential, stability, and phase transition differ between nanosize materials and bulk. For most metals, the variation in Li potential at the surface gives a substantial perturbation to the system and leads to the disappearance of first order phase transitions in particle with small size. We have verified this with experiments and ab initio computations on Co and Pt and a theory for the modification of Li potential by the surface of nanoscale systems will be presented. We have also studied the change of lithiation potential in LiFePO4 with size. Since nano particles have a very large fraction of material in or near the surface, we have systematically calculated the energy and electrochemical properties of the different surfaces of LiFePO4 using first principles Density Functional Theory. The results indicate that, surprisingly, some surface have a lower redox potential than the bulk, while other ones have a higher redox potential. We have put these results together into a model for the voltage profile and solubility in LiFePO4 as function of particle size, which we believe explains many of the recent observations on nanosize LiFePO4. In LiMnP04 most surfaces lithiate below the bulk potential. We believe that this has significance for the different rate capability of the material.

As first principles methods do not rely on experimental input they can be automated and applied to a wide variety of systems. It will also be shown how high-throughput computing can be used to search for new battery materials across a very large number of possible chemistries. We believe that such high-throughput searches can provide the essential information and new ideas to make the experimental development of better electrode materials more efficient.
Nano-Micro Composites as High Capacity Anode Materials for Li-ion Batteries

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Nanostructured materials have attracted much attention as high capacity anode materials for Li-ion batteries, i.e., tin composite oxide, nano-Si, nano-SnSb alloy, and transition metal oxides. Due to high surface energy, stand-alone nanostructured materials show serious electrochemical agglomeration and drastic surface side chemical and electrochemical reactions in nonaqueous electrolyte, leading to poor cyclic performance, low columbic efficiency and poor kinetic performances. In order to solve these problems, structure modification has been considered to stabilize nanostructured materials, such as growing nanoparticles or nanowires on a stable core or substrate, forming a core/shell structure where nanoparticles are covered by a stable surface protection layer. Since small surface area is favorable for achieving high efficiency, therefore, nano-micro composite with core/shell structure seems better choice. It has also an advantage of high tap density. Here we report our investigations on several nano-micro composites, where core materials are Cr$_2$O$_3$, MnO and Si and the shell is carbon mainly. Surface reaction, polarization analysis, effects of using alternative binder and surface film forming additive in the electrolytes will be discussed mainly.

Acknowledgement:
Financial support from NSFC (50672122, 50730005), “863” project (2006AA03Z228) and “973” project (2007CB936501) are appreciated.

MnO Anode for Lithium Ion Batteries

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Poizot et al reported for the first time that lithium can be stored reversibly in transition metal oxides mainly through heterogeneous conversion reaction: \( \text{Li} + \text{TMO} \rightarrow \text{Li}_2\text{O} + \text{TM} \) (1) (TM=Co, Fe, Ni, Cu). Later, reversible lithium storage was also observed in transition metal fluorides as well as sulfides, nitrides and phosphides. One of the interesting points for this type of lithium storage is that very inert and insulating LiF or Li$_2$O takes part in electrochemical reaction at room temperature. The enhanced reactivity of LiF or Li$_2$O is believed to be related to the special microstructure of converted LiX/TM nanocomposites where LiX and TM have extremely small grain size (<5 nm) and interspersed uniformly. TMX materials with low electrochemical motivation force (emf) values for conversion reaction are desirable as anode materials for Li-ion batteries. It is noticed that nearly all transition metal oxides show high overpotential over 1.0 V for both lithiation and delithiation. Consequently, Cr$_2$O$_3$ and MnO are a few of oxides among transition metal oxides which have high lithiation capacity and relatively lower emf values (1.085 V and 1.032 V vs. Li/Li$^+$ respectively). Cr$_2$O$_3$ has been studied comprehensively. As for MnO, the only report indicates that MnO powder electrode could be discharged and charged under a very small current density (1/300 C) by a potentialstatic intermittent titration technique (PITT) mode. Here we report that both nanocrystalline MnO thin film electrodes and MnO powder electrodes show high volumetric capacity, rate performance, good cyclic performance and relatively low polarization compared to other TMO compounds at room temperature. Thermodynamic and kinetic properties of MnO anode in lithium ion batteries as well as the structure evolution during charging and discharging will be discussed.

Acknowledgement:
Financial support from NSFC (50672122, 50730005), “863” project (2006AA03Z228) and “973” project (2007CB936501) are appreciated.

Molten Salt Synthesis of La$_{0.8}$Sr$_{0.2}$MnO$_3$ Powders for SOFC Cathode Electrode

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SOFC have high operating temperature, therefore the cathode electrode of SOFC is needed high oxidation safety and ionic conductivity. One of the suitable cathode electrode for SOFC is La$_{0.8}$Sr$_{0.2}$MnO$_3$(LSM), but its conductivity decreases due to the formation of 2nd phases during electrode formation process, thus the temperature of the electrode formation needs to decrease through synthesis of fine LSM powders. The method is frequently used liquid methods, such as coprecipitation and sol-gel methods, but it has very complex process and difficult to achieve the uniform compositions.

In this study, LSM powder was prepared by molten salt synthesis method which is easy to control of particle size and low synthesis temperature, and it’s conditions were changed with synthesis temperature and a variety...
of salt. Especially LSM powder could be synthesised at low temperature (650°C) used mixing salt of KF and KCl with mol ratio of 0.45:0.55. LSM powder which is suited cathode electrode of SOFC was synthesised from mixing powder of salt and raw powder with 1:1 of weight ratio.

A01393-02438

Synthesis of CIGS(CuInGaSe₂) Nano Particle for Thick Film Process CIGS Solar Cell

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The disadvantage of CIGS solar cells prepared by thin film process is more expensive and complex processes. It is increased an attention for preparing the CIGS nano particles suitable for a thick film CIGS solar cells. The synthesis of CIGS is used such as solvothermal and colloidal method. Among the various synthesis of CIGS, solvothermal synthesis method is frequently used to have many merits such as feasibility of particle size control and low temperature and pressure.

In this study, we used solvothermal method and CIGS nano particle was suitably synthesised for a thick film CIGS solar cell. The crystallinity of particles was analyzed by XRD. The properties of particles were evaluated for the suitability of thick film CIGS solar cell by SEM, particle size analysis, and B.E.T.

A01439-02496

Development of Sulfide Glass-ceramic Electrolytes for All-solid-state Lithium Rechargeable Batteries

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An all-solid-state lithium rechargeable battery using inorganic solid electrolytes is one of the ultimate goals of rechargeable energy sources because of its high level of safety, reliability and energy density. Solid electrolytes with high Li⁺ ion conductivity are a key to improve electrochemical performance of solid-state batteries. Li₅S₆ based sulfide glasses prepared by melt quenching and mechanical milling techniques are a promising solid electrolyte for solid-state batteries. In particular, LiₓS₋₅PₓS₅ glass-ceramic electrolytes, which are obtained by careful crystallization of glasses, exhibited high conductivity of over 10⁻³ S cm⁻¹ at room temperature and wide electrochemical window of over 5 V. Superionic LiₓPᵧS₁₋ₓPₓS₅ crystals were precipitated at selected compositions and these crystals are responsible for high conductivity of glass-ceramic electrolytes. A partial substitution of P₂O₅ or PₓS₅ for P₅S₅ is also effective in enhancing conductivity and electrochemical stability of the LiₓS₋₅PₓS₅ electrolytes.

All-solid-state batteries using the LiₓS₋₅PₓS₅ glass-ceramics were fabricated in order to evaluate the cell performance as a lithium rechargeable battery. The cells In / 80LiₓS₋₂₀PₓS₅ (mol%) glass-ceramic / LiCoO₂ exhibited excellent cycling performance of over 500 times with no decrease of the capacity (100 mAh⁻¹) at limited current densities. The coating of LiCoO₂ particles with oxide and sulfide thin films improved rate performance of the solid-state cells, suggesting that the formation of a suitable electrode-electrolyte solid-solid interface is important for developing battery properties. The In / coated-LiCoO₂ cell worked as a lithium rechargeable battery under the high current density of 38 mA cm⁻² at 100 °C.

Active materials of sulfur, metal sulfide and metal phosphide were useful for application to all-solid-state batteries with large energy density. Establishing favorable solid interface and large contact area between electrode and electrolyte is a key issue to enhance battery performance. Nanocomposite materials, where NiS electrode nanoparticles were embedded in the LiₓS₋₅PₓS₅ electrolyte matrix, were prepared using a planetary ball mill apparatus. In this process, electrode and electrolyte were formed at the same time during mechanochemical reaction. An all-solid-state cell using the NiS / LiₓS₋₅PₓS₅ nanocomposite material retained large capacity of about 400 mAh g⁻¹ for 50 cycles at 1.3 mA cm⁻². Mechanochemical process is a useful technique to establish close contact at the electrode-electrolyte interface.

A01443-02513

Inhibitor Effect of Sodium Benzoate on Corrosion Behaviour of Nanocrystalline Pure Iron Metal in Near-neutral Aqueous Solutions

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Nanocrystalline iron was produced by pulse electrodeposition using citric acid bath. The grain size of a nanocrystalline surface was analyzed by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The electrochemical behavior of nanocrystalline Fe in the presence of sodium benzoate was evaluated in 0.1 N Na₂SO₄ aqueous solution using tafel polarization curves and electrochemical impedance spectroscopy (EIS) and compared with that of coarse-grained iron. The thermodynamic data of adsorption are determined.
Results obtained revealed that the inhibition effect and corrosion protection of sodium benzoate inhibitor in near-neutral aqueous solutions increased as the grain size decreased from microcrystalline to nanocrystalline. This was discussed in terms of excess free energy caused by nanocrystalline surface.

Further grinding up to 25-min lead to large voids, increased resistivity and poor electrochemical behavior. The best electrochemical was observed after grinding for 20 min, which is linked with a low resistivity.

Electrochemically Co-deposition of Manganese Oxide /Polypyrrole Composite Films as Supercapacitor Electrodes
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The manganese oxide/polypyrrole (Ppy) composite films were electrochemically synthesized by the aidance of nonionic surfactant in the manganese acetate and pyrrole solution. FT-IR spectroscopic studies indicated that the ratio of manganese acetate and the pyrrole monomer influenced the content of Ppy in the composite films. It was found that the oxides and polymers components were regularly dispersed at the nanometer level in the composite films by scanning electron microscopy. Capacitance behavior was studied by cyclic voltammetry and galvanostatic charge/discharge cycling in a potential range from 0 to 1 V vs. SCE in 3 M potassium chloride solution. Specific capacitance of about 390 mF cm⁻² was obtained at the scanning rate of 10 mV s⁻¹.

Acknowledgement:
The authors wish to thank for the financial supports by the National High Technology Research and Development Program of China (Grant No.2007AA03Z249).

Olivine Nanofibrous Cathodes for Lithium Ion Batteries
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Concurrent with progress in rechargeable lithium batteries (secondary lithium batteries), several lithium-conducting compounds have been intensively studied. Among them, lithium transition metal phosphates (olivines) have attracted immense interest as storage cathodes for rechargeable lithium batteries because of their high energy density (150-170mAh/g), low raw materials cost, environmental friendliness and safety. A large variety of synthesis methods including hydrothermal routes, sol-gel and solid state syntheses have been devised to synthesize olivines (in various degrees of crystallinity) like LiFePO₄ and related compounds like LiCoPO₄ and LiMnPO₄. Electrochemical extraction of lithium from the olivine LiFePO₄ is accompanied by a direct transition to FePO₄ in which the Fe²⁺ ions are oxidized to Fe³⁺ ions leaving the olivine FePO₄ framework intact. So during charge/discharge LiFePO₄ electrodes are composed of LiFePO₄ and FePO₄ which are both poor electronic conductors. This extremely low electronic conductivity (10⁻⁹-10⁻¹⁰S cm⁻¹) has been the key limitation of olivine phases. Attempts have been made previously to enhance its electronic conductivity by coating with carbon (usually by means of pyrolysis of co-synthesized organic compounds), doping with metal ions and also reducing the particle size to the nanometer range. Among the various nanostructured architectures, the nanofibre morphology has been previously mentioned to be more electrochemically strain-resistant as compared to nanospheres, nanopowders and thin films.

In this study, we have adopted hydrothermal and electrospinning techniques for fabricating inorganic nanofibers of doped and undoped olivines. Electrospinning makes use of a high accelerating voltage to generate an electric field, which overcomes the surface tension of a polymeric solution and ejects a continuous jet, leading to the production of nanofibres on the collector surface upon evaporation of the solvent. The advantages of this process is the resulting nanofibre mats possess large surface area and small pore sizes which would facilitate lithium-ion transport by providing small electronic resistance and short diffusion pathway, and hence can deliver higher rate lithium-ion storage capability, faster charge-discharge kinetics,
and better cyclic stability. There exists the possibility of producing LiFePO$_4$ nanowires in a randomized or ordered network as well. In addition, the length and diameter of the oxide nanofibres are varied by controlling the fabrication conditions including gel viscosity, electric field, flow rate and collector plate and needle distance. The effects on the electrochemical and intercalation properties of the resulting nanowires are studied. Using this technique, nanocomposites of olivines along with carbon based materials (carbon nanotubes, that possess very large surface area [-1000-1600m$^2$/g], excellent electrical conductivity [-10$^{-1}$-10$^{8}$S/cm]) will be studied in an effort to improve the electronic conductivity, as the electrospinning technique also gives the possibility of co-spinning different materials simultaneously. Detailed fabrication procedures, characterization and electrochemical test results will be presented and discussed.

Acknowledgements:
The authors thank Région Aquitaine for financial support.

**Mechanochemical Synthesis of Na-beta-$\text{Al}_2\text{O}_3$**

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Na-beta-$\text{Al}_2\text{O}_3$ has been used as a solid electrolyte in the sodium sulfur (NAS) battery because of its high Na$^+$ conductivity. Na-beta-$\text{Al}_2\text{O}_3$ is known to be nonstoichiometric oxide, assigned the formula Na$_x$O$_{2-x}$Al$_2$O$_3$ ($5 \leq x \leq 11$). The most common fabrication method of Na-beta-$\text{Al}_2\text{O}_3$ is solid state reaction at a temperature usually between 1200-1700 °C with alpha alumina and sodium compound as raw materials. The overgrowth of grains at high temperature has been an obstacle for the fabrication of Na-beta-$\text{Al}_2\text{O}_3$ with preferable electrochemical performance. Mechanochemical method is a favorable approach to prepare powders with fine particle size. In this paper, fine Na-beta-$\text{Al}_2\text{O}_3$ powders were prepared by mechanochemical process. The difference in phase and microstructure between powders obtained in mechanochemical process and traditional route was investigated. The mechanism of mechanochemical fabrication of Na-beta-$\text{Al}_2\text{O}_3$ was discussed.

A stoichiometric amount of sodium source and aluminium source were mixed, mechanically activated (MA) and then calcined. The contrastive sample was directly sintered at the same temperature without mechanical activation. Difference in phase and microstructure of final powders were characterized by X-ray diffraction (XRD) and electron probe micro analysis (EPMA). The influence of the mechanical activation in the sintering thermodynamics of precursors was investigated with infrared spectrum (FTIR) and differential scanning calorimetry (TG-DSC).

Phase analysis results showed that the powders prepared by mechanochemical processing consisted of $\beta^+$-$\text{Al}_2\text{O}_3$ and $\beta$-$\text{Al}_2\text{O}_3$. Main phase of sample without mechanical
activation was NaAl\(_2\)O\(_4\). The powders directly calcined without mechanical activation have an average grain size of 2-3 μm. The average grain size of powders calcined at the same temperature was decreased to submicron dimension by MA. It was discovered that MA for the precursors before calcination increase greatly its thermodynamic activity. Transformation from crystalline to amorphous state of the precursors during the MA process was observed.

The overgrowth of grains appeared in the fabrication of Na-beta-Al\(_2\)O\(_3\) in a traditional high temperature solid reaction was restricted by the MA process, which is beneficial to the improvement of the microstructure and hence the performances of the Na-beta-Al\(_2\)O\(_3\) ceramic electrolytes.

The electrochemical results showed that both rate capability and initial discharge capacity were improved by the carbon-compositing of the LNCMO materials, because the carbon distributed in the pores of spherical powders favored the transference of electron among the particles. After the 100th cycling, the cells with LNCMO and carbon-coated C-LNCMO delivered about 86.9% and 92.4% of their initial discharge capacities, respectively. It was indicated that the carbon-coating had the effect to stabilize the structure of LNCMO.

Spherical LNCMO was prepared by slurry spray drying method and a post heat treatment in air. The citric acid was selected as carbon source. LNCMO powders were added to the ethanol solution of citric acid slowly under constant stirring, allowing the permeation of solution to the pores of LNCMO particles. The dried slurry was fired in air at 500 °C for 5h and the composite of carbon and LNCMO (C-LNCMO) was therefore obtained. Electron dispersive X-ray analysis (EDX) confirmed the excellent dispersion of C in the composite. The electrochemical performance of the powders was evaluated with coin-type cells with a lithium foil counter electrode. The galvanostatic charge-discharge tests were conducted between the cut-off voltages of 2.5 and 4.5 V (versus Li/Li\(^+\)) at a current density of 32 mA g\(^{-1}\).

In recent years, Li\([\mathrm{Ni}_{1/3}\mathrm{Co}_{1/3}\mathrm{Mn}_{1/3}]\)\(\mathrm{O}_2\) (LNCMO) cathode material has been studied for use in lithium ion batteries to replace the presently popular LiCoO\(_2\). This material has attracted significant interests because the combination of nickel, manganese and cobalt could provide many advantages such as higher reversible capacity with milder thermal stability at charged state, lower cost and less toxicity than LiCoO\(_2\). Despite the positive effect of LNCMO for the electrochemical property, the delivered capacities have shown a fading while the high rate current density was applied. Therefore, the addition of dopants or the surface modification of LNCMO has been adopted to prevent fading of the discharge capacity. In this investigation, based on the porous cathode powders, we filled the pores with carbon via the carbonization of citric acid and the electrochemical properties were characterized.

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This work was financially supported by NSFC (project No. 50730001, Ministry of Science and Technology of China (No.2007CB209700 and 2007BA07B001) and Science and Technology Commission of Shanghai Municipality (No. 06DZ12213/07DZ12004).

A01485-02578

Synthesis and Characterization of Carbon-Composited Li[\(\mathrm{Ni}_{1/3}\mathrm{Co}_{1/3}\mathrm{Mn}_{1/3}]\)\(\mathrm{O}_2\)

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In recent years, Li\([\mathrm{Ni}_{1/3}\mathrm{Co}_{1/3}\mathrm{Mn}_{1/3}]\)\(\mathrm{O}_2\) (LNCMO) cathode material has been studied for use in lithium ion batteries to replace the presently popular LiCoO\(_2\). This material has attracted significant interests because the combination of nickel, manganese and cobalt could provide many advantages such as higher reversible capacity with milder thermal stability at charged state, lower cost and less toxicity than LiCoO\(_2\). Despite the positive effect of LNCMO for the electrochemical property, the delivered capacities have shown a fading while the high rate current density was applied. Therefore, the addition of dopants or the surface modification of LNCMO has been adopted to prevent fading of the discharge capacity. In this investigation, based on the porous cathode powders, we filled the pores with carbon via the carbonization of citric acid and the electrochemical properties were characterized.

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This work was financially supported by Natural Science Foundation of China (NSFC, Project No. 20333040) and 973 Project of China No. 2007CB209700.

A01492-02595

The Inhibitive Efect of ZnO and Polyaniline on Corrosion of 57S Aluminium in 2M NaOH Solutions

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In various chemical industries, organic inhibitors are normally used. Among them heterocyclic compounds comprised a potential candidate for corrosion inhibitors. However, nitrogen and sulphur containing conducting polymers have been studied for the protection of metals against corrosion. Among all conducting polymers polyaniline stands out a separate class due their greater stability, cheapness, easy method of synthesis and unique redox behavior. Conducting polymers are used as inhibitors for prevention of corrosion because of the large availability of (π) electrons enable them to function as very effective corrosion inhibitors.

The present study deals with the effect of polyaniline incorporation with ZnO in 2M of NaOH solution on the corrosion of commercial aluminium alloys have been studied using various electrochemical characterization techniques. The inhibition of corrosion brought about by the addition of polyaniline is found to be under anodic control. Surface studies reveal the formation of very adherent protective layer on the metal surface.

A good galvanic anode should possess a high negative open circuit potential, minimal self corrosion and high...
anode efficiency. Based on these requirements 57S can be considered as suitable anode materials for galvanic anodes in 2M NaOH containing 0.2M ZnO and 700 ppm of polyaniline, 57S is to be preferred because of the fact that it has more favourable electrochemical characteristics. So zincating aluminium of 57S grades by immersing in 2M NaOH containing 0.2M ZnO and 700 ppm of polyaniline has been found to produce materials suitable for use as galvanic anodes in alkaline solutions. These zinc oxide and polyaniline coating grades of aluminium are characterized by high negative open circuit potential and high inhibition efficiency. 57S aluminium in 2M NaOH containing 0.2M ZnO and 700 ppm concentration is found to show high negative open circuit potential and high inhibition efficiency. 57S aluminium in 2M NaOH containing 0.2M ZnO and 700 ppm concentration in NMP is found to show most favourable characteristics for the performance as galvanic anodes in alkaline media.

A01492-03613

Effect of Dopants on the Synthesis of Polyaniline and Its Characterization

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Polyaniline has been the most active material because it combines with a verity of novel properties and behaves as metals and plastics. The paper reports on the synthesis of polyaniline and doping with different protonic acids. The polymers were characterized by NMR, FTIR, UV-Visible, TGA&DTA, XRD and conductivity measurements etc. Doping process which takes an important role in stabilizing the conducting form of polyaniline. The stable form of PANI would be more suitable potential candidate for any technological applications. Hence, the results showed that the doped-polyaniline play an important role to change the structure of polyaniline. Therefore, it is an advantage to fabricate devices using polyaniline in the form of doped state and it has great potential for energy device application.

A01498-02741

Facile Synthesis of LiMn$_2$O$_4$/MWNTs Hybrid Nanomaterials as Cathode Materials of Li-Ion Batteries

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The demands for higher energy density and higher power capacity of Li ion secondary batteries for applications in electric vehicles and power tools have led to a search for electrode materials with much higher electrochemical performance. Due to the unique one dimensional tubular structure, high electrical and thermal conductivities and extremely large surface area, carbon nanotubes (CNTs) have been considered as the ideal additive materials to improve the electrochemical and functional characteristics of both the anode and cathode materials for Li ion batteries with much enhanced energy conversion and storage. Hybrid nanostructures composed of CNTs and oxide compounds, such as Co$_3$O$_4$/CNT, TiO$_2$/CNT and Au/SnO$_2$/CNT, have recently been developed as the anode materials. These hybrid materials may possess not only the inherent properties of nanocrystals and CNTs acting alone, but also additional, novel properties arising from the interactions (e.g., electrical or optical) between them. In particular, the CNT additives provide electronic conductive paths that in turn decrease the inner resistance of Li ion batteries, leading to higher specific capacities even at high charge/discharge current rates. However, very few studies have hitherto been reported on the direct preparation of hybrid nanocomposites for cathode materials of Li ion batteries.

This presentation reports development of a new hybrid nanomaterial composed of nanocrystals that are uniformly attached onto the CNT surface by a facile sol-gel method followed by calcination at a low temperature. The elemental, morphological and structural characterization indicate that the hybrid nanocomposite had a unique structure with a compositional variation across the radial direction while there was a constant concentric arrangement of each participating component along the axial direction, resembling an electric cable configuration. The electrochemical properties of these hybrid nanocomposites were evaluated as the cathode material, proving that the performance of the battery was markedly improved, especially the rate performance.

Acknowledgements:
The project was supported by the Finetex Technology Global Ltd (Project Number: FTG001-MECH.07/08).
The demand for clean and sustainable energy has stimulated great interest in fuel cells. Solid oxide fuel cells (SOFC) represent the cleanest, most efficient and versatile chemical-to-electrical energy conversion system. It offers a potential for direct utilization of hydrocarbon fuels, coal gas, biomass, and other renewable fuels. One of the grand challenges facing the development of a new generation of SOFC is the creation of novel electrode materials that not only promote fast transport of ionic/electronic defects but also facilitate rapid surface electrochemical reactions. This presentation will highlight some recent progress in modeling, simulation, and in situ characterization of surface species, interfacial processes, and new phase formation on SOFC electrodes using Raman spectroscopy, which can provide structural and compositional information complementary to that from traditional ex situ and in situ characterization methods. Recently, we have built a state-of-the-art system capable of simultaneously performing in situ Raman spectro-microscopy and impedance spectroscopy to probe and map electrode reactions in SOFCs under practical operating conditions while the gas composition is monitored by mass spectrometry. Raman spectroscopy provides unique identification of molecular species (adsorbates or reaction intermediates) and new phases through their vibration states. The Raman signals from electrode surfaces may be enhanced by depositing silver or gold nano-particles on the electrodes, creating the so-called surface-enhanced Raman scattering (SERS) effect to dramatically increase the sensitivity. In addition, Raman spectroscopy offers capabilities for mapping where a specific reaction of interest is taking place. When applied to an SOFC with patterned electrodes perturbed by an electrical, chemical, or optical stimulus, these techniques become very powerful in investigating into active reaction sites and other properties of various electrode materials, providing invaluable information that has never before been accessible. Probing and mapping surface molecular processes relevant to electrode kinetics under practical fuel cell operating conditions may provide vital insights into the mechanisms of interfacial reactions, which are critical to achieving rational design of better electrodes, catalysts, and interfaces. While the discussions will focus primarily on SOFCs, the methodology and the techniques presented are applicable to other energy storage and conversion systems such as batteries, PEM fuel cells, super-capacitors, and catalysts or reactors for fuel processing. Successful creation of new materials with flexibility in composition and microstructure, and hence in electrical, transport, and catalytic properties, is essential to the development of a new generation of clean and renewable energy systems.

Lithium ion-conducting glasses are well known for their applications in electrochemical devices such as solid-state microbatteries, fuel cells, chemical sensors and smart windows. However the mechanism of ionic conductivity in these disordered materials and in particular the effect of halide dopants is yet to understand. Here, we study the effect of LiBr doping of the Lithium phosphate glass 0.6Li_2O-0.4P_2O_5. The glass transition temperature (T_g), ionic conductivity (σ) and activation energy (E_a) are measured for melt quenched xLiBr-(1-x)(0.6Li_2O-0.4P_2O_5) glasses with x = 0.1, 0.15, 0.2.

Higher LiBr concentrations lead to partial crystallisation. Molecular Dynamics (MD) simulations for the same systems have been performed with an optimized potential, fitted to match bond lengths, coordination numbers and ionic conductivity. Based on the equilibrated configurations of these MD simulations, ion transport pathways are modelled in detail by the bond valence approach to clarify the influence of the halide dopant concentration on the glass structure and its consequence for Li ion mobility. Experimental and computational results are compared with our previous reports on the system xLiCl-(1-x)(0.6Li_2O-0.4P_2O_5) and discussed in terms of the general structure property correlations derived from our pathway analysis of RMC structure studies for related alkali and silver ion conducting glass systems. T_g and σ values are observed higher for LiBr doped glasses when compared with LiCl doped glasses. Moreover, LiBr doping is found to increase the volume fraction and the local dimensionality of the Lithium transport pathways more efficiently than the same concentration of the dopant LiCl, as to be expected from the larger size and higher polarisability of bromide ions. None of the two glass systems shows entirely halide coordinated pathways, but LiBr-doped glasses exhibit a more pronounced tendency for local separation between regions of high and low halide contributions to the Li coordination, so that also the local mobilities of Li ions will show a wider distribution than for the nearly statistical distribution in LiCl-doped glasses. In all the investigated glasses, the calculated pathway volume fractions permit a semiquantitative prediction of the ionic conductivity, though the variation of the properties within the individual series is underestimated.
FTIR Studies of Al and Mg Doped LiCo_{1-x}M_xPO_4 (M= Al) Cathode Material for Li Ion Rechargeable Batteries

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Among the proposed olivine candidates, LiCoPO_4 is a strong candidate for new high voltage and superior capacity cathodes since it exhibited the highest 4.8V discharge plateau of 100mAh/g Vs Li/Li+. Sol gel method using citric acid as a fuel has been developed for the synthesis of the compound LiCo_{1-x}M_xPO_4 (M= Al, Mg). The FTIR spectra of LiCo_{1-x}Al_{x}Mg_{y}PO_4 recorded in the region from 400-2000cm^-1. For olivines, there are a singlet (A1) at a frequency v_A=965cm-1; a doublet(E) at v_E=465cm-1 and two triply degenerate (F2) modes, v_3, in the region 1050-1140cm-1 and v_2 in the range 500-560cm-1. These groups correspond to the internal stretching, internal bending and external oscillations modes of PO_4 respectively. These patterns are consistent with the assumption that the PO4 tetrahedra have very stable chemical bonds even when they are backbone of the vitreous phase. The bands appearing in the region between 900-1200cm^-1 is related to the stretching vibrations of the tetrahedral anion i.e. PO4^-2. The complex pattern of bands in the region 400-700cm^-1 corresponds to the bending motion of the tetrahedral group and to the external modes. An increase in the wave number for most of the dominant bands corresponds to the substitution of Co by Al and Mg. The effect of doping Al and Mg in LiCoPO_4 on electrical conductivity was investigated. Arrhenius plot has been made to investigate the electrical conductivity of LiCo_{1-x}M_xPO_4 (M= Al, Mg) which reveals the enhancement in the ionic conductivity values.

Synthesis and Characterization of Intercalated LiMn_{2-x-y}Al_{x}V_{y}O_4 Cathode Material for Lithium Ion Batteries

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Inorganic based LiMnO_4 as cathode materials is in the development of lithium secondary ion batteries because of its good properties, low cost and easy availability of manganese oxide, the raw material used to produce the above spinel oxide. The new spinel oxides cathode material LiMn_{2-x-y}Al_{x}V_{y}O_4 (x≤0.5, y≤0.5) were prepared using low cost Soft-Combustion method. Succinic acid acts as a combustion agent in this method. The precursors were sintered at 1073 K to get the desired product. The phase purity of the cathode materials were confirmed by X-ray diffraction pattern. The electrochemical properties in terms of AC impedance measurements were carried out for these cathode materials. Conductivity values were calculated and it was found to be in the order of 10^-4 S/cm. The aluminum and vanadium doped spinal oxide samples gave considerable activation energy. Thermal and local environment studies have been carried out by DSC and FTIR.

Characterisation of LiCo_{1-x}Mg_{x}PO_4, Olivine Cathode Material for Li Ion Batteries by Sol-gel Route

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Olivine orthophosphates LiMPO_4 (M=Fe, Co, Ni, Mn) has overcome many of the weaknesses inherent to earlier cathode candidates. In recent years, several low temperature methods such as sol-gel synthesis, the pechini process, hydrothermal method , ball milling, and solid state reaction have been used to prepare olivine materials LiMPO_4 (M=Fe, Co, Ni, Mn). Problems such as rate limitation and low electronic conductivity prevented the utilization of this kind of cathode in practice, in spite of the theoretical predictions of a high storage capacity. Olivine particles with carbon coating, adding metal particles to the mix or metal doping are the other ways to overcome the problem. Olivine LiCo_{1-x}Mg_{x}PO_4 compound has been prepared by citric acid assisted sol-gel method. This soft chemistry technique offers many advantages such as better homogeneity, low calcinations temperature, shorter heating time, regular morphology, sub micron sized particles, less impurities, large surface area and good control of stoichiometry. The compound has been characterized for phase purity and cation environment by XRD. The FTIR spectra of LiCo_{1-x-y}Al_{x}Mg_{y}PO_4 recorded in the region from 400-2000cm^-1. Thermal analysis has been done by TG-DTA. The electrical conductivity increases as temperature increases indicating a characteristic activated behavior over the complete temperature range studied. At room temperature, conductivity was found to be 10^-4 S/cm. Conductivity measurements have been taken by AC impedance analyzer. It was observed that there is increase in electrical conductivity values which may be due to the finer particle size and the aloivalent doping.
Increasing demand for high energy density Li-ion batteries (LIBs) for applications in electric vehicles (EV), hybrid EV, telecommunications and satellites has motivated researches for new and novel electrode materials possessing high gravimetric and volumetric capacity and good cyclability. Bulk and nano-size tin (Sn) - based metal alloys, oxides and composites have been extensively studied as the alternative negative electrode (anode) materials. The reaction mechanism involved during cycling is alloying/ de-alloying reactions (Sn + 4.4 Li ↔ LiₓSn). In recent years, Sony Company introduced the second-generation LIBs, containing the composite, ‘Sn-Co-C’ as the anode replacing the graphite in the first-generation LIBs. It is known that cobalt (Co) and carbon (C) in the above composite act as electrochemically- inactive but electronically- conducting ‘matrices’, during the Li-storage and cycling behavior. Thus, the choice of a good matrix element/compound appears to be the prerequisite to obtain high and stable capacities with the Sn-based compounds.

In the present study, we examined the Li-cycling behavior of the nanocomposites, (SnO.½ VO₃) and (SnO.½ VO). These are prepared by high energy ball-milling of mixtures of SnO and vanadium oxides, V₂O₅ or VO. These V-oxides are chosen since they exhibit ‘metallic-type’ electronic conductivity. The composites are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Li-cycling behavior is studied by galvanostatic cycling and cyclic voltammetry (CV) in two voltage ranges. When cycled at 60 mAg⁻¹(0.12 C) in the voltage window 0.005-0.8 V vs. Li, the reversible first-charge capacities are 500 (±10) mAhg⁻¹ for both (SnO. ½ V₂O₅) and (SnO. ½ VO). These capacities correspond to 3.2 moles of Li per mole of the composite. However, slow capacity-fading is observed and at the end of 50 cycles, the capacity retentions are 82% for (SnO. ½ V₂O₅) and 77% for (SnO. ½ VO). When cycled at 0.12 C in the voltage range, 0.005-1.0 V, the first-cycle reversible capacities are 565 (±10) mAhg⁻¹ (3.6 moles of Li) and 630(±10) mAhg⁻¹ (3.9 moles of Li) for (SnO. ½ V₂O₅) and (SnO. ½ VO), respectively. The capacity retention at the end of 40 cycles are 79% for (SnO. ½ V₂O₅) and 74% for (SnO. ½ VO). Though the V-content in the both nano-composites is same, the one with V₂O₅ performs better in both the voltage windows. The CV data corroborate the galvanostatic cycling results. Possible reasons for the better Li-cycling performance of (SnO. ½ V₂O₅) are discussed.

Rechargeable lithium-ion batteries (LIBs) are popular dc power sources for portable electronic appliances. However, for high power applications, the present day LIBs suffer from the safety problem during operation, exhibit less than optimal energy density and high cost. In order to overcome these drawbacks, researches are underway on the electrode materials. Metal oxides, especially, those containing Li-alloy forming elements like Sn, Zn, Cd, and/or those containing transition metals which can undergo ‘conversion’ reactions have been extensively investigated as anodes.

As part of a comprehensive program of work on the suitability of metal oxides with the spinel structure, AB₂O₄ (A and B are metals) as prospective anodes for LIBs, presently we have studied the Li-storage and cyclability of cadmium ferrite, Cd₃(Fe₄O₄). Since Cd can form the alloy, Li₂Cd, and also participate in ‘conversion reaction’ (CdO + 2Li ↔ Cd + Li₂O) along with Fe, we can expect a reversible capacity corresponding to 9 moles of Li per formula unit.

CdFe₂O₄ with the normal spinel structure is prepared by urea combustion synthesis followed by heating in air at 900°C for 6 h. It is characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), high resolution transmission electron microscope (HR-TEM) and selected area electron diffraction (SAED). Li-cycling is examined by galvanostatic cycling, cyclic voltammetry (CV) and impedance spectroscopy in the range 0.005-3.0V vs. Li at room temperature. CdFe₂O₄ showed a first discharge and charge capacity of 1180(±10) mAhg⁻¹ (corresponding to 12.7 moles of Li per mole of CdFe₂O₄) and 840(±10) mAhg⁻¹ (9.0 moles of Li), respectively when cycled at 60 mAg⁻¹(0.07C). A reversible capacity of 810(±10) mAhg⁻¹ (8.7 moles of Li) remained stable in the range 10-60 cycles with a coulombic efficiency of > 98%. Rate capability has also been examined up to 1.4 C (1 C = 840 mAg⁻¹) and found to be good. Effect of heat treatment of the composite electrode (containing the active material) at 300°C for 12 h in Ar-atmosphere on the Li-cycling behavior has also been examined. CV data show that the average discharge- and charge potentials ~1.0 V and ~2.0V, respectively. Ex-situ XRD, HR-TEM and SAED studies, and impedance data collected during the 1st and 10th cycle have been analyzed and discussed in the context of the proposed Li-cycling reaction mechanism.
Nanostructured Electrode Materials Made by Combustion Synthesis

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Combustion synthesis techniques may be used to prepare high-quality nano-particulate electrode materials for use in lithium ion batteries. Either phase-pure oxides and phosphates or carbon-containing composites may easily be prepared in a one-step process. The composites may contain carbon nanotubes or fibers as separate entities or may consist of carbon-coated particles of active material. In general, nitrate and/or phosphate precursors are used in combination with an appropriate fuel such as glycine or citric acid. The combustion temperature is determined by the fuel:nitrate ratio, which can be varied over a wide range. Temperatures as high as 1400°C may be realized. This allows the production of high quality carbon (i.e., with graphitic characteristics) not normally achievable during conventional synthesis at lower temperatures. Due to the rapidity of the reaction, the thermodynamically favored product may not be produced initially. XRD analysis of the ash often shows that it is amorphous or only partially crystalline, but a brief calcination causes crystallization to occur and the desired phase is produced. Carbon content is determined both by the type of fuel and the amount. Glycine usually results in very little residual carbon, whereas citric acid is suitable for the production of phosphates such as olivines because carbon is co-produced during the initial combustion. This is useful because it avoids a second step in which carbon is added and the mixture is processed. We have succeeded in making a series of partially Al-substituted layered mixed transition metal oxides via combustion synthesis. These compounds can be difficult to make by the more familiar mixed hydroxide route due to problems with homogeneity and the production of aluminum oxides as impurities. Using combustion techniques, single phase materials can be made up to about y=0.2 for the series Li[Ni0.4Co0.2-yAl0.5Mn0.5]O2 and Li[Ni1/3Co1/3-yAl0.5Mn1/3]O2. Compounds with low levels of Al substitution have similar practical capacities as analogs with no Al, but rate capabilities are improved, suggesting that the increased homogeneity results in better electrochemical properties. Composites of carbon and olivines such as LiFePO4 and LiMnPO4 can also be made easily. This is particularly advantageous in the case of the latter, which normally shows very poor electrochemical properties due to its low conductivity. The extremely small size of the particles (~30 nm) and the co-production of high quality carbon during combustion are beneficial to the performance. A particular challenge, however, is the need to produce samples with little agglomeration and even dispersion of carbon to ensure full utilization. Na0.44MnO2 and Na0.44Ti0.5Mn1-

Studies on the 4V-cathode, LiVPO4_F for Li-ion Batteries

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Recent research has shown that lithium (Li)-containing transition metal compounds with the phosphate-frame work, like LiFePO4 and LiVPO4_F can be viable alternative materials to replace the LiCoO2 presently being used as the positive electrode (cathode) in the commercial Li-ion batteries. While LiFePO4 works as the 3.5 V-cathode, Barker and coworkers have shown that LiVPO4_F works as the 4 V-cathode, similar to LiCoO2.

Presently, we report on the synthesis of LiVPO4_F, by two-step carbothermal reduction method, its characterization by X-ray diffraction, SEM, density and surface area, and electrochemical studies by way of charge-discharge cycling, cyclic voltammetry (CV) and impedance spectroscopy. Li-metal was used as the counter and reference electrode. Galvanostatic cycling in the voltage range, 3.0-4.5 V at a current rate of 15 mA/g (0.12C) up to 200 cycles was carried out. Results show that the reversible capacity stabilizes after 20 cycles and yields a capacity of 130 (±3) mAhg⁻¹ without any noticeable capacity fade up to 200 cycles. This value corresponds to 83 % of the theoretical reversible capacity of LiVPO4_F. Coulombic efficiency is >98%. Good rate-capability is also shown. CV-data show that the charge-discharge process occurs in the range; 4.1-3.4V vs. Li. The Li-extraction/insertion in the LiVPO4_F occurs through a two-phase reaction, similar to the 3.5V-cathode, LiFePO4_F. Impedance data at various voltages have been fitted to an equivalent circuit and the impedance parameters have been evaluated and discussed.
Fast ion conductors characterized by their high ionic conductivity have attracted a great deal of attention because of their potential applications in energy storage devices or sensors. To achieve a more detailed understanding of the microscopic ion transport process in complex disordered solids, determinations of ionic conductivity should be complemented by experimental investigations of relaxation processes.

Here, we study the electrical conductivity ($\sigma$) of yLiX-(1-y) (0.6Li$_2$O-0.4P$_2$O$_5$) glasses in the temperature range 300K to 423K by impedance spectroscopy (frequency range 1Hz to 12MHz) using Ag as blocking electrodes. The variation of the imaginary part of impedance with frequency at different temperatures is characterized by peaks that are broader than the ideal Debye curve and asymmetric. As temperature or LiX content increases, the peak shifts to higher frequencies. This variation of the peak frequency, $f_p$, as a function of temperature obeys an Arrhenius relation. The plots of log $\sigma$ versus log $f$ at various temperatures for all compositions exhibits a typical behaviour of ionic materials, i.e. the dc plateau and the frequency dependent region. The conductivity is found to be frequency independent in the lower frequency region at 300K and it is equal to the bulk conductivity of the samples, which increases with LiX content.

The conductivity relaxation phenomena have been indicated by crossover from the frequency independent to the dependent region. The observed behavior is not in general agreement with the prediction of the jump relaxation model. The increase of conductivity with the frequency for different temperatures cannot be fully described through simple Jonscher’s universal power law feature. The logarithmic variation of real part of permittivity with frequency at different LiX content shows high values at low frequency region (for T= 300K), which can be attributed to the charge accumulation at the electrode and electrolyte interface.

The variation of the real part of modulus ($M'$) with frequency shows that $M'$ tends to be very small at lower frequencies, confirming that the electrode effects may make a negligible contribution in all the glasses under investigation. The peak values in the frequency dependence of the imaginary part of modulus ($M''$) move towards higher frequencies with increasing LiX content, indicating that the transition from the long range to short range mobility occurs at higher frequency for high concentration of LiX. The peak in the $M''$ plot also shifts towards higher frequency with increasing temperature. At the same time the peak height increases when either LiX content or temperature is increased. The asymmetry in the $M''$ plot is suggestive of the stretched exponential character of relaxation times of the material.

The conductivity relaxation time and activation energy have been estimated from the modulus spectra. Increase of ionic conductivity with addition of LiX content are in line with the decrease of activation energy and relaxation time.

**Ta-doped Li$_6$Zr$_2$O$_7$ : A New Li-fast Ion Conductor**

Rechargeable all-solid-state lithium (Li)- or Li-ion batteries (AS-LIBs) are attractive power sources for applications, like ‘smart’ credit cards and medical implants. They need a Li-fast ion (super-ionic) conductor (FIC) as the solid electrolyte. However, the presently known crystalline Li-FICs do not possess sufficiently high ionic conductivity at ambient temperature for the realization of high energy density AS-LIBs. Hence, there is a need to search for new and better Li-FICs. Presently, we have studied, for the first time, the Li - ionic conductivity, $\sigma_{\text{ionic}}$, behavior of pure and aliovalently doped Li$_x$Zr$_2$O$_7$, a network compound with a monoclinic structure. The structure contains structurally non-equivalent, interconnected Li ion channels in x, y and z-direction, so that a favorable 3D network of pathways might be expected. Results, indeed, show that Ta doping enhances the Li ion conductivity to a technically relevant level.

Pure and doped Li$_x$(Zr$_2$M$_{1-x}$)$_2$O$_7$, M=Nb and Ta; $x$=0, 0.15 have been prepared by the urea combustion method followed by heating in air at 950°C for 8 h. The single-phase materials obtained were characterized by X-ray diffraction, density and surface area measurements. The $\sigma_{\text{ionic}}$ measurements were carried out on sintered pellets in the temperature range, 60-360°C by impedance spectroscopy. We observe that the Ta doped Li$_x$Zr$_2$O$_7$ has a measurable $\sigma_{\text{ionic}}$ at ~120°C, and at 300°C exhibits a value of $1 \times 10^{-3}$ S/cm. The temperature dependence of the conductivity in the range 120-360°C obeys the Arrhenius relation, yielding an activation energy of $E_a$ = 0.84 eV (for Ta).

Atomistic molecular dynamics simulations have been used to understand the Li-ion mobility and the conductivity...
mechanism in these compounds. The lowest energy pathway is found to extend in [012] direction. Bond valence approach indicates significant anisotropy in Li-ion conductivity in compounds with Li₂ZrO₂ type structure. Detailed results will be presented and discussed.

**A01623-02814**

**Electrochemical Properties of Nb₂O₅ Nanofibers**

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Recently nano/submicron sized metal oxides have been studied as electrode materials for lithium (Li)-batteries because of their chemical stability and high surface area leading to facile Li-intercalation/de-intercalation process. In this work, we prepared Nb₂O₅ nanofibers by electrospinning technique, followed by heating in air for 1h at temperatures (T), ranging from 500 to 1100 °C. The Nb₂O₅ nanofibers were characterized by XRD, SEM, TEM, XPS, density and BET surface area methods. Electrochemical properties were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge cycling and impedance spectroscopy techniques at room temperature with Li-metal as counter and reference electrode. For the Nb₂O₅ prepared at temperature 500, 800, 1000 and 1100 °C, the following discharge capacities at end of 5th cycle are: 130, 170, 172 and 235(±3) mAh/g, respectively, when cycled in range 1-2.6 V, at the current rate of 50mA/g. The CV and galvanostatic discharge-charge curves clearly showed the differences in peak potentials depending on the heating temperature and morphology of Nb₂O₅ nanofibers. Average charge and discharge voltages for Nb₂O₅ heated at 1100 °C are 1.7 and 1.65 V, respectively. The structural, electrochemical properties as well as Li-diffusion coefficients and the Li-cycling mechanism will be discussed.

**A01684-03025**

**Study on Graphite Nano-fiber as Catalyst Support for Proton Exchange Membrane Fuel Cell**

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By ball-milling method, the graphite nano-fiber (GNF) was prepared from the used carbon paper in a proton exchange membrane fuel cell. The surface of GNF was 229 m²/g, 20% platinum was loaded on the GNF and XC-72 carbon to fabricate Pt/GNF and Pt/XC-72 supported catalysts. The results of cyclic voltammetry showed that the Pt/GNF catalyst had the same electrochemical area (ECA) as the Pt/XC-72 catalyst. The morphology of these catalysts was characterized by transmission electron micrograph. The electrochemical stability was measured for XC-72, GNF, Pt/XC-72 and Pt/GNF electrodes by the constant-potential oxidation. The peak current increased by 2% for GNF while 60% for XC-72. The corrosion current for Pt/XC-72 was 1.4 times of that for Pt/GNF. In addition, almost 84.7% ECA was lost for Pt/XC-72 catalyst after oxidation for 60 h, while only 37.2% ECA was lost for Pt/GNF. The results indicated that the GNF possessed much higher resistance to electrochemical oxidation than XC-72.

**A01630-02825**

**Nanoscale Electrocatalysts and Mechanistic Understanding by Electrochemical Impedance Spectroscopy**

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Fuel Cells, in particular the solid polymer electrolyte fuel cell, have been developed for many decades because of their rich potentials in transportation and residential power applications. In recent years, with an increasing power demand from consumer electronics, low temperature portable fuel cells with promise of high energy density and uninterrupted use of power have been heavily studied by electronics companies and academic institutions. It is anticipated that these low temperature fuel cells once developed could challenge the position of lithium polymer batteries currently dominating the consumer electronics industry.

Electrocatalysts supported on high surface area support materials are the heart of fuel cell systems. In spite of many years’ progresses, significant technical challenges still exist, particularly for low temperature fuel cell catalysts. In this invited presentation, the first half of the talk will introduce new synthesis methods of electrocatalytic nanoparticles. Issues related to catalyst stability and activity will be discussed. Examples of electrochemical impedance spectroscopy (EIS) based interpretation and analyses of several important electrocatalytic reactions such as H₂/CO oxidation, methanol oxidation and formic acid oxidation will be highlighted in the second half. At the end of the presentation, it would be great if the audience can be convinced that EIS is a powerful technique to probe and understand electrocatalytic reaction pathways, leading to a better design of active electrocatalysts for fuel cells.
Nanostructured Anodes and Cathodes for Lithium-Ion Batteries
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Nanostructured materials are currently of interest as high performance anodes and cathodes for lithium-ion batteries because of their novel size effects and significantly enhanced kinetics (Adv. Mater. 2008, 20, 2878). However, their practical applications suffer from the problems of low thermodynamic stability and high surface reactions (J. Phys. Chem. C 2008, 112, 16824). Electrode materials with nano/micro hierarchical structures are the best systems of choice because they can take both the advantages of nanometer-sized building blocks and micro- or submicrometer-sized assemblies. While the former provides negligible diffusion times and possible new Li storage mechanisms and hence is the key to the favorable kinetics and high capacities, the latter guarantees good stability and easy of fabrication. This contribution highlights some recent developments in this field mainly by using work of the author for illustration:

1) Composite particles with mixed-conducting nano-networks: An optimized nanostructure design of electrode materials for high-energy and high-power lithium-ion batteries was shown to be the introduction of hierarchical mixed conducting networks (that is, networks that can conduct both ions and electrons). The concept was realized by the synthesis of mesoporous TiO2-RuO2, (Adv. Mater. 2007, 19, 2087) and C-LiFePO4-RuO2 (Adv. Mater. 2007, 19, 1963) nanocomposite electrodes. For practical applications, the expensive material of RuO2 can be replaced with carbon and carbon nanotubes (CNTs) for such nanostructure. The successful fabrication of mesoporous TiO2-C nanocomposite and CuO-CNT nanomicrospheres (Chem. Mater. 2008, 20, 3617) will be discussed in this context.

2) Nanoparticles in (nanoporous) carbon matrix: An alternative optimized nanostructure design of electrode materials was taking both the advantages of nanoporous carbon (itself being a mixed conducting 3D network) and nano-sized active particles. Superior cathode materials are obtained by dispersing nano-sized LiFePO4 particles into nanoporous carbon matrix, which can even be operated within a charge/discharge time less than 30 seconds like a supercapacitor material but with more energy density (Adv. Mater., Submitted). The relevant work of Sn-C nanocomposite anode, i.e., Sn nanoparticles encapsulated with elastic hollow carbon spheres, will also be discussed (Adv. Mater. 2008, 20, 1160).

3) Coaxial nanowires: A facile approach to high-rate electrode materials with mixed conducting 3D networks was proposed by using coaxial nanowires with electronically conductive cores such as CNTs and metallic nanowires. The power of this concept is demonstrated by the synthesis of CNT@TiO2 core/sheath coaxial nanowires.

4) Carbon coatings: Both enhanced cycle performance and rate performance were found in carbon coated Fe2O3 nano-spindles, because the carbon coating layers can not only significantly enhance the electronic conductivity of electrode materials, but also lead to stabilized SEI films (Adv. Func. Mater. 2008, 18, 3941).

Acknowledgment:
This work is supported by the National Natural Science Foundation of China (50730005 and 20701038), National Key Project on Basic Research (2009CB930400), and the Chinese Academy of Sciences. The author thanks Professors Li-Jun Wan, Joachim Maier and Hong Li for their support and discussion.

Effect of Cathode Material on Cell Parameters of P (MMA-CO-4VPNO+KBrO3) Polymer Electrolyte System
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Polymer electrolyte films based on a co-polymer poly (methyl methacrylate-co-4-vinyl pyridine N-oxide) [P (MMA-CO-4VPNO)] complexed with potassium bromate (KBrO3) were prepared by solution cast technique. The complexation of KBrO3 salt with the polymer was confirmed by X-ray diffraction and infrared studies. Measurements of conductivity in the temperature range 300-410 K and transference numbers were carried out to investigate the change transport in the polymer electrolyte system. Transport number data show that the change transport in this polymer electrolyte system is predominantly due to ions. Electrochemical cells were fabricated with different cathode materials like I2, (I2+C) and (I2+C+electrolyte). The cell with configuration K / P (MMA-CO-4VPNO+KBrO3) / (I2+C+electrolyte) exhibited better discharge characteristics than the other configurations. Different cell parameters like open circuit voltage (OCV), short circuit current (SCC), power density, energy density etc., were evaluated and reported.
Electro-ceramics are potential candidates for a variety of technological applications such as in Solid Oxide Fuel Cells (SOFC). Their functionality further increases if they are synthesized in nano-crystalline form employing an appropriate soft-chemical route. Among the available chemical routes, the combustion technique is capable of producing the nanocrystalline powders of the oxide ceramics at a lower calcination temperature. This process involves a combustion reaction between a fuel (e.g. glycine, citric acid, urea etc.) and an oxidizer (e.g. metal nitrates). In our group, a wide ranging electro-ceramics such as electrolytes, interconnect and cathode materials for SOFC applications have been prepared. Some of the specific examples are ceria, substituted ceria, zirconia, Zr_{0.8}Ce_{0.2}O_{2-x}, YSZ, Nd_{0.5}GaO_{3}, La_{1-x}M_{x}CrO_{3} (M = Ca, Sr), LaGaO_{3} derivatives and brown millerite and pyrochlore based ionic conductors. The powder properties were tailored to achieve the near theoretical density sintered pellets, while retaining the ultra-fine grains. A number of techniques like XRD, HT-XRD, surface area analyzer, SEM, TEM, Raman spectroscopy, dynamic light scattering, small angle x-ray/neutron scattering, dilatometer, AC Impedance analyzer etc. were used for detailed characterization of these products. The degree of agglomeration was shown to be a crucial factor affecting the sinterability of some these materials. Detailed structural refinement and Raman spectroscopic studies revealed that an optimum degree of disorder in the structure is required to enhance the ionic conductivity in some of these systems. These results will be discussed.

A01874-03109

Electro-ceramics for Energy Conversion: Role of Nanoscience

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Electro-ceramics are potential candidates for a variety of technological applications such as in Solid Oxide Fuel Cells (SOFC). Their functionality further increases if they are synthesized in nano-crystalline form employing an appropriate soft-chemical route. Among the available chemical routes, the combustion technique is capable of producing the nanocrystalline powders of the oxide ceramics at a lower calcination temperature. This process involves a combustion reaction between a fuel (e.g. glycine, citric acid, urea etc.) and an oxidizer (e.g. metal nitrates). In our group, a wide ranging electro-ceramics such as electrolytes, interconnect and cathode materials for SOFC applications have been prepared. Some of the specific examples are ceria, substituted ceria, zirconia, Zr_{0.8}Ce_{0.2}O_{2-x}, YSZ, Nd_{0.5}GaO_{3}, La_{1-x}M_{x}CrO_{3} (M = Ca, Sr), LaGaO_{3} derivatives and brown millerite and pyrochlore based ionic conductors. The powder properties were tailored to achieve the near theoretical density sintered pellets, while retaining the ultra-fine grains. A number of techniques like XRD, HT-XRD, surface area analyzer, SEM, TEM, Raman spectroscopy, dynamic light scattering, small angle x-ray/neutron scattering, dilatometer, AC Impedance analyzer etc. were used for detailed characterization of these products. The degree of agglomeration was shown to be a crucial factor affecting the sinterability of some these materials. Detailed structural refinement and Raman spectroscopic studies revealed that an optimum degree of disorder in the structure is required to enhance the ionic conductivity in some of these systems. These results will be discussed.

A01878-03124

Updated References for the Structural, Electronic and Vibrational Properties of TiO_2(B) Bulk Using First-principles DFT Calculations

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TiO_2(B) is one of the eleven polymorphs of titanium dioxide like rutile or anatase. It has been receiving a renewal of interest in energy storage applications as electrode material for rechargeable lithium ion (Li-Ion) batteries especially since P. Bruce and co-workers showed that TiO_2(B) nanowires or nanotubes can significantly improve the TiO_2(B) bulk faradic capacity. However, as a metastable phase, pure TiO_2(B) is difficult to obtain and the products are usually polluted with TiO_2 polymorphs, like anatase. To get updated references on the structural, electronic and vibration properties of the metastable TiO_2(B) compound, Infra-Red and Raman spectra of TiO_2(B) were computed within the density functional theory framework and all active modes were assigned. Our study shows that Raman spectroscopy is the most appropriate tool to characterize traces of anatase in TiO_2(B) products, as it allows to discriminate between anatase and TiO_2(B) vibration modes around 520 cm^{-1}. More interestingly, full structural relaxations reveal that TiO_2(B) exhibits different titanium local environments compare to other titanium dioxide polymorphs like rutile or anatase, with one Ti being 5-coordinated. The presence of two electronically different titanium ions is shown to play a crucial role in TiO_2(B) Li-reactivity, thus preventing from a complete filling of the available Li-sites, and therefore from a better capacity.

A01848-03205

Micro Lithium Ion Batteries Prepared by Pulsed Laser Deposition

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Micro lithium ion batteries are now attracting a great deal of attention for the application to ubiquitous micro IT devices such as RF-ID chips. For this purpose, glassy solid electrolytes of high lithium ion conductivity are employed instead of the liquid electrolytes used in the conventional lithium ion batteries.

We have developed all solid state thin film micro-batteries by means of a pulsed laser deposition (PLD) method. LiCoO_2, LiMn2O4, LiNiCoO2 etc. are used for the cathode. SnO, ITO and metallic lithium are used for the anode. A Li-V-Si-O glass and Li3PO4 glass and their variations are used for the solid electrolytes. All these battery components are fabricated into multi-layered thin-films of about 1 micro meters.

The cell performance is evaluated by cyclic voltammetry (CV) and/or charge-discharge measurements. The structural change of the battery components are investigated by in situ micro-Raman scattering as well as SEM, TEM and laser microscope etc.
Fabrication of the dense, homogeneous, strong and stable solid electrolyte film is the key process, which is achieved by the selection and optimization of the material and PLD conditions. Second importance is the combination of the cathode, solid electrolyte and anode materials, since the electrochemical reaction and mutual diffusion at the interface affect strongly on the degradation of the cells.

In order to achieve the highly stable cells, the band alignments of the battery components should be optimized, which can be achieved by using a wide band gap solid electrolyte (WBG-SE) such as Li3PO4. On the contrary, soft structure of the glass network and large polarizability of anions are suitable for the high lithium ion conductivity, which prefers small band gap. In order to overcome this difficulty, it is necessary to accept some compromise or introducing interfacial buffer layers.

Electrochemical study of hydrogen charge-discharge process in MgH2 provides distinct information on thermodynamic and kinetics of the MgH2-catalyst system. The potentials of the absorption and desorption were showed a good reversibility, indicating the product was significantly activated due to the catalytic effects.

**Synthesis of Li$_4$Ti$_{12}$O$_{19}$ by Spray-Dry Method and its Electrochemical Property as the Anode Material for Li-ion batteries**

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Li$_4$Ti$_{12}$O$_{19}$ is a promising negative electrode material for Li-ion batteries due to its good structural stability during charge-discharge cycling. We have synthesized Li$_4$Ti$_{12}$O$_{19}$ form an aqueous solution using spray-dry method that could give more homogenous particles than the conventional solid-state reaction method, resulting in reducing rutile-TiO$_2$ secondary phase in the final product. In this study, we have investigated the effect of the synthetic conditions on the electrochemical properties of the prepared materials. The physical and electrochemical properties of the synthesized Li$_4$Ti$_{12}$O$_{19}$ powders have been characterized by mean of XRD, SEM, BET, charge-discharge cyclings, and ac impedance method.

**Storage Performance of LiFe1-xMnxPO4 Nanoplates**

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Although LiFePO4 (LFP) is considered to be a potential cathode material for the lithium-ion batteries, its rate performance is significantly restricted by sluggish kinetics of electrons and lithium ions. Several attempts have been made so far to improve the performance of LiFePO4 by reducing the grain size and painting conductive materials such as carbon or RuO2. We report here synthesis of LFP nanoplates by solvothermal method tailoring the thickness as well as carbon coverage at surfaces to explore their influence on the storage performance. Due to the fact that Li$^+$ ion diffuses along the b-axis solvothermal method was aimed to control the thickness of nanoplates across
the b-axis. We synthesised several nanoplates with various plate thicknesses along b-axis, among those, nanoplates of LFP with ~30 nm thick b-axis having thin (2 - 5 nm) and uniform layer of carbon coating exhibits high storage capacity as well as high rate performances. Thus, a favourable morphology for LiFePO4 has been achieved via solvothermal method for fast insertion/extraction of Li+ as compared to spherical nanoparticles of carbon coated LFP. Galvanostatic cycling shows a capacity of 164 mAh/g at 0.1C rate, 100 mAh/g at 10C rate, and 46 mAh/g at 30C rate, with excellent capacity retention of up to 50 cycles. Further attempts have been made to synthesize LiMnPO4 as well as Li(Fe1-xMnx)PO4/C (x=0.25,0.5,0.75) nanoplates using solvothermal method. Although LiMnPO4 does not exhibit an high storage behaviour comparable with that of LiFePO4, the mixed systems have shown an impressive storage performance. Influence of carbon coating on the electrochemical performances will also be addressed based on the performances of ball-milled nanoplates.

**A01924-03610**

**Electrochemical Characterization of Mesoporous Anatase TiO2 for Lithium Storage: Effect of Template Chain Length and Surface Area**

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In recent years TiO2 has been considered to be a promising candidate as an anode material for lithium-ion batteries due to the fast and highly reversible uptake of Li (0.5 mole of Li per formula unit) during insertion/extraction, non-toxic, cheap and flat low-voltage profile with Li. In Recent years, mesoporous and nanosized electrode materials has been recognized for rapid Li insertion/extraction. Here we report the optimized mesoporous anatase TiO2 nanostructure synthesized using soft template method for high power/energy density lithium batteries. Various cationic surfactants with different chain lengths have been selected for this investigation to study their ability to assist the formation of the mesoporous-assembled structure. Among these cetyltrimethylammonium bromide (CTAB) templated C16-TiO2 shows the higher surface area of 158 m2/g and reversible capacity of 288 mAh/g at 0.2C rate, 132 mAh/g at 5C rate, and 128 mAh/g at 30C rate. Best electrochemical performance, excellent cyclic stability and remarkable rate capabilities have been achieved for the mesoporous TiO2. It is believed that due to the increase in surface area of such mesoporous TiO2 electrodes, the volume fraction of the atoms near the surface layers dominates compared to those at bulk, enhancing the surface Li storage behaviour; whereas reducing the particle size has decreased the diffusion length for Li insertion/extraction in the bulk phase.

**A01943-03352**

**Lithium Ion Solid State Electrolyte Fabrication Methods and the Effect on Microstructure and Conductivity**

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Lithium ion conductors of the formula Li1+xTi2-xAlxP3-ySiyo12 (LTAPS) are promising solid state electrolytes for use in secondary lithium ion batteries. Maximizing electrolyte ionic conductivity is an important step in making lithium batteries efficient and reliable. Currently, there are two primary fabrication methods used: powder sintering, and glass-ceramic recrystallization. Glass ceramic processing insures novel part geometries can be fabricated and final recrystallized parts have low porosity. Powder sintering has the advantage of using lower processing temperatures, but extra care must be taken in ensuring that there is a high degree of intergranular contact.

LTAPS has a Nasicon-type structure at room temperature. The network structure allows for lithium ion hopping between interstitial sites. As shown by Aono et. al. this means that bulk conductivity dominates over grain boundary conductivity. Therefore, good intergranular contact is required for maximum conductivity.

The current work compares the processing methods by observation of microstructure and conductivity after heat treatment at a range of sintering/recrystallization temperatures. The microstructures are observed by scanning electron microscope. Conductivity is measured by AC impedance spectroscopy conducted with a Gamry Reference 600.

The author would like to recognize Professors, Nobuyuke Imanishi and Osamu Yamamoto of Mie University, Tsu, Japan and Professor Nigel Sammes of the Colorado School of Mines for their support and expertise.
One dimensional (1D) nanostructures such as nanowires, nanotubes, nanorods and nanoribbons have been extensively investigated for a wide range of applications. Here, we present the synthesis, characterization and technological applications of several 1D nanostructures including SnO$_2$ nanowires and α-Fe$_2$O$_3$ nanorods.

SnO$_2$ nanowires were synthesized by thermal evaporation combined with a self-catalyzed growth procedure. Scanning electron microscopy (SEM) observation shows SnO$_2$ nanowires having diameters of 200 – 500 nm and lengths extending several tens of micrometers. High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analysis identified that SnO$_2$ nanowires grew along [100] direction with an interplanar spacing of about 0.47 nm. The electrochemical performance of SnO$_2$ nanowires was tested as anode materials in lithium-ion cells. SnO$_2$ nanowires show a much higher lithium storage capacity, smaller initial irreversible capacity, and higher cyclability than that of SnO$_3$ microcrystalline powders. This improved performance should be attributed to the 1D nanowires having larger surface area and high length/diameter ratio[1]. Flute-like porous α-Fe$_2$O$_3$ nanorods and branched nanostructures such as pentapods and hexapods were prepared via dehydration and recrystallization of hydrothermally synthesised β-FeOOH precursor. The α-Fe$_2$O$_3$ nanostructures show much better sensing performance towards ethanol than that of the previously reported polycrystalline nanotubes. In addition, the α-Fe$_2$O$_3$ nanostructure based sensor can selectively detect formaldehyde and acetic acid among other toxic, corrosive, and irritant vapours at a low working temperature with rapid response, high sensitivity, and good stability.

Manganese dioxide (MnO$_2$) is one of the most promising materials for electrode materials due to its cheap, nontoxic, and environment friendly. However, the main problem for MnO$_2$ using in lithium recharge battery is the capacity failure during cycling. Recently, intensive research has been done by fabricating MnO$_2$ into nanomaterials to accommodate the structure change. Here, different morphologies of MnO$_2$ nanomaterials were synthesized via hydrothermal method in magnetic field (4T). The as prepared materials were characterized by means of X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDX), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). The electrochemical tests including charge-discharge, cyclic voltammetric (CV), and electrochemical impedance spectroscopy (EIS) show that the as-prepared MnO$_2$ nanomaterials in magnetic field can be used in Li-ion rechargeable batteries with enhanced cycleability. The MnO$_2$ prepared without magnetic field only shows a capacity of 62.6 mAh g$^{-1}$, while the MnO$_2$ prepared under a magnetic field of 4 T shows 103.3 mAh g$^{-1}$ up to 50 cycles.
Enhanced Performance as a Lithium Ion Battery Cathode of Electrodeposited \( V_2O_5 \) Thin Film by e-beam Irradiation

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Electrodeposited \( V_2O_5 \) thin films were irradiated with 1 MeV electron beam to examine the performance as a lithium ion battery cathode. \( V_2O_5 \) thin films were deposited electrochemically onto ITO (Indium Tin Oxide) coated glass from an aqueous solution of vanadyl sulfate using Pt and Ag/AgCl as a counter electrode and reference electrode, respectively. Electrodeposition was performed potentiostatically at \( 1.5 \sim 2.0 \) V vs Ag/AgCl for 10 minutes at \( 65^\circ C \). 1 MeV electron beam irradiation was performed using an electron beam accelerator at the Korea Atomic Energy Reasearch Institute by varying irradiation time. For comparison, control sample was not irradiated with electron beam.

Crystallinity change before and after electron beam irradiation was investigated by X-ray diffraction, and the oxidation state of vanadium was determined by X-ray photoelectron spectroscopy (XPS). SEM (Scanning Electron Microscopy)-EDS (Energy Dispersive Spectroscopy) was utilized to examine morphology and composition changes of \( V_2O_5 \).

It was concluded that electron beam irradiation altered the oxidation state of vanadium and increased crystallinity. Significant morphological changes of \( V_2O_5 \) thin films were also observed with electron beam irradiation.

Cyclicvoltammetry and chronoamperometry were employed to evaluate the synthesized \( V_2O_5 \) films as lithium ion battery cathodes. Compared with control sample, which was not irradiated with electron beam, electron beam irradiated \( V_2O_5 \) showed much higher capacity and enhanced charge-discharge behaviors. And the capacity of \( V_2O_5 \) was found to be strongly dependent on irradiation time. These enhanced electrochemical properties can be attributed to the higher surface area and facilitated charge transfer, resulting from increased surface roughness and defect sites.

Electrochemical Deposition of Highly-Oriented Zinc Oxide Nanorods Suitable for use in Dye-Sensitized Solar Cells

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The supply of energy from the sun to the Earth is gigantic: \( 3 \times 10^{24} \) joules a year, or about 10,000 times more than the global population currently consumes. In other words, covering 0.1% of the Earth’s surface with solar cells with an efficiency of 10% would satisfy our present needs. However, to tap into this huge energy reservoir at a price that is competitive to fossil fuels remains an enormous challenge. The dye-sensitized solar cell (DSSC) is a new generation that offers the potential of economically feasible conversion of solar energy to electricity. This consists of a porous matrix of semiconductor nanoparticles (usually TiO\(_2\)) onto which a monolayer of a redox active dye is absorbed. Solar conversion efficiencies >10% have been reported for this arrangement. However, one of the main parameters limiting further improvements in efficiency are back reactions, in which the excited electron is re-captured by solution species before it reaches the back contact electrode where it can do the work. One promising method to improve this situation is to increase the rate of charge transport through the semiconductor by replacing the nanoparticle matrix with oriented nanorods or nanotubes. However, to date the fabrication of TiO\(_2\) nanotubes requires the anodization of metallic titanium, making it an expensive process. On the other hand, the hexagonal close packed structure of ZnO allows nanorods and possibly nanotubes to be grown directly from zinc salt solutions, which will represent a significant cost saving. Among the available methods to produce highly-oriented ZnO nanostructures, electrochemical deposition methods stand out as having the potential to be chosen as a facile, efficient and economical process meeting the requirements of a reliable, large-scale production line. In this paper, the effect of electrodeposition parameters including concentration, potential and temperature on the morphology and optical properties of orientated ZnO nanostructures will be presented. Characterization techniques used included Field Emission Scanning Electron Microscope, X-Ray Diffraction and also UV-Vis Spectroscopy. The advantages and disadvantages of the use of ZnO in a DSSC as compared to TiO\(_2\) will also be briefly discussed.
Carbon Nanotube Based MnO₂ Nanorod Battery

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So called printed electronics, devices that can be made using simple printing processes, have received increasing interest in recent years. The fabrication of devices using printing techniques not only helps lowering manufacturing costs but can also result in flexibility, which is highly desirable for certain applications. Conventional batteries are not fully compatible with these printed devices, which include RFID tags, smart cards, electronic paper and wearable electronics. In order to provide a charge storage device in accordance with these requirements we have recently proposed a battery architecture which is based on carbon nanotube (CNT) random networks used as charge collectors.

This presentation will show advances made to improve on the above concept by also replacing the active cathode material with novel materials. Instead of the commonly used MnO₂ powder, our devices have been made using nanstructured MnO₂ materials. In addition to replacing the metallic current collector with a printable CNT network, the conduction enhancer (usually carbon black) has also been substituted by CNTs. Due to their excellent electrical conductivity and large aspect ratio, CNTs are highly suited to provide short, efficient conduction paths. Electrochemical measurements comparing the performance of both MnO₂ nanorods and nanostructured powders will be presented. The high surface area of the active material allows better access of the electrolyte to the MnO₂, thus leading to better usage of the material, especially under high current discharge conditions.

Triol Based Polyurethane Gel Electrolyte for Lithium Batteries and Electrochromic Devices

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Polyurethane gel electrolytes are emerging as potential candidates for the fabrication of flexible, compact and lightweight lithium polymer batteries. A Novel Triol based Polyurethane (PU) gel was synthesized from polyoxyethylene triol, 4,4’-diphenyl-methane diisocyanate) (MDI), and propylene Carbonate (PC) as a solvent. Gel electrolytes with varying solvent content were prepared keeping the mole ratio of carbonyl group in PC to Li⁺ as 12:1. The maximum conductivity of the PU gel electrolytes was found to be 2.53 x 10⁻² S/cm at the room temperature, which is higher than that reported in the domain of published literature for the thermoplastic polyurethane family. The Tan(δ) relaxation study revealed that the migration of lithium ion is mostly through the solvent phase. Stability and electrochemical performance of test cells were evaluated gel with electrolytes developed in the the laboratory. The transmittance of polymer gel electrolytes for all the composition was observed to be more than 90% over the visible range. Because of transparent nature and high ionic conductivity, PU gel electrolyte also has potential applicability in in both lithium batteries and electrochromic devices.

Enhanced Supercapacitive Behaviors of Manganese Dioxides

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Manganese based oxide electrodes exhibit high specific capacitance due to utilization of both electric double layer and redox activities. However, there is a drawback to the application of manganese oxides for supercapacitor, that is, loss of manganese oxide electrode through partial dissolution of the oxide during cycling. Previously, we reported the birnessite type manganese dioxides for active material in supercapacitor prepared by the electrochemical stimulation of MnO₂ powder electrode. Here we report the new electrolyte additives to enhance the supercapacitor behavior of birnessite.

X-ray diffraction measurements confirmed that hydrated lamellar manganese dioxides, birnessite, was prepared by the electrochemical stimulation of MnO₂ in a Na₂SO₄ solution. The high capacitance of 190 F g⁻¹ was achieved in 1 mol dm⁻³ Na₂SO₄. The galvanostatic oxidation and reduction curves of the birnessite electrode were compared in additive free and Na₄HPO₄ added electrolyte solutions. In the case of additive-free, the potential of birnessite linearly varied by applying constant anodic and cathodic currents with the capacitance of ca. 190 F g⁻¹. After one thousand cycles, the capacitance decreased, actually, manganese oxide precipitation was visually confirmed in the electrolyte after cycling, indicating the capacity reduction was due to the loss of active material by the partial dissolution of the birnessite. When the birnessite electrode was tested in the Na₄HPO₄ added electrolyte, the capacitance was remarkably increased up to approximately 230 F g⁻¹ at the initial cycle. There are no additional plateaus in the curves, furthermore, the curves unchanged over 1000 cycles meaning no significant degradation of capacity.

The capacitance vs. cycle number plots were compared in the electrolytes with and without Na₄HPO₄. Because
of the manganese dissolution, the capacitance drastically decreased in the additive-free electrolyte. However, when Na₅HPO₄ was dissolved into the electrolyte, the capacitance did not decrease over 1800 cycles, simultaneously, less or no precipitation was visually observed. The pH value of the electrolyte was almost constant when the additive was dissolved. Generally, manganese phosphate is insoluble in water. Therefore, if Mn²⁺ ions are dissolved from the electrode surface, its phosphate should be promptly deposited on the electrode. In other word, the electrode is coated with the phosphate thin layer, so that the dissolution would be successfully suppressed by the additive.

From ICP analyses of the electrolyte solution, the dissolved manganese amount was remarkably decreased with the increase of Na₅HPO₄ concentrations, and the cycleability was enhanced as well. The manganese dissolution is completely suppressed by the additives. There is a general consensus that the manganese dissolution is essential problem to be solved for the application of electroactive MnO₂ based electrode to electrochemical capacitors. We believe that there is a general possibility that the new additives realize higher capacitance and enhanced cycle life of transition metal oxides as active material for the electrochemical capacitors.

Finally, some interesting properties of large ensembles of wired nanoparticles are elucidated. It is shown that an ensemble can exhibit a hysteretic behaviour even in cases in which individual particles do not. This issue is very important towards understanding of ensemble electrochemistry.

Electrochemical Characterizations of Lithium Secondary Batteries at High Temperatures Using Nanostructured Lithium Titanate Spinel (Li₄Ti₅O₁₂)

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Lithium titanate (LTO) is an attractive nanostructured material with excellent charge/discharge ability and superior safety properties compared to standard negative electrode of lithium secondary batteries. More particularly, in this study, we aim at using this innovating nanomaterial in rechargeable batteries working at high temperatures.

In fact, even if Li-ion is usually limited to utilizations below 60°C, some specific applications with very aggressive environment are also interested in rechargeable batteries based on this technology. As an example, oil exploration requires batteries working at temperature above 80°C. Secondary batteries capable to work with only a limited number of cycles in such conditions appear as a promising alternative to the traditional primary lithium batteries.

However, working at high temperature requires a stable electrolyte with appropriate electrochemical and thermal stability together with adequate materials. To overcome the well-known thermal limitations of standard Li-ion cells, alternative anodes to graphite, such as LTO, are suggested in this study.

Spinel Li₄Ti₅O₁₂, which operates at 1.5 V/Li⁰, provides an electrode system with much better stability characteristics. Indeed, at this high voltage, the solid electrolyte interphase (SEI) film associated with the graphite anode does not form, because the reduction of the organic species (such as carbonates solvents) only occurs below 1V/Li⁰. In fact, high redox voltage of LTO materials makes it possible to use nanostructured morphology (i.e. which develops high specific surface areas) to offer improved performances without abuse-tolerance concerns associated with solvents reactions over the electrode surface. In addition, the issue of lithium plating in existing Li-ion cells in case of charge performed at high rate and/or low temperature may be entirely resolved because of the high potential of the Ti⁴⁺/³⁺ redox couple versus lithium metal. Moreover, unlike the graphite anode case, no volume change is expected during the insertion of lithium atoms in the spinel structure with the formation of a rock-salt-type Li[Ti₅O₁₂] material with a zero-strain structural ability.
Therefore, LTO nanostructured active material can be coupled with a 4V positive electrode, to provide a system operating at 2.5 V. However, on the one hand, the replacement of graphite by Li$_{10}$Ti$_2$O$_{12}$ could be seen by some as a hurdle in itself because of the loss of some energy density at the level of the cell. On the other hand, the absence of graphite can be considered as a solution to the intrinsic cycle life limitation at high temperature (mainly due to the dissolution of the SEI in the electrolyte above 60°C) and safety problems of the standard Li-ion battery technology in abuse conditions.

The purpose of this paper is to study the effect of high temperature on the electrochemical behavior of nanostructured LTO electrodes. Voltamperometry, X-ray diffraction and charge-discharge tests at several temperatures (mainly 60 and 100°C) were employed to study the electrochemical characteristics of Li$_{10}$Ti$_2$O$_{12}$ and especially to investigate the thermal stability and reactivity between the cell components and the electrolyte.

A02063-03548

**Achieving High Proton Conductivities in Polymer Electrolyte Membranes for Fuel Cells Applications**

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Highly sulfonated polyarylenethioethersulfones (SPTES) based polymers, including SPTES, 6F-SPTES, and Block SPTES copolymers, were synthesized in a wide range of compositions. Investigations of the polymer membranes revealed that these polymers have outstanding mechanical integrity, very good thermal/thermo-oxidative stability and high proton conductivities. The Membrane Electrode Assemblies (MEAs), fabricated from SPTES based membranes, demonstrated peak power density twice that of Nafion-117 membrane, at 80°C and 55% relative humidity. To further improve the performance of the SPTES based membranes for fuel cell applications, nanoparticles, such as Zirconium Phosphate (ZrP) or nanoClay, were introduced into the SPTES based membranes to form nanocomposite membranes. The interesting feature of the nanoparticles is that it can retain water at the high temperatures required for fuel cell operations. The nanocomposite membranes were fabricated by casting the solution of SPTES based polymers and nanoparticles in DMAc. The nanocomposite membranes were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to confirm and characterize the dispersion of nanoparticles in SPTES based polymers. The thermal properties, proton conductivities, and mechanical properties of the nanocomposite membranes were also investigated.

A02085-03596

**Preparation and Characterization of Proton-conducting Phosphoric Acid-doped Silica Gel Electrolyte for Secondary Battery at Room Temperature**

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Solid-state electrochemical cells were fabricated using proton conducting phosphoric acid-doped silica gel as an electrolyte, zinc with zinc sulphate as a composite anode and γ-MnO$_2$ with graphite as a composite cathode material. H$_3$PO$_4$-doped silica gel with phosphoric pentaoxide was dried in home made vacuum chamber and heated at 40, 60, 80, 100, 150 and 200°C temperatures for 2h, 3h, 4h and 5h in 2RML ROTAMENTAL by Remi motors Ltd. Mumbai, India, before fabricating the battery in order to reduce the possibility of corrosion. The material was studied by X-ray powder diffraction (XRD), thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and complex impedance spectroscopy (CIS). It had found proton conductivity in the order of $1 \times 10^{-5}$ - 0.1 S/cm at room temperature and remained stable up to 100°C.

The fabricated all solid-state battery subjected to electrochemical characterization reveals several tens of charge-discharge cycles at relatively high current density. Cyclic Voltametry was carried out using LabVIEW-7.1 (National Instrument, USA).

A02091-04499

**Electrochemical Deposition of Polyaniline into Nanostructured Titanium Dioxide Matrices**

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The dye-sensitized solar cell (DSSC) is a new generation that usually consists of a porous matrix of TiO$_2$ nanoparticles onto which a monolayer of a redox active dye is absorbed. The light is absorbed by the dye and then the excited electron is rapidly injected into the conduction band of the semiconductor. This arrangement can yield solar conversion efficiencies in excess of 10%. However, such high efficiencies are only possible with cells filled liquid electrolytes, whereas an all solid state construction is desirable for practical applications. Although one way to produce a solid state device is to replace the electrolyte with a hole conductor, such as a conductor polymer, conversion efficiencies of such cells have so far been disappointing, only a few percent. One of the main difficulties is the need for the hole conductor to fully penetrate into the nanostructured semiconductor matrix, failure to do so leads to dead areas and thus a poor conversion efficiency.
In an attempt to solve this problem the conducting polymer polyaniline has been electrochemically deposited into a porous titanium matrix using a cyclic dipping process, previously only used for the deposition of inorganic materials. An update on the success of this novel approach will be presented.

A02095-04509

Optical Amplification of Eu3+ Emission via Energy Transfer at Molecular Printboards for the Efficiency Enhancement of the Solar Cell

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The main challenge in nanotechnology resides in the precise spatial (self-) organization of nanoscale components onto surfaces which requires an activated interface, like self-assembled monolayers (SAMs). The molecular printboards, monolayers of β-cyclodextrin (β-CD), can be employed to bind suitable guest molecules onto a surface with molecular accuracy based on the host-guest interactions. The trivalent cations of several lanthanides and their organic complexes are known to exhibit photoluminescent properties. The noncovalent immobilization of a guest sensitiser and a lanthanide moiety in the β-CD cavity enables sensitized lanthanide luminescence due to the close proximity for the efficient energy transfer in solution. Based on this host-guest interaction, the first example of the controllable SAMs of Eu3+ complexes is prepared on the molecular printboards and is successful to demonstrate the stoichiometry of the efficient energy transfer pair with a close proximity manner proved by local image spectra and emission life-time.

To further maximize the optical amplification, self-assembled organic/nanoparticles multilayers based on multivalent supramolecular host-guest interactions between dendritic guest molecules and host-modified TiO2 particles can result in a strong absorption and efficient sensitization thin film. The stable positioning nanostructure is used as antireflecting layer for enhancing the solar cell conversion.

A02105-03622

Enhanced Ionic Conductivity in Poly (Methyl Methacrylate) (PMMA) /Layered Lithium Trivanadate (LiV3O8) Nanocomposite Gel Polymer Electrolytes

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Polymers intercalated into low-dimensional host lattices form an attractive class of compounds since intercalation can combine properties of both the guest polymer and the inorganic host in a single material. Polymer-layered silicate nanocomposites have recently attracted attention as new ionic conducting materials. They exhibit enhanced ionic conductivity, improved mechanical and interfacial stability towards electrodes. These materials also serve as model systems for understanding the effect of confinement of polymer electrolyte chains on nanoscale in relation to the bulk polymer electrolyte. In the present work, a novel nanocomposite gel polymer electrolyte composed of PMMA, LiV3O8 as layered host, (PC+DEC) as plasticizer and LiClO4 as salt have been investigated with varying concentration of LiV3O8 (from 0 wt. % to 8 wt. %). X-ray diffraction (XRD) studies show that solution intercalation of PMMA into LiV3O8 results in the enhancement of d-spacing from 6.32 Å to 7.74 Å indicating intercalation of PMMA into the layered LiV3O8. FTIR spectral studies confirm the favorable interactions between the polymer matrix, LiV3O8, plasticizer and salt LiClO4. Maximum ionic conductivity of 1.5 × 10-3 S/cm has been obtained for 4 wt. % loading of LiV3O8 as revealed by ac ionic measurements. Beyond 4 wt. % of LiV3O8 loading a decrease of conductivity was observed which could be attributed to the usual blocking effect on the transport of charge carriers resulting from aggregation of LiV3O8. On the other hand increase of ionic conductivity up to 4 wt. % loading of LiV3O8 could be attributed to the high dielectric constant of LiV3O8 which help to dissociate lithium salt (LiClO4) resulting in increased concentration of free carriers. The temperature dependence of ionic conductivity was observed to obey Arrhenius behavior. SEM results show aggregation of nanocomposite particles resulting from extension of some polymer chains from interlayer to the edge.
Effect of Calcination Temperature on the Morphology and Electrochemical Properties of \( \text{Co}_3\text{O}_4 \) for Lithium-ion Battery

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Rechargeable Li-ion batteries have become the power source of choice for popular electronic equipment because of the high energy density. There is increasing attention on the morphology and size control of material synthesized since the discovery of transition-metal oxides by Poizot et al. The reactivity of the metal oxide particles is markedly determined by the morphology and size because \( \text{Li}_2\text{O} \) formed in reduction is electrochemically inactive and the reverse removal of lithium is thermodynamically difficult. In addition, new properties are required likely due to the size effect, such as chemical composition, relative size, and morphological structure when reduced down to the nanometer scale.

In this work, a facile method have been developed to synthesize \( \text{Co}_3\text{O}_4 \) in mass production by using hexamethylenetetramine (HMT, \( \text{C}_6\text{H}_{12}\text{N}_4 \)) as precipitator via the hydrothermal treatment. The samples calcinated at different temperatures from 300 °C to 600 °C were characterized by XRD and SEM. The structure became agglomerative and collapsed with the increase of calcination temperature. The electrochemical performance in combination with SEM and BET analysis suggests that there is an optimum calcination temperature for \( \text{Co}_3\text{O}_4 \). It is found that the capacity retention of well crystallized \( \text{Co}_3\text{O}_4 \) hollow microspheres with higher specific surface area at 300 °C is almost above 94% from 5th cycle at different current density of 40 and 60 mA·g\(^{-1}\). The EIS analysis demonstrated that lithium-ion conduction inside the SEI layers and charge transfer at the electrode/electrolyte interface was hindered with the increase of calcination temperature. It is proposed that drastic capacity fading and the variation of resistive components (SEI layers and charge transfer) can be influenced by morphologies due to the calcination temperature.

Preparation of Si(0)/Poly(aniline-2-sulfonic acid) Composite Anode for Lithium Ion Battery

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The carbonaceous materials as anode materials for lithium ion battery are commercially used because of excellent durability, but do not propose good energy density. Accordingly, studies using anode materials of metal particles such as Ag, Ni, and Sn have progressed to dissolve such drawback, but this work is restricted in enhancing electrochemical properties on account of agglomeration of metal particle each other, and volume expansion. This work focuses on enhancing electrochemical properties (i) by forming three-dimensional network between metal and poly(aniline-2-sulfonic acid) as conducting polymer, (ii) dispersing metal particles well inside complex, and (iii) keeping buffering effect so as to protect metal particles from agglomerating.

Si(0)/PANI nanocomposites and Si(0)/Poly(aniline-2-sulfonic acid)(PASA) nanocomposites were prepared by in-situ oxidative polymerization. To prepare these nanocomposites, Si(IV) metals were reduced as state of Si(0) by using sodium hydride as a metal reducing agent, and stabilized by t-BuOH stabilizer in the mixed solution. Si(0)/PANI nanocomposite or Si(0)/Poly(aniline-2-sulfonic acid) one was obtained by polymerizing to drop aniline or aniline-2-sulfonic acid monomer into above mixed solution and to add ammonium persulfate (APS) as an oxidant afterward. This process indicates on how well metal nanoparticles distribute to the polymer chain. Three nanocomposites samples were prepared as 100:0, 70:30, and 70:30 according to the ratio of Si(0) to PANI or Si(0) to PASA by weight percent. Si(0) nanoparticles in the nanocomposites were not only well-reduced as neutral state but also well-distributed in polymer chain. The morphology of these nanocomposites was investigated by means of X-ray diffraction (XRD), Scanning electron microscopy (SEM). In the XRD pattern, there was an increase in silicon region which could be an evidence of existence of silicon nanoparticles with the increase of silicon tetraacetate amount. The charge capacitance of Si(0)/PASA (70:30) nanocomposite was improved more than 30 % as compared with Si(0)/PANI by transferring ion mobility easily because of sulfonyl group.
A02134-03716

Structural and Electrochromic Properties of Molybdenum Doped Vanadium Pentoxide Thin Films by Electrophoresis Deposition

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Vanadium pentoxide (V₂O₅) is a typical Li⁺-intercalation compound due to its layer structure. However, there are some disadvantages for pure V₂O₅ film including their low conductivity and narrow optical modulation, and worse cycle reversibility and stability, therefore great efforts have been made in order to improve or modify their electrochromic property. The films can be modified by doping with high-valence cations (Mo⁶⁺) that generate a donor-like defect due to provide quasi free electron with the formation of substitution solid solution. In this paper, Mo doped V₂O₅ thin films were successfully prepared on ITO substrate with electrophoresis deposition (EDP) through sol-gel method. Through a series of experiments, the optimal process of EDP could be found out. It is found that V₂O₅ thin films deposited by EDP were a compact microstructure with finer adhesive force with ITO substrate and the thickness was uniform. X-ray diffraction and scanning electron microscopy were used for studying the nanostructures of the films. The optical and electrochemical properties were measured by the transmittance spectra and cyclic voltammetry measurements, respectively. Optical modulation property of film was tested by applied potential between -1.5 V to +1.5 V. The film showed the electrochromic phenomena from bottle green to orange, which would be a promising application at smart windows and information display.

A02136-03678

Combustion Synthesis of Ultra-fine Nickel Oxide Powder and Its Characterization

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Nickel-yttria-stabilized zirconia (Ni-YSZ) cermet is a popular material for solid oxide fuel cell anode. NiO-YSZ is usually synthesized by reduction of anode precursor, NiO-YSZ in hydrogen atmosphere. The morphology of NiO in the precursor influences the properties of cermet which governs the anode performance. In the current study, ultra-fine NiO powder was prepared by combustion synthesis technique. Three different fuels, namely, urea, glycine, and citric acid were used. Effects of fuel composition, metal/fuel ratio were studied. The synthesized powders were calcined at different temperatures ranging from 600-1000 °C. Phase analysis of the powders was done using X-ray diffraction technique. Thermal and microstructural investigations were carried out by TG/DTA and SEM, respectively. It was observed that auto-ignition temperature, particle size, and degree of crystallinity of NiO powder particles depend on the temperatures and volume of gases evolved during the reactions, which ultimately depend on the amounts and types of the fuel.

A02140-03711

Cross Surface Charge Percolation for High Energy Density Lithium Storage

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As one of the state-of-the-art power sources, lithium ion batteries have been widely investigated in recent years, due to the increasing demands in portable electronic market and the emerging application in hybrid vehicles. For pursuing high energy and high power densities, numerous efforts have been taken to increase the capacity and rate capability by using advanced device configuration or electrode materials. For instance, the amounts of binder and conducting additives have been rigorously optimized in the electrode sheet to maximize the fraction of active material. However, for olivine-type materials LiMPO₄ (M=Fe, Mn, etc.), which are electronically insulating wide bandgap semiconductors, a large amount of conducting additives has to be added to secure acceptable electrochemical performance, greatly reducing the energy density of batteries. The situation is even worse if nanostructured materials are used, since more conducting additives are needed to form a continuous conducting pathway of electrons. Meanwhile, more binder has to also be added due to the higher surface area of the material itself and any additives, further reducing the energy density of batteries.

There have been many approaches employed to address the above challenges. Here we will introduce our new strategies of “molecular wiring”, “redox targeting” and “polymer wiring” to improve the electrochemical performance of carbon-free LiFePO₄ whose electronic conductivity is ~10⁻² S/cm. Molecular wiring of battery materials is based on our recent discovery of cross-surface charge transfer in self-assembled molecular
charge transport layers on mesoscopic oxide films. Such molecular charge transport layers can be employed to electrochemically address insulating battery materials. While intriguing, molecular wiring is constrained by the risk of desorption of the surface adsorbed redox mediator, and the low current output limited by the rates of cross-surface charge percolation and interfacial charge transfer. Redox targeting with free relay molecules dissolved in the electrolyte was then introduced to address these issues. The advantage of using a freely diffusing redox shuttle over molecular wiring is that it allows charge transport to proceed at a much faster rate, thus enhancing greatly the power output of the battery. However, the challenge in this case is that a special separator has to be used to prevent the redox shuttle molecules from reaching the counter electrode, which leads to self-discharge. A novel polymer-wiring concept is introduced to electrochemically address insulating battery materials. It provides an all-in-one solution to the problems encountered by molecular wiring and redox targeting. It is expected that, with engineered polymer backbone and swing redox centers, this strategy will pave the way to conducting-additive and binder free electrode for high energy density batteries.

**Synthesis and Assessment of SrTiO$_3$-based Perovskite as Anode Materials for Solid Oxide Fuel Cells**

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SrTiO$_3$-based perovskite materials, were synthesized via an EDTA-citrate complexing process, and examined as potential SOFC anode materials in terms of electrical conductivity, phase stability, and electrochemical performance in sulfur-containing methane fuels. Substitution on the A and B sites with alkali earth (La, Y, Nd) and transition metal elements (Co, Nb, Cr, Mn) was found to substantially improve the electrochemical performance of SrTiO$_3$-based anodes. It is believed that simultaneous donor and acceptor doping in SrTiO$_3$ has improved both electronic and ionic conductivities, as well as the catalytic activity toward the electrochemical oxidation of methane fuels. Good sulfur tolerance was also observed in 50ppmH$_2$S-CH$_4$ fuel.

**Effects of Low Hydrocarbons on the SOFC Anode**

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Solid oxide fuel cells (SOFCs) of high temperature fuel cell have various advantages. The efficiency of fuel cell can be improved by a cogeneration design; in addition, cheap material, avoiding noble metal catalysts, can be utilized to satisfy the electrochemical performance. The high temperature operation can also lead to the capability of internal reforming, providing fuel flexibility. SOFCs can directly use CH$_4$ as well as CO as a fuel with sufficient steam feeds. Consequently SOFCs do not require the CO clean-up fuel processor, such as water-gas shift (WGS) reactor and preferential oxidation (PROX) reactor. The use of CO and CH$_4$ is possible because the anode material of SOFCs is active for steam reforming (SR) and WGS reactions. However, heavier hydrocarbons than CH$_4$, such as ethylene, ethane, propane, and etc., induce the carbon deposition on the Ni-based anode of SOFCs. In the case of ethylene steam reforming reaction on the Ni-based catalyst, rate of carbon deposition is faster than among the hydrocarbons, even aromatics. In the reformates of heavy hydrocarbons (diesel, gasoline, kerosene, and JP-8), concentration of ethylene is usually higher than low hydrocarbons such as methane, propane and butane.

In this paper, ethylene effect on the SOFC anode is investigated. Two cases of fuels are used for observing the effects of low hydrocarbons at reformate gas stream on the SOFC anode. Methane and ethylene are supplied to the electrolyte-supported SOFC anode. In the case of using ethylene as a fuel, catastrophic degradation of SOFC conductivity is observed. Performance of SOFC also decreases as the SOFC operation time increases using ethylene as a fuel. These results are caused by the carbon deposition from ethylene on the SOFC anode. So, removal of low hydrocarbons (over C$_2$), especially ethylene, at the reformate gases is important for stable operation of SOFC. New methodology as named “post-reformer” is introduced for removing the low hydrocarbons at the reformate gas stream. Catalyst of the NECS-PR2 is selected for post-reforming catalyst because the catalyst shows the high selectivity for removing low hydrocarbons and long-term stability. The diesel reformer and post-reformer are continuously operated for about 250 hours as integrated mode. The reforming performance is not degraded and low hydrocarbons in the diesel reformate were completely removed.

**Acknowledgments:**

This work was funded by the Korea Electric Power Research Institute (KEPRI), and the Korean Government. Analysis facilities, such as the GC-MS and SEM/EDX, were supported by the Ministry of Education and Human Resources Development.
Also this work is outcome of the project of high temperature electrolysis cell development and high temperature steam corrosion experiment for nuclear hydrogen production system by KEPCO & KHNP.

A02201-03773

Low Temperature Deposition of SnO₂ on C-Paper as an Anode for DMFC
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Electrochromic properties of SnO₂ films is attracting interest of researchers after the reports of Orel et al. and Olivi et al., who prepared samples by dip coating, whereas Isidorsson et al. prepared SnO₂ films by dc sputtering. Based on these reports, it is anticipated that the electrochromic properties would depend on crystallinity and preferred orientations. In addition, the oxidation/reduction properties of this material is well explored in gas sensing applications mainly because of its tendency to easily adopts dual valency of (II) and (IV) or a mixture of valencies (Sn4+, and Sn2+) upon partial reduction. CellTechPower® has build up a technology upon conventional solid oxide fuel cell materials and components using liquid tin anode. In this the oxygen ions are extracted at the cathode and pass through the electrolyte to the anode (fuel) side where they combine with hydrogen or carbon monoxide from the fuel to form water or carbon dioxide. Meanwhile, electrons are released at the anode and travel through the load producing useful electrical energy on their way to the cathode. Their anode is a p-orbital-electron metal such as tin which is molten at operating temperatures. The tin is held in place by a ceramic matrix. Electricity is produced in fuel cell by converting tin to tin oxide at the anode. The conversion of tin to tin oxide has attracted researcher’s interest for exploring such properties deposited by various techniques.

This work presents low temperature thin film deposition of tin oxide (SnO₂) using modified plasma enhanced chemical vapor deposition on carbon paper as an anode for direct methanol fuel cells. Pt was RF sputtered on SnO₂/C paper and Ru was thermally evaporated on Pt/SnO₂/C paper. For SnO₂ deposition, stannic chloride (SnCl₂ xH₂O) was used as precursor and oxygen (O₂, 300 sccm) as reactant gas. Deposition was carried out without heating the C-paper. Plasma power was varied (60 to 80W) to change the grown film properties. Amount of source material was varied to obtain different amounts of SnO₂ on the carbon paper. Fine granular morphology was observed with tetragonal rutile structure grown along the [110] direction. Tin oxide has proved to be a good matrix for the deposition of platinum nanoparticles since they present a rough surface. Cyclic voltammetric studies indicated that Pt/SnO₂/C system resulted in a maximum anodic oxidation in comparison with Pt/C.

A02225-03800

New Mechanisms of Li⁺ Insertion/Extraction into Highly Defective LiₓFePO₄ Powders
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LiFePO₄ is now recognized (and used) as a new electrode material for Li-ion batteries as it represents a low cost and safe material that exhibits high specific capacity and exceptional structural stability upon cycling. Li ions can be reversibly removed from the structure, leading to the formation of FePO₄ in a two-phase process with a theoretical specific capacity of 170 mAhg⁻¹.

The crystal chemistry and electrochemical behavior of various nanometric “LiFePO₄” powders prepared by direct precipitation under ambient pressure in water will be presented. We report on the discovery, probed by in situ X-Ray diffraction, of a full solid solution process during Li⁺ extraction / insertion at room temperature for triphylite-based nanopowders that contain significant amounts of defects on the Li and Fe octahedral crystallographic sites, as deduced from Rietveld analysis of powder neutron diffraction data.

The possibility of having single phase extraction/insertion mechanisms (e.g., a sloping voltage curve) presents some intrinsic advantages with respect to applications such as an easier and cheaper monitoring state of charge of the battery as compared to a flat constant voltage curve.
In order to understand electrode reaction mechanism for high temperature electrochemical devices, AC impedance and DC polarization measurement usually have been used. In these methods, the mechanism is presumed from the relationship between the energy and the rate. It is difficult to grasp the physical/chemical states of the electrode and electrolyte under operating conditions of devices, which give us important and directly information for understanding the reaction mechanism. In this work, we applied in situ XAS technique to investigate the electrode reaction on La0.9Sr0.1Co0.8Fe0.2O3 (LSCF) and La0.6Sr0.4MnO3 (LSM), which are one of promising cathode materials for SOFC. The oxygen chemical potential profile around the electrode was evaluated by means of in situ electrochemical XAS, and the rate determining step of the reactions was discussed.

Dense thin films of LSCF and LSM were prepared on YDC and YSZ substrates by PLD technique, and used as a working electrode. A counter electrode was porous Pt/YDC/LSCF and a reference electrode was porous Pt. in situ electrochemical XAS measurements were performed at the beam line BL7C at Photon Factory, Japan. Absorption spectra of Fe/Co K-edge of LSCF and Mn K-edge of LSM were measured by the fluorescence mode. During measurements, the temperature was maintained at 1073 K, while controlling the oxygen partial pressure, p(O2), between 102 and 105 Pa, and applying the electrical voltage.

The XANES measurement of LSCF and LSM represented that the change of oxygen nonstoichiometry in LSCF and LSM could be estimated from the change of the Co and Mn mean valence, respectively. The absorption edge shift estimated from in-situ XANES spectra at Co K-edge of the LSCF and at Mn K-edge of LSM thin film measured under various DC bias and p(O2). The amount of the Co K-edge shift due to the polarization was comparable with that due to the corresponding p(O2) change when assuming Ln[p(O2)eff/p(O2)] = 4Fη/RT. The results indicated that change of the oxygen potential under polarization occur at the electrode/gas interface, suggesting that the rate determining step of the electrode reaction on the LSCF electrode is the surface reaction. On the other hand, the shift of the Mn K-edge was about half, implying gradual change of the oxygen potential in LSM bulk. This result implies the rate determined step of LSM electrode reaction is the bulk diffusion.
**Symposium F - Nanostructured Materials for Electrochemical Energy Systems:**

### A02271-03878

**Effect of Acetic acid on Electrospinning of PAN Polymer Solution**

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Polyacrylonitrile (PAN) was used to study the effect of acetic acid on electrospinning. In this work, the interior structure of electrospinning PAN nanofibers by adding different content of acetic acid was investigated. At first, the mixed solution of both polyacrylonitrile (PAN) in N,N-dimethylformamide (DMF) and acetic acid was electrospun. The PAN/ Acetic acid electros spun fiber web was synthesized through the process of stabilization at 280°C and carbonization at 800°C. The carbon fiber web was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FT-IR), energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). The addition of acetic acid leads to both good electric conductivity and a change of diameter of PAN fiber. The electric conductivity of carbonized PAN nanofibers, electro spun by solutions with different content of acetic acid increases in the following order: 30 wt.% acetic acid < 5 wt.% acetic acid < 20 wt.% acetic acid < 10 wt.% acetic acid. But, PAN fiber was crumpled when content of acetic acid increased more than 30 wt.%. The X-ray diffraction patterns of carbonized PAN nanofibers with acetic acid changed some. Also, We found that acetic acid could create holes on the surface of PAN fiber. Therefore, we supposed mechanism which PAN with adding acetic acid showed above-mentioned properties.

### A02293-03924

**Nanostructured Oxide Thin Films for Miniaturized Solid Oxide Fuel Cells (SOFCs)**

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The development of micro-solid oxide fuel cells (SOFCs) open new scenarios for portable unit power generation. Micro-SOFCs are likely to produce energy densities per volume and specific energy per weight up to four times larger than state-of-the-art batteries. Reducing the operation temperature is critical for practical use of miniaturized SOFCs and can be achieved using thin-film electrolytes.

However, lowering the SOFC operating temperature makes slow the kinetics of charge transfer reactions at the electrolyte-electrode interfaces, mainly at the cathode. This results in a worst fuel cell performance, because the lower the fuel cell working temperature, the larger the cathode overpotential. An increase in their triple phase boundary (TPB) can improve the electrode performance. Pulsed laser deposition (PLD) is very promising for the fabrication of tailored oxide thin films, because it allows to obtain single crystal or polycrystalline films, with tailored microstructure from dense to highly porous. This talk shows examples of PLD fabricated SOFC components and their assembly, such as dense oxygen ion (ceria) and protonic (barium zirconate) electrolyte films in single crystal and polycrystalline forms. Cathode films (LSFC perovskite oxides), deposited as dense or porous layers on polycrystalline tape-cast YSZ electrolytes, showed polarization drops of about 2 orders of magnitude from dense to porous films.

### A02334-04001

**Influence of Plasticizer on the PVAc :PEG Blend Polymer Electrolyte for Li-Ion Battery**

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The development of lithium batteries has gained an unprecedented significance in the last two decades as the demand for portable telecommunication devices, computers and eventually hybrid electric vehicles has been an ever-increasing one. The advantages such as no-leakage of electrolyte, higher energy density, flexible geometry and improved safety hazards have drawn the attention of many researchers on the development of lithium polymer batteries. A number of methods have been reported for improving the mechanical and morphological characteristics of polymer electrolytes in the higher temperature and for improving conductivity in the lower temperature. The Blend Polymer electrolytes overcome the disadvantages of gel electrolytes and enhance the ionic conductivity as well as mechanical strength. In the present work, the effect of plasticizer on the Li ion conductivity of the blend polymer electrolytes based on PVAc and PEG containing LiCF3SO3 has been studied. XRD analysis has been done to confirm the amorphous nature of the blend gel polymer electrolyte. The complex AC impedance spectroscopy has been studied in the frequency range of 42Hz – 1MHz over the temperature of 303K – 343K. The conductance spectra obey the Jonscher’s power law. The conductivity of blend electrolyte is found to be 1.0 x 10^-3 S/cm at 303K. Addition of DMF influenced the conductivity (2.8 x 10^-3 S/cm) for 20mol%DMF at 303K) and the membrane is found to be free standing. It has been
noted that the the temperature dependence for the blend gel polymer membrane is found to follow Arrhenius nature and the activation energy is found to decrease from 0.56 to 0.36eV. The transport parameters of the blend gel polymer membrane has been calculated and discussed. Dielectric studies show α – relaxation peak in the low frequency region which may be due to the motion of the main chain dipole segment.

The starting materials, TiO$_2$-anatase, LiNO$_3$, and citric acid, were thoroughly mixed in an agate mortar with acetone as the dispersing agent. After drying, the precursors were heated at 800°C for 12h in the air. The contents of citric acid were 0 wt %, 5 wt %, 10 wt %, and 15 wt % of the total mass of TiO$_2$ and LiNO$_3$. And the products were MAC0, MAC5, MAC10, MAC15, respectively.

Preparation of Li$_4$Ti$_5$O$_{12}$

The spinel Li$_4$Ti$_5$O$_{12}$ has been demonstrated as a good candidate for lithium-ion batteries as an anode and for asymmetric hybrid supercapacitors.

Our previous experiments have demonstrated that the products are with better crystallinity and rate performances, when LiNO$_3$ with low melting point was used as the lithium source. In this paper, citric acid with low melting point was used as the additive. Then, Li$_4$Ti$_5$O$_{12}$ with higher performances was synthesized by the traditional method, without ball-milling.

Preparation of Li$_4$Ti$_5$O$_{12}$

The objective of the present work was to investigate the possibility of improving the hydrogen storage capacity of the mesoporous MCM-41 containing nickel (Ni) oxides (Ni/MCM-41). The Ni/MCM-41 was prepared using a hydrothermal process as a function of Ni content (0, 2, 5, and 10 wt.% in the pure silica MCM-41). The surface functional groups on the Ni/MCM-41 were identified by fourier transform infrared spectroscopy (FT-IR). The structure and morphology of the Ni/MCM-41 were characterized by X-ray diffraction (XRD) and field emission transmission electron microscopy (FE-TEM). XRD results showed that the well-ordered hexagonal pore structure and FE-TEM also revealed, as a complementary technique, the structure and pore size. The textural properties of the Ni/MCM-41 were analyzed using N$_2$ adsorption isotherms at 77 K. The specific surface areas and the pore size distributions were determined from BET equation and desorption isotherms with the BJH method, respectively. The hydrogen storage capacity of the Ni/MCM-41 was evaluated at 298 K/100 bar. It was found that the presence of Ni on mesoporous MCM-41 created hydrogen-favorable sites which enhanced the hydrogen...
storage capacity by spillover effect. Furthermore, it could be concluded that hydrogen storage capacity was greatly influenced on the amount of nickel oxide, resulting in the chemical reaction between Ni/MCM-41 and hydrogen molecules.

CdSe Quantum Dot Sensitized TiO₂ Photoelectrodes

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Dye-sensitized solar cells (DSSC) have attracted much attention recently as an alternative to conventional solid-state solar cells. In the aspect of solar energy utilization, the development of TiO₂ that can utilize visible light (λ>400 nm) efficiently is indispensable to make the solar cells. By using a CdSe-sensitized nanocrystalline TiO₂ photoelectrode, the photovoltaic performance of the cell is presumed to give better efficiency; since, CdSe is a semiconductor materials which absorb light in the visible region when the sizes of these materials were decreased down to the quantum-dot (QD) region, the quantum confinement effect makes it possible to generate multiple electron-hole pairs per photon through the impact ionization effect. In this work, CdSe was assembled into nanocrystalline TiO₂ films using a spin coating method. Colloidal CdSe - QDs were synthesized in a reversed micelle system were purchased from Aldrich and absorb the visible light from 480 to 640 nm and the diameters of the CdS-QDs were about 2.5 – 6.5 nm. Colloidal CdS-QDs were first self-assembled on TiO₂ surface by using a bifunctional linker, 3-mercaptopropyl trimethoxysilane. Mesoscopic TiO₂ films were prepared by doctor blade method on Florin doped tin oxide substrates, followed by sintering at 450 °C for 30 min. The thickness of the TiO₂ film was measured to be 12 μm. TiO₂ films were surface modified by immersing in a 1 wt % MPTMS/toluene solution for 5 min, followed by spin coating CdS-QDs at different rotational speeds and layer thickness. The present method is proved to have a great enhancement to the performance of the DSSC.

Effect of PVC Content on Ion Conductivity and Mechanical Properties of PEO-based Polymer Electrolytes

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In order to overcome the solid-state electrolyte problem of poor ionic conductivity (σ = 10⁻⁸ to 10⁻⁷ S cm⁻¹) and their mechanical strength, poly(vinyl chloride)[PVC]/poly(ethylene oxide)[PEO] polymer electrolytes for secondary battery were prepared and their properties were investigated. Polymer electrolytes, based on PVC/PEO blends were prepared by solution casting technique. The binary mixture of carbonate solvent was used as a plasticizer, and lithium perchlorate (LiClO₄) as a salt. The ionic conductivity of the polymer electrolytes was measured by frequency response analyzer (FRA) method. The morphology and mechanical properties of the polymer electrolytes were characterized by scanning electron microscopy (SEM) and universal tensile machine (UTM). The crystallinity of the polymer electrolytes was evaluated using differential scanning calorimetry (DSC). The polymer electrolytes containing 2 wt.% PVC showed the highest ionic conductivity, 2.35 x 10⁻¹ (S/cm) at 20°C. Also, the mechanical property of the polymer blend electrolyte was better than that of the pure PEO electrolyte.
Design of Naoporous Carbon Electrode for High Voltage Operation of Electric Double Layer Capacitor

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The authors modified the activated carbon electrode in order to improve the energy density of electric double layer capacitor (EDLC). The N-doping by NO-gas or the heat-treatment at 1500°C was effective for suppressing the capacitance decline by the high voltage (> 3V) charging at 70°C. It was also found that the multi-walled carbon nanotube (MWCNT) heated at 2800°C showed the excellent durability for the high voltage charging.

Ru/LSCM Catalysts for Propane Reforming in IT-SOFCs

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In recent years, considerable research has been directed toward the development of new catalysts for the hydrocarbon reforming in intermediate temperature solid oxide fuel cells (SOFCs). In fact, while conventional Ni/yttria stabilized zirconia composite anode gives adequate performance in pure H2, Ni tends to catalyze the formation of carbon in hydrocarbon fuels. Therefore, the development of Ni-free materials such as the La0.75Sr0.25Cr0.5Mn0.5O3-d perovskite powders as alternative anodes has recently gained significant attention. Considering that nanostructured Ru is a well known catalyst in various reactions such as the syngas production, Ru/La0.75Sr0.25Cr0.5Mn0.5O3-d composites have been investigated in this work as alternative anodes for the direct utilization of propane in SOFCs.

In order to increase the catalyst surface area, two synthetic approaches have been developed for the preparation of nano-structured composites: a modified sol-gel process for the synthesis of LSCM powders and a microwave-assisted process for the deposition of metallic ruthenium nanoparticles onto the LSCM surface. In particular, the LSCM powders were prepared by a sol-gel method based on a modified Pechini procedure and the deposition of 5 wt% metallic ruthenium nanoparticles was carried out in ethylene glycol by a microwave-assisted procedure.

Single-phase LSCM perovskite powders were obtained and SEM micrographs revealed particles having size in the 200-300 nm range. TEM investigations of Ru/LSCM composites showed a homogeneous distribution of metallic ruthenium nanoparticles with mean grains size around 2-3 nm. The catalytic activity of these potential anode materials was investigated for the following propane reforming processes, i.e. steam reforming (SR), autothermal reforming (ATR) and partial oxidation (POX) at 600°C, 700°C and 800°C. A good conversion of propane (≥ 92%) was observed in POX and ATR conditions at 700°C and 800°C, whereas in the steam reforming environment a satisfactory conversion was achieved at 800°C. The ruthenium presence was found to improve the selectivity to H2 and syngas formation for all the experiments performed, showing syngas productions higher than 80% at 700°C and no carbon formation was detected in all environments. Finally, a good chemical stability after catalytic tests was verified by XRD and TEM analyses.

This work has been supported by the “Celle a combustibile ad elettroliti polimerici e ceramici: dimostrazione di sistemi e sviluppo di nuovi materiali” FISR Project of Italian MIUR.
respectively. The microstructure of the Pt/Ni/porous GNFs was characterized by X-ray diffraction and transmission electron microscopy. The hydrogen storage behaviors of the Pt/Ni/GNFs were studied using a PCT apparatus at 298 K and 10 MPa.

Development of Solid-State Lithium Ion Battery Using Polymer Electrolyte

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Safety problems have become a significant issue in lithium ion battery technology. The development of an all-solid battery using a solid organic or inorganic electrolyte is a promising target with regard to fire-resistance. Dry polymer electrolyte, free from low molecular weight solvents, is flame-resistive and has unique morphological and mechanical features. The lack of grain boundaries in dry polymer electrolytes is also an advantage over inorganic crystalline solid electrolytes. It is our goal to develop a safer lithium ion battery using polymer electrolyte. To achieve this, choice of electrode materials which are compatible with polymer electrolyte is important. In this presentation, we introduce several electrode and electrolyte materials specifically synthesized for the purpose.

CATHODE

LiFePO₄ is selected, since it is stable at high temperature and operates at relatively low voltages which do not cause electrolyte decomposition. Due to the low electronic conductivity, LiFePO₄/carbon composite electrode was prepared by solid-state method and the amount of carbon loading was optimized. LiFePO₄/C composite was mixed with polymer electrolyte, which was composed of polyethylene oxide(PEO) and LiTFSI. When the salt concentration described as Li/O molar ratio was adjusted at 1/10, low-temperature performance of LiFePO₄ was achieved. The reversible capacity of the laminate cell was 140 mAh g⁻¹ (C/20) and 110 mAh g⁻¹ (C/2) at 40°C, which is comparable to the performance in the liquid electrolyte system.

ANODE

Lithiated carbon co-fired with polymer shows moderate exothermal behavior. Thus, carbon can work as a safe anode in polymer battery, but low wettability against polymer was the problem. A high anode performance was obtained in the surface modified meso-carbon microbeads(MCMB). MCMB and polyvinylchloride(PVC) mixture was heated under inert atmosphere. By this treatment, the surface of MCMB is covered with low crystalline carbon material derived from PVC pyrolysis. The surface modified MCMB electrode applied to dry polymer electrolytes shows a reversible capacity of 300 mAh g⁻¹, which is comparable to those obtained in liquid electrolyte systems.

ELECTROLYTE

PEO-based electrolytes were crosslinked using electron beam (EB) irradiation. The polymer network structure was developed after irradiation doses of 0, 140, 280, and 420 kGy. The electrolyte with higher EB dose amount exhibits lowering of crystallizing temperature due to stabilization of the amorphous state. Addition of the co-bridging agent is effective for developing a crosslinked structure with a smaller EB dose. Tensile strength becomes two to three times higher with irradiation compared to the non-treated polymer. Combination of the EB technique with a co-bridging agent is a simple and effective method to prepare strong dry polymer electrolyte films with improved room temperature conductivity.

Acknowledgments:
This study has been partly supported by Cooperation of Innovative Technology and Advanced Research in Evolution Area (City Area) Project of Ministry of Education, Culture, Sports, Science and Technology.
On the Use of Nano-materials and Nano-structures in Rechargeable Batteries and EDL (super) Capacitors

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There is no question that we experience in these days the nano-revolution. The improvement in imaging and manipulation technologies (e.g. high resolution electron microscopy, scanning probe microscopy etc.) in recent years, enables to study rigorously materials, surface architectures and composite structures in the nanometer scale. Hence, we see in recent years an explosion of innovative work related to nano-materials and nano-technology. Naturally, we would like to extend nano-technology also to the field of energy storage & conversion, with a clear incentive: the nano-structure may improve considerably the rate capability of energy storage devices.

However, nano-structure also means high surface area and hence high surface reactivity.

In this presentation we discuss the relevance of nanotechnology to 3 systems: rechargeable Li ion batteries, rechargeable Mg batteries and EDL capacitors.

In Li batteries most anode and cathode materials are thermodynamically unstable with the relevant electrolyte solutions (e.g. LiPF$_6$ in alkyl carbonate mixtures.) and hence develop rich surface chemistry. In case of the anode side, only compounds which red-ox activity is above 1.5V vs. Li (e.g. lithiated titanium oxide compounds) do not develop passivating surface films. In the cathode side, all lithiated transition metal oxide cathode materials react with standard electrolyte solutions (via their negatively charges oxygen atoms) and develop surface films that from one hand passivate well the active mass but from the other hand cause severe problems of inter-particle electrical contact. The oxygen atoms of olivine compounds (e.g. LiFePO$_4$, LiMnPO$_4$) are much less reactive than those of Li$_x$MO$_2$ and hence, LiMPO$_4$ materials can be used as nano-materials in Li ion batteries. In fact, all LiMPO$_4$ compounds suffer from very poor transport properties (both ionic & electronic) and hence, only their use as nano-particles make them relevant as cathode materials in Li batteries. The synthesis and study of nano-materials is thoroughly discuss in this presentation.

In turn, there is no passivation phenomena in rechargeable (non-aqueous) Mg batteries. The electrolyte solutions for these systems are selected accordingly, because Mg electrodes cannot behave reversibly while being covered by surface films. Thereby, the use of nano materials cathodes (e.g. Mg-Mo-S-Se Chevrel phases) for Mg batteries is very feasible and enables to obtain high rates.

Finaly, we discuss nano-structural aspects of activated carbon electrodes in super capacitor systems. For instance, graphitic nano-crystallites in disordered porous carbons may lead to phenomena of partial charge trapping due to possible intercalation of ions (e.g. tetra-alkyl ammonium cations). Fortunately, such charge trapping phenomena are reversible.

Dispersed Phase Polymer Composites: Mechanism of Improvement in Ionic Conductivity and Stability Properties

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Ionically conducting polymer composites are important materials both from fundamental studies as well as practical applications point of view. The polymer-salt complexes prepared by complexing polar polymers having solvating heteroatoms (e.g. polyethylene oxide (PEO), polypropylene oxide (PPO), etc.) with alkali metal salts/ acids (LiClO$_4$, NaClO$_4$, NH$_4$ClO$_4$, H$_3$PO$_4$, etc.) offer electrical (ionic) conductivity in the range of $10^{-4}$ to $10^{-7}$ S cm$^{-1}$ at room temperature. Almost all the solid polymer electrolytes (SPEs) are endowed with some inherent drawbacks that impose limitations on their applicability in devices. These are: (i) their semi-crystalline nature that hinders mobility of ions thereby lowering their conductivity, (ii) poor thermo-mechanical stability, (iii) slow kinetics and (iv) poor interfacial properties etc. In order to overcome these chronic problems of ion conducting polymers, various modifications such as co-polymerization, plasticization, ceramic dispersion etc. have been suggested. However, these modifications have their own strength and weaknesses. Plasticization improves electrical conductivity of polymer electrolytes at the cost of mechanical strength/dimensional stability. Co-polymerization, on the other hand, is a cumbersome process. The idea of dispersing inert ceramic fillers into the matrix of polymer-salt complexes was proposed originally by Weston and Steele as an attractive approach leading to improvement in mechanical properties of the polymeric films. Subsequently this approach resulted in improving electrical, electrochemical and thermal properties of SPEs. The enhancement in electrical conductivity on dispersion of inert filler particles has been generally explained in terms of the disruption of crystallization in the polymer host matrix. The improvement in mechanical properties is normally explained on the basis that the filler particles act as a supporting matrix for the conductive polymer electrolytes and hence impart it dimensional stability so as to retain an overall solid structure even at higher temperatures. However, the actual mechanism involved in the phenomena leading to lowering of thermal degradation behavior and enhancement in the tensile properties on
cereal filler dispersion in polymer-salt complexes is yet to be understood completely.

In the present work, we aim to investigate the role played by the inert cereal filler particles in the improvement in ionic conductivity and thermal/mechanical stability. The effect of filler concentration on enhancement in thermal and dimensional stability of the films has been investigated at the microscopic level using Fourier transform infra-red (FTIR) spectroscopy technique. The FTIR results have been interpreted to propose an explanation for improvement in conductivity and stability properties of the dispersed phase ion conducting polymers. A mechanism for the same has been proposed in terms of polymer–ion–filler interactions arising due to: (i) polar/acidic nature of the filler particles and (ii) transient cross-linking of polymer segments. The origin of such an effect appears to be consistent and convincing in the light of feasibility of polymer–ion–filler interactions evidenced by experimental results.

A02535-04336

New Concepts of Redox Centres in Electrode Materials for Li-Ion Batteries: A Step by Step Theoretical Approach

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Development of density functional theory (DFT) and computers capacities now allow accurate electronic structure calculations of infinite periodic solids, and predictions of solid state crystal structures. This powerful tool is being extensively used to rationalize the electrochemical properties of layered or 3D transition metal oxides [1] but seldom to more covalent systems, i.e. low potential materials for anodic applications. One rational explanation for this success lies in the fact that free enthalpy computations are sufficient to reproduce the potential vs. composition curve of these materials. In other words, the ratio of lithium to TM ions being slightly varied upon charge and discharge (1 Li/TM), a very few number of TM-like electronic states, equivalent in nature, are involved in the redox reactions, thus preventing from drastic structural and electronic changes upon intercalation. Based on simple concepts of chemical bonding, electron transfer and band structure our approach aimed at determining the structural and electronic criteria required for an electrode material to accommodate large charge variation (i.e. large lithium insertion) without undergoing dramatic volume expansion. By this way, we were able to show that systems built on weakly interacting molecular anions should exhibit promising electrochemical properties vs. lithium, provided that the redox centre is no longer the transition metal, as in oxides. This study was applied to a series of (early) transition metal phosphides Li_xMP_y for which up to 10 Li/TM can be reversibly exchanged upon charge and discharge without significant volume changes of the host matrix. [2] The covalent character of the metal-ligand bonds was shown to be at the origin of this surprising behavior, involving both the ligand and the transition metal in the redox reactions. Depending on the transition metal involved, three different mechanisms were then reported for these systems: classical insertion reactions with early-TM, conversion reactions with middle-TM, [3] and displacement reactions with late-TM [4];

(1) Insertion \[ MP_x \cdot xLi \rightarrow Li_xMP_y \]
(2) Conversion \[ MP_y \cdot 3yLi \rightarrow yLi_3P \cdot M^0 \]
(3) Displacement \[ MP_y \cdot xLi \rightarrow Li_xM_y \cdot yP \cdot xM^0 \]

To elucidate the driving force of these reactions, first-principles DFT phase diagram computations and chemical bond analyses were investigated. For each class of TM, the nature of the M-Pn bonds have been directly correlated to the crystal structure of the related phases, and to the redox centre (ligand or transition metal) involved in the redox reactions.


A02542-04431

Effect of Processing Parameters on Pore Structure and Thickness of Anodic Alumina Membranes

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Nanoporous anodic aluminum oxide tubular membranes were fabricated from aluminum alloy tubes in oxalic acid or other acid solutions electrolytes using a two-step anodization process. Anodization is a widely used process for producing corrosion resistant aluminum parts. These membranes are used on a large scale due to their thermal, chemical, and microbiological resistance as well as structural stability.
In this study, AAMs were investigated for characteristics such as pore size and thickness by varying applied voltage and oxalic acid concentration. Morphology of the membranes was examined by scanning electron microscopy. Membranes having narrow pore size and uniform pore distribution with parallel channel arrays were obtained. The pore sizes were ranging from 50nm to 200nm and the wall thicknesses were as high as 150 µm. It was found that the pore size increases directly with the applied voltage and inversely with the electrolyte concentration. Furthermore the pore size increased in direct proportion with the applied voltage and inversely with the electrolyte concentration while the interpore distance increased linearly with the applied voltage. It was also observed that increase in acid concentration increased tubular membrane wall thickness that improved mechanical handling. By using anodic alumina technology, robust ceramic tubes with uniformly distributed pore structure and parallel nanochannels of lengths and sizes practical for industrial applications were reliably produced in quantity.

New Materials for PEM Fuel Cells

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Most of the applied research on proton exchange membrane (PEM) fuel cells to increase the efficiency and reduce the cost is concentrated on synthesis and optimization of new materials and components. Three fundamental parts constitute the MEA (membrane electrode assembly). The gas diffusion layer, the catalytic layer and the polymer membrane electrolyte. Apart from this the important part is the body of the cell consisted of the bi-polar plates and current collectors. Each of these parts is interrelated physically as well as functionally. The MEA in presence of the fuel and oxidant permits an electrochemical reaction, by which the chemical energy is transformed into electrical energy. Normally used bi-polar plates are high quality graphite plates, which have a lot of problems with respect to weight, cost and difficulty in machining. Results are presented on light weight metals protected with corrosion resistant coatings, which may be used as bipolar plates and current collectors instead of graphite. Results will also be presented on new catalytic materials based on transition metal alloys, in addition to Pt and Pd prepared by new synthesis methods. New design strategies will be presented for MEA, bipolar plates and the whole cell.

The Catalytic Performance of Ni-based on Al2O3 Support for Steam Reforming of Biogas

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The trend of research is increasing on the renewable energy to develop alternative and clean energy, such as fuel cell. Hydrogen fuel can be supplied from many sources e.g. biogas from fermentation or ethanol. For an application in a fuel cell especially solid oxide fuel cell, biogas has to be reformed to hydrogen under reforming system.

In this work, a catalytic steam reforming of biogas (CH4/CO2 = 60/40) is investigated to produce H2-rich synthesis gas. The Ni-based catalyst on Al2O3 support developed in our laboratory has operated in a fixed bed reactor. To optimize the performance, the kinetic control has been observed at stable conditions for longer than 48 hr at 700 - 900 ºC of synthesis biogas feeding. The catalytic activities were compared with the commercial Ni-based at the same controlling conditions. Reaction parameters are studied for the trends of CH4 conversion and H2 yield. Finally, an optimal reactor temperature is identified and a durability of potential catalyst will be presented. The experimental results will be applied to design a steam reformer for a 1 kW solid oxide fuel cell system.

Ion Dynamics in Intercalated Polymer Nanocomposite Based on Pan

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Ionically conducting polymer nanocomposites (PNCs) are expected to play major role in new generation solid-state energy storage/conversion devices (such as high energy density solid polymer batteries, fuel cells, supercapacitors etc.). Such devices are expected to have an enhanced performance with added advantage of design flexibility, mouldability of shape and possibility of miniaturization as per the present demand in consumer
Carbon Nanospheres for Negative Electrode of Lithium-ion Batteries
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Lithium-ion batteries have attracted much attention for a practical use in hybrid electric vehicles (HEV). High rate performance is required for the lithium-ion batteries in HEV. Nano-sized active materials including nanocarbons have been extensively studied since the diffusion path of lithium-ion can be shortened and the charge transfer resistances can be drastically decreased due to the large reaction sites. We have so far prepared nanocarbons by several methods as negative electrodes for lithium-ion batteries. The rate performance can be enhanced, but the large reaction sites of nanocarbons caused the large irreversible capacities, and therefore, it was quite difficult to use the nanocarbons as negative electrodes.

Carbon nanospheres prepared by Tokai carbon possess unique microstructures and basal planes cover the carbon surface. The unique microstructures may suppress the reaction between electrolyte and nanocarbons. Here we show the negative electrode properties of graphitized carbon nanospheres.

Graphitized carbon nanospheres with particle sizes of 500 and 700 nm were used. The graphitization was made by a heat-treatment of 2600 °C. Electrochemical properties of graphitized carbon nanospheres were studied by cyclic voltammetry, charge-discharge measurements, and AC impedance spectroscopy. Electrolytes used were 1 mol dm$^{-3}$ LiPF$_6$ / EC+DEC (1:1 by vol.) and 1 mol dm$^{-3}$ LiPF$_6$ / PC.

The graphitized carbon nanospheres showed the first coulombic efficiencies exceeding 88 %, which is the highest value for nanocarbons. The high efficiencies are ascribed to the unique microstructures. In addition, some graphitized carbon nanospheres showed good cycle performance even in PC-based electrolyte. The detail results will be given in the conference.

Acknowledgments:
This work is done by the collaboration of Kyoto Univ., AIST, and Tokai carbon under the NEDO project.
Oxygen ion conducting ceramic oxides endowed with $O^2-$ ion permeation are suitable for a number of applications including solid oxide fuel cell (SOFC) provided they have structural, thermal and mechanical stability and exhibit selective oxygen permeation over a wide range of operating conditions. The materials showing selective oxygen permeation have defects preferably in the form of oxygen deficiency created originating from the presence of transition metal dopants (alio-valent / mixed-valent) causing defect in the system. Alternately, the presence of oxygen non-stoichiometry in a ceramic lattice also results in similar type of defect structure. Oxide ceramics with such a defect concentration can be expected to facilitate easier oxygen transport controlled effectively by parameters such as oxygen partial pressure maintained across the ceramic membrane externally or by tailoring of defect architecture in it. However, developing an oxygen deficient ceramic having defect in its lattice coupled with structural, thermal and chemical stability is a very challenging task. Literature reveals that only selected structural families such as fluorites ($YSZ$), perovskites/brownmillerite (LaGaO$_3$/Ba$_2$In$_2$O$_7$), intergrowth perovskites ($\delta$-Bi$_2$O$_3$), LAMOX (La$_5$Mo$_2$O$_{12}$), pyrochlores and recently $K_xNiF_3$ structures fulfill the stringent requirements of oxygen permeation and stability in redox environment. Electrical conduction via oxide ($O^2-$) ion mobility occurs due to hopping of the $O^2-$ from one energetically favorable site to another within the lattice. Such feasibility can exist only if there is $O^2-$ ion concentration gradient favored by the presence of oxygen deficient sites in the lattice with appropriate energy to facilitate $O^2-$ mobility under thermal activation via diffusion. Diffusion assisted $O^2-$ ion migration in the ceramic membrane occurs through oxide ion ($O^2-$) – lattice vacancy ($V_o^-$) interaction governed by Kröger-Vink formulation; \( \frac{1}{2}O_2 + 2e^- \rightarrow O^2- - V_o^-. \)

This paper aims to present a comprehensive study on the structural, thermal and electrical properties of SrMnO$_{2.5}$ prepared by conventional ceramic processing route. A preliminary XRD analysis confirmed hexagonal structure with lattice parameters; $a=5.584(0)$ Å, $b=15.899(6)$ Å and $c=5.366(8)$ Å with the space group $P6_3/mmc$ (194). The XRD pattern shows a typical hexagonal feature of perovskite. The complex impedance spectrum provides evidences of bulk conductivity at lower temperatures. However a grain boundary effect dominates at $T\leq355^\circ$C. The typical variation of bulk and grain boundary conductivity at a function of temperature follows a linear pattern obeying Arhenius relation in the range from room temperature to 900°C. The highest value of conductivity observed in the present investigation is of the order of $10^{-2}$ S cm$^{-1}$ at 900°C. The estimated activation energy ~0.89 eV provides indications of oxygen ion mobility through the lattice. A correlation of microstructure-structure with electrical properties is proposed to be discussed with an objective to analyze the suitability of the material for SOFC applications.
Nanostructured Si Materials as Anode for Li-ion Batteries

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Nanostructured Si materials and their composites have attracted big interests as anode materials for Li-ion batteries due to low cost and high capacity of the materials. In this work, we will report that some novel techniques to make silicon nanotube / nanowires electrodes, their characterization and electrochemical results of these nanostructured Si materials. For example, SiNWs electrodes were fabricated by two different techniques. The structure, morphology and electrochemical performances of such materials were characterized by XRD, SEM and charge-discharge tests. The results show that the electrodes made by direct evaporation-growth method have higher capacity, better cycle life and good rate capabilities. It is shown that clearly that during lithiation process, the initial crystalline Si nanowires transformed to amorphous Li$_x$Si, and the average diameter of the SiNWs increased. Despite the large volume changed, the SiNWs remained intact and did not break into smaller particles. Moreover, carbon-coated SiNWs electrodes were prepared. The structure, morphology and electrochemical performances of carbon-coated SiNWs were characterized. Such coated Si materials show better electrochemical performances than uncoated materials. Significantly, the observed capacity during this first charging operation was 3,542 mAh g$^{-1}$, the first discharge capacity was 2,938 mAh g$^{-1}$, indicating a coulombic efficiency of 83%. Both charge and discharge capacities of the materials remained little fading up to 30 cycles. The significance and detailed analysis of results will be presented at the meeting.

kW SOFC System and Related Development at Huazhong University of Science and Technology

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Solid oxide fuel cell (SOFC) is recognized as one of the emerging technologies for green power generation in the twenty first century. Extensive attention has been drawn worldwide on its development for decades. In 2004, a R&D center for SOFC was established in Huazhong University of Science and Technology, focusing on the development of SOFC key materials (including those for cathode, interconnect, contact and seal). Cell fabrication, stack design and assembly and kW-scale system integration as well. As of today, significant progress has been achieved, higher than 740 mW cm$^{-2}$ performance with 10 × 10 cm$^2$ cells has been obtained. In this presentation, details regarding materials development, cell and stack manufacturing and system integration will be provided.

Acknowledgments: all the research activities have been financially supported by the ministry of science and technology of China, national science foundation of China, the department of science and technology of Hubei province, the bureau of science and technology of Wuhan city.

Novel Composite Membrane Based on Pore-Filling Electrolyte for Direct Methanol Fuel Cells

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A sulfonated poly(styrene-ran-ethylene) (SPSE) shows a higher proton conductivity compared with the Nafion based membranes. However, the SPSE membrane has exhibited low mechanical strength and high methanol crossover, which make it not suitable as electrolyte membrane for direct methanol fuel cells (DMFCs). In this work, we have successfully synthesized porous polyimide film and used it as matrix to construct SPSE infiltrated composite membrane for DMFC application. The composite membrane was characterized by various techniques for its water uptake, dimension stability, proton conductivity and methanol crossover. Due to the complete inertness to methanol and the very high mechanical strength of the polyimide matrix, the swelling of the composite membrane is greatly suppressed and the methanol crossover is also significantly reduced. Because of its higher proton conductivity and less methanol permeability, single fuel cell performance test demonstrated that this composite membrane outperformed Nafion membrane. Based on these results, SPSE/polyimide composite membrane has great potential to be used in direct methanol fuel cells.

Doped Cobaltite Nanofibres for Energy Conversion Applications

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The thermoelectric potential of doped cobaltite ceramics has been widely recognized for several years now. The unique structures observed give rise to the favourable conductivity profile required to obtain high thermoelectric Figures of Merit. These properties depend on the type of dopant used, and much work has focused on the use
of sodium, calcium and lithium as p-type dopants in these materials. There has, however, been little study on how these materials behave when in nanostructured form, or how they may be engineered into competitive thermoelectric devices.

This work will present hitherto unseen structural and electrical data for a variety of common p-type doped cobaltite electrospun nanofibres and will present work on n-type versions of these materials. In addition to the stoichiometrically stable Ca$_2$Co$_3$O$_7$ material, the dependence of electrical conductivity on the type and amount of dopant will be shown alongside structural evidence via XRD and high resolution electron microscopy techniques. The effect of doping with vanadium, tantalum, zirconium and molybdenum (VI) on the structural, impedance and thermal properties will be presented and initial findings on how p-type and n-type materials can be engineered into solid state thermoelectric devices will also be discussed. All materials are prepared using the electrospinning of cobaltite sol gels based on polyvinyl alcohol – a technique that results in highly crystalline cobalt oxide-based nanofibres of between 50-100nm in diameter consisting of plate-like grains of around 20-30nm thick.

**A02725-04691**

**Electrical Characterization of Zirconia Based sol Gel Electrospun Fibres**

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Zirconia finds many uses in modern engineering ranging from thermal barrier coatings through to ionic conductors and gemstones. It is also receiving significant interest as a potential supercapacitor and battery material. However, to be useful, bulk zirconia needs to be partially stabilized into a cubic/tetragonal form through the use of dopant elements, typically yttrium and calcium. Doping has the added effect of enhancing the conduction properties, especially if the dopant is of similar ionic radius and of different (often lower) valency.

Studies have shown that when produced in nanofibrous form through electrospinning techniques, tetragonal zirconia can exist at ambient in pure form, and that this form can be stabilized at higher temperatures by the addition of much less dopant than in bulk form. The structure of these nanofibres is highly complex, consisting of a dense, thin shell surrounding a mesoporous granular structure of pore size 3-5nm. The current work aims to fully characterize these structures in terms of high resolution microscopy and XPS and to provide a correlation between these complex structures, the type and amount of dopant, and properties such as thermal conductivity, ionic/electrical conductivity, impedance behaviour and dielectric responses. The distribution of the dopant ions within the material and material boundaries will be established. Dopant materials will include calcium, sodium, lithium, barium, tantalum and zinc and all materials will be produced through the electrospinning of zirconia sol gels based on polyvinyl pyrrolidine (PVP). The fibres produced are continuous and between 300nm and 800nm in diameter. Ideas for prototype solid-state zirconia devices for energy storage will also be presented.

**A02757-04726**

**The Impact of Surface and Interface Energy on Nano-sized Insertion Compounds**

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Recent research has shown that particle size reduction towards the nano-scale has strong impact on insertion reactions related to Li-ion and H-storage. In many cases relevant properties such as storage capacities, equilibrium compositions and voltage profiles change significantly. Here we present a simple approach introducing the surface and interface energetics in a thermodynamical treatment of nano-insertion-materials. The calculations, applied to LiFePO$_4$, are compared with diffraction results (X-ray and neutron) reveal the impact of the surface energy, interface energy and particle size distribution on nano-sized insertion materials, explaining many recent findings.

**A02766-04731**

**Transport Properties in an Ion Conducting Polymer Nano-Composite**

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The solid polymer electrolytes formed by complexation of alkali metal salts ($\text{Li}^+ / \text{Na}^+$) with an appropriate polymer host has been studied widely due to their potential application in electrochemical devices. Ion conducting polymers impart special features in device such as low weight, flexibility, ability to form desired shape and low manufacturing costs. Till now different polymers such as PEO, PMMA, PAN and PVDF have been studied with this advantage in mind. However, the poor ionic conductivity of the solid polymer electrolytes imposes limitation on their application. The main cause of poor ionic conductivity in polymers is attributed to the ion pair formation which

reduces the number of mobile charge carriers. Many efforts have been made to eliminate ion pairing effect. Formation of intercalated polymer nanocomposite is considered an effective approach where ion pairing effect can be minimized if not eliminated. Intercalation of ion conducting polymer matrix into organically modified hydrophobic nanometric channels of the clay ensures an effective separation between the cations (Li\(^+\)) and its counter ion due to Coulombic repulsion of the anions with the –ve charges on the surface of the clay. As a consequence, concentration of mobile charges in polymer clay nanocomposites may be expected to be higher resulting in an enhancement in the conductivity in accordance with the relation, \(\sigma = \sum n_i \mu_i z_i\), where \(n_i\), \(\mu_i\), and \(z_i\) refer to the number of the charge carrier, ionic mobility and the ionic charge. However, the clay addition also results in lowering of chain mobility due to increase in viscosity of the composite phase. Hence, the addition of clay induces two adverse effects one is favorable and another is detrimental for ionic conductivity. This requires optimization of clay concentration in such a composite matrix.

In this paper, we report the results of our investigation on polymer nano-composite films based on PMMA-LiClO\(_4\)+x wt% clay over a wide range of clay concentration (0-20 wt%). The intercalation of polymer in the clay galleries has been confirmed from transmission electron microscopy (TEM). FTIR results indicate the polymer–ion, ion-ion and ion–clay interactions. The fraction of free charge carriers has been estimated and correlated with conductivity results. The increase in fraction of free anion has been observed with addition of small percentage of clay and it is highest for PNCs with (2 & 7.5 %MMT). The improvement in voltage stability has also been noticed with addition of clay (MMT). The ionic transport number for all the PNCs has been estimated to be >\(99\%\) (\(t_{\text{an}}\), >\(99\%\)). The improvement in voltage stability has been recorded with addition of clay. AC conductivity and dielectric relaxation behavior of these nanocomposites have been carried out to analyze the effect of clay on ion dynamics and transport properties.

A similar analysis in the case of LiCoPO\(_4\) prepared using conventional ceramic route indicated that it follows an entirely different electrochemical oxidation behavior with redox potential ~ 4.7 – 4.8 V unlike that of LiFePO\(_4\) and LiMnP\(_4\). This result prompted us to think for a potentially different mechanism for delithiation in LiCoPO\(_4\) when compared with those in LiFePO\(_4\) and LiMnP\(_4\).

In this paper, we report, nanocrystalline LiCoPO\(_4\) prepared by citrate route. Preliminary structural analysis suggests the formation of single phase nanocrystalline LiCoPO\(_4\). Preparation conditions have been optimized using thermal analysis technique. Microanalysis has confirmed the sample stoichiometry. BET surface area and electrochemical analysis suggest suitability of LiCoPO\(_4\) as the cathode for lithium battery application. The details of the result are proposed to be presented and discussed.

A02772-04737

Power Generating Property of Direct CH\(_4\) Fueled SOFC using LaGaO\(_3\) Electrolyte

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Solid Oxide Fuel Cells (SOFCs) can utilize various hydrocarbons for fuel without an external reforming reaction, which means a simple fuel process is enough for the system as a power generator and so, low cost as well as a compact system could be achieved in case of SOFC. However, in case of direct hydrocarbon type cell, codeposition shows critical issues to overcome. In this study, effects of oxide mixed with Ni on coke deposition for anode of SOFC using LaGaO\(_3\) based electrolyte were investigated.

Ni-oxide mixture was prepared by ball mixing method by using NiO-Fe\(_2\)O\(_3\) and oxide prepared by solid state reaction. The obtained powder was coated on La\(_{0.9}\)Sr\(_{0.1}\)Ga\(_{0.8}\)Mg\(_{0.2}\)O\(_3\) (LSGM) electrolyte disk with slurry coating method. After
calcination at 1273 K, the cell was set into the measurement setup, in which multilite tube was used and molten Pyrex glass was also used for gas sealing. Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ was always used for cathode and dry CH$_4$ and O$_2$ was fed to anode and cathode with 100ml/min.

Power generation property of the cell was measured under a constant current out-put condition. Although NiFe bimetal shows the high surface activity to CH$_4$ electrochemical oxidation, coke is easily formed on this anode and so the significant degradation of power density was observed. It was found that mixing MgO, CeO$_2$, and LaGaO$_3$ based oxide is effective for preventing coke deposition and also power density. Among the examined oxide, mixing LSGM is highly effective for preventing coke deposition under dry CH$_4$ feeding condition and the stable power density is observed over 15 hours operation. The optimum amount of LSGM mixed with NiFe seems existing around 10 wt%. The maximum power density of this cell is achieved ca. 500 mW/cm$^2$ at 1073 K by using 0.5 mm thick electrolyte.

Deposition of coke was analyzed by Raman spectroscopy after 15 h operation. In case of Ni, there were strong Raman peaks observed at 1350 and 1580 cm$^{-1}$, which could be assigned to carbon. However, in case of Ni-Fe/LSGM anode, not Raman peaks assigned to carbon was observed suggesting no coke deposition. In addition, SEM observation also shows no change in morphology of Ni-Fe/LSGM anode powder. Consequently, it can be concluded that Ni-Fe/LSGM anode is highly tolerant against coke deposition in CH$_4$ flow.

Effects of LSGM on the anodic reaction were studied by impedance analysis and it was found that two semicircles were observed for anodic impedance plots and it seem that charge transfer step determined the anodic reaction because of no $P_{\text{CH}_4}$ dependency on anodic overpotential.

**A02774-04849**

**Direct Methanol Fuel Cell (DMFC) vs In-direct (Reforming) Methanol Fuel Cell (RMFC)**

Deryn CHU

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The efficient hydrogen-air polymer electrolyte membrane fuel cell systems are already in development to meet the need for portable applications. However, the main difficulty that remains to be overcome is the development of safe and compact units for storage hydrogen or producing that gas on demand. Therefore, direct and in-direct (reforming) methanol fuel cells become more attractive now. U. S. Army and Defense Advanced Research Project Agency have supported numerous DMFC and RMFC research and development projects. At this time, the Army is still supporting DMFC and RMFC projects. Recently, the 20W DMFC and RMFC systems are successfully developed and demonstrated at different environmental conditions. This presentation focuses on the technical challenges of the DMFC and RMFC power system, Lessons Learned and the Road Ahead.

**Reality Check on Using NaAlH$_4$ as a Hydrogen Storage Material**

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NaAlH$_4$ has been considered as a potential material for hydrogen storage. Although its theoretical hydrogen storage capacity is 5.5 wt% at 250°C, the material still has its drawback in the regeneration issue. With the use of certain catalysts, the regeneration can somewhat be alleviated with added benefits in the decrease in the hydrogen decomposition rate and temperature. This work summarizes what we have learned from the decomposition of NaAlH$_4$ with/without catalysts and co-dopants. The decomposition was carried out using a thermovolumetric apparatus. For the tested catalysts – $\text{HfCl}_4$, VCl$_3$, TiO$_2$, TiCl$_4$, Ti, the decomposition temperature of the hydride decreases; however, they affect the temperature in subsequent cycles differently and TiO$_2$ appears to have the most positive effect on the temperature. Sample segregation and alloys formation between metal from a catalyst and aluminium from the hydride are postulated to hinder the reversibility of the hydride. To prevent the problems, co-dopants – activated carbon, graphite, and MCM-41 – were loaded. Results show that the hydrogen re-absorption capacity of $\text{HfCl}_4$- and TiO$_2$-doped NaAlH$_4$ added with the co-dopants increases 10-50% compared with that without a co-dopant, and graphite is the best co-dopant in terms of re-absorption capacity. In addition, the decomposition temperature in the subsequent cycle of co-dopant doped samples decreases about 10-15°C as compared to the sample without a co-dopant. Porosity and large surface area of the co-dopant may decrease the segregation of bulk aluminium after the desorption and improve hydrogen diffusion in/out bulk of desorbed/re-absorbed samples.
Size Effect on Hydrogen Adsorption in Coiled Carbon Nanotubes

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Carbon nanotubes (CNTs) are rolled up sheets of graphite formed into seamless cylinder. Depending upon rolling it can be divided as armchair (metal), zigzag (semiconductor) and chiral (metal or semiconductor) tubes. Further it can be classified as Single walled nanotube (SWNT), Multi walled nanotube (MWNT), Double walled nanotube (DWNT). Due to their nano size, porous nature, unique physical and chemical properties it has tremendous potential applications in energy storage, field emission, smart fabrics, environmental, molecular electronics, to name a few. Among these applications we are interested to study about energy storage in these novel nano structures. Through its high surface area, chemical inertness and stable solid-gas adsorption characteristics, CNTs provide good medium for hydrogen adsorption. It has been observed CNTs provides hydrogen storage capacity below 6Wt% is the value set by the U.S Department of energy and hence there is wide range of exploration of new materials that will provide high storage capacity than CNTs. This motivates us to take up the present investigation on Coiled carbon nanotubes (CCNT), one of the classifications of CNTs. CCNTs with spiral like structures is predicted to exhibit unique physical and chemical properties as that of linear tubes. It has been observed that pentagon-heptagon pairs are responsible for coiling and it can exhibit two kinds of chirality. Moreover the tube pitch and coil diameter affects the material properties. It is interesting to know that synthesis, properties and size of coiled carbon nanotubes will affect the hydrogen storage capacity. In the present work, Coiled CNTs are constructed by inserting pentagons and heptagons on opposite sides of tubules at knee of the bend. Tubes with diameter 0.74Å and 254 carbon atoms are constructed including 4 pentagons and 5 heptagons. Adsorption studies are carried out through the hydrogen molecule positioned above hexagon ring with its molecular axis perpendicular to the tube surface. This molecular configuration is found to be a stable one. We could get an adsorption binding energy value as 4.76eV and for comparison the identical studies are carried out on linear tube with five unit cells and approximately of same diameter of (9,0) Zigzag CNT. For this case the binding energy works out the 0.26eV. The above values show an eighteen times increase in binding energy in the case of coiled CNT than the linear one. It will be interesting to study this aspire with different adsorption site like pentagons and heptagons. Adsorption binding energies at these defect sites will be calculated and results will be compared with the existing literature for better hydrogen adsorption and storage. This study is important for identifying the suitable nanomaterials for hydrogen economy.

Comparative Study of Lithium Transport Kinetics in Olivine Cathodes for Li-ion Batteries

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Phospho-olivine compounds are important emerging cathode materials for high power Li-ion batteries, some of which are already finding applications in high power, safe, long-lived batteries for power tools and hybrid electric vehicles. This family of compounds, like many other intercalation compounds, undergo phase transitions upon electrochemical cycling. It has been shown that the phase transitions alone can be quite complex, and involve metastable and amorphous phases [1-2]. The kinetic behavior during electrochemical cycling in battery electrodes is further complicated by the existence of other processes such as interfacial charge transfer. Fundamental understanding of the various contributions to the kinetics of olivine electrodes is important to the future development of phosphate battery technology.

In this work, olivine samples of undoped and aliovalent-doped compositions for which a number of structural and electrochemical properties are already well-established through prior work [1-5] having mean particle sizes ranging from the nanoscale (34 nm) to >100 nm were studied using potentiostatic intermittent titration technique (PITT) and impedance spectroscopy (IS). Using established theoretical treatments [6-9], the lithium chemical diffusion coefficients were separated from other kinetic parameters such as the solution, surface, and interfacial charge transfer resistances. Clear and measurable differences as a function of particle size and doping are found. In particular, the importance of the lithium miscibility gap and vacancy defects introduced by doping are emphasized.

References:
Phase Stability of Nanostructured Storage Materials during Electrochemical Cycling

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In the drive towards improved electrical energy storage for applications ranging from wireless devices to electric vehicles to grid stabilization, nanoscale materials are of growing interest as ion storage electrodes. The effects of nanoscale size on phase stability, coupled with the large magnitude of the driving forces (often underappreciated) imposed on battery electrodes during electrochemical cycling, can cause a variety of complex, non-equilibrium responses. This is true even for systems in which a “simple” two-phase reaction is expected during cycling, based on their bulk phase diagrams. Olivines based on LiMPO_{4} (M=Fe, Mn, Co, Ni) are one such class of compounds. Recent experimental and theoretical developments reveal very different phase transitions and lithium solid-solubility behavior in nanoscale (<50 nm) crystallites compared to larger particles. For example, far from undergoing a simple two-phase reaction, a metastable amorphous phase appears to be readily stabilized during cycling. However, a surprising result is that even “large” particles (e.g., >100nm) exhibit far-from-equilibrium behavior under certain conditions. A systematic approach to understanding such behavior must take into account the effects of composition, temperature, elastic energy (including transformation misfit strains), crystalline anisotropy, and surface energetics. In addition, we find that the overpotential applied to the storage compound also has large, previously unrecognized effects.

In this talk, we will discuss results from a diffuse-interface thermodynamic model that has shed light on the conditions under which nonequilibrium phase transitions may occur, using LiMPO_{4} systems as an example. Critical experiments carried out using in-situ synchrotron X-ray diffraction to track the overpotential and time dependence of phase evolution in samples of various compositions and crystallite size scales will be presented. Several results in published literature that up to now have been unexplained can be understood. The impact on practical battery performance in olivine-based systems will be discussed.
This is caused by the increase in particles size as revealed in Pt loading leads to a decrease in the oxidation current. Enhancement in electrocatalytic activity. Further increase in optimum Pt loading of 40% gives the most pronounced for their activity towards ethanol electro-oxidation. An (TBAB). The synthesized catalysts have been evaluated of a protecting agent like tetrabutylammoniumbromide. Catalyst particles can be further achieved through the user particles with uniform size distribution. Size control of the corresponding metal salts. The use of a mesoporous carbon, Vulcan XC-72 as support, leads to well dispersed catalyst particles with uniform size distribution. Size control of the catalyst particles can be further achieved through the use of a protecting agent like tetrabutylammonium monium bromide (TBAB). The synthesized catalysts have been evaluated for their activity towards ethanol electro-oxidation. An optimum Pt loading of 40% gives the most pronounced enhancement in electrocatalytic activity. Further increase in Pt loading leads to a decrease in the oxidation current. This is caused by the increase in particles size as revealed by HRTEM images. Different PtRu alloy compositions were investigated; an optimum Ru content in binary PtRu catalysts for ethanol oxidation is reached at low Ru levels, at 10% or even less. At relatively low Ru content there is sufficient number of Pt sites for the dissociative adsorption of ethanol. As this requires an ensemble of Pt sites, facile adsorption and subsequent dehydrogenation can occur only in presence of large number of Pt active sites on the catalyst surface. At high Ru concentration there are not enough Pt sites for easy ethanol adsorption and hence oxidation currents remain low.

Development of Nanoporous Pt supported Electrocatalysts as Anode Component for Direct Alcohol Fuel Cell

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Platinum is used in the fabrication of components for fuel cells, especially for the direct alcohol fuel cell (DAFC), where a relatively high catalyst loading is still required. Electro catalysts based on Pt and its alloys have been a subject of extensive research because of their importance in low and medium temperature fuel cells. In order to attain commercial viability in DAFC, reduction in catalyst loading is thus necessary. To achieve maximum utilization of Pt, the highest possible surface to volume ratio of the dispersed metal is desirable. Several methods have been reported for deposition of the Pt catalyst. Size and distribution of Pt particles are important parameters that affect the reactivity of platinized electrodes of fuel cells.

In this work we report synthesis of Pt and PtRu nano catalyst and evaluate their electrocatalytic property towards ethanol electro-oxidation. Pt metal and PtRu alloy nano particles were prepared by borohydride reduction of the corresponding metal salts. The use of a mesoporous carbon, Vulcan XC-72 as support, leads to well dispersed catalyst particles with uniform size distribution. Size control of the catalyst particles can be further achieved through the use of a protecting agent like tetrabutylammonium monium bromide (TBAB). The synthesized catalysts have been evaluated for their activity towards ethanol electro-oxidation. An optimum Pt loading of 40% gives the most pronounced enhancement in electrocatalytic activity. Further increase in Pt loading leads to a decrease in the oxidation current. This is caused by the increase in particles size as revealed by HRTEM images. Different PtRu alloy compositions were investigated; an optimum Ru content in binary PtRu catalysts for ethanol oxidation is reached at low Ru levels, at 10% or even less. At relatively low Ru content there is sufficient number of Pt sites for the dissociative adsorption of ethanol. As this requires an ensemble of Pt sites, facile adsorption and subsequent dehydrogenation can occur only in presence of large number of Pt active sites on the catalyst surface. At high Ru concentration there are not enough Pt sites for easy ethanol adsorption and hence oxidation currents remain low.

A02955-05059

Nonaqueous Electrolyte Containing Boron Based Anion Receptors (BBAR)

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In searching the new chemistry of lithium-ion batteries with higher energy density, the none-LiPF6 electrolytes with higher lithium ion transference number, higher electrochemical stability and wider operating temperature are desired. One of the approaches developed at BNL is using boron based anion receptors (BBAR) to complex anions of none-LiPF6 salts. Several families of neutral anion complexing agents have been synthesized by Lee et al, each based on boron based Lewis acid centers. It has been demonstrated by us that the complexing agents have the ability to promote the dissolution of LiF, Li2O, and Li2O2 in organic solvents.

The BBAR-LiX nonaqueous electrolytes show moderate ionic conductivity (10-5Scm-1) and high lithium ion transference number (0.6-0.8). They are compatible with bench-mark anode and cathode materials for lithium batteries. The applications of these BBAR-LiX nonaqueous electrolytes in other energy storage systems, such as lithium primary batteries are being explored by our group. The preliminary results of these studies will be reported in this poster.

Acknowledgement:
The work in CAS was supported by Nature Scientific Foundation of China (50672122, 50730005) and “973” Project (2007CB936501). The work at BNL was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, under the program of “Hybrid and Electric Systems”, of the U. S. Department of Energy under Contract Number DEAC02-98CH10886.
Nanometal Oxides for Electrochemical Li-Ion Capacitors and Batteries: Effects of Porosity and Particle Size

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There have been many efforts devoted to improve the properties of electrochemical capacitors (ECs) and ion storage batteries. We present here an overview of the porosity and particle size correlations in the context of Li-Ion capacitors (LIC) and batteries (LIB). Our results show that the particle size down to < 10 nm along with distributed porosity (Synthesized via our proprietary low temperature protocol) yields much enhanced electrode-active characteristics of positive electrode materials such as NiO, NiO/Ni nano-composite, NiCo₂O₄ and Li₄Ti₅O₁₂ and their nanodot derivatives of impregnated complexes into mesoporous carbon structures. We also provide supporting evidences from literature as to how the porosity and particle size play a vital role in improving energy/power densities of the above mentioned advanced electrochemical power sources. Nanodot derivatives yield an impressive amount of near theoretical capacity in the case of Li₄Ti₅O₁₂ (LTO) zero-strain spinels. On the other hand, impressive cycle performance has been realized for Li-Ion capacitors compared to LICs employing conventional LTO spinels. Some new results based on Li ion storage in NiO/Ni nano-composite as well as NiCo₂O₄ spinel will also be discussed.

Neutron Scattering Study of Diffusion and Disorder in Cu-Se Superionic Conductor

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Copper selenide is a mixed ionic-electronic conductor and received attention from the technological and physical point of view in particular due to a high ionic conductivity. According to literature only a fraction of Cu atoms takes part in the ionic transport in Cu₂-xSe compounds. The number of mobile atoms is about 1/3 - 1/8 of the total cation concentration in stoichiometric Cu₂Se and decreases with x causing the ionic conductivity to drop.

The quasi-elastic neutron scattering study is of interest because the width and intensity of quasi-elastic peak associated with Cu diffusion are directly related to Cu coefficient of self-diffusion and the number of mobile ions, respectively. We present results of the measurements of the quasi-elastic broadening in Cu₁.77Se, Cu₁.90Se and Cu₁.98Se compounds at 313 and 430K. In Cu₁.98Se compound the quasielastic component was not observed at T = 313K in ordered non-superionic α-phase, however it is clearly seen in superionic β-phase at T=430K. By contrast the Cu₁.77Se compound which is superionic at ambient temperature has relatively small quasielastic component showing little difference between 313 and 430K. The analysis shows that fraction of Cu atoms which takes part in the ionic transport indeed decreases with x in general agreement with literature, but not vanishes at x = 0.23.

In superionic phase of Cu₃Se compounds X-ray and neutron diffraction patterns demonstrate the presence of strong diffuse scattering component. It is connected to static lattice disorder and/or dynamical correlations of atomic displacements. According to calculations a strong correlation between Cu-Cu and Se-Cu thermal atomic displacements exists in superionic phase. We present results of energy dispersive diffraction experiment showing that diffuse scattering in Cu₂-xSe compounds is mainly inelastic and most probably comes from correlations among the thermal atomic displacements. The inelastic neutron scattering experiments show the presence of the low-energy phonons with optic-like behaviour what is characteristic for superionic compounds. Recent results of phonon measurements are presented for Cu₁.85Se compound.
A Group of New Polyanion Materials Li_{x}M_{1-x}(MoO_{3})_{y} (0 ≤ x<3) [M=Co, Ni] for Lithium Batteries: Findings and Issues

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Over the recent years we have identified quite a number of NASICON framework materials in the molybdate family, characterized the submicron structures of these new materials synthesized through a solution based low temperature scheme and reported our findings for the first time. As for the positive electrode of Li-ion batteries, we have explored two systems, namely, Li₂M₁₋ₓ(MoO₄)ₓ and LiₓMₓ(MoO₄)ₓ [M= Co, Ni] which correspond to Lithium-rich and Lithium-free phase of transition metal molybdates respectively.

All the materials were shown to crystallize in a single phase structure with submicron sized particles. The electrode-active behavior of the new materials was examined in a two-electrode configuration utilizing a Li⁺ non-aqueous environment. Both the systems were found to exhibit reduction/oxidation peaks corresponding to the transition metals M and Mo indicating the excellent electrochemical reversibility as evidenced from Slow Scan Cyclic Voltammetry (SSCV) studies. The charge-discharge profiles obtained by means of Galvanostatic cycling tests signified removal/reinsertion of lithium in the new materials. The former Li-rich system was studied in the potential window 4.5 – 1.5 V whereas 3.5 – 1.5 V voltage window was set for the latter Lithium-free phase.

We have reported a first discharge capacity of 115 mAh g⁻¹ and 55 mAh g⁻¹ corresponding to the Lithiated phases, Li₂Ni₂(MoO₄)₂ and Li₂Co₂(MoO₄)₂, respectively. On the other hand, the non-lithiated states of Ni₂(MoO₄)₂ and Co₂(MoO₄)₂ delivered 170 mAh g⁻¹ and 110 mAh g⁻¹ capacity after accommodating lithium in the structure down to 1.5 V. Although the explored systems revealed electrochemical reversibility giving rise to good capacity values at the end of first discharge, all of them invariably failed to retain the capacity during prolonged cycling. The poor capacity retention is strongly associated with a very low lattice conductivity of the new materials similar to the other polyanion systems reported to date.

The poor conductivity issue has been addressed in our latest publications and we have successfully overcome the complexity by means of a nanocomposite approach. This novel approach has shown promising results in terms of discharge capacity and extended cycling. The nanocomposite positive electrodes were fabricated wherein highly conducting nanoporous carbon black (NCB) was mixed with the electrode-active material in addition to the conventional acetylene black (AB) carbon. Interestingly, when tested against lithium in a half cell the cycling characteristics of the materials improved as a result of an intimate contact between the active grains and better electrolyte wetting into the pores leading to an overall enhancement in the conductivity. Accordingly, the capacity offered by the materials followed an increasing trend.

It was confirmed that the capacity delivered by the nanocomposite electrode material, Li₂Ni₂(MoO₄)₂, is approximately a four-fold excess when compared to its conventional counterpart. A 2.5 times excess capacity was observed for the nanocomposite Li₂Co₂(MoO₄)₂ and the same progress was shown for the non-lithiated states of Ni₂(MoO₄)₂ and Co₂(MoO₄)₂ as well. Nanosized carbon black addition resulted in good capacity retention at the end of 20th cycle almost in all the four cases.

We ascertained that the nanocomposite approach is very effective towards improving the electrochemical characteristics of the polyanion materials by way of increasing the conductivity of the materials as a whole due to much better established connectivity between the electrode-active particles. The results will be presented.

CuO-Polyacrylic Acid Hybrid Films for Supercapacitor Application

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The supercapacitors are very attractive for delivering high specific power, long cycle lives and rapid rate of charging and discharging. Metal oxide store charge in the form of ions via redox pseudocapacitive charge storage mechanism. Cupric oxide (CuO) has been known as p-type semiconductor. It is potentially useful in lithium-copper oxide electrochemical cell. Its possible application in supercapacitor has been recently the topic intensive research.

In the present study, thin films comprising of CuO-Polyacrylic acid (PAA) hybrid thin films were synthesized by polymer assisted deposition method. Different surface morphology was observed for samples annealed at various temperature over 300-700°C for 4 hrs. The sample annealed at 300°C shows the monodispersed island like
surface and sample annealed at 400°C copper crystalline embedded in polymer matrix. An interesting PAA grafted nanocomposite rings were observed at 500°C annealing temperature. Microporous structure was observed for film annealed at 600-700°C respectively. PAA is hydrophilic and hence CuO-PAA hybrid samples exhibit hydrophilicity. An increment in hydrophilicity with contact angle varying from 90-20° with increase in annealing temperature from 300-700°C respectively was observed. This is due to the fact that at higher temperature, organic groups get oxidized leading to the effective adsorption of water. It is a matter of considerable interest because it reduces the diffusion resistance of electrolyte. The CuO-PAA hybrid films were, further characterized by XRD, SEM, FT-IR and FT-Raman spectroscopy. Supercapacitive behavior has been studied using cyclic voltammetry. Films annealed at 700°C show the largest specific capacitance ~ 120 F/g as compared to the reported value for CuO samples prepared by Electrodeposition (~60 F/g). hence the combination of appropriate porosity with superhydrophilicity of CuO-PAA hybrid leads to an improved supercapacitive behaviour. Simple route of preparation, non-toxicity, cost effectiveness are the added advantages of CuO-PAA hybrid thin films over well known RuO₂ based supercapacitor.

A03027-05158

Li Intercalation/Deintercalation in V₂O₅ Nanowires Supported by Ni Microtubes Arrays

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Ni microtube arrays have been prepared via a combined electroless deposition and sacrificial template technique. The Ni arrays were used as a substrate on which V₂O₅ hydrogel was coated. Super critical drying of V₂O₅ hydrogel yielded a web of nanowires (~20 nm) V₂O₅ aerogel. SEM micrographs showed that the web of V₂O₅ aerogel nanowires consists of a highly porous interconnected solid network coated onto Ni arrays. Cyclic voltammetry of the nanocomposite (in 1 M LiClO₄ in propylene carbonate) demonstrate the ability of this material to intercalate/deintercalate Li reversibly with no contribution from the Ni microtubes. Ni arrays were used in this configuration as current collectors that provide an electronic conduction path needed to the host material (V₂O₅). In this case, there is no need to use auxiliary carbon and binder materials for the composite electrode. In this work we developed novel method to prepare nanowires of V₂O₅ host material coated on a highly conductive substrate of Ni and Pd microtube which could be used as an electrode in Li battery.
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