SYMPOSIUM S

Nanostructured Materials in Alternative Energy Devices

April 13 - 15, 2004

Chairs

Edson R. Leite
Dept. of Chemistry
Federal University of São Carlos
CP-676
via Washington Luis Km 235
São Carlos, SP, 13565-905 Brazil
55-16-260-8214

Yet-Ming Chiang
Dept. of Materials Science & Engineering
Massachusetts Institute of Technology
77 Massachusetts Ave
Cambridge, MA 02139
617-253-6471

Jean-Marie Tarascon
Lab. de Reactivité et Chimie des Solides
Université de Picardie Jules Verne
33 rue St.-Leu
Amiens, F-80039 France
33-3-2282-7571

Erik M. Kelder
Delft Inst for Sustainable Energy Lab
Delft University of Technology
Jlianalaan 136
Delft, 2628BL The Netherlands
31-15-278-2647

Proceedings to be published in both book form and online
(see ONLINE PUBLICATIONS at www.mrs.org)
as volume 822
of the Materials Research Society
Symposium Proceedings Series.

* Invited paper
I. Fabrication of three-dimensional multifunctional architectures from formed from 100-260 layers. Their tips are opened due to the nature “nothing” (void space) and deliberate disorder as design components.

Debra R. Rolison, Jeffrey W. Long, Christopher P. Rhodes, Michael S. Doescher and Jeremy J. Pietzon; Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia.

The fundamental processes that produce or store energy can now be rethought in light of architectural nanoscience, i.e., the design and fabrication of three-dimensional multifunctional architectures from the appropriate nanoscale building blocks, including the use of "nothing" (void space) and deliberate disorder as design components [1,2]. When the multifunctionality inherent to charge insertion and energy storage, including molecular transport of solvent and ions, is structured within such architectures, improved performance and new opportunities are possible. The appropriate electronic, ionic, and electrochemical requirements, including high-surface-area electrodes readily accessible to molecules, may now be assembled into nanoarchitectures on the bench top through the synthesis of low density, ultraporous nanocoarchitectures that meld high surface area for heterogeneous reactions with a continuous, porous network for rapid diffusional flux of reactants and products. Our success at creating ultrathin, electronically insulating, cation-permeable films on charge-insertion oxide nanocoarchitectures [3] has led us to devise electrochemical storage devices that will be fully integrated, and integrated metatronics and three-dimensional ultrathin, electronically insulating, cation-permeable films on charge-insertion oxide nanocoarchitectures [3] have been fabricated and investigated in the form of solar cells.


Carbon nanocoarchitectures and carbon-carbon (C-C) composite materials have valuable properties which make them attractive for development of energy storage systems. Therefore it is of great importance to elaborate new methods for obtaining such materials in industry. The main aim of the study presented is to establish a possibility of using graphite intercalation compounds for producing carbon nanocoarchitectures and C-C composite materials. Using the methodology developed by R. Kaner and his group [1] we have found that treatment of graphite nitrate prepared in the appropriate way with ultrasonic in certain solvent leads to carbon-carbon nanocoarchitectures. These nanocoarchitectures have thickness 40-400 nm and length 200-400 nm. Taking into account interlayer spacing of graphite (0.34 nm) it might be concluded that nanocoarchitectures are likely formed from 200-200 layers. Their tips are opened due to the nature of graphene nanocoarchitectures which can lead to high-surface-area electrodes readily accessible to molecules. Our success at creating ultrathin, electronically insulating, cation-permeable films on charge-insertion oxide nanocoarchitectures [3] has led us to devise electrochemical storage devices that will be fully integrated, and integrated metatronics and three-dimensional ultrathin, electronically insulating, cation-permeable films on charge-insertion oxide nanocoarchitectures [3].

Michael V. Savoskin1, Alexander P. Yurashenko2, Nina I. Lazaren1, and Tatjana K. Kustovtsova1; 1OBST Research Laboratory, Washington, District of Columbia.

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Session S1: Impact of the Nanostructured Material in Alternative Energy Chair: Jean-Marc Troncon Tuesday Morning, April 13, 2004 Room 3006 (Moscone West)

9:30 AM S1.1 Integrating the Multifunctional Necessary for Electrochemical Power into Mesoporous Nanostructured Architectures.

Debra R. Rolison, Jeffrey W. Long, Christopher P. Rhodes, Michael S. Doescher and Jeremy J. Pietzon; Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia.

A carbon nanotube (CNT) reinforced three-dimensionally (3-D) ordered porous carbon structure has been developed at NASA Langley Research Center. The material offers a sub-micron porous structure with significantly enhanced mechanical-compressive-strength due to its promising carbon dioxide storage material can be utilized as a catalyst carrier, electrode or gas storage material. Based on the existing material, a super three-dimensionally ordered porous graphite/carbon was developed. The material contains a CNT reinforced 3-D porous carbon structure housing sub-micron graphite spheres in each of its pores. The size of the spherical graphite fits the dimension of the pores well. These characteristics make the material a promising candidate particularly in the area of high performance batteries and for the electrode/storage material in fuel cells. The fabrication method to produce the materials and the results of some relevant physical characterization (mechanical properties, gas adsorption properties and structure studies) will be presented and discussed.

Doescher and Jeremy J. Pietzon; Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia.

When the multifunctionality inherent to charge insertion and energy storage, including molecular transport of solvent and ions, is structured within such architectures, improved performance and new opportunities are possible. The appropriate electronic, ionic, and electrochemical requirements, including high-surface-area electrodes readily accessible to molecules, may now be assembled into nanoarchitectures on the bench top through the synthesis of low density, ultraporous nanocoarchitectures that meld high surface area for heterogeneous reactions with a continuous, porous network for rapid diffusional flux of reactants and products. Our success at creating ultrathin, electronically insulating, cation-permeable films on charge-insertion oxide nanocoarchitectures [3] has led us to devise electrochemical storage devices that will be fully integrated, and integrated metatronics and three-dimensional ultrathin, electronically insulating, cation-permeable films on charge-insertion oxide nanocoarchitectures [3].


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11:00 AM S1.6
Thermochemical Nanowire Arrays for Waste Heat Conversion, Erik Mengis and Reginald Penner; Chemistry, UC-Irvine, Irvine, California.

No longer relegated to specialized roles like powering satellites, thermoelectric materials are gaining interest for more mundane uses like solid-state refrigerators and collecting waste heat in automobiles. A number of research groups are currently working on a variety of methods to improve the efficiency of thermoelectric materials. Our attempts to create more efficient thermoelectric devices have focused on fabricating high aspect ratio nanowires of bismuth telluride, presently the best conventional thermoelectric material for room temperature applications. I will present our method for preparing bismuth telluride nanowires by the vapor-liquid-solid process of nanowires on highly oriented pyrolytic graphite via electrochemical step-edge decoration. This will be followed by the characterization of these nanowires by scanning electron microscopy, x-ray diffraction, and energy dispersive x-ray analysis. Finally, I will end by briefly discussing our attempts to measure the thermoelectric figure of merit for these nanowires.

11:15 AM S1.7
Direct Synthesis of Mesoporous Carbon, Jiebin Pang, J. Eric Hampsey, Qingyuan Hu, Zhiwang Wu and Yunfeng Lu, Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

Mesoporous carbon materials with high surface areas and high pore volumes are of importance for energy storage, catalysis, gas separation, and other applications. Templating techniques have been recently employed to synthesize nanocarbon materials, which are generally based on carbonization of carbon precursors infiltrated inside mesoporous silica. Subsequent silica removal generates mesoporous carbon materials with ordered pore structure. Although such a two-step process allows the precise pore-structure control, it is tedious and often insufficient. Here we report the direct synthesis of mesoporous carbon materials with 2 nm sized pore channels by self-assembly of low-cost sucrose and silicate species. Carbonization and silica removal using HF results in mesoporous carbon with high surface area, high uniformity, and ordered uniform pores. The pore volumes can be tuned by changing the silica content. While pore structure can also be controlled by introducing silica colloidal particles as the second template, mesoporous carbons with hierarchically uniform 7.7 nm mesopores connected through 2 nm mesopores have been synthesized using this approach. More importantly, continuous and crack-free mesoporous carbon thin films have been successfully prepared by the direct synthesis strategy, which is of much interest in filtrations, sensors, and photovoltaic devices.

11:30 AM *S1.8
Direct Fabrication of Patterned LiCoO2 Films by Soft Solution Processing without Post-Firing, Masahiro Yoshimura, Tomoaki Watanabe, Takeshi Fujiiwa and Seung-Wan Song, Tokyo Institute of Technology, Yokohama, Japan.

In order to obtain LiCoO2 patterns, heating process have been essential for synthesis, pattern forming and sintering of fine-nano powders or their precursors. Such multi-step processes inevitably cost in energetic, environmental and economical points of view. Single-step patterning process via PVD or CVD using gases, vapors or ions cost more seriously. We are proposing an innovative concept and technology, Soft Solution Processing (SSP) for ceramics, which aims have successfully fabricated thick and thin film of BaTiO3, SrTiO3, Bi2WO6, SrMoO4, LiCoO2, and LiNiO2 by SSP in aqueous solutions from room temperature to 200°C. In these experiments, interfacial reactions between a solid reactant (substrate) and component(s) in solution have been designed and realized. By locally activating the reaction and moving the reaction point dynamically in these reactions, we can produce patterned ceramics directly in solution without masking, etching, pattern forming or any post-heating such as firing or sintering. In the present paper, we report recent successful results in the direct fabrication of LiCoO2 films and patterns in/from solutions without post firing. (1) Electrochemically activated interfacial reactions between LiOH and CoSO4 solutions at 120°C, (2) LiCoO2 deposition on porous, and (3) LiCoO2 deposition on Pt, Graphite and Co plates in LiOH solutions at 150°C. Hexagonal LiCoO2 crystals have face-centered cubic morphology of nano- to micro-meter sizes. References : (1) T. Watanabe, et al., J. solid State Chern., vol.192, pp. 364-370 (2001) (2) S-W Song, et al., Adv. Mater., vol.14, pp. 268-271 (2002) (3) T. Fujiiwa, et al., Chem. Phys. Lett., vol.365, pp. 359-373 (2002)
The cyclic voltammetry and charge-discharge measurements of the films were measured using a homemade three-electrode cell and also a commercial cell. The correlation between the particle size and the electrochemical properties will be presented.

3:15 PM S2.3 X-ray Absorption Spectroscopy Investigation of the Sub-Nanoparticle Stress in Thin-Film Lithium Ion Battery Cathodes, Fasal M Alamgir1, Jason VanSlyutman1, Nick Barbosa1, Richard Vinci1, Jay Whitacre1, Chi-Chang Kao2, Steve Greenbaum1 and Marten denBoer1, 1Physics and Astronomy, Hunter College of the City University of New York, New York, New York; 2Department of Physics, University of California, Berkeley, California.

The drive towards the miniaturization of batteries for highly localized and portable power, such as in MEMS and micro-sensors has meant that a new generation of batteries are being fabricated through vapor deposition. There has, so far, not been commensurate progress in our understanding of the effects of vapor deposition on the local structure of the cathode and in the SEI. To address structural issues in the all-important cathode layers in Li-ion batteries, LiCoO2 and LiNiO2, two popular starting materials for cathodes, were studied in their respective bulk and thin-film form. X-ray absorption spectroscopy (XAS) has been used to probe the local atomic structure and structural defects in the thin-film and bulk cathodes, while the intrinsic stress in the films were measured using wafer curvature method. Results comparing Li(Co,Ni)O2 in the bulk and thin film forms suggest a correlation between intrinsic stress and local strain in the thin-fil. This local strain is manifested by a collapse of the six-fold rotational symmetry within the metal-metal layer of the Li(Co,Ni)O2 system into a two fold. The relationship between the deposition conditions and the resulting strain at the sub-nanoscale and bulk stress in these films is reported.

3:30 PM S2.4 The Study of SEI Formation in Cycled LiCoO2 Cathode Materials by High Field 13C and 6Li NMR, Benjamin Meyer1,2, Steven Aliprantis2,3,4, Heiki Kasemagi1,2, Alvo Aabloo2 and Josh Thomas1, 1Materials Chemistry, Uppsala University, Uppsala, Sweden; 2Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York; 3Department of Materials Science and Engineering, UCLA, Los Angeles, California; 4Department of Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania.

Materials by High Field 13C and 6Li NMR. Benjamin Meyer1,2, Steven Aliprantis2,3,4, Heiki Kasemagi1,2, Alvo Aabloo2 and Josh Thomas1, 1Materials Chemistry, Uppsala University, Uppsala, Sweden; 2Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York; 3Department of Materials Science and Engineering, UCLA, Los Angeles, California.

3:30 PM S2.5 Cu3P as Anode Material for Lithium-ion Battery: Insertion Mechanism, Powder Morphology and Electrochemical Performances, Marie-Pierre Bichat1, Tatiana Poltova2, Herberto Pires3, Laura Moncoutié3, Laurence Ponsel3, Matthieu Marrecet3 and Frederic Feuvier1, 1LAMMI, UMR 5072 CNRS-Université Montpellier 2, Montpellier, France; 2LGM, Ecole Polytechnique de l Université de Nantes, Nantes, France; 3LRC, CNRS, Université de Picardie Jules Verne, Amiens, France.

Cu3P is studied as a potential material to be used as anode in a Li-ion battery. Depending on the synthetic route, solvothermal, ball-milling (with or without annealing), spray method or ceramic, used for its preparation, Cu3P shows various particle sizes and crystallinities. The electrochemical reactivity towards lithium of these various Cu3P powders is discussed through galvanostatic and potentiodynamic measurements, electron microscopy techniques, and X-ray diffraction on powders. The lithium insertion into Cu3P phase involves the progressive reduction of Cu(I) to Cu(0) undergoing the successive formation of Li2Cu2xP2x by solid solution as well as two-phase processes. During the charge, as Li is progressively extracted from Li2Cu2xP2x phases by a reverse pathway, copper metal is partially re-oxidized. As expected for such a solid state process involving both growth and reactivity of metal nanoparticles or non-dendrites, electrochemical performances, especially initial capacity and capacity retention, are shown to strongly correlate to the powder morphologies: small particle size favors high capacity values while the battery capacity is better retained from crystallized powders.
Capacitive Characteristics Synthesized by Chemical Oxidation of Ruthenium Chloride with H2O2. Chi-Chang Hu and Kuo-Hsin Chang; Chemical Engineering, National Chung Cheng University, Chia-Yi, Taiwan.

The purpose of this work is to employ the chemical oxidation method for the preparation of amorphous and hydrous ruthenium oxide (denoted as a-RuOx) with high specific capacitance and excellent stability. The electrochemical and textural characteristics of a-RuOx were systematically investigated in this study to demonstrate its applicability as supercapacitors. Hydrous ruthenium oxide was synthesized by chemical oxidation from an aqueous RuCl3 solution with H2O2. The specific capacitance of a-RuOx measured at 25 mV/s in 0.1 M H2SO4 is 540 F/g when the a-RuOx powders were annealed in air between 200 and 400 degrees of C for 2 hrs. The average particle size of pristine RuOx, 20 nm, was estimated from high-resolution transmission electron microscopy (HRTEM). The capacitive performance of these annealed a-RuOx is excellent when the annealing temperatures are set between 200 and 350 degrees of C, evidenced by the cyclic voltammetric (CV) and chronopotentiometric (CP) results. The amorphous structure of annealed a-RuOx was examined by both x-ray diffraction (XRD) patterns and electron diffraction (ED) analysis.

SESSION S3: Poster Session
Chair: Emanuel A. M. Kelder and Ross A. Leite
Tuesday, Evening, April 13, 2004
8:00 PM
Salons 8-9 (Marriott)

S3.1 Sol-Gel Non-hydrolytic Synthesis of a NaNanocomposite Electrolyte for Application in Lithium-Ion Devices. Edison Roberto Leite1, Flavio Leandro Souza1, Paulo Roberto Bueno2, and Ronaldo Cesar Ferraz2,1.1
department of Chemistry, Universidade Federal de Sao Carlos, Sao Carlos, Sao Paulo, Brazil; 2Department of Chemistry, Universidade Federal de Sao Carlos, Sao Carlos, Sao Paulo, Brazil.

A new nanocomposite electrolyte was synthesized by a non-hydrolytic sol-gel simple route without a specific treatment of the reagents. The nanocomposite conductor ion is prepared with citric acid, tetraethyl orthosilicate and ethylene glycol, forming polymer chains. The time consuming drying step is replaced in most of the conventional synthesis methods, is not necessary for the preparation of the present nanocomposite electrolyte, pertaining to the polyelectrolyte class, because only Li+ is mobile in the polymeric chains. The effects of the Li concentration and also the concentration of SiO2 and SnO2 nanoparticles are investigated in terms of the Li+ ionic conductivity. Conductivity measurements as a function of the metal oxide nanocrystals content in the nanocomposite show that there is a significant increase in conductivity at approximately 10 wt % of nanoparticles. The new nanocomposite conductor is shown to be fully amorphous at room temperature with the vitreous transition temperature at around 228K. The material is solid, transparent and displays an ionic conductivity ranging from 10^-4 to 10^-3 (ohm.cm)^-1 at room temperature, besides exhibiting a great reproducibility of all these characteristics. Cyclic Voltammetry measurements shows that the hybrid electrolyte presents an outstanding electrochemical stability.

S3.2 Li-Co-Ni citrate precursor as a new synthesis route for nanometer LixNi0.8Co0.2O2 electrode material. Andrea Riez, Vedaigis Mosqueda, Eduardo Perez-Cappe, Pilar Aranda, and Eduardo Ruiz-Hitzky1. 1Department of Technology, UNESP - Chemistry Institute, Araras, SP, Brazil, 2Laboratory of Solid State Ionic, IMRE- Havana University, Havana, Cuba, 3Instituto de Ciencias de Materiales de CSIC, Madrid, Spain.

The Li[Ni1-y-Coy]0.7O2 family is a member of the LiM02 (M= V, Cr, Mn, Co, Ni) series. It exhibits very interesting physical and electrochemical properties that have made most of them applicable as positive electrodes in high energy density batteries. The nickel rich phase, Li[Ni0.8Co0.2]02, exhibits several advantageous properties in comparison other members of this family: higher capacity, lower material cost and better thermal stability. Although many authors have reported the presence of divalent nickel ions at the lithium sites), this occupancy of Li sites by Ni is the main cause that during lithium insertion the electrical conductivity of the material decreases, which affects the performance of the electrode. Progress in this field is being made by means of Brunner-Emmett-Teller method (BET), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Raman spectroscopy analyses. The results show that for material A3 (theoretical PLR of 1:3), the average size of grains and spores are from 40 to 60nm and 3.86nm, respectively, reaching nanometer level. The pyrolytic material mainly consists of aromatic-ring structural carbons, mixed with unfunctionalized sp3 hybrid carbons. ZnO2 dopant results in an increase in the specific surface area of the pyrolytic materials, which provides much space for lithium insertion. When the material is used as electrode material for lithium ion battery, the reversible capacity could be kept at 370 mAhg-1 after 10 charge/discharge cycles.

S3.3 Effect of Nano-sized Particles on the Li-Ion Insertion Kinetics of LixCo02-Based Electrodes. Paulo Roberto Bueno1, Elizabeth Ignacio Santiago2 and Luis Otavio Sousa Bulhões3. 1Department of Physics, University of Sao Paulo, Ribeirao Preto, SP, Brazil, 2Department of Chemistry, University of Sao Paulo, Sao Carlos, SP, Brazil, 3Department of Chemistry, Federal University of Sao Carlos, Sao Carlos, SP, Brazil.

Phosphoric resin based nanocapsular carbonaceous materials have been prepared by doping different proportions of ZnCl2 into phosphoric resin powders at various heat-treatment temperatures. Phosphoric resin porosity was determined by means of Brunner-Emmett-Teller method (BET), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Raman spectroscopy analyses. The results show that for material A3 (theoretical PLR 1:3), the average size of grains and spores are from 40 to 60nm and 3.86nm, respectively, reaching nanometer level. The pyrolytic material mainly consists of aromatic-ring structural carbons, mixed with unfunctionalized sp3 hybrid carbons. ZnO2 dopant results in an increase in the specific surface area of the pyrolytic materials, which provides much space for lithium insertion. When the material is used as electrode material for lithium ion battery, the reversible capacity could be kept at 370 mAhg-1 after 10 charge/discharge cycles.
battery electrodes, whose nanostructure clearly restricts the distance that Li+ must diffuse, which may be as small as 50 nm. This work deals with the mechanism of Li+ ion diffusion in a nanometer length-thick film. A capacitive nanostructured electrodes designed mainly by different LiCoO2 nanosized spherical-like particles protruding from current collector substrate. In previous works we have shown that the scheme for ion diffusion in a nanometer length has the capability to store capacitance charge rather than diffusion process (because of the diffusion length is short enough, which has the effect that diffusion resistance not respond in the frequency-range commonly used in the frequency-domain response - fast charging mode), an effect that was dubbed "nano-scale effect". In a spherical-like particle nanostructured electrode, the "nano-scale effect" is specially pronounced for particles diameter lower than 20 nm for host porous substrates. As a catalyst for the CNTs growth, cobalt particles were deposited by sol-gel polymeric precursor method and either by combustion synthesis.

S3.6 Improved EDLC Characteristics of CNTs Grown on Nanoporous Alumina Templates. Sun-il Mho, Sun-Wen and Mi Jung, Molecular Science & Technology, Ajou University, Suwon, South Korea.

Carbon nanotubes (CNTs) are very useful materials for electrochemical capacitors such as batteries and electrophotical double layer capacitors (EDLCs). In this work, we used the chemical vapor deposition (CVD) method. For EDLC applications, aluminum metal substrate below the porous alumina layer can work directly as conductive electrode substrate. As a catalyst for the CNTs growth, cobalt particles were electrochemically deposited on the bottom of the pore where aluminum surface was exposed to the solution containing Co+ ion by applying ac voltage. The homogeneous CNTs grown on the well-ordered porous alumina templates are excellent electrode materials for EDLCs with the enhanced capacitance. The EDLC characteristics were examined by measuring the capacitances from cyclic voltammograms and the charge-discharge curves.

S3.7 Synthesis and Characterization of Nanocrystalline Li1+xNi0.5Mn0.5O2 Cathode Material Based on Freeze Drying Method. Sun-Hoe Chung, Young-Ji Oh, Shyuckahn O. Aeg and Young Sung Park, Materials Science and Technology, Korea Institute of Science and Technology, Seoul, South Korea.

Lithium nickel manganese oxides are considered as promising cathode materials for secondary Li-ion batteries. Good electrochemical performance of various Li(Ni,Mn)O2-based electrodes, combined with reduced cost of raw materials, is ensured by the easy formation of solid solutions with the layered structure in Li-Ni-Mn-O system. In LiNi0.5Mn0.5O2, Ni ion is placed at Li position, which induce irreversible capacity fade during initial charge. In order to decrease capacity fade, we added extra Li. LiNi0.8Mn0.2O2 was prepared from the mixed-dried Ni-Mn hydroxides (Ni/ Mn=1). The reaction mixture was pressed into pellets and was subjected to thermal processing at 500°C and 800°C in air. LiNi0.5Mn0.5O2 is related closely LiNiO2 having a layered structure, not to LiMn2O4 having a spinel-framework structure. LiNi0.5Mn0.5O2 shows the rechargeable capacity of 185-190 mAh/g. Li-overdoped samples have higher capacities and good rate characteristics. In addition, we will discuss our results with a point of view of structure stabilization during synthesis.

S3.8 Controlled synthesis of manganese (oxihydr)oxides in aqueous solution by thermodisproportionation, Yukiho Eggashima, Yahei Meguro, and Jean Pierret, Chemie de la matiere condensee, Universite Pierre et Marie Curie, Paris, France.

Manganese hydroxide under numerous degrees of oxidation (from 0 to VII), forms a group number of solid compounds, in particular oxides and oxhydroxides with interesting applications: components of batteries, metallurgy, pigments, catalysts [1]. The properties of these materials depend closely on their crystalline structure as well as size and morphology of the particles. Nanometric-sized particles are of interest, because of the high ratio surface to volume and specific effects related to the small size of the crystalline domains (phonon confinement, magnetic relaxation). Because of the variety of manganese oxides (composition, structure), their conditions of synthesis must be strictly controlled. Most of the synthesis of manganese (oxihydr)oxides found in literature bring in organic compounds [2] or template [3]. In aqueous medium, manganese (oxihydr)oxides are obtained from the molecular complexes of Mn(II) or Mn(IV), the most stable degrees in solution. We can quote the oxidation of MnSO4 by ammonium peroxodisulfate S2O82- [4] or the reduction of KMnO4 in alkaline medium [5]. This work is interested in the formation of manganese oxides in aqueous solution by thermodisproportionation of MnCl2 or KMnO4, and in the influence of certain initial parameters (pH and concentration) on the formation, the size and the morphology of the nanoparticles obtained. For example, nanoparticles of MnO0H, MnO2 (with different morphologies) and different crystallographic phases of MnO2 (g- or d-MnO2) have been obtained. This study presents multiple interest: (i) to determine the synthesis method leading to obtaining of pure phases, (ii) to control the morphology and the size of particles in the nanometric domain, (iii) to obtain information about the mechanisms of formation of manganese (oxihydr)oxides. [1] J. E. Post, Proc. Natl. Acad. Sci. 1990, 96, 2447-2452 [2] Y. Sun, C. Ma, Y. Wang, H. Li, Inorg. Chem. Comm. 2002, 5, 747-750 [3] S. Suganaha, P.A. Ramakrishnan, A.M. Hermann, C.P. Warnsingh, D.S. Ginley, Int. J. Hyd. Ener. 2003, 78 (6), 597-600 [4] X. Wang, Y. Li, J. Amer. Chem. Soc. 2001, 124 (12), 2899-2901 [5] E. Narita, T. Okabe, Bull. Chem. Soc. Jpn. 1980, 53, 525-532.


Nanostructured manganese oxides powders are under study as anode materials for electrochemical supercapacitors. Several preparation routes have been explored that lead to manganese oxides of various average manganese oxidation state, composition, particle size and morphology. This contribution will compare the chemical and electrochemical properties of manganese oxide nanoparticles with high surface area and mesoporous manganese oxides, including Co, Fe and Al doped compositions. The electrochemical performances of these various manganese oxides are discussed through cyclic voltammetry and charge-discharge measurements, electron microscopic techniques, and powder X-ray diffraction. Electrochemical performance, especially initial capacity and capacity retention, are shown to strongly correlate with the material composition, morphology and extent of doping.

S3.10 Nanostructured Carbon Materials Synthesis and Applications in Fuel Cells, Li-batteries and Supercapacitors. Xin-Huang Wang, Man-Yin Lo, Chun-Chieh Huang and Sheng-Min Wang, Union Chemical Laboratories, Industrial Technology Research Institute, Hsin-Chiu, Taiwan.

The nanostructured carbon materials such as spheres, tubes (CNTs) or fibers (CNFs) have been realized in Li-battery, fuel cell or supercapacitor applications. An effective production of these carbon materials was achieved in a vertical flow reactor by floating catalyst method via decomposition of ethanol or benzene over metal nanoparticles. The concentration of catalyst precursor, concentration of the promoter, H2 flow rate, feeding speed, reaction time and reaction temperature were controlled to obtain high production yield and morphology of the products. When applying CNFs or CNTs to the anode of Li-battery, addition of small amount of graphitized CNFs in the electrode can improve the charge-discharge cycle life. The energy storage capacity was increased by 20-30 mAh/g when adding 1% of graphitized CNFs. Moreover, addition of as-synthesized CNFs or CNTs in the cathode of direct methanol fuel cell (DMFC) also increases the current density per gram Pt-Ru/C catalyst by 50%. The improvement in performance of Li-battery and DMFC may be due to the conductivity and mechanical strength enhancement of anode electrode with CNFs or CNTs addition.

S3.11 Highly Efficient Organic Small Molecule Based Solar Cells with CuPcC60 Mixed Thin Film Active Layer. Saichi Uchida and Stephen R Forrest, Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University, Princeton, New Jersey.
S3.12

**Dye Sensitised Nanocrystalline SnO2 and TiO2:** A Comparative Study of Interfacial Charge Recombination.

Alex Nicholas Michael Green, Emilio J Palomares and James R. Durrant

Dye sensitised nanocrystalline solar cells (DSSC) have attracted widespread commercial and academic interest in recent years, with the best performance achieving an overall energy conversion efficiency of 10%.[1] Several methods have been used in an attempt to improve the current achievable efficiency. One notable method has been the incorporation of conformal metal oxide insulating layers onto the nanocrystalline metal oxide substrates.[2] In an attempt to move away from TiO2, alternative nanocrystalline metal oxides substrates have also been investigated.[3-7] In this regard, SnO2 has been of particular interest due to its lower conduction band edge and greater crystalline perfection.[8] However, dye sensitised solar cells employing nanocrystalline SnO2 films have proved less comparable to devices fabricated employing TiO2. In this paper we will report a detailed comparison of the electronic properties of TiO2 and SnO2 nanostructured electrodes, and discuss the implications of these observations for the function of dye sensitized solar cells. Issues that will be addressed will include: 1. Charge recombination dynamics observed for dye sensitized films as a function of the bias applied to the photoelectrode. 2. The correlation of these recombination dynamics with film electron densities determined by chromomiporometric studies. 3. Retardation of interfacial charge recombination using conformal deposition of metal oxide layers. 4. The effects of conformal deposition on the solar cell efficiency. References [1] Nazeeruddin, M.K.; Pechy, P.; Renouard, T.; Zakeeruddin, S.M.; Pechy, P.; Renouard, T.; Zakeeruddin, S.M.; BCP / Ag shows (1). 1)pC 60 = 81 (2003). [5] P. Peumans and S. R. Forrest, small molecule based BH solar cells. For example, 374-379. [6] Tennakone, K.; Kumara, G. R. R. A.; Kottegoda, T. R.; S. R. Forrest, contact shows hole selective injection. Combined with observations for the function of dye sensitized solar cells. Issues that have previously achieved the highest efficiencies among small molecule based bilayer organic PV devices.[5]. A vacuum co-deposited D:A mixed layer is macroscopically uniform, and the device characteristics are determined by both electron and hole injection properties of the cathode and anode materials, respectively. As for the anode, UV/O2 treated ITO provides a good ohmic contact for holes from CuPc, and an energy barrier to electrons from CuO. Thus, an ITO/CuPc/C60 contact shows hole selective injection. Combined with 2.9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), C60/BCP thin layers act as an electron donor. This simple architecture has very small series resistance, e.g. a forward current density of 1A/cm2 is obtained with a rectification ratio of 10^6 at ±1V, and Jsc is linearly increased with increasing irradiation light intensity of up to 2.4 suns. A device with a structure of ITO / 370 Å CuPc:C60 (1:1) / 100 Å CuO / 75 Å BCP / Ag shows n = 3.8% at 0.37 suns (AM1.5G). Although the fill factor increases with increasing the light intensity because of the possible increase of hole-electron recombination in the mixed region, n = 3.8% under 2.4 suns irradiation. References [1] G. Yu, J. Gao, J. Hummelen, F. Wudl and A. J. Heeger, Science, 270, 1789 (1995). [2] F. R. R. Oreg, Solar Energy Materials and Solar Cells, 51, 13 (1998). [3] P. Peumans and S. R. Forrest, Appl. Phys. Lett., 79, 81 (2001). [5] P. Peumans and S. R. Forrest, Appl. Phys. Lett., 79, 81 (2001).
quantum confined SnO₂ particles was studied. This dependence agreed very well with the weak confinement regime behavior predicted by the effective mass theoretical model, which estimates the size dependence of the band gap energy of nanocrystals. This is a strong indicative that the photoluminescence emission energy corresponds to the quantum dot band gap energy, and therefore that the observed photoluminescence occurs by free exciton decay.

**S3.16 The next generation in nanocrystal-based solution processible solar cells.** Dan Gur¹,², Delin J. Milliron¹,² and A. Paul Alivisatos³,⁴,⁵. ¹Materials Science and Engineering, UC Berkeley, Berkeley, California; ²Chemistry, UC Berkeley, Berkeley, California; ³Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Developments in colloidal nanocrystal synthesis have facilitated major advances in the field of hybrid organic-nanocrystal photovoltaics. Synthesis techniques allow the control of nanocrystal size, shape, and composition, enabling the creation of 3-dimensional and chemically heterogeneous structures suitable for photovoltaic applications. For example, tetrapod-shaped cadmium telluride nanocrystals offer broadband absorption well matched to the solar spectrum and a branched structure that ensures direct electron transport through a dispersed heterojunction. The role of CdTe tetrapods and other novel nanostructures in next generation nanocrystal-based solar cells is presented.

**S3.17 Synthesis of Nanoparticles of TiO₂ in Aqueous Solution by Soft Chemistry: Influence of the Nature of Anions in Solution on the Crystal Morphology.** Magali Koelsch, Sophie Cassaignon and Jean Pierre Jolivet; Lab Chimie de la Matière Condensée, Université Pierre et Marie Curie, Paris, France.

Titanium oxide TiO₂ has found extensive use in a great variety of applications among which electrode materials for dye-sensitized solar cells. The polymorphs of TiO₂, rutile, anatase and brookite exhibit specific physical properties (band gap, surface states...). TiO₂ anatase is the most used phase for photovoltaic applications [1] and brookite seems potentially interesting [2, 3]. Nanometric particles of anatase, brookite and rutile polymorphs, were synthesized by thermolysis of TiCl₄ in aqueous medium. The control of the conditions of precipitation (acidity, nature of anions, ionic strength, titanium concentration) allow the control of crystalline structure, size and morphology of particles. This presentation is focused on the influence of the anions in solution (Cl⁻, SO₄²⁻, NO₃⁻, ClO₄⁻) on the control of the synthesis of nanoparticles of TiO₂. We will discuss the role of these anions in the mechanism of formation. [1] O’Regan B., Graetzel M., Nature 1991, 353, 737. [2] K.J. Jiang, T. Kitamura, H. Yin, S. Bao, S. Yamagishi, Chem. Lett., 2002, 872. [3] M. Koelsch, S. Cassaignon, J. F. Guillemeols, J. P. Jolivet, Thin Solid Films, 2002, 403-404, 312.

**S3.18 Electrical and morphological characterization of electrochemically deposited ZnO/dye hybrid films.** Jens Reents, Juergen Parisi and Achim Kittel; Energy and Semiconductor Research, University of Oldenburg, Oldenburg, Germany.

Dye sensitized solar cells of the Gratzel type are usually fabricated with TiO₂ covered with dye after its synthesis as one electrode. Due to its enhanced surface area and a strong attachment of non-aggregated sensitizer dyes ZnO is, aside from TiO₂, a promising semiconducting material for solar energy conversion. We investigate ZnO/dye electrodes where the dye is already added during the electrodeposition process of the ZnO. We examine the influence of the dye species and the dye concentration on the surface morphology of the ZnO film by means of AFM and STM. The electrical properties of the different films were characterized by means of I-V-measurements. In order to analyze the lateral electrical conductivity we electrodeposit ZnO/dye thin films across an insulating gap. The transversal conductivity was measured with a conductive tip AFM.

**S3.19 Non-Steady State Operation of Polymer/TiO₂ Photovoltaic Devices.** Kiril Kirov, Bernard Henry, Victor Burkovik, Michelle Carey, Chris Grovenor and Hazel Assender; Department of Materials, University of Oxford, Oxford, United Kingdom.

Polymer/TiO₂ composite solar cells (CSCs) are currently being investigated by academic research groups and industrial companies due to the prospect of achieving good power conversion efficiencies at a low production cost. We present a study of the initial period of operation (up to 2 hours) of such devices, which show that during this time interval the CSCs operate in a non-steady state. The behaviour is complex and may include a gradual rise of Voc and Isc with time, a passage through a maximum of either or both parameters, and even a gradual decrease. This time dependent behaviour can be attributed to the formation of quasi steady state due to both diffusion and drift of charges in the CSCs. Such results bear implications on the photovoltaic characterisation of polymer/TiO₂ devices and on the reporting of photovoltaic performance in scientific literature.

SESSION S4: Lithium-ion Batteries II

Chair: Robert K. Maruska, Wednesday Morning, April 14, 2004
Room 3006 (Moscone West)

8:30 AM S4.1 Improving Electrochemical Properties Through Mesoporous Nanoarchitectures. Bruce Dunn, Materials Science and Engineering, UCLA, Los Angeles, California.

Aerogels are well known mesoporous materials whose low density and high surface area result from synthesis methods that do not collapse the solid network phase upon removal of the solvent. They have been widely used in the heterogeneous catalytic materials field because of their molecular accessibility and rapid mass transport. However, electrochemical, chemical and electronic properties in general, and battery materials in particular, have yet to exploit this nanoarchitecture, despite the fact that one would expect such physical features to be desirable for electrochemical reactions. This paper reviews some of the interesting, and unexpected, electrochemical results obtained with vanadium oxide aerogels. These results underscore the benefits to be gained by creating battery materials with mesoporous nanoarchitectures. Our studies show that the inherent electrochemical properties of V₂O₅ aerogels combine elements of both capacitor-like and battery-like behavior. Depending upon the nanoarchitecture, specific capacitance values in excess of 2000 F/g have been obtained along with lithium capacities of over 400 mAh/g. The charge storage mechanism in these materials is very different from that which occurs with traditional intercalation materials and we have proposed that the origin of this unique response is associated with the high surface area of the aerogel. That is, surface defects that may not be evident in traditional materials now become dominant because of the drastic increase in surface area. We have also been exploring novel electrode architectures that incorporate V₂O₅ aerogels. One approach, involving the integration of single wall carbon nanotubes as the electronically conducting network, leads to electrodes with excellent performance at high discharge rates. Lithium capacities on the order of 300 mAh/g are obtained at discharge rates above 2C. Another approach has involved the preparation of aerogel electrodes that possess an inverted opal structure. This architecture is also effective at retaining high lithium capacity at high discharge rates.

9:00 AM S4.2 Three Dimensionally Nanostructured Anode and Cathode Materials Prepared by Colloidal Crystal Templating. Andreas Stein¹, Justin C. Lytle¹, Nicholas S. Ergang¹, Hangwei Yan¹, Kye Tae Lee²,³ and Seung M. Oh²,³;¹Department of Chemistry, University of Minnesota, Minneapolis, Minnesota; ²School of Chemical Engineering, Seoul National University, Seoul, South Korea.

Recently, colloidal crystal templating techniques have been developed to produce three-dimensionally ordered macroporous (3DOM) solids composed of insulator, semiconductor, or metal compositions. Monodisperse polymer spheres are close-packed into ordered arrays and infiltrated with a fluid which is solidified. After removal of the template, a solid skeleton is obtained around an ordered array of voids that possess an inverted opal structure. This architecture is also effective at retaining high lithium capacity at high discharge rates.
(b) the large open pores which permit facile transport of liquid electrolyte; (c) the thin walls which significantly shorten ion diffusion distances; (d) the porous nanocellular network which is expected to improve the electrical conductivity; and (c) the relatively large accessible surface. Since charge transport in 3DOM electrodes would occur on a nanometer scale, rather than a micrometer scale, these materials also appear to be more labile to Li-ion diffusion and the problem of shorting during intercalation.

In a first step towards 3D interpenetrating battery components, we have prepared several electrode compositions with 3DOM structures, including 3DOM cathode materials (LiCoO2, LiNiO2, LiNi1-xCoxO2, LiMn2O4, V2O5) and 3DOM anode materials (carbon, SiO2).

This presentation will provide a general overview of relevant issues of structural and phase control in these materials and will then focus on synthesis optimization and electrochemical properties of 3DOM materials, including 3DOM SnO2 films and 3DOM carbon nanofibers for anodes and will then be discussed in greater detail.

9:15 AM S4.4 Liquid Crystal Templated Nickel/Nickel Oxide Electrodes. John Robert Owen, School of Chemistry, University of Southampton, Southampton, United Kingdom; 2Nanotec Ltd, Southampton, United Kingdom.

Electrodeposition of platinum in a liquid crystal template has been described [1] as a general synthesis technique for metal films containing a lattice of periodic channels with nanometer dimensions. Since then we have used the Southampton Method for the deposition of nanostructured materials such as Pt, Co, Ag, Au, and semiconductors such as Se, and metal oxides such as MnO2 and Ni(OH). Mesoporous nickel metal films were grown from a liquid crystalline electrolyte formed by adding a surfactant in high concentration to a nickel salt solution. After washing away the electrolyte a thin layer of nickel oxyhydroxide was grown on the surface of the pores to give a high surface area redox insertion electrode supported by a nanostructured current collector of nickel [2]. The nanostructured nickel was then used as part of an electrode that was used to study the effect of counter ion placement on the conductivity of 3DOM materials. By adjusting the grain size of electrode materials, the properties of macroscopic structures can be tuned precisely. The discussion of cathode materials will focus mainly on methods to obtain 3DOM powders as well as thin films. The structure and electrochemical behavior of 3DOM SnO2 films and 3DOM carbon monoliths for anodes will then be discussed in greater detail.

10:30 AM S4.5 Nanocomposite Electrodes for Solid-State Lithium Batteries. Ema A. Olivetti, Anna M Mayes and Donald R Sadoway; Department of Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We investigate the fabrication of high energy density electrode materials for solid-state rechargeable batteries by incorporating continuous, nanoscale phases within one component of self-organizing amphiphilic graft copolymer systems. The in-situ growth of cathodic components in ion-conducting domains of copolymer systems allows for the control of morphology and concentration polarization by varying concentration and distance between the electrodes. The system is comprised of a graft copolymer electrolyte, in which a portion of the polymer is comprised of a lattice of periodic channels with nanometer dimensions, and has been described in detail in the literature. Briefly, the polymer consists of a lattice of periodic channels with nanometer dimensions, and has been described in detail in the literature. The in-situ growth of cathodic components in ion-conducting domains of copolymer systems allows the electrical conductivity to be improved by incorporating metallic phases as electronic conductors by electrodeposition techniques. In situ growth of active cathode phases by sol-gel synthesis and electrochemical methods is also explored.

10:45 AM S4.6 Nanoscale solid polymer electrolytes from electropolymerization: New routes to integrated nanostructured energy storage architectures. Christopher P Rhodes, Jeffrey W. Long, Michael S. Doescher and Debra R. Rolison; Naval Research Laboratory, Washington, District of Columbia.

Nanoscale solid electrolytes are an integral part of functional nanoscale architectures for energy storage and conversion devices. The use of nanoscale (5 to 50 nm) solid polymer electrolytes offers the possibility to significantly improve rate capabilities and power densities for batteries and other solid-state ionic devices and represents a considerable improvement over current micrometer-thick solid electrolytes. Electropolymerization provides a route to synthesize nanoscale polymer-free polymer films directly at the electrode surface and offers advantages over self-assembly and vapor deposition for obtaining thin films on the walls within 3-D architectures. We have explored electro-oxidation of phenol and phenol derivatives to create 5-50 nm-thick polymers on planar and porous substrates. When doped or functionalized with ions, these ultrathin polymers function as solid electrolytes in nanoscale devices. Solid-state electrical measurements of electropolymerized poly(phenylene oxide) and related polymers on ITO and Au substrates are made using a two-electrode configuration with soft organic contacts such as Hg or slowly evaporated Au or Al as counter electrode. In-situ and ex-situ transmission electron microscopy measurements are used to determine the electronic conductivity, ionic conductivity and dielectric breakdown. Experimental results demonstrate that electropolymerization provides new synthetic strategies to create nanoscale solid electrolytes and nanostructured energy storage architectures.
outside of the ion-conducting POEM block, i.e., TiO2-PLMA-b-PLiMA-b-POEM and PLiMA-b-PLMA-b-POEM, the lithium ions were able to dissociate from the anions and room temperature conductivities approaching 10-5 S/cm were achieved. Conversely, in the [PLMA-b-P(PEO-r-LiMA)] system, in which the anion is incorporated into the conducting phase, the conductivity was roughly two orders of magnitude lower due to strong ion-pairing interactions as supported by FT-IR measurement. By reducing charge density through complexing the carboxylate anion with BFs, the ion dissociation was enhanced significantly and conductivity comparable to the latter system was achieved. Charge separation could thus be equivalently obtained either by using a low charge density anion or by spatially isolating the counter ion. All of the single-ion block copolymer electrolytes exhibited transference numbers of roughly unity and also excellent electrochemical stability to 5V.

11:45 AM S4.8
The variation in the structure and ionic conductivity of LiClO4-PEO hybrid electrolytes by addition of Al2O3-doped TiO2, Yun-Mo Sung and Jin-Kyung Lee; Materials Sci. & Eng., Daejin University, Kyunggi-do, South Korea.

Nowadays, the application of Li-ion polymer battery is rapidly increasing with increase in the use of mobile electronics such as cellular phones, camcorders, and laptop computers. Thus, high-performance Li-ion polymer battery is highly demanded and much study has been concentrated on the improvement of polymer electrolytes. In this study TiO2 was added into LiClO4-PEO hybrids to modify their molecular structure and ionic conductivity. Also, TiO2 doped with Al2O3 was introduced into the hybrids. The variation in the hybrid morphology and PEI crystallization behavior in addition of TiO2 and Al2O3-doped TiO2, respectively into LiClO4-PEO hybrids was investigated using scanning electron microscopy (SEM) and x-ray diffraction (XRD). Also, scanning differential calorimetry (DSC) was performed to study the glass transition and crystallization behaviors of PEI in each of the hybrids. The LiClO4-PEO hybrids with TiO2 and Al2O3-doped TiO2 addition showed enhanced ionic conductivity and the effect of TiO2 and Al2O3-doped TiO2 addition was elucidated based upon structure-property relationship for each hybrid.

SESSION S5: Solar Cell I
Chair: Michael Graetzel
Wednesday Afternoon, April 14, 2004
Room 3009 (Moscone West)

1:30 PM S5.5.1
Nanoporous Semiconductor Electrodes for Photoelectrochemical Solar Cells: Design, Synthesis, Characterization, and Application, Arie Zaban; Chemistry Department, Bar-Ilan University, Ramat-Gan, Israel.

Dye sensitized solar cells (DSSCs) are based on the photoelectrode of a semiconductor and the electrolyte in contact with the electrode. The light harvest compartment is responsible for efficient light conversion. In the case of nanocrystals, the light absorption is high but the electron transport is very low. The diffusion of electrons to the counter electrode occurs via diffusion of electrolytes. In this study, we will present our results on the synthesis of controlled shapes.

2:15 PM S5.5.2
Synthesis of nanometric TiO2 in aqueous solution by soft chemistry: obtaining of anatase, brookite and rutile with controlled shapes, maguhi koolah, cassaignon sophie and jean pierre jolivet; lab chimie de la matiere condensee, universite Pierre et Marie Curie, Paris, France.

Titanium dioxide, a non-toxic and chemically inert material, has an important place in many commercial applications. Anatase is attractive because of a large effective surface which enhances surface reactivity. Among many applications, electrode materials for Dye Sensitized Solar Cell (DSSC) present a great interest [1]. The anatase (made of isotropic spherical particles) is the phase preferentially used for the photovoltaic devices, while the rutile commonly synthesized in the form of anisotropic rods gave very poor efficiency. As for the brookite, very few studies related to its use as the mesoscopic ordering stable to 750°C using carbon as a confining material to prevent framework reconstruction. The surfactant-based structure-directing agent is used directly as the carbon precursor enhancing confinement. Compared to non-carbon treated films, these films exhibit enhanced photocatalytic activity in water splitting measurements. Furthermore, crystallized films are used to fabricate electrochemical dye-sensitized solar cells (DSSC) and improved power conversion efficiency is observed.

2:30 PM S5.5.4
Titania aerogels: New ultrahigh-surface-area interfaces for dye-sensitized photovoltaics, Jeremy Pietron; Arnold Stux;
Ratanya Compton1, Gerald J. Meyer2,3 and Debra Rolison; 1Surface Chemistry Branch, Code 6171, Naval Research Laboratory, Washington, District of Columbia; 2Materials Science, Johns Hopkins University, Baltimore, Maryland; 3Chemistry, Johns Hopkins University, Baltimore, Maryland.

The discontinuous pore-solid networks that comprise the ultrahigh, high-surface-area aerogel enable rapid flow of solutes through the three-dimensional, nanostructured architecture. The high specific surface area of titania aerogel (150-200m2/g) amplifies the effective concentration of dye adsorbed in the film (and thus the number of...
photonsensitizing centers), while the continuous pore network permits rapid transport of electron-transfer mediators through the film to recycle the sensitized dye. The self-connection of the thinnest semiconductor films such as selenium\(^1\), tellurium\(^2\) and cadmium telluride that have been fabricated by this method. The liquid crystalline template mixtures and electrodeposited films were optimised and elicit new functional properties, e.g. allowing quantum size effects by virtue of their reduced dimensionality and nanometre length scales (from 2 to 15 nm). The ability to electrodeposited mesoporous nanostructured semiconductors highlights the possibility of creating a new class of transparent solar cells that would exhibit unusual optical and electronic properties. References \([1]\) S. Nandakumar, J. Elliott, G. S. Attard, Chem. Mater., 2001, 13, 3840. \([2]\) T. Gabriel, I. S. Nandakumar, G. S. Attard, Electrochem. Comms., 2002, 4, 610.

3:45 PM S5.5

**Nanowire Solar Cells**. Matt Law\(^1,2\), Lori E Greene\(^1,3\), Ekaterina N Kudinova\(^1,2\), Jinsong Liu\(^1,2\), Jean M J Frechet\(^1,2\) and Peidong Yang\(^1\).

A new method of depositing epitaxial ZnO nanocolumns, for use in solar cells and other devices, on sputter-coated ZnO substrates is described that utilizes supersaturated zincate species in sodium hydroxide solutions. Uniform arrays of columns were grown reproducibly over the entire substrate. Columns were 50 to 2000 nm long and 50 to 200 nm wide. They grew on substrates pre-coated with ZnO, not on bare glass orITO or SnO\(_2\)-coated glass. This growth occurs by the preferential etching of ZnO to form a metallic Zn core, and the columns on these substrates formed a three-dimensional structure to provide functional materials with an ideal surface-area to volume ratio. Through the development of a donor-acceptor heterojunction to provide a large internal surface area for the efficient collection of photogenerated carriers. In state-of-the-art cells, the bulk interface forms via phase separation during the spin coating of mixtures of the constitutive donor and acceptor materials. Spinning coating typically yields a disordered morphology that results, due to the presence of circular and incomplete percolation pathways, in the poor charge transport properties of these devices. A promising strategy for improving cell performance is to hasten the outward flow of carriers by providing an ordered bulk interface with direct channels to the electrodes. Here we describe solar cells based on ZnO nanowire-polymer composite films in which both electron dissociation and charge collection are efficient. The columns can be fabricated on glass and plastic substrates using mild solution methods. We also report on the modification of our ZnO nanowire arrays for use as single-crystalline phototubes in Gratzel-type solar cells.

4:00 PM S5.6

**Optical Properties of Nanostructured Mesoporous Semiconductor Film**s. Alan Jankowski, LLNL, Livermore, California.

Optical and electrical properties of vertically aligned ZnO-nanowires, deposited at low temperature and in hydrogen with continuous open porosity. As applied for transparent conductive substrates. The preparation of these wires is compatible with large-area optical and photovoltaic applications. The nano-wires are mostly single-crystalline with aspect ratios up to 20. The orientation is vertical to within \(30^\circ\). Deposition with AI was achieved during deposition. Strong band gap photoluminescence around 384 nm can be observed at room temperature. The defect photoluminescence is found to depend on surface treatment and is centered around 384 nm. The use of UV-VIS near infrared reflectivity measurements, is typically around 20 cm\(^{-1}\)/Vs. Optical polarization effects, light scattering, light trapping and deposition of other thin-film semiconductors on these nano-wires will be discussed.

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**SESSION S6: Poster Session**

**Chairs: Enrico Traverso and Harry Toller**

**Wednesday Evening, April 14, 2004**

8:00 PM

Salons 8-9 (Marriott)

**S6.1**

**Sputter-deposited porous nanostructures for catalytic membranes.** Alan Janowski, LLNL, Livermore, California.

Membranes in the form of porous nanostructures are of interest in catalytic functions for new alternative energy devices. Sputter-deposited porous membranes are now applied for use in microfuel cells as electrodes and to reform hydrocarbons to deliver hydrogen. The nanostructured membranes require optimization of a three-dimensional structure to provide functional materials with an ideal surface-area to volume ratio. Through the development of a sputter deposition method, nickel membranes for use as electrodes are demonstrated with continuous open porosity at the nanoscale. A three-dimensional material is produced under the following general condition. A moderate, sputter gas pressure and an elevated substrate temperature about half the absolute melting point of the nanomaterial with continuous open porosity. As applied for depositing porous nanostructured copper, a new means arises for synthesizing oxide materials that are of interest for use as catalytic materials. Specifically, copper-oxygen is a compound that surpasses the performance of nickel in the direct reformation of methanol at low temperatures. A porous nanostructure is demonstrated in a several-micron thick coating as sputter deposited from a copper-zinc...
Synthesis of Metal-Oxide Matrix with Embedded Nickel Nanoparticles by a Bottom-up Chemical Process.
Edson Roberto Leite, Chemistry, Universidade Federal de Sao Carlos, Sao Carlos, Sao Paulo, Brazil.

The combination of the Sol-Gel technology with the nanotechnology can result in the development of new nanostructures for catalytic materials. These new nanostructured materials, in special the nanocomposites, can improve the performance of the catalytic materials, specially in materials for fuel cell application or hydrogen generation. Here we describe a new chemical route to obtain highly dispersed nanometric particles embedded in different matrices that such as MgO and ZnO. The synthesis method is based on a modification of the polymeric precursor method. The nanometric particles (particles at the range of 1-4nm) were obtained in a single process, without the use of an external reducing agent (hydrogen atmosphere).

Abstract Withdrawn

Conductivity dependence on oxygen partial pressure and transport number measurements of La2M02O9.
Alberto tarancon1, Guilhem Dezanneau1, Alejandro Morata1, Francesca Petri2, Joan-Ramon Morante1 and Truls Norby2; 1Dept. Electronica, Universitat de Barcelona, Barcelona, Spain; 2Dept. of Chemistry, Centre for materials research, University of Oslo, Oslo, Norway.

Transport number measurements and impedance spectroscopy in controlled temperature and atmosphere were used to investigate the electrical properties of La2Mo2O9 sintered samples. These samples were prepared from nanocrystalline La2Mo2O9 powders as obtained from a new soft chemistry route, involving the polymerisation of acrylamide in a solution containing cation salts complexed with EDTA. By means of EMF method measurements, the sintered compound was found pure oxygen conductor in the range of 673-1073 K with oxide-ion transport numbers greater than 0.99. The effect of the oxygen partial pressure on the electrical conductivity of La2Mo2O9 was investigated by impedance spectroscopy from 1 to 10-72 atm. The results show a highly stable conduction properties of the compound up to 10-17 atm at 1073K. For more reductive atmospheres, the conduction is strongly affected, leading to consider important electronic conduction for the reduced La2Mo2O9-derived phase with mean composition La7Mo7O30. Finally, we also studied the protonic conduction of such sample and showed that it is several orders of magnitude lower than the oxygen conduction in the 673-1073 K temperature range. Based on these results, we question and discuss the suitability of the recently discovered La2Mo2O9-derived compounds as electrolytes in solid oxide fuel cell applications.

Percolation Properties of Anisotropic Composites.
David Spencer Mebane, Arun Gokhale and Rosario Gerhardt; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

A method for determining the electrically active (percolating) volume fraction of anisotropic conducting inclusions in a material containing spherical inclusions[1]. In this work, a three-dimensional, continuum Monte Carlo model is used to obtain the electrically active fractions for a composite containing cylindrical inclusions. The model input parameters included randomly generated cylindrical orientations, cylinder diameters and aspect ratio as well as cylinder overlap distributions. Experimental verification was obtained by comparing the simulation models with the electrical response of ceramic matrix micro-composites containing various ratios of silicon carbide whiskers dispersed in an alumina matrix. The work shows that microstructurally measurable parameters such as orientation and particle size for a given composite can be used to predict at what volume fraction and associated surface area percolation may occur. The model is generic and may be extended to other materials, such as the compositions used in ternary SOFC electrode composites. In this case, additional parameters associated with the porosity of the ionically conducting matrix need to be incorporated into the model. Variations in the particle micro-structure from that of BaF2 and CaF2 with layers from 2 to 500 nm were produced and their ionic conduction properties were characterized. Two important deviations from bulk properties were observed. First, the ionic conductivity of the superlattices is much larger than those of the bulk compounds for layer widths in the range of 15-50 nm. Second, the activation energy for ionic conduction in the superlattices is almost identical that of bulk CaF2 from that of BaF2. These results were interpreted as resulting from the transfer of negative fluoride interstitials from the BaF2 layers to the CaF2 ones. These results show that an ionic channel model can be developed, with potential applications in the technology of ionic conductors. In the present work, we perform first-principles calculations for the formation energies of negative fluoride self-interstitials (Fi(-)) and positive fluorine vacancies (V_F(+)) in CaF2-BaF2 superlattices and in the corresponding bulk compounds. In dislocation-free (strained-layer) superlattices, the calculations show that both the Fi(-) and the V_F(+) defects are energetically more stable in the CaF2 layers than in the BaF2 layers. If the misfit stress is released (by dislocations, for instance), our results indicate that ion transfer between layers becomes energetically favorable with Fi(-) in the CaF2 layers and the V_F(+) in the BaF2 layers. This is consistent with the experimental results [1].

Synthesis and characterization of nanocrystalline SDC powder for IT-SOFC application obtained via mimic alkoxide method.
Alberto Rainer, Vincenzo Esposito, Chavalit Trakanprapai, Silvia Licocci and Enrico Traversa; Dept. of Chemical Science and Technology, University of Rome "Tor Vergata", Rome, Italy.

Doped Ceria represents an attractive material for Intermediate Temperature SOFC applications. Various techniques for synthesizing nanocrystalline ceria-based oxide powders have been reported in the literature, including aqueous solution co-precipitation and sol-gel techniques. In fact, the electrochemical performance of metal oxides strongly depends on the route employed for the synthesis of the powders, in this paper, a novel synthesis for the preparation of Samaria Doped Ceria (SDC) using a mimic alkoxide method, is presented. The peculiarity of this technique is to combine the low cost of nitrate based conventional co-precipitation with the small particle size and low calcination temperature of the sol-gel chemical route. The reaction is based on the hydrolysis of coordination H2O from the salts used as precursors by a polyfunctional amine in alcoholic solvent, this leads to the formation of a mixed hydroxide, which is then deprotoinated by the amine. The steps of the reaction have been performed via FT-IR analysis to confirm the role of the amine. XRD and Raman analysis were performed to characterize the calcined powders in terms of purity and crystallinity. Very angular powder size (10nm) was determined for the calcined powder by XRD. Such a small crystallite size leads to high sintering resistance of the powder. Therefore, EIS measurements on SDC pellets were performed to fully understand the influence of sintering parameters on the electrical properties of the material.
Nanosized particles of 13 mol% MgO-doped ZrO\(_2\) with a narrow distribution of pore sizes were prepared by the co-precipitation technique using optimized parameters of synthesis. Transmission electron microscopy analysis of the calcined powder reveals that the majority of the particles having grain sizes in the 10 to 20 nm range. From nitrogen adsorption analysis an average particle size of 13 nm was estimated, which is similar to the average pore size diameter (12 nm). Besides the unimodal distribution of pore sizes, the linear shrinkage curve of powder compacts exhibits several inflexions indicating different rates of densification up to 1873 K. After sintering at 1873 K for 2 h, the microstructure features of a compact are characteristics of the intermediate stage with interconnected porosity. Some pores have not been fully densified by these treatments. These results are explained as a size effect of nanoparticles of magnesia-doped zirconia during sintering.

Ceria-gadolinia solid electrolytes prepared with nanosized powders, Reginaldo Muccillo and Eliana N. S. Muccillo, CCTM, IPEN, S. Paulo, SP, Brazil.

Nanosized powders of ceria-10 mol% gadolinia were prepared by a co-precipitation chemical route. After calculation of the powders at 400 degrees C for 1 hour, the average pore size determined by nitrogen adsorption is 4 nm. Average values of crystallite size of 6 and 33 nm were estimated after Scherrer equation for the (111) X-ray diffraction reflection in specimens calcined for 1 hour at 400 degrees C and 900 degrees C, respectively. Particle size in the powders sintered at 1673 K for 1 h, attaining full densification at that temperature. The X-ray diffraction pattern of a sintered powder shows a decrease in both the intergranular (grain boundary) and intragranular (bulk) resistivities for increasing sintering temperature.


Dense thin films of ZrO\(_2\)85Y0.15O1.92 (8YSZ) as electrolyte for solid oxide fuel cells and gas sensor devices have been fabricated using the screen printing technology. In first step a slurry was prepared using commercial 8YSZ powders (MEL-chemicals), terpolymer (dispersing agent), ethylcellulose and dibutyl phthalate (DBT). After being in a ball milling stage for some hours the slurry was printed onto alumina substrates and submitted to a thermal treatment at 1573K in air. A double printing process, with an intermediate co-firing at 1273K was also attempted to improve the compactness of the grains. The aim of this work is to understand the influence of the processing parameters in order to optimize the grain size and porosity of the layers. The number of involved parameters is very high, (composition of binder and dispersant agents in the slurry, ball milling time, sintering temperature and duration of the thermal treatments, etc) an statistical analysis of data has been applied to define and carry out the minimum set of experiments to account for the most significant parameters and to detect cross-linked effects between them. After a conventional mechanical polishing cross-section sample preparation procedure, the samples have been examined by Scanning Electron Microscopy. These results are compared with those obtained by “in-situ” cross section preparation in a focused ion beam (FIB)-SEM equipment.

Preparation of A New Carbon Nano-particle by Arc Discharge, Jhy-Yeong Gau and Hong-Jen Lai; Materials Research Laboratories, Tung, Hsinchu, Taiwan.

Synthesis and characterization of a new carbon material are investigated in this study. With an unique graphiteic structure, this carbon particle which possesses a very high surface area (600 cm\(^2\)/g), is suitable for catalysts loading in application of fuel cell. It is known that carbon material is used as a support material to achieve high dispersion of metal catalyst such as Platinum to enhance the activity of it. Synthesis was proceeded by conventional arc discharge process between two graphite electrodes in vacuum. A high-current arc was utilized to evaporate the cathode electrode to produce carbon soot on the chamber wall. The morphology and microstructure of the material were investigated by SEM, HRTEM, XRD and Raman spectroscopy. Observation of the soot by SEM has shown that it consists agglomerations of carbon particles which fused together to form an interconnected chain structure. Most carbon particles had approximate 30 nm in diameter. HRTEM observation shown the carbon particle is composed of onion-type fullerene and extremely curled graphene sheet, which appears as double-sheet lamella. The as-prepared soot shown sharp 002 diffraction at 2q=26.04 degree, which is typically observed in graphite. Furthermore, the diffraction spectrum shown merely a regular increase of intensity with decrease in scattering angle from 2q=20 to 2q=20 degree. This corresponded to the wider inter-layer spacing for the van der Waals distance of this carbon particle as compared with that of the ordinary graphite.

The effect of structural change and Ni doping on Hydrogen storage properties of carbon nanotubes, Hyun-Seok Kim, Ho Lee and Jiu-Young Lee; Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

Hydrogen storage properties in carbon nanotubes (CNTs) were investigated from the view points of not only physical hydrogen molecules adsorption in nano-holes but also chemical hydrogen adsorption on graphite surface. CNTs with intrinsic closed structure, which mean the blocked hole and entry induced by highly defective layers and tube cap and CNTs with open structure were studied through hydrogen thermal desorption technique equipped with gas chromatograph. The precise analysis on thermal desorption spectra on CNTs with closed structure showed that hydrogen gas was released at three major temperature ranges such as 100-230K, 290-350K, and 600-925K, where the evolved hydrogen amount were about 1.65wt%, 0.64wt%, and 0.03wt%, respectively. However, in case of aligned and open CNTs, the evoluted peak around 290-350K was highly developed about 1.9wt% and that at 600-925K disappeared. Ni doping (dispersion) effect on hydrogen storage properties were investigated comparatively. The metal nanoparticles were homogeneously dispersed using incipient wetness impregnation method. Hydrogen desorption spectra of MWNTs with Ni nanoparticles showed that about 2.85wt% of hydrogen was released in the range of 340-520K.

A Formalism to Describe Demixing of Mixed Oxides of Large and Small Grain Size in an Electric Field, Mandy J Brown, Inna V. Belova and Graeme E Murch; School of Engineering, The University of Newcastle, Callaghan, New South Wales, Australia.

It has been for some time that mixed oxides demix in an electric field under high current conditions. Taking a phenomenological approach we develop a formalism for open and closed systems which describes steady state demixed cation concentration profiles. The open system corresponds to small grain material and a corresponding significant grain boundary diffusion flux to enable the cation vacancies to be in communication with the surface oxygen partial pressure. The closed system corresponds to large grain material where the vacancies respond only to local forces and kinetic conditions. The closed system results in possible supersaturated concentrations of vacancies demixed in the temperature region. In these two cases give substantially different degrees of cation demixing. Unusual demixed profiles may develop in quaternary mixed oxide systems.

Titanium POEMS: High Proton Conductivity in Porous Titania Dioxide Prepared by the Sol-Gel Route, Flavio Marion Vichi, Maria Isabel Tejedor and Marc Anderson; 1Institute of Chemistry, Univ of Sao Paulo, Sao Paulo, Brazil; 2Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, Wisconsin.

Porous Oxide Electrolyte Materials (POEMS), obtained as nanoporous ceramics via the sol-gel route, are interesting materials, because they have a proton conductivity which is similar to that of Nafion\(^\circ\), the material used presently in most Proton Exchange Membrane Fuel Cells (PEMFC). Inorganic oxides have the advantage of being less costly, and have the potential to operate at higher temperatures, since they are all hydrophilic, in contrast to their polymeric counterparts. In this presentation we describe the preparation and some interesting properties of TiO\(_2\) ceramic materials which can be easily dipcoat on porous supports to obtain POEMS. Monolithic chips of the ceramic material were obtained by the controlled drying of the precursor sol, followed by a heat treatment of the resulting xerogel at 300°C for 3h. Samples of this material were submitted to a further treatment with acidic solutions of different pH values in order to increase the number of surface acidic sites. The protonic conductivity was determined by impedance spectroscopy at temperatures ranging from 10 to 40°C and relative humidities (RH) ranging from 83 to 81%, and from these results the proton conduction were obtained. The conductivity of these ceramics increases from 0.0012 S/cm to 0.063 S/cm at 25°C and 81% RH after modification of the surface acidity by a treatment at a pH of 1.5 for 24h. Conversely, the activation energy for proton conduction decreases.
Partial vacancy in the oxide film leads to a shift of 1.6 eV. At higher temperatures, the activation energy increases for the transfer process. The activation energy shows a sharp increase at the onset of water clusters, and starts at approximately 65% RH.

**S7.16 Platinum-embedded PAN-based Carbon Nanofibers**

Lei Zhang¹, Bin Cheng² and Edward T Samulski¹,²; ¹Curriculum in Applied & Materials Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina; ²Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina.

Hexagonally-porous anodic aluminum oxide (AAO) templates are made by two-step anodization of highly pure aluminum foil. Close-packed PAN nanofibers containing a platinum compound were fabricated by polymerization of acrylonitrile in this AAO template. Under the same conditions, the conductivity of Pt on top of the titania and then heating the polymer at 100 and 200 degrees C. We find that 32 % of the volume of the film can be filled with polymer in just a few minutes at 200 degrees C. At lower temperatures, the infiltration process takes longer and the amount of polymer that can be incorporated is less. We hypothesize that the polymer coats the walls of the pores and that the coating is thicker when the polymer is incorporated at higher temperatures. Using absorption and photoluminescence spectroscopy we have determined that the polymer chains take on a coiled conformation in the pores and that there is little or no polymer crystallization. The photoluminescence measurements also show that the photoinjected electron transfer takes place from the polymer to the titania, but that not all of the excitons are quenched by electron transfer. Since the pores are less than 10 nm in diameter and excitons can diffuse over this distance before emitting a photon in a spin cast polymer film, we think that exciton diffusion is hindered inside the pores. We attribute this to the coiled polymer chain morphology.

Modifying the titania surface with an organic monolayer improves the morphology of the polymer, enabling more effective exciton diffusion and electron transfer to the titania. We will present the effect that these titania surface modifiers have on the performance of photovoltaic cells made with polymers in mesoporous titania.

9:00 AM S7.2 A Novel solar cell based on CdTe nanoparticle/MEH-PPV composites, Sandeep Kumar¹,², Gerald Anton Urban² and Thomas Nann¹,²; ¹Freeburg Materials Research Center, Freiburg, Germany; ²Institute for Mikrosystemtechnik, Freiburg, Germany.

Market expansion in the use of conventional inorganic solar cells remains limited due to high costs imposed by fabrication procedures involving elevated temperatures, high vacuum and numerous lithographic steps and discrete processing due to glass carriers. Organic solar cell components as conducting polymers can serve as a cost effective alternative to conventional inorganic solar cells because of the processing advantages of polymers. These polymers can be solution processed and their good mechanical properties and electrical conductivity allow the design to fit flexible shape and sizes. Solar cells based on CdSe nanoparticles and conducting polymers were realised and a maximum efficiency of 1.7% was obtained.[1-4]. The performance of such a solar cell can be improved further by extending partly the nanoparticle absorption in the IR region by using CdTe nanoparticles. The onset of absorption of CdSe in bulk is 720 nm whereas that of CdTe is 820 nm. The shift of 100 nm for CdTe can improve the absorption of sunlight by 20% relative to CdSe[5]. Furthermore the electron mobility of CdTe is higher compared to CdSe and hence can be looked at as a better material to be used in polymer solar cells. In this report we present for the first time a solar cell based on CdTe nanoparticle/ MEH-PPV composites. Being a new system a systematic approach was carried out from synthesising nanoparticles to building solar cells. CdTe nanoparticles were synthesised by a modified organometallic route[6]. Cyclic voltammetry measurements were carried to determine the HOMO and LUMO levels of the nanoparticles and MEH-PPV to see if they meet the proper energy level alignment for a possible charge transfer.

Evidence for charge transfer was further confirmed by PL quenching. Once the evidence for charge transfer was confirmed solar cells were built using spin coating on ITO substrate and an efficiency of 0.05% was obtained for first cells under AM 1.5 conditions. Reference [1]


0:15 AM S7.3 Photovoltaic Devices Fabricated from Charge Transporting Polymer Brushes, Henry James Saath¹,², Greg L Whiting¹, Wilhelm T S Huck² and Richard H Friend³; ¹Department of Physics, Cambridge University, Cambridge, Cambridge, United Kingdom; ²Department of Chemistry, Cambridge University, Cambridge, Cambridge, United Kingdom.

Photovoltaic diodes based on molecular semiconductor require a heterojunction between semiconductors with band-edge offsets sufficient to ionize photogenerated excitons. Efficient operation requires both a 'distributed' arrangement of heterojunction so that all absorbed light can produce ionised excitons, and charge transport pathways back to collection electrodes. We report the growth, characterisation and use of triarylamine side-chain acrylate polymer 'brushes' grown on an indium-tin oxide, ITO, coated glass substrate. Brush thicknesses of up to 35 nm can be obtained, and these support very high hole currents injected from the ITO (an order of magnitude larger than from spin-coated films of polymer of the same thickness). Absorption and interpenetration by CdSe nanocrystals and evaporation of CdTe onto CdSe provides diodes with efficient photovoltaic properties.

10:00 AM S7.4 Solution Processed Nanocrystal-Based Solar Cells, Dejin J Milliren, Ian Gur and A. Paul Alivisatos; University of California at Berkeley, Berkeley, California.

Hybrid semiconductor nanocrystal-polymer photovoltaic cells combine advantageous properties of inorganic semiconductors with the inexpensive solution processability of polymers. Inorganic nanocrystals provide tunable visible and near infrared absorption, and improve upon the poor electron mobility of most polymers. Results achieved by incorporating state-of-the-art nanocrystals into solar cells extend the efficiencies achievable in this type of cell.

10:15 AM S7.5 Extremely Thin Absorber Layers in Solid-State Solar Cells, Rolf Koenenkamp¹,², Abdelhak Belaidi² and Katja Ernst¹; ¹Hahn-Meitner Institut, Berlin, Germany; ²Hahn-Meitner Institut, Berlin, Germany.

We report on recent progress in fabricating an inorganic solid-state solar cell on a nano-structured substrate, the so-called eeta-cell. The cell uses HgCdTe as an absorber and porous TiO₂ as a substrate. By adjusting the Hg/Cd ratio, the conduction band edge can be brought into alignment with the band edge of TiO₂. This tuning provides an ideal tool to optimize the optical and electrical properties of the cell. At the same time it allows to study the electron transport and the energy levels at the TiO₂/absorber interface. In qualitative agreement with earlier work we find a band-offset of 0.25 eV to give maximum transfer rates across the interface. The optimized cell has a short-circuit current of 15 mA/cm² and an open-circuit voltage of 0.7 V. We will discuss the optical and electrical properties of the cell, and outline future work to further improve the performance.

10:30 AM S7.6 Synthesis of nanostructured MoS₂ / Ag₃S multilayered coatings by sol-gel for solar energy storage applications, Phani Ratna Ayyalasomayajula¹, Christan Hindering², Henry Hadfield³, Sandro Santucci⁴ and Maurizio Pascaletto⁵;
The optical and electrical properties of transition metal chalcogenides make these semiconductors promising candidates for efficient solar energy conversion. In recent years, considerable interest has been shown to synthesize thin semiconductor films of MoS₂, AgₓSᵧ by electrochemical and chemical deposition of colloidal semiconductors. By these methods, the properties of the polymer solar cell can be tailored. The films were deposited on glass, quartz substrates at room temperature. The deposited nanocrystalline films were subjected to annealing treatment from 100°C to 400°C and the effect of annealing on the electrical, optical and chemical properties has been studied in detail. X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements indicated that the deposited films are nanocrystalline with uniform and smooth coatings. High-resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM) techniques revealed the presence of monodispersed nanoparticles of MoS₂ (5-6nm) and AgₓSᵧ (5-8 nm) in the deposited films. UV-vis, Fourier transform infrared (FTIR) spectroscopies have been employed in order to study the optical absorption as well as band gap of the individual films and multilayered films and vibrational and stretching bands respectively. Film thickness and chemical composition was estimated by survey and depth profile X-ray photoelectron spectroscopy (XPS) respectively. Electrical resistivity of the films have been measured using four-probe sheet resistance technique. Thermoelectric measurements indicated that the deposited films were p-type in case of MoS₂ and n-type in case of AgₓSᵧ.

10:45 AM S7.7 Theoretical Investigations of Polymer Based Solar Cells, Davide Barreca1, Elza Bontempi2, Laura E. Depero2, Cinzia Marangon2 and Eugenio Tondello3; 1Department of Chemistry, ISTM-CNR and INSTM, Padova, Italy; 2Department of Mechanical Engineering, INFM and Structural Chemistry Laboratory - Brescia University, Brescia, Italy; 3Department of Chemistry, Padova University and INSTM, Padova, Italy.

We investigate the behavior of typical polymer-polymer and polymer-PCBM bulk heterojunction solar cells. We use a perspective model that self-consistently solves Poisson's equation and the charge continuity equation while incorporating temperature and electric field dependent mobility. We obtain good quantitative agreement with present experimental data for I-V curves and photocurrent action spectra. We also study the limiting conditions of polymer solar cell development by simulating an ideal solar cell using an AM1.5 global spectrum and assuming all absorbed photons hitting a typical polymer (band gap 1.9 eV) based solar cell at normal incidence contribute to current. If such a solar cell has 100 nm length, open circuit voltage=0.6 V and 50% fill factor, then the maximum theoretical power conversion efficiency is 6.63%. These results further highlight the need to develop smaller band gap materials and help explain why the best polymer based solar cells have power conversion efficiencies that remain stuck below about 4%. Our model is used to investigate the important increase in power conversion efficiencies we can expect as lower band gap polymers with similar mobility characteristics become available.

11:00 AM S7.8 Surface structure and composition of nanocrystalline SnO₂ thin films obtained by Chemical Vapor Deposition, Davide Barreca1, Elza Bontempi2, Laura E. Depero2, Cinzia Marangon2 and Eugenio Tondello3; 1Department of Chemistry, ISTM-CNR and INSTM, Padova, Italy; 2Department of Mechanical Engineering, INFM and Structural Chemistry Laboratory - Brescia University, Brescia, Italy; 3Department of Chemistry, Padova University and INSTM, Padova, Italy.

Tin dioxide (SnO₂), an n-type semiconductor with the rutile structure, has received a great attention as a functional for various applications, featuring transparent electrodes and conductors, solar cells, heterogeneous catalysis, gas sensors for oxidizable gases. The functional properties of these systems are strongly dependent on defects nature as well as on crystallite size, chemical composition and surface morphology. A thorough investigation of these properties is therefore needed in order to develop materials with tailored properties. Different techniques have been employed to obtain pure and doped SnO₂ thin films. These include spray pyrolysis, reactive and magnetron sputtering, electron beam evaporation, ion-assisted deposition and CVD. The Chemical Vapor Deposition (CVD) process is a valuable method since it allows a modulation of system properties by a suitable choice of the molecular precursor, together with an accurate control of the growth conditions, resulting in nanocrystalline films with tailored properties. The aim of this work is to study structure, composition and morphology of SnO₂ nanocrystalline thin films obtained by HW-CVD (Hot Wall-Chemical Vapor Deposition) using bis(diethylamino)dimethylstannane(IV) [(CH₃)₂Sn(N(C₂H₅)₂)] as precursor. In particular, the attention is focused on the structural analysis of the coatings, using the results obtained by X-ray reflectivity (XRR) to those obtained by Atomic Force Microscopy (AFM) analyses and relating them to the different synthetic conditions. Further important information on the microstructural features of the films was obtained by X-ray Diffraction (XRD) and Glancing Incidence X-ray Diffraction (GIXRD), while their chemical composition was elucidated by X-ray Photoelectron Spectroscopy (XPS). Results concerning the influencing factors on the present work, in order to have quantum confinement effect, the present experimental data for such a solar cell has 100 nm length, open circuit voltage=0.6 V and 50% fill factor, then the maximum theoretical power conversion efficiency is 5.63%.
advantages of composite technology are clear: very low processing temperature and possibility to control porosity of the layers. A composite cathode was prepared by combing the powder and metal-organic YSZ polymer. It was shown, that preparation temperature can be lowered to 400°C (decomposition temperature of the polymer used). Dense electrolyte prepared by this way had high ionic conductivity and it was possible to depo. it on porous substrates (anode and cathode) without cracks for the electrolyte thickness from 1 to 10 µm. Composite electrodes (anode and cathode) were also prepared using composite technology and tested. It was shown that Ni-YSZ/Nafion composite cathode exhibits high low potential and is stable at REDOX circles. SSC-YSZ and LSP-YSZ cathodes were also prepared using composite technology. Conductivity of these cathodes was high and the potential stability was shown. These composite cathodes can be used as an interlayer in cathode supported SOFCs and is effective. Multilayer SOFC systems were prepared using composite technology. It was shown that entire SOFC system can be made by composite technology starting from cathode, anode or electrolyte as a substrate.

2:15 PM **S8.3**
Interfacial Conductivity in hybrid polymers. Philippe Barboux, Lauriane Pautrot, David Carriere, Kisloud Lahihi and Jean-Pierre Boilot; Physique de la Matiere Condensee, CNRS UMR 7643, Ecole Polytechnique, PALAISEAU, France.

Dispersions of mineral particles are often used to increase the performance of ion conducting membranes (in lithium batteries as well as in proton-conducting fuel cells). To understand and optimize this effect, we have studied the role of the surface conduction by such colloidal materials. Firstly, we compared in situ TPD, ZrO2, TiO2 and Y2O3 dispersed in non-conductive and ion conducting polymers. Grattesting organic s or acids at the surface of mineral colloids also yields materials with better conducting properties, enhanced by the large density of surface sites. Thus, proton conducting materials can be prepared by the grafting of phosphonic acid or stronger acids such as sulfophenolphosphonic acid onto oxide nanoparticles. The mechanism and the density of grafting was studied by solid state MAS NMR and nitrogen adsorption isotherms. The grafting is coherent and quantitative with the number of surface sites whereas the high specific surface (> 400 m2/g) allows a high concentration of grafted groups. This leads to the formation of stable Metal-OH bonds with a surface acidity strongly enhanced by the presence of P-OH and sulfonic acid groups. The conductance mechanism is based on direct proton transfer between these strongly grafted species and results in a significant conductivity quite stable against the relative humidity. Apart from the higher loadings which can be achieved in the membranes, the nanometric size of the particles increases the proton conduction properties due to a better grain-to-grain transfer and a higher surface groups content. Further work has been devoted to study the interface between the polymer and the particles. The cooperative transfer between the weak acid sites of the mineral particles and the basic sites of the organic polymers allows the formation of a conductive pathway with increased performance.

3:15 PM **S8.4**

Nafion is a perfluorosulfonate ionomer commonly used in proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) technologies. Critical to the performance of Nafion are its high proton conductivity and its low methanol permeability. Recently, Nafion has been modified by the incorporation of inorganics by sol-gel processing, ostensibly to increase its thermal stability and reduce its methanol permeability. Nafion can be infiltrated, as well as dissolved in sol-gel formulations for recasting. Infiltration requires swelling of the membrane before the inorganic content can be introduced. Typically, the weight of the membrane is increased between 10 and 50%. Hygroscopic oxides infiltrated into Nafion include silica, phosphosilicates, zirconia-containing and titania-containing silicates. Infiltrated membranes have been treated after infiltration in phosphoric acid or stronger acids such as sulfophenolphosphonic acid onto oxide nanoparticles. The mechanism and the density of grafting was studied by solid state MAS NMR and nitrogen adsorption isotherms. The bonding level of STA on the silane-modified SiO2 was strongly affected by the presence of STA on the sols gels was "free," i.e., only weakly adsorbed, and could be easily washed off. High bonding levels (>95%) of STA were obtained when epoxy-type functional silanes were used above a certain concentration ratio. Ion exchange capacity (IEC) of the water-washed, SiO2-based STA and SFA proton-carrier composite powders is in the range of 1.8 to 3.5 mmol/g, two to three times higher than that for Nafion 117 (0.9 meq/mol). Among several polymer hosts studied, a glycidyl methacrylate copolymer (PEMAGMA), which is stable up to 225°C from thermogravimetric analysis (TGA), was found to produce mechanically robust and freely hybrid membranes. The PEMAGMA matrix cross-linked to a Teflon Felt under the present formulation after baking at 80°C for 40 min. The cured hybrid membranes effectively retained the "free" STA with only a small weight percentage loss even when extracted in an 85°C water bath, and showed a 10 wt% water loss at 150°C and a 15 wt% loss at 225°C, following the weight loss trends of STA and the SiO2-based sol gel composite in TGA. Fuel cell performance tests of the preliminary films gave a Voc in the 0.8 to 0.9 V range, but with low current density. The resistive characteristics were attributed to the inhomogeneous distribution of the sol gel matrix in the PEMAGMA matrix. The NREL has tested this film on a fuel cell, with an overall efficiency of 50%.

4:15 PM **S8.7**
High Performance Fuel Cell Electrodes using Solid-phase Synthesized Carbon Nanostructured Materials. Taeghwan Hyeon*, Sangjin Han1, Youngkwang Yun2, Byungchul Jang1, Young Eun Sung1 and Kyung-Won Park1; 1School of Chemical Engineering, Seoul National University, Seoul, South Korea; 2Department of Materials Science & Engineering and Research Center for Energy Conversion and Storage, Kwangju Institute of Science & Technology, Kwangju, South Korea.

Environmental problems lead to the need for new technologies in the fields of energy production and storage for sustainable development, to reduce the pollutant emissions from fossil fuel combustion. Fuel cells are very promising as electrochemical power sources either for application in portable technology and in electric vehicles (polymeric fuel cells, PEFCs), or for the stationary energy production (solid oxide fuel cells, SOFCs). The use of nanosized materials offers great promise for the development of improved materials for fuel cells. For PEFCs, improved performance has been observed when nanocrystalline oxides were added to polymer electrolyte membranes. The high specific surface area of nanocrystalline ceramics oxides to NaF membranes showed improved water retention characteristics, due to their operation in a direct methanol fuel cell at higher temperatures. Introducing 10 wt% of titanias into NaF membranes improved their use up to 145°C when introduced in membrane-electrode assemblies (MEA) and fed with methanol, with a remarkable power density of 330 mW/cm². The trend in the present research on SOFCs is the reduction of their operating temperature. If SOFCs can operate at a temperature of 600°C, the use of stable nanocrystalline or mesoporous oxides can be foreseen as electrode (both anode and cathode) materials to improve the triple phase boundary, thus decreasing the ohmic drops at the electrode/electrolyte interfaces.

3:30 PM **S8.5**
Nanoized and Mesostructured Oxides for Fuel Cells. Enrico Fragneto, Chemical Sciences and Technology, University of Rome Tor Vergata, Roma, Italy.

Hybrid proton-carrier polymer composite materials were fabricated in an effort to develop high-performance high-temperature proton exchange membranes (PEMs) for fuel cell applications in the 1000 to 1500°C range. The hybrid membranes comprise a polymer host and a SiO2-based proton-carrier composite that was synthesized via sol gel approach using a functional silane and tetraethylorthosilicate (TEOS) in acidic conditions. The membranes were prepared by a simple solution cast and dried by thermal press curing (cross-linking) to enhance the membranes’ thermal stability and mechanical strength. The primary proton-carrying compound was either a Keggin-structured heteropoly sulfonic acid (STA) or a sulfonic acid (SFA) that was thermooxidatively converted from a mercapto (-SH) group. The “bonding” level on the silane-modified SiO2 sol gel composites was strongly affected by the presence of the functional group of the silane. In the absence of a functional silane, most of STA on the sols gels was “free,” i.e., only weakly adsorbed, and could be easily washed off. High bonding levels (>95%) of STA were obtained when epoxy-type functional silanes were used above a certain concentration ratio. Ion exchange capacity (IEC) of the water-washed, SiO2-based STA and SFA proton-carrier composite powders is in the range of 1.8 to 3.5 mmol/g, two to three times higher than that for Nafion 117 (0.9 meq/mol). Among several polymer hosts studied, a glycidyl methacrylate copolymer (PEMAGMA), which is stable up to 225°C from thermogravimetric analysis (TGA), was found to produce mechanically robust and freely hybrid membranes. The PEMAGMA matrix is cross-linked to a Teflon Felt under the present formulation after baking at 80°C for 40 min. The cured hybrid membranes effectively retained the “free” STA with only a small weight percentage loss even when extracted in an 85°C water bath, and showed a 10 wt% water loss at 150°C and a 15 wt% loss at 225°C, following the weight loss trends of STA and the SiO2-based sol gel composite in TGA. Fuel cell performance tests of the preliminary films gave a Voc in the 0.8 to 0.9 V range, but with low current density. The resistive characteristics were attributed to the inhomogeneous distribution of the sol gel matrix in the PEMAGMA matrix. The NREL has tested this film on a fuel cell, with an overall efficiency of 50%.

4:00 PM **S8.6**
Hybrid Proton-Carrier Polymer Composites for High-Temperature FCPEM Applications. John Pernt1, John Turner2 and Andy Herring2; 1National Renewable Energy Laboratory, Golden, Colorado; 2Chemical Engineering, Colorado School of Mines, Golden, Colorado.
We report on the synthesis of new carbon nanostructured materials including hollow carbon nanoparticles (carbon onions) and carbon nanocoils and their successful applications to fuel cell electrodes. These carbon nanostructured materials were synthesized from the catalytic graphitization of polymeric carbon precursors. These carbon materials possess high surface areas exceeding 300 m²/g and exhibit good graphitic crystallinity. The synthetic procedure is very simple and can be readily applied to the large-scale and economic production of the carbon nanostructured materials. These carbon nanostructured materials were successfully applied as electrode materials for direct methanol fuel cells. The electrochemical properties of the carbon nanocoils were compared with those of Vulcan XC-72 carbon and commercial catalysts. The carbon nanostructured materials outperform all the carbon materials tested. For example, the specific oxidation currents of the carbon nanocoils and Vulcan-XC72 at 0.4 V are 80 and 21 A/g, respectively. The synthesis, characterization, and fuel cell performances of these new nanostructured carbon materials will be discussed in the presentation (Some of the results were published in Angew. Chem. Inter. Ed. 2003, 42, 4352; Adv. Mater. 2003, in press; J. Phys. Chern. B, 2004, in press.)

4:30 PM S8.8
Assemblies of Semiconductor and Metal Nanoparticles for Renewable Energy. Mariezabel Markarian, Maysa Harake, Dima Najjar and Lara J. Halou; Chemistry, American University of Beirut, Beirut, Lebanon.

Studies of the photoelectrochemical and electrochemical behavior of multilayers of polyacrylate-capped Q-CdS (d = 3.6 nm) and polyacrylate-capped Pt nanoparticles (d = 2.5 nm) self-assembled layer-by-layer in poly(diallyldimethylammonium chloride) on electrode surfaces will be presented. Photoelectrochemical and electrochemical measurements at nanoparticles/PDDA films revealed the feasibility of charge transport in the films, likely by means of charge hopping between the nanoparticles through the embedding matrix. The photoelectrochemistry of the quantum-dot films was investigated as a function of solution redox couples, solution pH, the nanoparticle layer density, and the number of nanoparticle/polyelectrolyte multilayers. Photoelectrochemical measurements revealed the feasibility of generating anodic and cathodic photocurrents at the QD films depending on the solution energetics and the electrode potential, in a departure from the behavior of the bulk solid; this is attributed to quantum confinement effects at this size scale. The potential at which the photocurrent reversed in direction from anodic to cathodic shifted with pH (by - 66 mV per pH unit) similar to the shift in Vfb of the bulk solid; attributed in part to an increase in the reducing power of the QD electron with increasing pH, as indicated from photocurrent-voltage plots acquired in the presence of methyl viologen. Hydrogen evolution at heterostructures of Pt nanoparticles in polyelectrolyte was also studied. Electrochemical measurements at polyacrylate-capped Pt nanoparticles/polyelectrolyte films showed the hydrogen adsorption behavior characteristic of the catalytic Pt surface. Dependence on the nanoparticle size and surface modification will be addressed. The possibility of photocatalyzed hydrogen fuel generation at heterostructured films containing a photocatalyst and a metal co-catalyst nanoparticles separately assembled in polyelectrolyte layers will be presented.

4:45 PM S8.9
Nano electrocatalyst for PEFC; Pt-coordinated heteropolyacid clusters. !taru Honma and Hitoshi Nakajima; EEI, AIST, Tsukuba, Ibaraki, Japan.

Polymer electrolyte fuel cells have attracted much attention recently as an alternative energy devices with much higher energy efficiencies. However, Pt electrode are very expensive and other non precious electrode materials have been explored to reduce the cost of the fuel cells and more function such as CO tolerance has been required for practical application of the cell to the mobiles as well as on site power generation employing fossil fuels. In this presentation, new electrocatalyst has been investigated based on the heteropolyacid clusters (HPA). The HPA has been known as a oxidative catalysts, however, its application to electrode materials for PEFC has not been studied so far. Here, we disclose that these HPA clusters can exhibit good electrocatalytic properties for methanol oxidation although the materials are metal oxide nano-clusters. Several kind of the Pt-coordinated heteropolyacid of the composition (H4PtPW11O40/H2O, or H4PtPMo11O40/H2O) have been synthesized by liquid precipitation process and the these nano clusters exhibit methanol oxidation properties in the same order of that of Pt materials and proved to be new family of electrocatalysts.