

# SYMPOSIUM V

## Materials for Energy Storage, Generation, and Transport

April 2 – 4, 2002

### Chairs

**Gerbrand Ceder**

Dept of MS&E

MIT

Rm 13-5056

Cambridge, MA 02139

617-253-1581

**Steven A. Ringel**

Dept of Electrical Engr

Ohio State Univ

Columbus, OH 43210

614-292-6904

**Ricardo B. Schwarz**

Structure/Properties Relations Group

Los Alamos National Laboratory

MST-8 MS G755

Los Alamos, NM 87545

505-667-8454

---

### Symposium Support

Los Alamos National Laboratory

Proceedings to be published in both book form and online

(see *ONLINE PUBLICATIONS* at [www.mrs.org](http://www.mrs.org))

as Volume 730

of the Materials Research Society

Symposium Proceedings Series

\* Invited paper

## SESSION V1: LITHIUM BATTERIES

Chairs: G. Ceder and G.A. Nazri

Tuesday Morning, April 2, 2002

Golden Gate A3 (Marriott)

### 8:00 AM \*V1.1

THIN FILM MATERIALS AND DESIGNS FOR RECHARGEABLE BATTERIES. Nancy Dudney, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; Young-Il Jang, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Rechargeable batteries fabricated of thin film materials offer some exceptional performance characteristics. These will be discussed and illustrated by examples from work done at ORNL on thin film rechargeable lithium batteries. Assembled by successive deposition of 0.1 to 4  $\mu\text{m}$ -thick films, the battery structure creates a large active interface area enhancing both the power density and the efficient use of the battery materials. The need for inactive materials such as binders and separators as well as second phases to augment the electron transport are eliminated because each layer is thin and dense. These savings may be more than offset, however, by the mass and volume of a substrate that serves no dual purpose. Power densities of the thin film battery approach 8 kW/kg, if the substrate can be excluded. Synthesis of the active battery materials by vapor deposition techniques also produces materials with compositions and microstructures not readily achieved by bulk processing methods. An amorphous inorganic electrolyte offers wide electrochemical stability and very small leakage current to provide for robust performance over a long lifetime and wide temperature range. Electrode materials with submicron and nanocrystalline grains are exceptionally tolerant of deep cycling and the associated volume changes and phase transitions. A high cost of fabrication is the principal disadvantage of these batteries and materials. Thin film batteries are expected to find uses in niche markets for small devices requiring either ultra-thin power sources or very long unattended battery life. The application of thin film materials either as an individual component or as a thin film cell in larger scale power sources may await development of more rapid and economical deposition processes, lower processing temperatures, and the use of low cost and light weight substrates. Ultimately, the full potential of the thin film batteries lies in their direct integration with devices or complementary power sources.

### 8:30 AM V1.2

MOLECULAR SIMULATIONS OF THE CATHODE/ELECTROLYTE INTERFACE IN A LITHIUM CONDUCTING OXIDE THIN FILM BATTERY. Stephen H. Garofalini, Weiqun Li, Dept of Ceramic and Materials Engineering, Rutgers University Piscataway, NJ.

Molecular dynamics (MD) computer simulations using a charge transfer model have been used to study the interface formed between oxide electrolyte glasses and  $\text{V}_2\text{O}_5$  cathode. The simulations reproduce the experimental crystal structures, vibrational frequency, and the appropriate phase transformation of  $\text{V}_2\text{O}_5$  as Li ions enter the crystal. The simulations have also shown that Li transport into the crystal is affected by the orientation of the crystal at the interface as well as by surface roughness. Each of these could potentially create electrochemically inactive regions. In addition, the simulations showed local structural changes around the V ions in the  $\text{V}_2\text{O}_5$  crystal that create trapping sites for Li ions in the crystal by significantly altering diffusive behavior. Activation energies for Li migration in different directions in the crystal and in the glassy phase will be presented.

### 8:45 AM V1.3

ELECTRONIC STRUCTURE OF LITHIUM INTERCALATED METAL OXIDES. J. Graetz, R. Yazami, P. Rez\*, C.C. Ahn, B. Fultz, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA. \*Department of Physics and Astronomy and CSSS, Arizona State University, Tempe, AZ.

Lithium transition-metal oxides ( $\text{LiTMO}_2$ ) are currently the preferred cathode in secondary Li ion batteries. Several of these materials have a layered structure suitable for intercalation compounds owing to their good kinetics and ability to withstand internal strains of Li intercalation. Despite extensive research on this system, it is still not understood how the electronic charge is redistributed during lithiation. Traditionally it has been accepted that the charge on the intercalated Li is accommodated by the transition-metal, allowing the O valence to remain 2-. However, recent computational studies suggest that there is substantial charge transfer from the ionic Li to the anion [1]. We report an electronic structure analysis in samples of chemically delithiated  $\text{Li}_{1-x}\text{CoO}_2$  ( $x = -0.02, 0.09, 0.12, 0.20, 0.28$ ) and  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  ( $x = 0, 0.25, 0.37, 0.54, 0.64$ ). Measurements of the electronic structure were performed using electron energy loss spectrometry (EELS) in conjunction with a conventional transmission electron microscope (TEM). The O  $K$ , Co  $L_{2,3}$ , and Ni  $L_{2,3}$ -edges

were used to probe the density of unoccupied states about each ion. Only small changes in the net electron density at the transition metal atoms were found. Conversely, the O  $K$ -edge shows an increase in the integrated intensity of the near-edge structure, which scales linearly with Li extraction. This suggests that the Li  $2s$  electron occupies O  $2p$  holes during intercalation. Ab-initio electronic structure calculations of the O  $2p$  partial densities of state curves were also performed and are in agreement with the experimental results. It is our contention that the O ions accommodate the majority of the charge on the intercalated Li.

[1] M. Aydinol, *et al.*, J. Phys. Rev. B, **56**, 1354 (1997).

### 9:00 AM V1.4

PROBING LITHIUM ORDERING PHENOMENA IN  $\text{O}_3$  LAYERED  $\text{Li}_{0.5}\text{CoO}_2$  PHASE: AN ELECTRON DIFFRACTION STUDY. Yang Shao-Horn, Stéphane Levasseur and Claude Delmas, Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS) and ENSCPB, Pessac, FRANCE.

$\text{LiCoO}_2$ , the most commonly used positive electrode material, experiences several structural transitions during lithium de-intercalation. In particular, a rhombohedral to monoclinic phase transition occurs near  $x=0.5$  in  $\text{Li}_x\text{CoO}_2$ , which is attributed to the ordering of lithium ions and vacancies. However, to our knowledge, there is no experimental evidence to support this hypothesis. In addition, many questions remain unanswered: 1. Does the monoclinic distortion necessarily concur with the ordering of lithium ions? 2. How does the monoclinic transition in  $\text{Li}_x\text{CoO}_2$  occur on the microscopic scale? In this study, we undertook electron diffraction studies of a  $\text{Li}_{0.5}\text{CoO}_2$  compound at  $-170^\circ\text{C}$  and simulation of various superstructures to reveal if lithium ions and vacancies order at the  $\text{Li}_{0.5}\text{CoO}_2$  composition. X-ray powder diffraction refinements showed that this compound was a single-phase having the monoclinic symmetry. We simulated step by step the changes in the X-ray diffraction pattern as a result of the structural changes associated with the rhombohedral-monoclinic transition. It was found that the peak splitting in the X-ray powder diffraction patterns was the most sensitive to the distortion of oxygen lattice. The monoclinic distortion did not necessarily concur with the ordering of lithium ions and vacancies. We adopted S.G.  $P2_1/m$  to describe the most probable lithium and vacancy ordering configuration. Simulated single-crystal electron diffraction patterns showed that the intensities of new reflections related to lithium ordering were significantly stronger than those of X-ray and they might allow experimental detection. We examined the electron diffraction patterns collected from  $\text{Li}_{0.5}\text{CoO}_2$ , and the superlattice reflections were present and were consistent with the structural model proposed for lithium ordering. Therefore, for the first time, we provided experimental evidence to support the concept of lithium and vacancy ordering in  $\text{Li}_x\text{CoO}_2$ . In-situ studies upon cooling of  $\text{Li}_{0.5}\text{CoO}_2$  are underway to understand how this transition proceeds on the microscopic scale.

### 9:15 AM V1.5

BEHAVIOR OF  $\text{LiMn}_2\text{O}_4$  SINGLE CRYSTALS AS BATTERY CATHODES. María Angeles Monge, José Manuel Amarilla, Enrique Gutiérrez-Puebla, Isidoro Rasines, Consejo Superior de Investigaciones Científicas, Instituto de Ciencia de Materiales, Cantoblanco, Madrid, SPAIN; Juan Antonio Campa, Universidad Complutense, Facultad de Ciencias Geológicas, Madrid, SPAIN.

The increasing production of portable electronics like cellular telephones, laptop computers and video cameras, and the needs of better lightweight batteries for energy-storage, emission-free vehicles and spacecrafts, are driving an organized effort for developing more efficient rechargeable batteries and especially lithium-ion batteries.  $\text{LiMn}_2\text{O}_4$  is now one of the most promising materials to replace more expensive and less biocompatible  $\text{LiCoO}_2$  in commercial lithium-ion batteries, but all the work on its electrochemical behavior has been performed until recently on powdered samples. A large number of articles has concluded that single crystal studies are quite necessary to precisely define the kind of defects present as well as their behavior while the material works as electrode. This is the end at which this communication aims. We shall describe how to grow  $\text{LiMn}_2\text{O}_4$  crystals sized up to 1 mm using an electrocrystallization technique; the electrochemical response of these crystals in lithium cells; and a method to follow their structural and morphological changes while working as electrodes in the charge-discharge process of the battery. Two of these crystals were as grown and the other five were prepared at select steps of the electrochemical cycling, two after first charge at 4.4 and 4.9 V, two after first discharge at 3.3 V, and the last one after ten cycles between 3.0 and 4.9 V finishing in charge. The defects present in these crystals are determined by thorough single-crystal X-ray diffraction analysis after refining the occupation at every site of the spinel structure. This analysis allows to establishing two possible paths for the process of lithium insertion-deinsertion. It will be shown how the crystals studied follow one of these paths during cycling of the

battery by virtue of a dynamic mechanism consisting in manganese migrations cooperatively induced by lithium insertion and extraction.

#### 10:00 AM V1.6

TEM STUDY OF LATTICE DEFECTS IN LiCoO<sub>2</sub>. Heike Gabrisch, Rachid Yazami, Brent Fultz, California Institute of Technology, Materials Science, Pasadena, CA.

LiCoO<sub>2</sub> is the material in most widespread use for positive electrodes ("cathodes") in rechargeable Li ion batteries. The structure of the material is layered (R3m) with Li ions in the Van der Waals gaps between slabs of oxygen-cobalt-oxygen planes. During charge and discharge cycles lithium ions are extracted from and re-intercalated into the LiCoO<sub>2</sub> lattice - a process during which non-stoichiometric Li<sub>(1-x)</sub>CoO<sub>2</sub> compounds are formed. The stability of the crystal structure with variation in Li content (1-x) limits the specific capacity of the electrode. It has been shown by X-ray diffractometry that the lattice is preserved when the lithium content is cycled between x = 0 and x ~ 0.5. Here we report results from a transmission electron microscopy (TEM) analysis of the dislocation structure in LiCoO<sub>2</sub>. The study of dislocations in this material is of interest because dislocations may provide an energetically favored diffusion path for the transport of Li ions between the electrolyte/electrode interface and their lattice site in the crystal structure. Dislocations are also potential initiation sites for mechanical degradation of the material during charge/discharge cycling. First results found in uncycled material have shown that perfect dislocations of a/3 <1120> type Burgers vector of mostly screw character are lying in the {0001} basal planes. Some of these perfect dislocations dissociate into Shockley Partial dislocations with a/3 <1010> type Burgersvectors. The stacking fault energy appears to be low. Here we compare the dislocation structure in virgin LiCoO<sub>2</sub> to that found in LiCoO<sub>2</sub> after cycling.

#### 10:15 AM V1.7

STRUCTURAL TRANSITIONS IN STOICHIOMETRIC LiMn<sub>2</sub>O<sub>4</sub> AND LITHIUM-RICH, OXYGEN-DEFICIENT Li<sub>1.05</sub>Mn<sub>1.95</sub>O<sub>4-d</sub> NEAR AMBIENT TEMPERATURE. Yang Shao-Horn, ICMCB-CNRS, ENSCPB, Pessace, FRANCE.

A first-order transition was observed upon cooling of stoichiometric LiMn<sub>2</sub>O<sub>4</sub> and lithium-rich, oxygen deficient spinels below ambient temperature. Discrepancy exists in the structural details and the transition mechanism of the low-temperature material, particularly if it is a single, orthorhombic phase or a mixture of a cubic and a tetragonal phases. In order to provide insights to the transition mechanism, we compared the changes in the crystal structure and physical properties of a stoichiometric LiMn<sub>2</sub>O<sub>4</sub> and a lithium-rich, oxygen deficient Li<sub>1.05</sub>Mn<sub>1.95</sub>O<sub>4-d</sub> compounds upon phase transitions near ambient temperature. Thermal, electrical conductivity and magnetic measurements clearly showed that a stoichiometric LiMn<sub>2</sub>O<sub>4</sub> sample exhibited the characteristic, first-order transition at 295K. X-ray powder diffraction analyses showed that the low temperature form of LiMn<sub>2</sub>O<sub>4</sub> could be refined as either a single-phase orthorhombic or a mixture of a cubic and a tetragonal phases. In-situ electron diffraction studies of LiMn<sub>2</sub>O<sub>4</sub> crystals upon down to 100K revealed that the cubic phase transformed to a superstructure with unit cell dimension close to 3ax3axa at intermediate temperatures, and eventually decomposed to two structurally similar phases upon further cooling. The observation was significant as it provided explanations to the discrepancies in previous studies and also insights in the transition mechanism. Thermal measurements of the Li<sub>1.05</sub>Mn<sub>1.95</sub>O<sub>4-d</sub> sample showed a similar first-order transition at 280K to LiMn<sub>2</sub>O<sub>4</sub>. Electron diffraction studies and measurements of physical properties of this compound are underway at this time.

#### 10:30 AM V1.8

LiMBO<sub>3</sub> (M=Fe,Mn): POTENTIAL CATHODE FOR LITHIUM ION BATTERIES. Jan L. Allen, Kang Xu, Sam S. Zhang, Michael S. Ding, T. Richard Jow, US Army Research Laboratory, Sensors and Electron Devices Directorate, Adelphi, MD.

There is a continuing interest in novel high capacity, inexpensive, environmentally benign cathode materials. LiCoO<sub>2</sub> while suitable for small applications is too expensive for use in electric vehicles and is not environmentally benign. LiNiO<sub>2</sub> and LiNi<sub>1-x</sub>CoO<sub>2</sub> have potential safety issues and LiMn<sub>2</sub>O<sub>4</sub> is beset by stability problems especially at higher temperatures. Polyanion structures have attracted much recent interest despite their low electronic conductivity. The highly-covalent polyanion raises the redox couple of the transition metal through an inductive effect [1]. This is especially noticeable for the Fe<sup>2+</sup>/Fe<sup>3+</sup> couple. Whereas the potential of Fe<sup>2+</sup>/Fe<sup>3+</sup> lies impractically low at ~1V in the oxide [2], the potential in LiFePO<sub>4</sub> lies around 3.4 V. The low electronic conductivity leads to high polarization and low capacity at reasonable rates. This problem has recently been improved by carbon coating [3], particle size control by lowered sintering temperature [4] and via preparation of LiFePO<sub>4</sub> nanocomposite

electrodes [5]. Recently synthesized borates[6], LiMBO<sub>3</sub> (M=Fe,Mn) share similarities with LiFePO<sub>4</sub>. They are polyanion structures, contain extractable lithium and suffer from low electronic conductivity. This study brings to bear techniques to improve electrode conductivity to produce LiMBO<sub>3</sub> composite electrodes thus allowing access to some of the high, theoretical specific capacity (220-222 mAh/g).

References:

- [1]. A. Maniheram, J.B. Goodenough, J. Solid State Chem. 71, 349 (1987).
- [2]. L.A. Picciotto and M. Thackeray, Mat. Res. Bull, 21, 583 (1986).
- [3]. N. Ravet, S. Besner, M. Simoneau, A. Vallee, M. Armand, Hydro-Quebec, Can. Pat. 2,270,771.
- [4]. A. Yamada, S.C. Chung, and K. Hinokuma, J. Electrochem. Soc. 148(3) A224-A229 (2001).
- [5]. H. Huang, S.-C. Yin, and L.F. Nazar, Electrochem. Solid-State Letters, 4 (10) A170-A172 (2001).
- [6]. V. Leganeur, Y. An, A. Mosbah, R. Portal, A. Le Gal La Salle, A. Verbaere, D. Guyomard, Y. Piffard, Solid State Ionics 139, 37-46 (2001).

#### 10:45 AM V1.9

ENERGY STORAGE MATERIALS BASED ON IRON PHOSPHATE. Pier Paolo Prosini, Marida Lisi, Silvera Scaccia, Maria Carewka, Stefano Passerini, ENEA C.R. Casaccia, Roma, ITALY; Luciano Cianchi, CNR, Firenze, ITALY; Mauro Pasquali, Universite di Roma La Sapienza, Roma, ITALY.

Introduction. Among the selection criteria for new compounds to be used as electrodes in electrochemical energy storage devices, particular emphasis should be given to the environmental compatibility of the elements and on the simplicity of the processing techniques which need to transform the raw materials into compounds suitable for use as electrodes in battery. From many different aspects (including practical consideration such as low toxicity and low cost) iron is a very attractive metal to be used in the field of lithium battery. The results concerning the preparation and characterization of several iron phosphates and their behavior upon lithium ion insertion will be discussed. Experimental. Iron(II)phosphate was obtained by spontaneous precipitation from iron and phosphate aqueous solutions under supersaturation conditions and ambient temperature. The compound was dried in air at 100°C. During this treatment, the iron was oxidized, forming iron(III)phosphate. This compound also contained iron(III)oxide as a by-product. Pure amorphous iron(III)phosphate was obtained by spontaneous precipitation from iron and phosphate aqueous solutions, using hydrogen peroxide as oxidizing agent. Amorphous LiFePO<sub>4</sub> was obtained by chemical lithiation of amorphous FePO<sub>4</sub> by using LiI as reducing agent. Crystalline nanosized LiFePO<sub>4</sub> was obtained by heating the amorphous compound at 550°C for 1h under reducing atmosphere (Ar/H<sub>2</sub>). Results. The electrochemical test showed that iron phosphates are able to intercalate lithium reversibly. The excellent performance of the materials in terms of practical capacity and long cycle life was related to their the unique microstructure. The small particle sizes achieved by the solution based synthesis allowed the materials to insert/release lithium with short diffusion length and minimal displacement adjustment. The environmental compatibility of the materials and the simplicity of the processing techniques, together with the good electrochemical properties, make iron-based phosphates ideal candidates for use as a cathode in the realization of large-size lithium batteries.

#### 11:00 AM V1.10

EXPLANATION OF THE SLOW CRYSTALLIZATION KINETICS AND HIGH IONIC CONDUCTIVITY OF PEO-LiTFSI AND -LiBETI POLYMER ELECTROLYTES. Wesley A. Henderson, William H. Smyrl, Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN.

The search for highly conductive solvent-free polymer electrolytes for solid-state lithium battery applications has lead in recent years to a new class of highly dissociated anions based upon the imide motif. Simple mixtures of poly(ethylene oxide) (PEO) and lithium salts with N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup> (LiTFSI) and N(SO<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup> (LiBETI) anions result in membranes with ionic conductivities approaching or exceeding 10<sup>-4</sup> S cm<sup>-1</sup> near ambient temperature. These are amongst the highest conductivities reported to date for solvent-free lithium polymer electrolytes. This is due in part to the extremely slow crystallization kinetics found for certain salt concentrations in PEO mixtures. The cause of the slow kinetics is not well understood, but has been attributed to the highly delocalized nature of the charge on the anions, their internal flexibility, and their large size which creates a "plasticizing" effect. A better understanding of the properties of these electrolytes may be obtained through a knowledge of the solvate coordination within these mixtures, but the structure of amorphous phases is a difficult topic to address. Typically comparisons are made with known structures of crystalline phases. Using this approach, we

have extensively studied the phase behavior of LiBETI with glymes of various lengths. Phase diagrams, crystallization kinetics, and crystal structures of the solvates which form provide a wealth of information regarding the solvation of the cations. In particular, an explanation for the slow crystallization kinetics emerges based upon slow nucleation due to competing amorphous solvate structures. Furthermore, a detailed study of the ambient temperature conductivity of such electrolytes as they slowly crystallize from the melt has been undertaken. Comparisons are made with other lithium salts. This allows one to separate and clarify the influence of salt concentration, anion effects, and crystallization of different phases upon the ionic conductivity.

#### 11:15 AM V1.11

##### PREPARATION AND CHARACTERIZATION OF METAL/CARBON COMPOSITES FOR LITHIUM-ION CELLS.

Ronald A. Guidotti<sup>1</sup>, David J. Irvin<sup>2</sup>, William R. Even, Jr.<sup>2</sup>, and Karl Gross<sup>2</sup>. <sup>1</sup>Albuquerque, NM. <sup>2</sup>Livermore, CA.

There has been increasing interest in recent years in the development of improved materials for use as anodes in lithium-ion cells. Both synthetic and natural graphites as well as disordered carbons have been studied for this purpose. Graphite has a maximum theoretical capacity of 372 mAh/g of carbon, but the disordered carbons can have values two or more times that. Unfortunately, the disordered carbons also exhibit high irreversible, first-cycle losses. A number of transition metals and transition-metal alloys have potential capacities much greater than that of graphite. Sn, for example, can intercalate up to 994 mAh/g to a composition of Li<sub>4.4</sub>Sn. However, such materials show rapid fade with cycling due to attrition of the alloy caused by large volume changes. One way of mitigating this problem is to use the metal on a support or substrate. Coating of the carbons with metals that do not alloy with or intercalate Li (e.g., Cu or Ni) has also been found to improve the performance for certain carbon materials. However, by combining Sn or Sn alloys with graphite, it may be possible to realize the capacities of both materials when used as lithium-ion anodes. In this work, we report on the preparation and characterization of metal/carbon composites made with platelet, spheroidal, and disordered carbon. Elemental Ni and Sn at various levels were deposited on the surfaces of the carbons by chemical reduction in both nonaqueous and aqueous solutions. In some cases, the metal salts were incorporated into the carbon precursors prior to pyrolysis. The metal-carbon composites were tested over a range of current densities as lithium-ion anodes in three-electrode cells using 1M LiPF<sub>6</sub> in ethylene carbonate-dimethyl carbonate electrolyte (1:1 v/v) with Li counter and reference electrodes. The results of those tests will be presented in this paper.

#### 11:30 AM V1.12

SYNTHESIS AND PROCESSING OF HIGH CAPACITY, HIGH CYCLE LIFE AND HIGH DISCHARGE RATE DEFECTIVE MAGNETOSPINEL FILMS FOR RECHARGEABLE BATTERY APPLICATIONS. Deepika Singh, H. Hofmann, Dept of Materials, EPFL Lausanne, SWITZERLAND; Rajiv Singh, W. Kim, V. Craciun, Dept. of Materials, University of Florida, Gainesville, FL.

Lithium manganese oxides spinels have been extensively studied in the last decade as cathode materials for battery applications. However these materials show low capacity, low discharge rates and short cycle life, which limits their use in commercial applications. In this talk, we will demonstrate that by formation of defective magnetospinels oxygen rich phase, we can significantly enhance the capacity, cycle-life and high discharge rate capability about conventional lithium manganese oxide spinels. Thin film of Li-Mn-O we synthesized using the ultraviolet assisted pulsed laser deposition process. This led to increased oxygen incorporation in the film even though the Li/Mn ratio was maintained at 0.5. The films were characterized by various electrochemical techniques to determine the redox behavior, charge capacity and cycle life. Unlike LiMn<sub>2</sub>O<sub>4</sub> film, the defective spinel exhibited a much higher capacity at 3V region compared to the 4V regions. A capacity loss of less than 5% was obtained after cycling for over 1500 cycles in the 4.5 to 2.5 V region. The correlation of the microstructure with the electrochemical properties will be detailed in this talk.

#### SESSION V2: HYDROGEN FUEL CELLS AND HYDROGEN STORAGE

Chairs: Ricardo Schwarz and Tom Zawodzinski  
Tuesday Afternoon, April 2, 2002  
Golden Gate A3 (Marriott)

#### 1:30 PM \*V2.1

##### MATERIALS ASPECTS OF FUEL CELLS FOR

TRANSPORTATION. G. Abbas Nazri, General Motors Research & Development and Planning Center, Warren, MI.

Current fuel cell technology may satisfy the requirements for stationary use, however, its application for transportation requires breakthroughs in various components of the fuel cell system. These breakthroughs are mostly related to the material aspects of this technology. The areas of importance are hydrogen storage materials (for hydrogen-oxygen fuel cell), catalysts (noble and non-noble metal systems), bi-polar plates, and moderate to high-temperature proton exchange membrane. There are engineering and packaging issues as well.

The most urgent need for a practical fuel cell, particularly for transportation, is the issue of hydrogen storage. Despite tremendous activities in the field, no new concept has been introduced during the last decade, and still the only promising candidates are the catalyzed alloys, carbonaceous materials (including fullerene derivatives, polyaromatics and nanotubes), and the complex chemical hydrides. This is an area that material scientist, solid state chemists and physicist can have the greatest impact. This presentation will provide an overview of science and technology of hydrogen storage materials. The next challenging area for ambient temperature fuel cell is the optimization of catalytic activity and stability of non-noble metal catalysts such as oxides, nitrides, carbides, and carbonitrides, as well as development of an affordable bipolar plate with metallic conductivity.

#### 2:00 PM V2.2

UNDERSTANDING THE LIMITS OF HYDROGEN STORAGE IN METALS. Huw Smithson, University of Cambridge, Department of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM; Dane Morgan, Chris Marianetti, Ashley Predith, Anton Van der Ven, Elena Arroyo, Stefano Curtarolo, Gerbrand Ceder, MIT, Dept. of Materials Science and Engineering, Cambridge, MA.

Hydrogen is expected to play an important role in the future distribution of energy. While hydrogen fuel cells have seen significant improvements, the problem of hydrogen storage remains. One attractive option is to store H in materials, either by hydride formation of metals, or by insertion into carbon nanotubes. To be useful as a hydrogen storage medium, hydrides must potentially satisfy competing requirements. First, high-density storage requires a large hydrogen to metal ratio, which usually necessitates a metal which is a strong hydride former. However, fast reaction kinetics for hydrogen absorption and release are also required, which may be easiest to obtain from weak hydride formers. Therefore, in this research we investigate the fundamental aspects of the bonding in metal hydrides. First-principles density functional theory is used to obtain the hydride formation energy for a large number of metals. We find that hybridizing behavior can be almost completely explained by electronic structure of the metal and the electron transfer reactions between the metal and hydrogen. These observations explain the observed trends in the hydride formation energy and give a theoretical basis for the empirically established rule of "reverse stability". We discuss the potential for making hydrides with higher energy density than MgH<sub>2</sub>.

#### 2:15 PM V2.3

##### HYDROGEN STORAGE AND NEUTRON POWDER

DIFFRACTION OF DEUTERIDED KC<sub>24</sub>. Channing C. Ahn, John J. Vajo<sup>a</sup>, Rachid Yazami, Brent Fultz and Donald W. Brown<sup>b</sup>, California Institute of Technology, Div. of Eng. & Appl. Sci., Pasadena, CA. <sup>a</sup>HRL Laboratories, LLC, Malibu, CA. <sup>b</sup>Los Alamos National Laboratory, Los Alamos, NM.

Onboard hydrogen storage for transportation applications is a challenging problem from both scientific and engineering standpoints. Many materials, including carbon nanofibers and single-walled nanotubes (SWNTs), generated initial excitement with claims of high storage capacities, but have ultimately fallen short of the requirements of transportation engineering needs. We can appreciate this by realizing that the adsorption enthalpy of hydrogen with respect to *sp*<sup>2</sup> carbons varies little whether in graphitic or nanotube form. We can, however, gain insight into the adsorption process and improvements in adsorption by considering modifications to the graphitic surface which will change the adsorption enthalpy. Potassium intercalated graphites represent an excellent starting point from which to extract such insights. In this system, the thermodynamic driving force for hydrogen sorption is increased by an order of magnitude over that of graphite. KC<sub>24</sub> is a stage 2 intercalation compound in which K atoms sit in a dodecal structure within alternating graphene sheets. Hydrogen has long been known to physisorb into the K containing planes to a value of 1.2 wt% at 77 K, although the precise nature of the interaction between the K, the graphite layers and the hydrogen is less certain. Our initial analysis of the KC<sub>24</sub> (003) peak by neutron powder diffractometry shows a 0.6% reduction in lattice parameter from 300 K, down to 35 K when the sample is held at vacuum. In the presence of ~3.8 bar of D<sub>2</sub>, the sample undergoes a lattice expansion of 1.6% at 125 K, and saturates at 3.3% at 35 K, indicating that the maximum

number of D<sub>2</sub> molecules has been accommodated by this structure. We are completing an analysis of the pair distribution functions in terms of D<sub>2</sub> site occupancies and these results will be presented.

**2:30 PM \*V2.4**

**MATERIALS ISSUES IN HIGH-PERFORMANCE MEMBRANES AND ELECTRODES FOR POLYMER ELECTROLYTE FUEL CELLS.** Thomas A. Zawodzinski, Jr., MST Division, Los Alamos National Laboratory, Los Alamos, NM.

Polymer electrolyte fuel cells are a promising technology for a range of applications. Increasingly, the needed performance, lifetime and cost improvements require solution of materials problems. Key areas for this activity include polymer electrolytes and composite electrodes. This talk will describe recent work related to new polymer electrolytes and their applications in fuel cells. The relationship between polymer structure and morphology and transport processes in these membranes will be highlighted. Also, the development of composite electrodes employing new polymer types will be critically assessed. A set of materials design considerations will be elaborated based on these experimental tests.

**3:15 PM \*V2.5**

**TECHNOLOGY DEVELOPMENT AND MATERIALS ISSUES IN DIRECT METHANOL FUEL CELLS.** Shimshon Gottesfeld, MTI Microfuel Cells, Inc., Albany, NY.

We describe recent efforts at MTI Microfuel Cells (Albany, NY) devoted to the development of small-scale direct-methanol fuel cells, targeting consumer electronics applications. Merit parameters defining advantages over Li batteries, including power density and effective energy density, will be reported for systems developed recently. Central materials issues associated with this fuel cell technology include advanced polymer membranes and catalysts, as well as optimized cell hardware materials and structure that enable one to achieve the key merit parameters of low weight and volume and effective manufacturing. Examples for each of these facets will be given for smaller scale as well as larger scale direct-methanol fuel cell systems.

**3:45 PM V2.6**

**HYDROGEN ABSORPTION OVER LITHIUM-CARBON COMPLEXES.** Jizhong Luo, Ping Chen, Zhitao Xiong, Kuanli Tan, Jianyi Lin, Dept of Physics, National University of Singapore, SINGAPORE.

Hydrogen adsorption over Li-graphite and <sup>6</sup>Li-CNTs complexes were studied by pressure composition isotherm (PCI) and in-situ XRD methods. A remarkable reduction in reaction temperature was found for the hydrogenation of Li metal in Li-C mixtures. H<sub>2</sub> uptake started at 50°C, became vigorous at 150°C and slowed down at temperatures above 200°C. About 10 wt% of H<sub>2</sub> adsorption were observed over Li-graphite (10:1) sample. In-situ XRD characterizations revealed that Li-C intercalation compounds such as LiC<sub>6</sub> and LiC<sub>12</sub> existed in the Li-C samples, and LiH was formed after the hydrogenation had taken place. Increasing carbon content in the Li-C mixture, from Li/C = 10:1 to 5:1 and then to 2:1, would enhance the reactivity of hydrogenation accordingly. Comparing with graphite, carbon nanotubes (CNTs) which have smaller size and larger specific area, showed much greater promotion to the hydrogenation of lithium metal than graphite. In addition, smaller diameter (range from 10 to 100 nm), greater promotion CNTs exhibited. The reasons were analysed and the mechanism for the low temperature hydrogenation of Li-C samples was proposed.

**4:00 PM V2.7**

**STORAGE AND TRANSPORT OF HYDROGEN AND OXYGEN IN HIGH PRESSURE COMPOSITE CYLINDERS EQUIPPED WITH ANTI-PERMEATION AND ANTI-CORROSION THIN LAYERS.** Armin Reller, University of Augsburg, Chair of Solid State Chemistry, Augsburg, GERMANY; Eva Maria Moser, Technical Highschool of Engineering, Geneva, SWITZERLAND.

For the storage and transport of hydrogen, one of the most promising future fuels, as well as of oxygen and other gases applicable to regenerative energy systems the use of high pressure composite cylinders proves to be advantageous. However, the problem of above all hydrogen permeation through the cylinder wall as well as of the degradation or corrosion of the liner material by reactive gases has to be solved. The deposition of thin protective metal and/or metal oxide films can be achieved by various techniques such as laser ablation, sputtering or reactive plasma treatment. In all cases the contact between the surface of the liner material, e.g. high density polyethylene, and the protective metal or metal oxide layer is of crucial importance. Detailed characterizations of differently deposited layers by means of scanning electron microscopy, atomic force microscopy, X-ray diffractometry and thermal analysis are presented.

**SESSION V3: MATERIALS FOR SOLAR ENERGY**

Chair: Dennis Flood

Wednesday Morning, April 3, 2002  
Golden Gate A3 (Marriott)

**8:30 AM \*V3.1**

**DOWN TO EARTH PHOTOVOLTAICS R&D: A LOOK AT THE PRESENT AND ROAD AHEAD.** Lawrence L. Kazmerski, National Center for Photovoltaics, National Renewable Energy Laboratory, Golden, CO.

In this paper, we contemplate the directions of photovoltaics (PV) R&D and technology into this new millennium. We also explore how some current technologies are laying the foundations for what might be expected for the first decades of this century, with some emphasis on potential technology and industry growth in the United States. The focus is on what current and coming generations can anticipate for the both conventional and non-conventional aspects of solar-electric technologies. Near- and coming-technology research approaches are discussed and evaluated, indicating the horizons of PV technology for thin films through bulk materials. Starting with contemporary, "traditional" PV, this paper speculates on coming generations of technology and their applications. The prognosis highlights nanotechnology through megascale deployment, biomorphic extensions through new physics, and quantum concepts through designer materials concluding that PV is embarking toward technological frontiers not known today.

**9:00 AM V3.2**

**SYNTHESIS OF ELECTRONIC OXIDES FOR SOLAR ENERGY APPLICATIONS.** Colin A. Wolden, Joshua J. Robbins, James Kestner, Yen-jung Huang, Anna Chorney, Mailasu Bai, Weican Xiao, and Tyrone Vincent, Colorado School of Mines, Department of Chemical Engineering, Golden, CO; Lawrence Woods and Joseph Armstrong, ITN Energy Systems, Inc., Littleton, CO.

Plasma-enhanced chemical vapor deposition (PECVD) is a flexible coating technology that has been employed for the synthesis of a variety of oxides. In this paper we discuss the synthesis of transparent conducting oxides (TCOs), insulating oxides and electrochromic oxides. TCOs form the transparent electrodes in all PV devices. Insulating oxides have application both as buffer layers and as protective coatings. Electrochromic materials may be reversibly converted from transparent to opaque to modulate sunlight in architectural applications. These three materials were deposited in the same reactor by simply adjusting the process gases and operating conditions. An advantage of PECVD is that film deposition was accomplished at low temperature, between 25°C and 250°C. The films' structural, optical, electrical and tribological properties were examined as a function of plasma power, substrate temperature, pressure, and gas composition. The relationships between plasma operating conditions and film properties are discussed. Examples are presented that demonstrate the application and integration of these materials into terrestrial CdTe solar cells, spaced-based photovoltaics, and smart windows. PECVD provides unique flexibility in its ability to be tailored for a particular application. It is amenable to in-situ process control through techniques such as optical emission spectroscopy and reflectometry. Furthermore it is particularly attractive for the formation of novel alloys and functionally graded materials. Examples of these features will be presented.

**9:15 AM V3.3**

**ORIGINS OF TRANSPARENT CONDUCTIVITY IN SnO<sub>2</sub>.**

Çetin Kılıç and Alex Zunger, National Renewable Energy Laboratory, Golden, CO.

Stannic oxide (SnO<sub>2</sub>) exhibits seemingly contradictory properties of high metallic conductivity and nearly complete transparency in the visible range. The coexistence of conductivity with transparency suggests that some conductivity-promoting intrinsic defects can be tolerated in SnO<sub>2</sub> in huge quantities, without creating visible absorption. We employ first-principles calculations to determine the conditions required for this unusual effect by investigating the role of intrinsic defects and hydrogen impurity. We find that the tin interstitial and oxygen vacancy predominate in the defect structure of SnO<sub>2</sub> due to low formation energies and mutual attractive interaction. Our results indicate that the multivalence of Sn makes it possible that tin interstitial together with oxygen vacancy in SnO<sub>2</sub> creates a local environment akin to SnO which is also stable (unlike SiO<sub>2</sub> vs SiO). This explains the natural oxygen deficiency of SnO<sub>2</sub>. In addition, we find these intrinsic defects and also interstitial hydrogen donate conduction electrons in undoped SnO<sub>2</sub> with almost no reduction in optical transparency, yielding an explanation for the transparent conductivity of SnO<sub>2</sub>.

### 9:30 AM V3.4

FABRICATION OF HIGH QUALITY COPPER INDIUM DISULFIDE FILMS ON Mo/GLASS SUBSTRATES VIA PULSED LASER ABLATION. R. Mu, A. Ueda, M.H. Wu, D.O. Henderson, Fisk University, Department of Physics, Chemical Physics Laboratory, Nashville TN; C.M. Lukehart, Vanderbilt University, Department of Chemistry, Nashville TN; L.C. Feldman, Vanderbilt University, Department of Physics and Astronomy, Nashville, TN; A. Hepp, NASA John H. Glenn Research Center at Lewis Field, Cleveland, OH.

Thin film photovoltaic devices offer several advantages over other solar cells from possible lower cost due to the thin active layer thickness, a large-scale application, flexibility to few limitations of shapes and configurations. Its light weight, high radiation resistance, and easy management in temperature due to its small volume also make thin film solar cell more attractive to be used in space. Chalcopyrite semiconductors, such as  $\text{CuInS}_2$  may be one of the very promising materials to be used as the active layer for solar cells. It has an optical band gap which is closely matched to the peak of the solar energy spectrum and a high absorption cross section  $> 10^4 \text{ cm}^{-1}$ . Thus, a film with 1-2  $\mu\text{m}$  in thickness is sufficient to absorb over 99% of incident solar energy above the band gap. On the other hand, it is also known that there exist many other isomorphous structures when a non-optimized film fabrication procedure is used and/or the film is off-stoichiometry. Thus, a pico-second pulsed laser ablation (PLA) technique has been employed to fabricate the copper indium disulfide (CIS) thin film on a molybdenum coated glass substrate. By optimizing the experimental parameters of PLA, changing the elemental ratio of the target materials, and a proper control of the annealing conditions of the fabricated film, high quality CIS films have been obtained. The structural, optical and morphologic characterizations have been conducted and will be reported. These techniques include XRD, RBS, infrared, UV-Vis, AFM and STM analyses.

### 10:15 AM V3.5

METAL-ORGANIC CHEMICAL VAPOUR DEPOSITION OF II-VI SEMICONDUCTOR THIN FILMS USING SINGLE-SOURCE APPROACH. Mohammad Afzaal, David Crouch, Paul O'Brien, Jin-Ho Park, University of Manchester, Dept of Chemistry and Manchester Materials Science Centre, Manchester, UNITED KINGDOM.

CdSe and CdS are found in applications for the use of solar cells, infrared filters and photoconductive films. ZnSe and ZnS are used to fabricate blue to ultra-violet light emitting diodes (LEDs) and laser diodes (LDs), which are key devices for full colour display and high density optical data processing. Typical preparation for II-VI materials using CVD technique employs pyrophoric metal alkyl,  $\text{MR}_2$  ( $\text{M} = \text{Cd, Zn}$ ;  $\text{R} = \text{alkyl}$ ) and  $\text{H}_2\text{S}$  or  $\text{H}_2\text{Se}$ . In this study, a series of  $\text{M}[(\text{E}_2\text{P}^{\text{iso}}\text{Pr}_2)_2\text{N}]_2$  ( $\text{M} = \text{Cd, Zn}$ ;  $\text{E} = \text{S, Se}$ ) have been prepared and used as single-source precursors for the deposition of II-VI semiconductor thin films on glass substrates by low-pressure chemical vapour deposition (LP-MOCVD). The films have been investigated using XRPD, SEM, EDS and XPS, as well as other material characterization techniques. SEM analyses show all films are microcrystalline for CdS/CdSe and nanocrystalline for ZnS/ZnSe and they also tend to be formed as different morphologies depending on growth temperatures. XRPD results show evidence of the crystalline nature of these metal chalcogenide films with having hexagonal phase. EDS analyses indicate that ratio of M:E is close to 1:1. The results of this comprehensive study will be presented and discussed.

### 10:30 AM V3.6

ORGANIC-SEMICONDUCTOR-BASED ALL-SOLID-STATE PHOTOELECTROCHEMICAL CELLS. Robert Hudej, Gvido Bratina, Nova Gorica Polytechnic, Nova Gorica, SLOVENIA; Urška Lavrenčič Štangar, Boris Orel, National Inst of Chemistry, Ljubljana, SLOVENIA.

The dye-sensitized photoelectrochemical cells (DSPECs) developed by Graetzel attracted particular attention because of their good photovoltaic conversion efficiency at low illumination levels and the possibility of using materials other than silicon. DSPEC in a thin film sandwich configuration consists of an electrolyte which is encapsulated between the electron generating  $\text{TiO}_2$  electrode sensitized with ruthenium bipyridyl complex and a thin Pt electrode serving as a counter electrode. Conventional DSPEC employs a liquid electrolyte with an incorporated  $\text{I}^-/\text{I}_3^-$  redox couple. In this paper we report about DSPEC, in which vacuum deposited p-type semiconductor 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) was employed in combination with a sol-gel produced  $\text{TiO}_2$  layer for making all-solid-state DSPEC. The DSPECs were examined in the light of photocurrent response as a function of organic semiconductor thickness. The effective surface of the solar cell was a rectangle with  $3\text{-cm}^2$  area. The photocurrent measurements were performed with

monochromatic light at wavelengths from 405 nm to 1070 nm under a direct exposure to sunlight. Measurements on the sample with 300 nm thick PTCDA showed a photocurrent/dark current ratio of 300, while measurements on the sample with 50 nm thick PTCDA showed the ratio of 10. The photocurrent response in the latter type of the samples exhibited a time dependence that may be associated to the space-charge limited current in organic semiconductors. The photocurrent as a function of wavelength exhibits a pronounced peak at 465 nm. The measured photocurrent density at this wavelength was  $1 \mu\text{A}/\text{cm}^2$  at light intensity of  $90 \mu\text{W}/\text{cm}^2$ . The measurements performed at sunlight yielded photocurrent densities as high as  $33 \mu\text{A}/\text{cm}^2$ .

### 10:45 AM V3.7

STRUCTURAL AND OPTICAL CHARACTERIZATION OF  $\text{Cu}_x\text{Ga}_y\text{Se}_2$  THIN FILMS UNDER EXCITATION WITH ABOVE AND BELOW BAND GAP LASER LIGHT. C. Xue, D. Papadimitriou, Y.S. Raptis, National Technical University of Athens, Department of Physics, Athens, GREECE; T. Riedle, N. Esser, W. Richter, Technical University of Berlin, Institute of Solid State Physics, Berlin, GERMANY; S. Siebentritt, J. Albert, M.Ch. Lux-Steiner, Hahn-Meitner Institute, Berlin, GERMANY.

Abstract  $\text{Cu}_x\text{Ga}_y\text{Se}_2$  MOCVD and PVD grown layers, with potential applications in photovoltaics, were characterized by means of Raman, photoluminescence and photoreflectance spectroscopy. Raman and PL spectra were excited by laser light above and below the material band gap (1.72 eV). The high quality of Raman spectra, (excited by 676 nm  $\text{Kr}^+$ -laser and  $\text{Ar}^+$ -pumped Ti-Sapphire laser in the range 750-850 nm), enables comparative studies of weak defect related modes of Cu-rich samples with the same intense modes of Ga-rich samples. These modes are represented by a  $\text{Cu}_x\text{Ga}_y\text{Se}_2$  double peak at 193 and  $199 \text{ cm}^{-1}$ , which in defect rich Ga-rich MOCVD samples can be also excited by above band gap light (514.5 nm  $\text{Ar}^+$ -laser). The absence of these modes in Cu-rich PVD samples is probably due to strong scattering of the laser beam ( $I \sim \omega^4$ ) by  $\text{Cu}_x\text{Se}_y$  surface coverage of  $\text{Cu}_x\text{Ga}_y\text{Se}_2$  as detected by SEM [1]. A Raman mode at  $150 \text{ cm}^{-1}$ , excited only in parallel polarization configuration and eliminated by etching, is considered to be the Raman fingerprint of preferential oriented  $\text{Cu}_x\text{Se}_y$ -crystallites. The presence of crystallites is discussed in terms of line shape considerations and in dependence of excitation-wavelength and scattering-geometry. The defect related modes of the ternary compound are composition dependent and may be used as indicator of structural changes by variation of the Cu/Ga content of Ga-rich layers, while the mode of the binary dominates in the spectra of layers containing Cu above stoichiometry independently of the fraction of Cu-in excess, and is only weakly present or absent from the spectra of Ga-rich samples. Photoluminescence emission (PL) studied at room and low temperatures in dependence of composition showed that: a) with increasing Ga-content, PL exhibits, independently of temperature, intensity enhancement, red energy shift and band broadening attributed [1,2] to potential fluctuations and increasing disorder, b) in stoichiometric and Cu-rich MOCVD samples, valence band splitting is observed at 20 K in agreement with the room temperature photoreflectance spectra. PL measurements under variable excitation wavelengths (VEPL) confirm the presence of a shallow donor and two different acceptor levels predicted in ref. [1,2], and c) in Ga-rich MOCVD samples, VEPL at 20 K reveals transitions between quasi-continua of deep donor and acceptor levels. References:

- [1] 99, A. Bauknecht, Ph.D. thesis, Freie Universitat Berlin, 1999.
- [2] A. Bauknecht, S. Siebentritt, J. Albert, M. Ch. Lux-Steiner, J. Appl. Phys. 89(8), 4391 (2001).

### 11:00 AM V3.8

INKJET PRINTING OF SILVER METALLIZATIONS ON SILICON SOLAR CELLS. Calvin Curtis, Alex Miedaner, Tanya Rivkin, Lee Smith, Jeff Alleman, John Perkins, and David Ginley, National Renewable Energy Laboratory, Golden, CO.

Direct-write inkjet printing of Ag metallizations on Si solar cells is a low-cost, materials-efficient approach that has two potential advantages. First, it is a non-contact printing approach that can be used to deposit metallizations reliably on thin, fragile Si substrates. Second, it offers line resolution as small as 20 microns, which is far better than the current state of the art obtained by screen printing. The major challenge in applying inkjet processes for direct-write metallizations is in formulating suitable inks. We have used Ag metal-organic decomposition (MOD) complexes and hybrid MOD/nanoparticle inks in organic solvents for this purpose. Silver printed on Si using  $\text{Ag}(\text{hfa})(\text{COD})$ -based ink (where hfa = hexafluoroacetylacetonate and COD = 1,5-cyclooctadiene) at 300-400°C gave smooth, dense Ag deposits characterized by good adhesion and conductivities as good as vacuum deposited Ag. In addition, low-resistance, ohmic contacts to the n-type layer of a diffused p-n junction Si solar cell have been achieved using  $\text{Ag}(\text{hfa})(\text{COD})$  ink printed at 400°C without further annealing. This

process has now been used to apply Ag metallizations to active Si solar cells. The performance of these devices and factors that affect the thickness and resolution of printed Ag lines will be discussed. This work was funded by the National Center for Photovoltaics at NREL. The National Renewable Energy Laboratory is a U.S. Department of Energy Laboratory operated by Midwest Research Institute-Battelle-Bechtel under Contract No. DE-AC36-99-GO10337.

#### 11:15 AM V3.9

TEXTURED ZINC OXIDE BY EXPANDING THERMAL PLASMA CVD: THE EFFECT OF ALUMINUM DOPING. R. Groenen, Eindhoven University of Technology, Department of Physics, Eindhoven, THE NETHERLANDS; E.R. Kieft, Eindhoven University of Technology, Department of Physics, Eindhoven, THE NETHERLANDS; J.L. Linden, TNO-TPD, Division Materials Research and Technology, Eindhoven, THE NETHERLANDS; M.C.M. van de Sanden, Eindhoven University of Technology, Department of Physics, Eindhoven, THE NETHERLANDS.

Zinc oxide (ZnO) is a transparent conducting oxide (TCO) of considerable technological interest. As recently shown, a new approach for low temperature deposition of textured ZnO is developed, using an expanding thermal argon plasma created with a cascaded arc [1]. (Co)precursors are oxygen, diethylzinc, and trimethylaluminum, which undergo ionization via charge exchange and consecutive dissociative recombination by respectively argon ions and electrons created in the arc. Films are deposited on glass substrates at a temperature of 200°C at a rate up to 1 nm/s. Surface texture, morphology and crystal structure have been studied by AFM, SEM and XRD. In addition, spectroscopic ellipsometry is used to evaluate optoelectronic properties of aluminum doped films. A rough surface texture, which is essential for application as front electrode in thin film solar cells, is obtained during deposition. The presence of aluminum donors in doped films is confirmed by a shift in the ZnO band gap energy. In combination with reflection and transmission measurements in the visible and NIR ranges film conductivities have been obtained from the free-carrier absorption. These results are consistent with direct measurements.

[1] R. Groenen, et al., Appl. Surf. Sci. 173 (2001) 40.

### SESSION V4: SOLID OXIDE FUEL CELLS

Chair: Michael Krumpelt  
Wednesday Afternoon, April 3, 2002  
Golden Gate A3 (Marriott)

#### 1:30 PM \*V4.1

MATERIALS CHALLENGES IN SOLID OXIDE FUEL CELLS. Michael Krumpelt, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

Solid oxide fuel cells were originally developed for electric utility applications and continue to have potential in distributed power generation and in "clean" coal-based central stations. New applications are now emerging for small portable systems as auxiliary power units in vehicles, power generators for RVs, and remote-area cabins. Unlike continuously operating utility systems, these small power generators will have to go through frequent start ups and shut downs. Lowering the operating temperature of the fuel cell becomes imperative. The electrochemical activity of the currently used cathode material ( $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ ) is too low at temperatures of less than 900°C, and new cathode materials need to be developed. Lanthanum ferrite is currently a leading candidate but other compounds with good electro-catalytic activity for the reduction of oxygen to oxide ions, and good ionic as well as electronic conductivities could become useful. The currently used anode material ( $\text{Ni}/\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$ ) will also have to be modified to make it more oxidation resistant during shut downs, and to improve the sulfur tolerance. At operating temperatures of less than 800°C, ferritic stainless steels become viable as bipolar plates, but need to be optimized. This presentation will provide an overview of the issues and discuss recent advances in the field.

#### 2:00 PM V4.2

MICROFABRICATED THIN-FILM FUEL CELLS FOR PORTABLE POWER APPLICATIONS. Alan Jankowski and Jeffrey Morse, Lawrence Livermore National Laboratory, Livermore, CA.

Fuel cells have gained renewed interest for applications in portable power since the energy is stored as fuel rather than as an integral part of the power source, as is the case with batteries. While miniaturized fuel cells have been demonstrated for the low power regime (1-20 Watts), numerous issues still must be resolved prior to deployment for applications as a replacement for batteries. As traditional fuel cell designs are scaled down in both power output and physical footprint, several issues impact the operation, efficiency, and overall

performance of the fuel cell system. These issues include fuel storage, delivery, and distribution, system control, i.e; startup, heating, and peak power requirements, stacking and packaging, and thermal management. The combination of microfabrication, thin-film deposition, and micromachining approaches offers potential advantages with respect to fuel cell stack size and weight, flow field structure and manifolding, fuel storage and delivery, packaging, and thermal management. Furthermore, these technologies enable material and fuel flexibility, while providing a manufacturable, modular fuel cell approach. These approaches will be discussed, along with experimental results from both solid oxide and proton exchange membrane thin-film fuel cells.

#### 2:15 PM V4.3

INVESTIGATIONS IN THE MICROSTRUCTURAL CHANGES DURING THE STARTUP PROCESS OF SOLID OXIDE FUEL CELLS (SOFC). Sven Schäfer, André Weber, Ellen Ivers-Tiffée, Universität Karlsruhe, Institut für Werkstoffe der Elektrotechnik, Karlsruhe, GERMANY; Klaus Schmid, Volker Krebs, Universität Karlsruhe, Institut für Regelungs- und Steuerungssysteme, Karlsruhe, GERMANY.

Solid Oxide Fuel Cells (SOFC) are high temperature electrochemical devices that convert the chemical energy of a fuel directly into electrical energy.

The electrochemical active part of a SOFC is the membrane electrode assembly (MEA), a ceramic multilayer structure which consists of a dense yttria stabilized zirconia (YSZ) electrolyte and porous electrode layers. Strontium doped lanthanum manganite ( $\text{LSM}:\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ ) was used as cathode and a nickel/YSZ-cermet as anode. Sintering of the LSM cathode layer onto the YSZ electrolyte substrate a poorly conducting lanthanum zirconate (LZO) layer is formed between LSM and YSZ. This layer is decomposed during the initial electrical loading of the cell resulting in a substantial increase in cell performance.

The influence of the initial load profile on the decomposition of the LZO-layer as well as the microstructural changes resulting in an extension of the electrochemical active three phase boundary during this formation process were investigated.

The effect of different startup procedures on the final cell performance were investigated by electrical characterization of SOFC single cells under realistic working conditions. The microstructure of the cathode layer before and after electrical loading has been analyzed by electron microscopy to get information about the influence of the initial load profile on the microstructural changes.

A first (control theory based) non-linear model of the startup process of SOFCs including the decomposition of the LZO-layer and the variation of the polarization resistance due to microstructural changes will be presented.

#### 2:30 PM V4.4

ELECTRICAL AND MICROSTRUCTURAL AGING OF POROUS AND DENSE LANTHANUM STRONTIUM MANGANITE/YTRIA DOPED CUBIC ZIRCONIA ELECTRODES. Marcia Caldeira Brant, CDTN, BRAZIL; Tulio Matencio, Dept of Chemistry, UFMG, BRAZIL; Larrent Dessemond, INPG, FRANCE; Rosana Zacarias Domingues, Dept of Chemistry, UFMG, BRAZIL.

The formation of the lanthanum zirconate at the triple phase boundary of the interfaces between cathode and electrolyte materials during solid oxide fuel cell (SOFC) operation leads to deleterious effects on SOFC properties. We report in situ impedance spectroscopy measurements of the degradation of porous and dense  $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3/\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$  electrodes submitted to annealing temperatures from 1373 to 1673 K. Impedance diagrams were plotted at 900 K at heating up and cooling annealing process. It was verified that the rate limiting reaction steps are different for samples annealed at low and high temperature. Impedance diagrams of samples annealed above 1473 K showed one additional semicircle at lower frequency range. SEM and EDS analyses corroborated the hypothesis that the formation of zirconate phases at the interface cathode/electrolyte is responsible for the change of electrode properties.

#### 3:15 PM V4.5

ELECTRICAL AND MICROSTRUCTURE STUDY OF LANTHANUM MANGANITE FILMS ON (001) YTRIA STABILIZED ZIRCONIA. Ramanan Ganesananthan, Siu-Wai Chan, Columbia University, NY, NY; Nan Yao, Princeton University, Princeton, NJ.

Microstructure of lanthanum manganite films is correlated to the impedance response measured at temperatures from 300 to 800°C and oxygen partial pressure from 1 to 0.001 atm. Two types of cathodes, stoichiometric undoped lanthanum manganite (LMO) and lanthanum deficient strontium doped manganite (LSM) films are deposited by laser ablation onto (001) yttria stabilized zirconia (YSZ) single crystal substrates at 725°C. Transmission electron microscopy (TEM) of the

LMO sample shows a columnar manganite film microstructure with a distinct reaction layer at the interface with the substrates. This reaction layer is Zr and La rich. Impedance response produces a series of 3 arcs over the temperature range measured. The high temperature arc (W) (700-800C) is highly dependent on oxygen pressure. The medium temperature arc (Y) (500-650C) has an activation energy of 0.97eV for oxygen ion transport possibly through the reaction-layer. The low temperature arc (X) (300-450C) is only weakly dependent on oxygen partial pressure and has a higher activation energy 1.68eV for LMO and 1.36eV for LSM.

### 3:30 PM V4.6

**GRAIN SIZE AND CHEMICAL COMPOSITION EFFECTS ON THE GRAIN BOUNDARY RESISTANCE OF CERIA BASED MATERIALS.** Xiao-Dong Zhou, Harlan. U. Anderson, Wayne Huebner, University of Missouri-Rolla, Electronic Materials Applied Research Center, Rolla, MO.

Solid oxide fuel cells (SOFC) that can be operated over the intermediate temperature (IT) regime (300°C ~ 600°C) have been of great interest very recently because lower cell operation temperature results in a higher Nernst voltage, better anticipated reliability due to minimized materials interactions, the use of low-temperature sealing materials, and a lower overall cost primarily due to the potential use of metallic interconnects. A low resistance electrolyte is a key component in IT-SOFC in order to achieve a useable current density; doped ceria are being considered as such an electrolyte. However, lower temperature operation does pose a problem due to the higher activation energy of the grain boundary resistivity. A high grain boundary resistivity can be due to many factors, including (1) amorphous phases, (2) dopant segregation, (3) an altered local defect chemistry due to space charge effects, and (4) intergranular porosity (small effect). These effects are all strongly related to grain size and the associated grain boundary area. In this paper, a series study of grain size (20nm - 5.0mm) effects on the undoped CeO<sub>2</sub>, 1.0mol% Gd-CeO<sub>2</sub> and 10.0mol% Gd doped CeO<sub>2</sub> are performed over two impurity levels of raw materials (99.5% and 99.995%). A series of impedance spectra as a function of temperature and grain size were analyzed. Doping with Gd lowered the r<sub>gb</sub> and the activation energy, in which the grain boundary resistance was very likely due to the oxygen ion trapping and only contribute to about 27% of total resistance at 300°C. Grain size effect was much stronger in undoped ceria. In low purity undoped ceria, impurities acted as both dopants and blocking materials, hence a size-dependent grain boundary resistivity was observed. An exponential increase of grain conductivity was observed in high purity undoped ceria when the grain size was decreased.

SESSION V5: POSTER SESSION  
Chair: Steve Ringel  
Wednesday Evening, April 3, 2002  
8:00 PM  
Salon 1-7 (Marriott)

### V5.1

**HIGH THERMAL CONDUCTIVITY SYNTHETIC MATERIALS IN ENERGY MANAGEMENT.** Kal Renganathan Sharma, Vellore Institute of Technology (Deemed University) Vellore, Tamil Nadu, INDIA.

There is a need for material with light weight and high heat sinking property in the design of laptop computer casings. Thermoplastic composites with higher thermal conductivity than Aluminum are needed in energy management. Pitch based carbon fibres dispersed in polyimide matrix are the candidate materials. An expression for the effective thermal conductivity as a function of volume fraction of the dispersed phase, fiber diameter, fiber orientation, and matrix properties is provided. The thermal conductivity change with temperature patterns of homogeneous solid materials are not same. For a dispersed heterogeneous system the options for the design engineer can be; a) choose matrix material that increases in k with increase in T and fiber material with k decreases with increase in T b) matrix material that decrease in k with increase in T and fiber material with k decreases with increase in T c) choose matrix material that increases in k with increase in T and fiber material with k increases with increase in T d) matrix material that increase in k with decrease in T and fiber material with k increases with increase in T. The search for a material design that is a superconductor of heat in a similar manner to the superconductor of electricity is discussed.

### V5.2

Abstract Withdrawn.

### V5.3

**QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIPS FOR**

**NEW AEROSPACE FUELS.** Steven Trohalaki, Robert J. Zellmer, Ruth Pachter, Saber Hussain, John M. Frazier, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

The design of new materials can be made more efficient if toxicity screening is performed in early rather than in late stages of development. This is especially true for volatile materials such as lubricants, fire retardants, fuels, and fuel additives. In our continuing efforts to develop methods for the prediction of the toxicological response to materials of interest to the U.S. Air Force, we have measured in vitro toxicity endpoints for thirteen newly proposed propellant compounds and constructed Quantitative Structure-Activity Relationships (QSARs). The endpoints measured include the mitochondrial function of hepatocytes and the total glutathione content of hepatocytes. Molecular descriptors were obtained using semi-empirical and ab initio molecular orbital theory as well as using density functional theory. QSAR models were then derived for each endpoint. For all levels of theory, correlation coefficients for 3-parameter QSARs exceed 0.9, possibly enabling toxicity predictions for similar compounds. Insight into the biophysical mechanism of toxic response can be obtained from interpretation of the descriptors comprising the QSARs.

### V5.4

**STUDY ON THE DOPED  $\beta$ -FeSi<sub>2</sub> OBTAINED BY METAL-VAPOR VACUUM-ARC ION SOURCE IMPLANTATION AND POST-ANNEALING.** S.B. Wang, AIST, Photonics Research Institute, Tsukuba, Ibaraki, JAPAN; Periran Zhu, Chinese Academy of Sciences, Institute of Physics, Beijing, CHINA.

$\beta$ -FeSi<sub>2</sub> is directly formed by implanting Si wafers with Fe ions at 50 kV to a dose of  $5 \times 10^{17}/\text{cm}^2$  in a strong current Metal Vapor Vacuum Arc (MEVVA) implanter. Additional Ti, V, and Zr implantation were also performed on these Fe implanted samples. While annealing was carried out in a temperature range of 650 ~ 950 °C, in Fe + Ti implanted samples, XRD patterns show there is only  $\beta$ -FeSi<sub>2</sub> structure ( $\beta$ -Fe(Ti)Si<sub>2</sub>). Until annealing was carried out at temperature above 1050 °C, the  $\beta$ -Fe(Ti)Si<sub>2</sub> transits into  $\alpha$ -structure. This implies that Ti introducing stabilizes the  $\beta$ -FeSi<sub>2</sub>. In V case, except of  $\beta$ -FeSi<sub>2</sub>, VSi<sub>2</sub> was formed. It reflects a large decrease in resistivity, MEVVA implantation doping is thought a potential method in manufacturing thermo-electricity films and devices.

### V5.5

**SYNTHESIS AND THERMOELECTRIC PROPERTIES OF Bi<sub>2</sub>S<sub>3</sub> NANOBEADS.** Jiye Fang, Kevin L. Stokes, Feng Chen, Jibao He and Charles J. O'Connor, Advanced Materials Research Institute, University of New Orleans, New Orleans, LA.

Bismuth sulfide (Bi<sub>2</sub>S<sub>3</sub>), a semimetal-like material in nanophase, attracts high interest in thermoelectric investigations. In this work, nanometer-sized bismuth sulfide with unique morphology has been successfully prepared by a precipitation between bismuth 2-ethylhexanoate and thioacetamide in high-temperature organic solution with presence of proper capping/stabilizing agents. By employing this technique, we are able to produce nanobeads of bismuth sulfide with an aspect ratio of ~ 5, typically ~10 nm wide and ~50 nm long according to the TEM observation. Characterization of XRD and TEM/HRTEM reveals that the as-prepared particles exist in single orthorhombic phase and possess high crystallinity. The composite ratio between Bi and S can be adjusted by varying the ratio between two precursors and was determined by using EDX (TEM) technique. Thermoelectric properties of these bismuth sulfide nanobeads were also investigated and will be discussed comparatively with those from commercial bulk materials.

### V5.6

**A GRAIN BOUNDARY ENGINEERING APPROACH TO PROMOTE SPECIAL BOUNDARIES IN A Pb-BASE ALLOY.** D.S. Lee, H.S. Ryoo, S.K. Hwang, Inha Univ, School of Materials Science and Engineering, Incheon, KOREA.

Grain boundary engineering was employed as a means to promote special boundaries in a commercial Pb-base alloy used for positive electrode grids in automobile batteries that are vulnerable to intergranular corrosion, cracking and creep. The present approach was adopted as a new alternative to the conventional alloy design methodology of grain refining or alloying with minor additions of Ca, Sn or Ag, etc., which is either costly or ineffective for the creep resistance. With an aim to increase the fraction of the special boundaries, a unique TMT processing route was developed that consisted of commercial strip rolling, additional laboratory cold rolling and recrystallization annealing heat treatment. Grain boundary character distribution (GBCD), as analyzed by electron back-scattered diffraction (EBSD), was sensitively affected by the TMT parameters. Cold rolling of the strip rolled specimen by 70% increased the low angle boundaries and, as a result, decreased the



relative proportion of the CSL (Coincidence Site Lattice) boundaries. However, increasing the amount of deformation to above 80% and utilizing a novel mode of plastic deformation, increased the portion of the CSL (Coincidence Site Lattice) boundaries significantly above the level of commercial grid materials. Concurrently the high angle grain boundaries regained their frequency over that of low angle grain boundaries. With repeated TMT the CSL boundaries of  $\Sigma 3$ - $\Sigma 9$ , analyzed by EBSD method, steadily increased and reached to 90% of the total boundary areas. The TMT-treated specimens exhibited numerous annealing twins identified as  $\Sigma 3^n$  boundaries, supporting a reproduction mechanism of the  $\Sigma 3$  boundaries.

#### V5.7

**THERMOELECTRIC PROPERTIES OF THE SEMICONDUCTING ANTIMONIDE-TELLURIDE  $\text{Mo}_3\text{Sb}_{5-x}\text{Te}_{2+x}$ .** Enkhe Dashjav, Holger Kleinke, Department of Chemistry, University of Waterloo, CANADA.

Thermoelectric materials are capable of converting heat into electrical energy and vice versa. This fascinating energy conversion is commercially used in power generators, food refrigerators, air conditioning, CPU cooling and sensors. Nowadays, the efficiency of thermoelectric energy conversion is smaller than in combustion engines or Freon compressors, which inhibits broader usages. Significant increases in efficiency would greatly improve the competitiveness against environmentally more harmful energy conversion methods. We are searching for compounds based on refractory antimonides that combine the advantages of commercially used materials with high temperature stability and rattling of cations in Sb atom cages, a combination which - if achieved - will lead to significantly enhanced efficiencies of the power generation. Generally, the antimonides of the early transition metal atoms fulfill most of the phenomenological requirements for excellent thermoelectric energy conversion, namely: high thermal stability, heavy constituent elements, small differences in the electronegativities of the constituent elements, crystal structures exhibiting low symmetry, often mixed occupancies on several sites in the structures, and (eventually) rattling of metal atoms in Sb atom cages. Problematic is the metallic character of the known antimonides like  $\text{ZrSb}_2$ ,  $\text{NbSb}_2$  and  $\text{Mo}_3\text{Sb}_7$ , for semiconducting or semimetallic properties are essential for good thermoelectrics. Our electronic structure calculations reveal that  $\text{Mo}_3\text{Sb}_7$  can be made semiconducting by heavy doping, e.g., by replacing Sb in part with Te. We succeeded in the preparation of semiconducting  $\text{Mo}_3\text{Sb}_{5-x}\text{Te}_{2+x}$ , the thermoelectric properties of which will be discussed in this poster contribution. We also succeeded in adding small M atoms into the cubic Sb/Te cage of  $\text{Mo}_3\text{Sb}_{5-x}\text{Te}_{2+x}$ , thereby creating the rattling effect as found in the filled skutterudites.

#### V5.8

**THE PROMISING NEW PHOTOCATALYST  $\text{InVO}_4$  FOR WATER MOLECULE DECOMPOSITION IN THE VISIBLE WAVELENGTH REGION.** Mitsutake Oshikiri, Nanomaterials Lab, National Institute for Materials Science, Tsukuba, Ibaraki, JAPAN; Ari P. Seitsonen, Michele Parrinello, Centro Svizzero di Calcolo Scientifico, Manno, SWITZERLAND; Mauro Boero, Research Center for Atom Technology, Advanced Industrial Science and Technology, Tsukuba, Ibaraki, JAPAN; Jinhua Ye, Materials Engineering Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, JAPAN; Zhigang Zou, Photoreaction Control Research Center, Advanced Industrial Science and Technology, Tsukuba, Ibaraki, JAPAN.

A photocatalyst for water molecule decomposition that can work in the visible wavelength region ( $> 420$  nm) is desired for solar energy storing. Because the redox level difference between  $\text{H}^+/\text{H}_2$  and  $\text{O}_2/\text{H}_2\text{O}$  is about 1.2 eV (1.0 micron), even a near-infra-red-active semiconductor photocatalyst could exist. However, the present semiconductor photocatalysts work mainly in the UV region. Most of them are based on materials including transition metal oxides of Ti, Zr, Nb, Ta. Since the bottom of their conduction band mainly consists of d orbitals of the transition metal, it would be advantageous to lower the bottom of these d bands closer to the redox level of  $\text{H}^+/\text{H}_2$ . In order to test such a simple concept, we have investigated the vanadium oxide related materials. We have deduced from our first principles electronic structure calculations that  $\text{InVO}_4$  might function as a photocatalyst in a wider visible wavelength range than  $\text{InNbO}_4$  and  $\text{InTaO}_4$ , whose photocatalytic activity was found to be limited to 500 nm [1]. Indeed,  $\text{InVO}_4$  is observed to be photocatalytically active in the hydrogen evolution in a wider visible range ( $> 600$  nm) in our experiment. In this Symposium, we present the wavelength dependency of photo catalytic activity, electronic structure and the influence of the crystal structure on them, and compare these with those of  $\text{InNbO}_4$  and  $\text{InTaO}_4$ . The electronic structure of  $\text{BiVO}_4$  is also discussed in order to achieve a systematic understanding of the whole photocatalytic reaction since  $\text{BiVO}_4$  is known to be active for the oxygen evolution in the visible range [2]. Moreover, we show some results from first principles molecular dynamics simulations for the

adsorption of water molecule on the  $\text{InVO}_4$  surface.

References:

- [1] Z. Zou et al. Chem. Phys. Lett. 332 (2000) 271.
- [2] A. Kudo et al. Catal. Lett. 53 (1998) 229.

#### V5.9

**TEXTURE EVOLUTION IN ZR GRAIN-REFINED BY EQUAL CHANNEL ANGULAR PRESSING.** S.H. Yu, H.S. Ryoo, D.H. Shin and S.K. Hwang, School of Materials Science and Eng. Inha Univ., Incheon, KOREA.

To explore a possibility of obtaining an ultra fine grain size in hcp materials, equal channel angular pressing (ECAP) was applied to commercially pure Zr. Starting from  $20\mu\text{m}$ , a grain size of  $200\text{nm}$  was obtainable by the severe plastic deformation performed at ambient temperature as well as at  $350^\circ\text{C}$ . For ensuring crack-free specimen during the severe deformation it was necessary to adopt different die designs at the two processing temperatures. With a proper choice of the processing route, the refined grains could be made into an equiaxed shape surrounded by high angle boundaries. During the initial stage of ECAP at room temperature numerous mechanical twins were generated. Crystallographic texture of specimens underwent a drastic change from a strong  $\langle\{1\}\{1\}\{2\}0\rangle$  fiber texture in the initial state into a strong (0002) and a medium  $\langle\{1\}\{0\}\{1\}0\rangle$  texture with respect to the planes of the maximum shear stress. Based on the texture information it was concluded that a dual  $\langle\{a\}\rangle$  slip mechanism accommodated the major portion of the large shear strain during ECAP. In the subsequent recrystallization annealing heat treatment, the nano-scale grain size of the severely deformed Zr increased to  $6\mu\text{m}$ . Using electron back-scattered diffraction equipment, the grain boundary character distribution (GBCD) of recrystallization-annealed specimen was analyzed. Accumulated fraction of the high angle boundaries in the range of  $20$ - $40^\circ$  occupied most of the boundary area. Using a Monte-Carlo computer simulation of the microstructure it was predicted that abnormal grain growth would not occur in this system and that the general pattern of GBCD in the annealed specimen would be maintained during normal grain growth.

#### V5.10

**ELECTRICAL PROPERTIES OF SODIUM LAMP BALLAST WITH PIEZOELECTRIC CERAMICS.** Dong Soo Paik, Chung Eui Seol, Hong Gyu Lee, Joon Koo Park, Kyoung Soo Baek, E2S Technologies Ltd, Whasung, KOREA.

Dielectric and piezoelectric materials are widely used for various applications such as resonators, transducers, filters, and transformers. In particular, the piezoelectric transformers are applied for display devices as an inverter for CCFLs (Cold Cathode Fluorescent Lamps) with output power of less than 20W because of benefits such as miniaturization, lightweight, and high reliability. General discharge lamps have similar properties with the CCFL, i.e. requiring a high initial voltage to light them up. However, since the general discharge lamps such as sodium and metal-halide lamps are operating with a large current up to a few amperes under the commercial ac source, ballasts for these discharge lamps require a piezoelectric materials which can stand against very large current and have functions of resonating, condensing, and setting up voltage. A sodium lamp with an output of 200W was ballasted using a piezoelectric material without an igniter circuit currently included in sodium lamp ballasts. The electrical characteristics of the sodium lamp driven by the piezoelectric ballast were satisfied with the requirements such as tube current and voltage, lumen and life. The operating frequency and starting-up voltage was  $41\pm 1\text{kHz}$  and 3,300V, respectively. From the fabricated piezoelectric ballast, the efficiency above 90% was obtained because the substitution of piezoelectrics for the wound transformer minimized the electrical loss.

#### V5.11

**STRUCTURE AND COMPOSITION OF CHEMICALLY DEPOSITED ANTIMONY SELENIDE THIN FILMS.**

Y. Rodriguez-Lazcano, Y. Peóoa, M.T.S. Nair, P.K. Nair, Universidad Nacional Autónoma de México, Centro de Investigación en Energía, Temixco, Morelos, MEXICO.

Thin films of antimony selenide were obtained from deposition baths containing sodium selenosulfate and different soluble complexes of antimony with citrate, tartrate and thiosulfate as sources of selenide and antimony(III) ions. X-ray diffraction patterns of the films annealed at  $300$  -  $350^\circ\text{C}$  under nitrogen (100mTorr) have shown the presence of antimony(III) oxide and antimony(III) selenide. The elemental composition of the films was analyzed by electron microprobe technique. The films are photoconductive and exhibit a high resistivity in the dark. The optical band gap in the films vary in the range of  $1.0$  -  $1.8$  eV, depending of the bath composition. This suggests possible application of the films as absorber materials in photovoltaic conversion. Variation in the electrical and optical

properties of the films depending on the bath composition will be presented.

#### V5.12

ELECTRICAL AND OPTICAL PROPERTIES OF ZnO:Al THIN FILM BY FACING TARGETS SPUTTERING SYSTEM. M.J. Keum, J.S. Yang, H.W. Choi, K.H. Kim, Kyungwon Univ., Dept of Electrical Information Eng., Kyunggi-do, KOREA; S.K. Shin, Dong Hae Univ., Dept of Electrical Eng., Kangwon-do, KOREA; I.H. Son, Shinsung College., School of Electrical., Chungnam, KOREA.

ZnO with hexagonal wurzite structure is a wide band gap n-type semiconductor and interesting material over a wide ranges. ZnO films can be prepared to obtain high transparency in the visible range, low resistivity, stability of chemical and stability in hydrogen plasma including many foreign materials such as Al, In. In this work, we prepared ZnO:Al thin film by Facing Targets Sputtering system with Zn metal target and ZnO:Al( $\text{Al}_2\text{O}_3$  2wt%, 4wt%) ceramic target at total working gas pressure 1mTorr, substrate temperature R.T and  $200^\circ\text{C}$ . ZnO:Al thin film's crystallography, electrical and optical characteristics with  $\text{O}_2$  gas flow rate were measured and evaluated.

#### V5.13

INFLUENCE OF SYNTHESIS AND SINTERING CONDITIONS ON LSM MICROSTRUCTURE. Marcia C. Brant, Fernando S. Lameiras, CNEN/CDTN, BRAZIL; Jaqueline Paulo, Rosana Z. Domingues, UFMG, BRAZIL.

Three different calcination temperatures were used to produce  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSM) powder, with variable particle sizes. The LSM powder was synthesized by a Pechini-type technique. This technique is based on polyesterification between citric acid and ethylene glycol. The control of the temperature of processing and calcination allowed the production of monophasic LSM powders. These powders showed large surface area (around  $14\text{ m}^2/\text{g}$ ). The powders were compacted in the shape of cylindrical pastilles and sintered at temperatures ranging between 1273 and 1573 K for two hours. The microstructural analysis was performed by treating images obtained by scanning electron microscopy. Also, the porosity and density of the pastilles were analyzed. The next step is to study the behavior of these pastilles as a cathode.

#### V5.14

ABSORBER FILMS OF  $\text{Ag}_2\text{S}$  AND  $\text{AgBiS}_2$  PREPARED BY CHEMICAL BATH DEPOSITION. Airez Nuñez Rodriguez, M.T.S. Nair and P.K. Nair, Universidad Nacional Autónoma de México, Centro de Investigación en Energía, Temixco, Morelos, MEXICO.

$\text{Ag}_2\text{S}$  thin films of 50 nm to 250 nm in thickness were deposited at  $70^\circ\text{C}$  on glass substrates immersed in a bath mixture containing silver nitrate, sodium thiosulfate and dimethylthiourea. When the films are heated in nitrogen at temperatures  $200^\circ\text{C}$  to  $400^\circ\text{C}$ , crystallinity is improved and XRD pattern similar to that of acanthite is observed. These films possess electrical conductivity of  $10^{-3}\text{ (ohm cm)}^{-1}$ , are photoconductive and exhibit an optical band gap of 1.3 eV. When  $\text{Ag}_2\text{S}$  thin film is deposited over a thin film of  $\text{Bi}_2\text{S}_3$ , also obtained by chemical bath deposition from bismuth nitrate, triethanolamine and thioacetamide, and heated at  $300^\circ\text{C}$  to  $400^\circ\text{C}$  in nitrogen, a ternary compound,  $\text{AgBiS}_2$ , is formed. This material has an electrical conductivity of  $10^{-3}\text{ (ohm cm)}^{-1}$ , also is photoconductive and possesses an optical band gap 1.1 eV.

#### V5.15

STRUCTURAL PARAMETERS DECIDING THE ELECTRO-CHEMICAL PERFORMANCES OF CARBON ANODES IN LITHIUM ION SECONDARY BATTERIES. Zheng Honghe, Wang Jianji Department of Chemistry, Henan Normal University, Xinxiang, PR CHINA; Xu Zhongyu, College of Materials Science and Engineering, Hunan University, Changsha, PR CHINA.

The performances of carbon anodes in lithium ion secondary batteries, as we know, depend strongly on the microstructure, texture, crystallinity and morphology of the negative materials. Active investigations have been going on in the recent years attempting to identify the key parameters of carbon materials deciding the electrochemical properties of carbon anodes while structural parameters of the carbon materials depend on their preparation process and precursor materials. We reported herein the experimental results of electrochemical performances of petroleum coke and mesocarbon microbeads used as negative electrodes in lithium ion secondary batteries after high temperature treatment (HTT) under different maximum temperatures. Spectroscopic studies (XRD, IR and Raman) have been employed in this study to get structural and surface analysis of the anode materials. Comparison of the electrochemical performances and microstructural characteristics of these electrode materials indicates that, apart from the specific surface which is an important factor determining the first irreversible

capacity loss in electrochemical cycles, the existence of a certain amount of SP3 bond in the carbon materials is also essential in preventing the co-intercalation of solvent molecules into graphite layers and /or crystalline defects.

#### V5.16

ENHANCEMENT OF INITIAL COULOMETRIC EFFICIENCY OF  $\text{Co}_3\text{O}_4$  BY BALL-MILLING WITH NICKEL. Yong-Mook Kang, Ki-Tae Kim, Youn-Seon Kang, Ho Lee and Jai-Young Lee, Dept of MS&E, Korea Advanced Institute of Science and Technology, Taejeon, SOUTH KOREA.

Graphite has been widely used as the anode material of commercial Li-ion secondary battery. With the growing demands of high capacity secondary battery, the low capacity of graphite (theoretical capacity: 372 mAh/g) has been thought to be the limiting factor in wide applications and a new anode material with high capacity has been sought for. Of many materials, Co oxide showed the best anode performance. It showed very high capacity of about 700mAh/g and good cycle life (93.4% of initial capacity is maintained after 100 cycles.) However, because its irreversible capacity comes to about 30% of initial capacity, the initial coulometric efficiency should be improved in the first place to commercialize Co oxide as the anode material of Li secondary battery. Because Co oxide was reported to be cycled through formation and decomposition of  $\text{Li}_2\text{O}$ , a poor decomposition of  $\text{Li}_2\text{O}$  at the first cycle can be looked upon as the cause of high initial irreversible capacity. Therefore, at first, addition of Ni to Co oxide was selected as a method to decrease the initial irreversible capacity, but it didn't make an eminent effect. Ball-milling method is known to be very effective method that connects original material with additive material. As a result of ball-milling with Ni, Co oxide well connected with Ni was obtained and as expected, its irreversible capacity was decreased from 30% to 20%.

#### V5.17

INTERACTION BETWEEN BINDER AND GRAPHITE IN THE ADNODES OF LITHIUM ION BATTERIES: RHEOLOGICAL PROPERTIES AND SURFACE CHEMISTRY. Mikyong Yoo, Curtis W. Frank, Stanford University, Dept. of Materials Science and Engineering, Stanford, CA; Shoichiro Mori, Mitsubishi Chemical Corp., Tsukuba Research Center, Ibaraki, JAPAN.

In rechargeable lithium ion batteries, anodes predominantly consist of graphite bound by polymeric binders like poly(vinylidene fluoride) (PVDF). Polymeric binder, which is necessary to provide sufficient mechanical strength to the electrodes, can be subjected to the reaction between lithium ions and electrolyte, which takes place at the carbon surface. It is known that the type and amount of the binder affect not only mechanical properties but also electrochemical performance of anodes such as electrochemical capacity, efficiency, charging-discharging rate and cyclic life. However, the interaction and interface between graphite and binders have not been studied extensively. In this report, we first manifested the interaction between graphite and binder by studying the viscosity of slurries before doctor-blading. We correlated this processing condition with the surface chemistry and morphology of PVDF in graphite/PVDF composite film. It shows that low viscosity slurries turn out to have more inhomogeneous distribution of PVDF than those with high viscosity. We observed that polymeric binders prefer to reside at the edge and grain boundaries of graphite rather than in the basal plane, and the degree of homogeneity is affected by the molecular weight and modified functionality of PVDF, and different solvents used in mixing. We will also show the adhesion strength in terms of binders and solvent, which can be explained by different crystallinity of PVDF.

#### V5.18

HYDROGEN STORAGE IN METAL NITRIDE SYSTEMS. Ping Chen, Zhitao Xiong, Jizhong Luo, Jianyi Lin, Kuang Lee Tan, National University of Singapore, Dept of Physics, SINGAPORE.

Hydrogen can be reversibly stored in metal nitride system at moderate temperature and pressure. Lithium nitride, as an example, can absorb more than 11 wt% of hydrogen at temperature lower than  $200^\circ\text{C}$  with lithium amide and hydride formed accordingly. More than half of the absorbed hydrogen can be released at temperature around  $270^\circ\text{C}$ . TPR, PCI and XRD were applied to study the hydrogen absorption/desorption properties and the structural changes during hydrogenation process.

#### V5.19

PZT AND ELECTRODE ENHANCEMENTS OF MEMS BASED MICRO HEAT ENGINE FOR POWER GENERATION. A.L. Olson, L.M. Eakins, B.W. Olson, D.F. Bahr, C.D. Richards, R.F. Richards, Mechanical and Mats Engr, Washington State Univ, Pullman, WA.

Lead Zirconate Titanate (PZT) with its high energy density is an ideal material for energy generation. Our laboratory has been

producing a micro power generator, the P3, in which a PZT generator is used to convert mechanical energy to usable electrical energy. The membrane generator consists of a Si/SiO<sub>2</sub> membrane, a Ti/Pt bottom electrode, layers of PZT between 300 and 1000 nm thick, and a top electrode, with lateral dimensions of mm and thickness dimensions of microns. In this work, the effects of materials and their properties on power generation for the membrane generator performance are evaluated. The effects of pre-anneal temperature on the bottom electrode structure was studied via AFM and AES to compare roughness, grain size, and diffusion effects on PZT adhesion and yield. With an optimized bottom electrode for yield and adhesion, the electrode yield was studied for various PZT thickness and electrode areas, two geometric parameters effecting defect densities. Various etching geometries on the PZT layers of the generator membrane were also studied as a method to reduce strain energy stored in the PZT film, thus increasing the strain at failure in these devices. The overall performance of the device is discussed, with single membranes capable of generating in excess of 1 V having been demonstrated operating between 200 and 500 Hz.

#### V5.20

HIGH TEMPERATURE-LOCAL CRYSTAL STRUCTURE OF Sc<sub>2</sub>O<sub>3</sub>-DOPED ZrO<sub>2</sub>. Yoshinori Arachi, Takeshi Asai, Faculty of Engineering, Kansai University, Suita, JAPAN.

Zirconia-based ionic conductors have been utilized as an electrolyte material in Solid Oxide Fuel Cells (SOFCs) because of their suitable properties such as high electrical conductivity or chemical stability under reducing and oxidizing atmospheres. Sc<sub>2</sub>O<sub>3</sub> doped zirconia shows the highest oxide ionic conductivity of other zirconia-based electrolytes in the range of 700-1000°C. However, there has been little understanding of the fast ionic conductivity behavior in detail. In this study, we investigated local atomic structure of Zr and dopant cations in 11mol%Sc<sub>2</sub>O<sub>3</sub>-doped(11ScSZ) and 8mol%Y<sub>2</sub>O<sub>3</sub>-doped ZrO<sub>2</sub>(8YSZ) by means of High temperature-X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS). The synchrotron radiation experiments were performed at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute. The XRD patterns of 11ScSZ at room temperature showed a rhombohedral symmetry which was slightly distorted to a cubic lattice, whereas 8YSZ a cubic phase. The XAFS spectroscopy indicated that oxygen vacancies introduced by Sc were located at nearest neighbors, while those by Y at nearest neighbors of Zr atoms. The change in the coordination number of the next nearest neighbor of Zr, Zr-Cations for 11ScSZ showed a remarkable decrease with increasing temperature, compared with the case of 8YSZ. 11ScSZ had a more disturbance to the surrounding next nearest neighbors than 8YSZ. Based on these results, the high temperature-local crystal structure will be discussed in connection with the noble ionic conductivity. On the other hand, a decrease of the bonding distance between cation and oxygen was observed by XAFS analysis, although the mean bonding distance calculated from the results of XRD increased linearly with increasing temperature. It is related to anharmonic vibration observed by the temperature dependence of XAFS. The detailed analysis is under investigation and will be discussed.

#### V5.21

PREPARATION OF DOPED LANTHANUM GALLATE ELECTROLYTE FOR SOFC BY PULSED LASER DEPOSITION. Seiji Kanazawa, Takeshi Ito, Kenji Yamada, Toshikazu Ohkubo, Yukiharu Nomoto, Department of Electrical and Electronic Engineering, Oita University, Oita, JAPAN; Tatsumi Ishihara, Yusaku Takita, Department of Applied Chemistry, Oita University, Oita, JAPAN.

Sr-Mg-Doped LaGaO<sub>3</sub> oxide, with the composition La<sub>1-x</sub>Sr<sub>x</sub>Ga<sub>1-y</sub>Mg<sub>y</sub>O<sub>3-(x+y)/2</sub> (LSGM) has shown superior oxide ion conductivity. It is a promising candidate for an electrolyte in solid oxide fuel cells (SOFC). If high quality LaGaO<sub>3</sub> thin films can be prepared, an operation of solid oxide fuel cells at intermediate temperatures may be possible. In this study, LSGM films were prepared by pulsed laser deposition (PLD) technique. Pulsed laser deposition is considered to be a promising technique for the preparation of the films with preserving stoichiometry. In the vacuum chamber, Sr-Mg-doped LaGaO<sub>3</sub> target was set on the rotating target holder. A KrF excimer laser was introduced into the chamber at an incident angle of about 45°. The laser energy density at the target was about 3J/cm<sup>2</sup>. The LSGM film was deposited on the NiO substrate without heating in argon ambient gas. The NiO substrate can be used directly in the fabrication of the SOFC as an electrode. The deposited LSGM films were characterized with measurements of X-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS) and scanning electron microscopy (SEM), respectively. As-deposited film had the amorphous structure. After post annealing at 1000°C for 6 hours, crystalline structure of LaGaO<sub>3</sub> was obtained. Other crystalline structures such as La<sub>2</sub>O<sub>3</sub>, La<sub>4</sub>Ga<sub>2</sub>O<sub>9</sub> phases were also observed in some other films depending on the preparation condition.

The films with a thickness greater than several 10nm showed a uniform and dense morphology. Using thick films prepared no gas leakage was confirmed, which is an important factor as an electrolyte of the fuel cell. The atomic component ratio of the deposited films was slightly deviated from that of the target. It should be improved by optimizing the deposition conditions.

#### V5.22

SINGLE-SOURCE APPROACH FOR THE GROWTH OF I-III-VI THIN FILMS. Mohammad Afzaal, Paul O'Brien, Jin-Ho Park, The University of Manchester, Dept of Chemistry and The Manchester Materials Science Centre, Manchester, UNITED KINGDOM; Theivanayagam C. Deivaraj, Jagadees J. Vittal, National University of Singapore, Dept of Chemistry, SINGAPORE.

The ternary chalcopyrite semiconductors I-III-VI are currently used for photovoltaic solar cell applications. In this study, various types of I-III-VI (I = Ag, Cu; III = In, Ga; VI = S) thin films were prepared from a series of single-source bimetalorganic precursors, e.g. [(Ph<sub>3</sub>P)<sub>2</sub>AgIn(SCOR)<sub>4</sub>] (R = alkyl) by aerosol assisted chemical vapour deposition (AA-CVD) and low pressure metalorganic chemical vapour deposition (LP-MOCVD). The compounds can be used as single-source precursors for the deposition of ternary compounds (I-III-VI) by one-pot reaction using CVD process and they are found to be air stable, which is favourable in comparison with metal alkyl compounds, which are found to be pyrophoric. The optimum growth temperature for the preparation of these films on glass and Si(111) substrates, was found to be above 400°C in terms of crystallinity, although deposition occurred at low temperatures. The films have been investigated using XRPD, SEM, EDS and XPS, as well as other characterization techniques. SEM analysis shows that all films are microcrystalline but have different morphologies depending on the growth temperatures. XRPD results show evidence of the crystalline nature of these films. The results of this comprehensive study will be presented and discussed.

#### V5.23

DIRECT-WRITE INKJET PRINTING AS A DEPOSITION METHOD FOR PHOTOVOLTAIC MATERIALS. Lee Smith, Alex Miedaner, Tanya Rivkin, Jeff Alleman, John Perkins, Calvin Curtis and David Ginley, National Renewable Energy Laboratory, Golden, CO.

Inkjet printing is an inexpensive, direct-write approach for fabrication of medium resolution electronic devices. Many components of photovoltaic cells, including metals, transparent conductors, semiconductors, dielectrics and polymers, can be printed from liquid or nanoparticle precursors using the inkjet. This eliminates the need for complicated, expensive deposition and processing steps. An inkjet printing system based on commercially-available Microfab print heads has been assembled. A substrate heater mounted on a high-resolution x-y translation stage completes the system. The inkjet system has a modular design that allows flexibility for printing a wide variety of materials, dissolved or suspended in both aqueous and organic solvents, over a range of substrate temperatures from 25 to 300°C. Printing parameters and substrate motion are controlled by computer through a custom Labview interface. The system has been used to print Ag and metal oxide materials such as ZnO, SnO<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and (Ba,Sr)TiO<sub>3</sub> using both chemical and nanoparticulate precursors. Line widths of 100 microns and layer thicknesses up to 5 microns have been achieved. The design, development and performance of this inkjet printing system will be discussed.

#### SESSION V6: MATERIALS FOR POWER IN SPACE

Chair: Larry Kazmerski  
Thursday Morning, April 4, 2002  
Golden Gate A3 (Marriott)

#### 8:15 AM \*V6.1

MATERIALS FOR SOLAR PHOTOVOLTAIC ENERGY CONVERSION IN SPACE. Dennis J. Flood, North Coast Initiatives Ltd., Oberlin, OH.

For decades, single crystal silicon was the most studied and used material for solar photovoltaic energy conversion for both terrestrial and space applications, despite the wide differences in device requirements for the two operating environments. Space solar photovoltaic energy conversion has been driven predominately by performance: high efficiency, reliability and lifetime are chief among them. Terrestrial solar energy conversion, on the other hand, has been driven hard by extreme low cost considerations, in addition to the above performance requirements. The two fields embarked down separate materials pathways almost from the start of the early DOE programs. The space community has historically sought performance gains by exploring new single crystal materials such as GaAs, InP,

and GaInP, and efficiency enhancing structures such as multiple band gap cells (MBG.) The terrestrial community, meanwhile, has moved aggressively toward thin film materials in its search for low cost. While the fastest growing segment of today's space market is the triple junction GaInP/GaAs/Ge high efficiency cell, new cost pressures brought on by more and more commercial space activity and the growth in space solar array size have turned the space community's focus on high performance thin film materials as well. This paper will highlight the important past materials developments for space solar cells and to what extent they represent current performance requirements that must be met by thin film solar cells if they are to be successfully used in space. The paper will conclude with a description of recent work on thin film solar cells for space application by both NASA and the Air Force.

#### 8:45 AM \*V6.2

**MATERIALS LIMITATIONS IN BATTERIES FOR SPACE APPLICATIONS.** Margot Wasz, The Aerospace Corporation, Energy Technology Department, Los Angeles, CA.

The different batteries used in satellites and launch vehicles have unique materials issues that impact usage and usable life of the batteries. This paper discusses the materials-specific limitations and challenges in traditional and emerging battery chemistries for space applications including nickel-cadmium, nickel-hydrogen, lithium-ion, and silver-zinc chemistries. Irreversible changes in nickel and cadmium electrodes reduce capacity and may lead to shorting mechanisms over the life of the cell. Lithium-ion batteries suffer from irreversible changes due to the development of surface layers on the electrodes. Furthermore, these batteries can be irreparably damaged by overcharge and overdischarge driving the need for more sophisticated charge control electronics that increases the weight of the power system. Finally, despite the maturity of the technology, attack of the cellophane separator in silver-zinc cells by the caustic electrolyte limits useable life of these batteries and affects prelaunch operations due to processing constraints.

#### 9:15 AM V6.3

**ULTRALIGHT AMORPHOUS SILICON ALLOY PHOTOVOLTAIC MODULES FOR SPACE APPLICATIONS.** K.J. Beernink, G. Pietka, J. Noch, K. Younan, D. Wolf, A. Banerjee, J. Yang, and S. Guha, United Solar Systems Corp., Troy, MI; S.J. Jones, Energy Conversion Devices, Inc., Rochester Hills, MI.

Future space missions will require photovoltaic devices with high specific power (W/kg). Multi-junction, thin-film amorphous silicon alloy solar cells are well suited to the space environment due to irradiation resistance, a low temperature coefficient of output power, and light weight. In particular, United Solar's amorphous silicon-based modules have been tested on MIR with only minimal degradation. Here we report on two approaches to increase the specific power of these cells. The near-term approach uses a thinned 1 mil thick stainless steel substrate, while the longer-term approach uses a light-weight Kapton (polyimide) substrate. In both cases, a textured Ag/ZnO back reflector/contact, triple-junction spectrum-spitting semiconductor layers, and a transparent conductor anti-reflection coating/contact layer are deposited. Current-collecting wire grids and bus bars are added to complete the modules. Various enhancements to the materials in the semiconductor layers are utilized to increase the efficiency. The amorphous silicon i-layer of the top cell is deposited so that it is near the transition to microcrystallinity; the p-layers are microcrystalline; and the ratio of Si to Ge in the i-layers for the middle and bottom cells is graded to improve carrier collection. Data is presented on the properties of the materials as regards solar cell performance. Modules of area 460 cm<sup>2</sup> on stainless steel substrates with aperture area efficiency  $\approx 10\%$  and specific power  $\approx 500$  W/kg are presented, as well as 412 cm<sup>2</sup> modules on Kapton with aperture area efficiency of 9.5 to 10% and specific power  $\approx 700$  W/kg, all under AM0 conditions. Details of the fabrication and device design considerations to further increase specific power to over 1000 W/kg will be discussed.

SESSION V7: DISORDERED AND NANOSCALE  
MATERIALS FOR ENERGY APPLICATIONS  
Thursday Morning, April 4, 2002  
Golden Gate A3 (Marriott)

#### 10:00 AM V7.1

**FABRICATION OF NEW NANOPOROUS CARBONS USING NANOSTRUCTURED SILICAS AS TEMPLATES AND THEIR APPLICATIONS TO SUPERCAPACITORS.** Taeghwan Hyeon, Jinwoo Lee, Sangjin Han, Kwonnam Sohn, and Minsuk Kim, Seoul National University, Seoul, KOREA.

We have developed new synthetic procedures to fabricate various nanoporous carbons using nanostructured silica materials as

templates. The carbonization of carbon precursors/silica nanostructures followed by the removal of the silica templates generated nanoporous carbons with various pore size and structures. The structures of silica templates dictate the pore structures of the nanoporous carbons. Nanoporous carbons with high pore volumes of  $> 4$  cc/g and uniform pore sizes of 4 nm  $\sim$  10 nm have been produced using silica sol nanoparticles and in-situ generated silica nanofiber network as templates (Chem. Mater. 2000, 12, 3337; Chem. Commun. 1999, 1955; Carbon 1999, 37, 1645). Mesoporous carbons with regular 3-dimensionally interconnected  $\sim 2$  nm pore arrays have been synthesized using mesoporous silicas as templates. The incorporation and carbonization of carbon precursors inside the nanopores of the mesoporous silica followed by the removal of templates generated mesoporous carbons with regular pore dimensions of 2 $\sim$ 5 nm (Chem. Commun. 1999, 2177; Adv. Mater. 2000, 12, 359). New mesocellular carbon foams (MCF) were fabricated using mesocellular aluminosilicate foam as a template. These MCFs are composed of uniform cells with diameter of  $\sim 30$  nm and window size of  $\sim 15$  nm (J. Am. Chem. Soc. 2001, 123, 5146). We fabricated carbon capsules with hollow  $> 100$  nm macroporous core/3 nm mesoporous shell (HCMS) structures using the submicrometer-size solid core/mesoporous shell (SCMS) silica spheres as templates (Adv. Mater. 2001, in press). These nanoporous carbons have been successfully applied as electrode materials for supercapacitors. These nanoporous carbons exhibited excellent performance for electrochemical double layer capacitors (EDLC) (J. Electrochem. Soc. 2000, 147, 2507). RuO<sub>2</sub> nanoparticles have been immobilized onto the large pore sized nanoporous carbons and they were utilized as electrode materials of supercapacitors that combine characteristics of both electrochemical double layer capacitance and pseudo-capacitance.

#### 10:15 AM V7.2

**APPLICATION OF CARBON NANOTUBE-PEROVSKITE COMPOSITES AS ELECTRODE MATERIAL FOR RECHARGEABLE Zn/AIR BATTERIES AND FUEL CELLS.** Anke Weidenkaff, Stefan G. Ebbinghaus, Armin Reller, University of Augsburg, Solid State Chemistry, Augsburg, GERMANY; Thomas Lippert, Macarena Montenegro, Paul Scherrer Institute, Dept. General Energy Research, Villigen, SWITZERLAND.

The development of oxygen electrode materials that will operate in anodic and cathodic modes will play a key role in the technical realization of electrically rechargeable air based batteries and in solid oxide fuel cell technologies. Efforts to develop oxygen electrode catalysts that will operate in both anodic and cathodic mode are confronted with a major problem: The oxygen reduction and generation reactions in aqueous media are irreversible ( $E(\text{O}_2\text{-gen.}) > E(\text{O}_2\text{-red.})$ ) even at moderate temperatures. This irreversibility causes efficiency losses and serious lifetime problems of the catalyst and its support material. Consequently, it is necessary to systematically investigate new catalytically active materials and synthesis routes in order to create nano-meter sized catalyst particles, which will be homogeneously dispersed in a conductive and stable support material. Suitable electrocatalyst-candidates have been studied and identified among the perovskites. Calcium, Barium and Strontium substituted Lanthanum Cobaltate nanoparticles were synthesized by sol-gel- and microemulsion processes. Epitaxial thin films of these materials were prepared by pulsed reactive crossed-beam laser ablation. A carbon nanotube-perovskite composite material was prepared by a catalytic hydrocarbon dissociation reaction on metal oxide nanoparticles. The materials were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Extended X-ray Absorption Fine Structure (EXAFS), and high resolution transmission electron microscopy (HRTEM). The electrochemical activity of the samples for oxygen evolution was measured by a three-electrode arrangement. With the combination of the properties of the perovskite and the carbon nanotubes in a carbon nanotube/metal oxide-composite the time consuming purification process for carbon nanotubes can be avoided, and the electrode stability as well as the carbon/metal oxide interface can be enhanced.

#### 10:30 AM V7.3

**PREPARATION AND CHARACTERIZATION OF NANOSTRUCTURED FeS<sub>2</sub> AND CoS<sub>2</sub> FOR HIGH-TEMPERATURE BATTERIES.** Ronald A. Guidotti<sup>1</sup>, Jinxiang Dai<sup>2</sup>, Jeff Roth<sup>2</sup>, and David E. Reisner<sup>2</sup>. <sup>1</sup>Sandia National Laboratories, Albuquerque, NM. <sup>2</sup>US Nanocorp Inc., Farmington, CT.

Conventional thermally activated ("thermal") batteries employ pyrite (FeS<sub>2</sub>) as the primary cathode material with Li(Si) and Li(Al) alloys as the anode. These batteries are ideal for power sources for many military applications (e.g., missiles) because of their long shelf life. This technology is also being considered for potential domestic applications such as power supplies for geothermal borehole data logging. Pyrite is a relatively abundant, inexpensive naturally occurring mineral. However, before it can be used for electrochemical applications, it must be ground, sized, and then purified to remove

electroactive impurities and inert gangue material. The overall processing adds greatly to the cost of the final cathode material. Synthetic pyrite has a number of advantages over natural pyrite. This material is typically nanostructured, which results in a much higher surface area and a correspondingly higher current-carrying capability. It can be easily prepared in high purity in large scale from inexpensive precursors. This avoids much of the nonhomogeneity associated with natural pyrite from various sources. The Co analogue to pyrite,  $\text{CoS}_2$ , is preferred to pyrite for applications involving high current densities, due to its much higher electronic conductivity and thermal stability. In this paper, we report on the preparation of synthetic nanostructured  $\text{FeS}_2$  and  $\text{CoS}_2$  using a relatively inexpensive aqueous process. This avoids the material and handling difficulties associated with a high-temperature approach. An aqueous approach also allows ready scale-up to a pilot-plant size facility. The  $\text{FeS}_2$  and  $\text{CoS}_2$  were characterized with respect to their physical and chemical properties. These materials were then incorporated into catholyte mixes for testing in single cells and batteries over a range of temperatures and discharge conditions. The results of these tests are presented and compared to the performance of natural pyrite. The results of preliminary tests using plasma-sprayed electrodes made with synthetic pyrite are also discussed.

#### 10:45 AM V7.4

CHARGE DENSITY IN DISORDERED BORON CARBIDE  $\text{B}_{12}\text{C}_3$ : AN EXPERIMENTAL AND AB-INITIO STUDY. Gianguido Baldinozzi, Michael Dutheil, Structures, propriétés et modélisation des solides, CNRS-Ecole Centrale Paris, Châtenay- Malabry, FRANCE; David Simeone, Lab de microstructure et étude de l'endommagement, CEA, CEN Saclay, Gif-sur-Yvette, FRANCE; Andreas Leithe-Jasper, NIRIM, Tsukuba Ibaraki, JAPAN.

The experimental charge density study of boron carbide  $\text{B}_{12}\text{C}_3$  single crystals at different temperatures allows a quantitative description of the electron density responsible for the chemical bonding. These results, based on direct observations, are compared to the previous models for the bonding. The description suggests structural features far more complex than the ones suggested by actual qualitative models. The effects of chemical substitution, the characteristics of the interatomic bonding, the bond strength, the charge transfer are discussed. We will present the structural refinements performed on a high quality single crystal of stoichiometric  $\text{B}_{12}\text{C}_3$ , using different models of increasing complexity and discussing the validity of the approximations for each step. We will start with a standard structure refinement using spherical atomic factors, then discuss the static and dynamic disorder in the structure before refining the structure within the Hansen-Coppens multipolar formalism for the atomic scattering factors. The results obtained within this approximation are then interpreted and the topology of the chemical bonding is compared to the results obtained by ab-initio modelling in boron carbide and in similar structures.

### SESSION V8: THERMOELECTRICS

Chair: Ricardo Schwarz  
Thursday Morning, April 4, 2002  
Golden Gate A3 (Marriott)

#### 11:00 AM V8.1

ANOMALY OF THERMAL PROPERTIES IN THIN FILMS OF  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  SERIES FABRICATED AS THERMOELECTRIC MATERIALS. Yoshiaki Takata, Hajime Haneda, Yutaka Adachi, Yoshiaki Wada, Takefumi Mitsuhashi, Advanced Materials Laboratory, NIMS, Tsukuba, JAPAN; Makoto Ohtani, Tomoteru Fukumura, Masashi Kawasaki, Hideomi Koinuma, Tokyo Institute of Technology, Yokohama, JAPAN.

We evaluated the thermal diffusivity for composition-spread thin film  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ , mono layer  $\text{LaCoO}_3$  and  $\text{SrCoO}_3$ , and substrate  $\text{SrTiO}_3(100)$  using a novel technique of pump-probe laser system. The wave lengths of laser consist of a set of third harmonics 266 nm and a fundamental 800 nm. The result of our analysis shows that thermal diffusivities extremely change at between  $0.33 < x < 0.78$ .

#### 11:15 AM V8.2

ELECTROCHEMICAL DEPOSITION OF COBALT TRIANTIMONIDE NANOWIRES FROM NON-AQUEOUS SOLUTIONS. J.P. Klitzke, R. Gronsky, T.D. Sands, Univ of California, Berkeley, Dept of Materials Science & Engineering, Berkeley, CA; M.S. Martin-Gonzalez, A.L. Prieto, A.M. Stacy, Univ of California, Berkeley, Dept of Chemistry, Berkeley, CA.

Thermoelectric materials provide an important means for reliable solid-state refrigeration and power generation. It has been shown that two-dimensional electronic quantum confinement can enhance a materials thermoelectric figure of merit and the effect for one-dimensional confinement is predicted to be greater. The

skutterudite compound  $\text{CoSb}_3$  is a thermoelectric material whose thermal and electrical properties may be decoupled through doping to produce a filled skutterudite structure. We report the fabrication of  $\text{CoSb}_3$  nanowire arrays by simultaneous electrolytic deposition of Co and Sb from dimethyl sulfoxide (DMSO) solutions into porous alumina templates. Wire diameter is controlled by the growth parameters of the alumina templates.  $\text{CoSb}_3$  nanowires of 200 nm and 50 nm diameters have been produced. Wire composition may be adjusted by varying the cation concentration, deposition time, and potential in the electrolytic bath. Transformation of the as-deposited wires to the skutterudite phase is prompted by heat treatment. X-ray diffraction, EDS, and SEM experiments confirmed the formation of the  $\text{CoSb}_3$  skutterudite nanowires.