

SYMPOSIUM K

Solid-State Ionics

November 29 - December 2, 2004

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* Invited paper

8:30 AM *K1.1

Dynamical Aspects of Nanocrystalline Ion Conductors Studied by NMR. Paul Heitjans, Sylvio Indris and Martin Wilkening; Institut fuer Physikalische Chemie und Elektrochemie, Universitaet Hannover, Hannover, Germany.

In recent years the potential of nuclear magnetic resonance (NMR) to study ionic motion [1] has increasingly been exploited also in the case of nanocrystalline solids, i.e. polycrystalline materials with average grain sizes typically in the range from 5 to 50 nm [2]. We review NMR studies performed hitherto mainly in our laboratory on nanocrystalline ceramics. NMR relaxation measurements, NMR lineshape studies and multiple-time NMR methods give access to microscopic diffusion parameters like ionic jump rates and jump barrier heights. The nanocrystalline ceramics were prepared by high-energy ball milling or by inert gas condensation. Single-phase materials like CaF_2 , BaF_2 , LiNbO_3 , Li_xTiS_2 , Li_2O , LiBO_2 as well as nanocrystalline composites like $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O}:\text{Al}_2\text{O}_3$ were studied. In nearly all cases the diffusivity is dominated by the large volume fraction of interfacial regions. In addition to the interfacial diffusion pathways in the single-phase nanocrystalline ceramics, in the composite systems enhanced diffusivity pathways are generated by the interfaces between the ion conducting and the ion insulating components. The heterogeneous ion dynamics in the grains and the interfaces can be discriminated by the various NMR techniques. Comparison of the nanocrystalline with the microcrystalline and, in some cases, the amorphous counterpart materials yields information on the volume fraction and the microstructure of the diffusion pathways. [1] *Diffusion in Condensed Matter - Methods, Materials, Models*, P. Heitjans, J. Kaerger (eds.), Springer, Berlin 2004. [2] P. Heitjans, S. Indris, J. Phys.: Condens. Matter 15 (2003) R1257.

9:00 AM K1.2

Sodium Ion Conduction in Plastic Phases: Dynamic Coupling of Cations and Anions in the Picosecond Range.

Dirk F. Wilmer¹, Harald Feldmann¹, Ruediger E. Lechner² and Jerome Combet³; ¹Institute of Physical Chemistry, Muenster University, Muenster, Germany; ²Hahn-Meitner-Institut, Berlin, Germany; ³Institut Laue-Langevin, Grenoble, France.

The characterization of ion dynamics in fast ion conductors is both a fascinating and complicated task since we are dealing with a large number of interacting charged particles in a disordered environment. The situation is even more complex if we consider fast cation conducting rotor phases which combine high cation mobility with dynamic rotational disorder of their polyatomic anions. The conduction mechanism in the plastic phases of compounds like, e.g., lithium sulfate and sodium orthophosphate has thus been discussed for a long time, and an intense debate focused on the relevance of a possible dynamic coupling between the rotational and translational motion of anions and cations. We present results from simple computer simulations and model calculations for ion conducting rotor phases and compare them to experimental data from several quasi-elastic neutron scattering experiments on solid solutions of sodium orthophosphate and sodium sulphate, $x \text{Na}_2\text{SO}_4 \cdot (1-x) \text{Na}_3\text{PO}_4$. While pure sodium orthophosphate exhibits a sharp phase transition into its cubic rotationally disordered FIC phase at 598 K, the addition of even small amounts of sodium sulphate stabilizes the cubic phase of Na_3PO_4 even down to ambient temperature. At the same time, vacancies are created in the cation sublattice, and the conductivity increases. The first set of measurements, performed on the time-of-flight neutron spectrometer NEAT (Hahn-Meitner-Institut, Berlin) with an elastic energy resolution of about 100 μeV FWHM, turned out to monitor the anion reorientational motion only. In the case of sodium orthophosphate/sodium sulphate solid solutions, comparison of the experimental quasielastic intensities with results from a Monte-Carlo-type simulation indicates the involvement of sodium ions in the anion reorientational motion: cation and anion motions are coupled on the picosecond time scale. In a second set of experiments on the backscattering neutron spectrometer IN16 (Institut Laue-Langevin, Grenoble, France), we examined the same samples of at a much higher energy resolution, i.e., 1 μeV FWHM. Under these conditions, the quasi-elastic neutron scattering experiment is sensitive to the sodium ion diffusion only which allowed an extensive characterization of the cation long-range jump diffusion. The cation hopping motion is dominated by jumps between neighboring tetrahedrally coordinated sites, with a jump distance corresponding to a half the FCC lattice constant. Quasi-elastic neutron scattering experiments not only allowed a complete characterization of both the rotational and translational motion of anions and cations in a fast ion conducting rotor phase, but also a

strong dynamic coupling between anion and cation motions.

9:15 AM K1.3

Using Structure-Property Relationships to Select Among Candidate Systems for High-Temperature Proton Conductor Development. Scott A. Speakman¹, E. Andrew Payzant¹, Timothy R. Armstrong¹, Robert D. Carneim², Richard A. Lawson¹ and Bryan E. Freeman¹; ¹Metals and Ceramics Division, Oak Ridge National Lab, Oak Ridge, Tennessee; ²Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee.

High-temperature proton conductors could provide an enabling technology for cleaner and more efficient coal gasification and petrochemical processing, where an unadulterated hydrogen product must be produced from a reformat stream. They might additionally prove useful in devices such as fuel cells. Barium cerate-based ceramics that manifest the fastest proton conduction continue to prove unreliable and unstable in the harsh application environments. However, at present there is no clear choice for an alternative material system for development. Therefore, several crystal systems were selected for structure-property studies to evaluate the potential for optimization of protonic conduction. X-ray and neutron diffraction were used to characterize the crystal structures and in situ X-ray diffraction was used to evaluate materials for stability in environments representative of the operating conditions, particularly the stability in the presence of CO_2 . Ion transport properties were evaluated using in situ dc electrical conductivity measurements and hydrogen flux/diffusivity measurements. The following systems will be discussed: oxygen-deficient perovskite-derivatives based on calcium ferrite; doped lanthanum zirconate pyrochlores; pyrochlore-fluorite binary systems based on lanthanum zirconate and lanthanum cerate; layered perovskite-derivatives based on bismuth aluminate; and layered structures based on lanthanum tungstate and molybdate. Project funded by the U. S. Dept. of Energy Fossil Energy's Advanced Research Materials Program.

9:30 AM K1.4

Structure, proton incorporation and transport properties of ceramic proton conductor $\text{Ba}(\text{Ce}_{0.7}\text{Zr}_{0.2}\text{Yb}_{0.1})\text{O}_{3-\delta}$.

Yaping Li¹, Alexander I. Kolesnikov¹, James W. Richardson¹, Tae H. Lee², Chendong Zuo² and Uthamalingam Balachandran²; ¹Intense Pulsed Neutron Source Division, Argonne National Laboratory, Argonne, Illinois; ²Energy Technology Division, Argonne National Laboratory, Argonne, Illinois.

Perovskites based on Ba or Sr cerates doped with trivalent rare-earths have been studied intensively as high-temperature proton conductors. Dense ceramic samples with composition $\text{Ba}(\text{Ce}_{0.7}\text{Zr}_{0.2}\text{Yb}_{0.1})\text{O}_{3-\delta}$ (BCZY) were synthesized by solid state reactions, and their structures were characterized by Rietveld refinements of time-of-flight (TOF) neutron diffraction data collected for the samples at high-temperature and controlled atmosphere. The structural phase transition from orthorhombic Imma to cubic Pm3m was observed between 500 and 700°C in flowing 10ppm H_2/Ar gases. At 900°C, the sample was subsequently exposed to different oxygen partial pressures ($p\text{O}_2$, ranging from 10^{-17} to 10^{-23} atm) and water vapor pressures ($p\text{H}_2\text{O}$) up to 0.18 atm. The high-temperature phase with cubic structure was stable over the entire $p\text{O}_2$ and $p\text{H}_2\text{O}$ regime examined. The lattice parameters of BCZY, instead of following the normally expected trend with changing $p\text{O}_2$, were actually correlated with the increase of $p\text{H}_2\text{O}$, implying proton incorporation into the structures. The oxygen occupancy of BCZY was dependent upon both $p\text{O}_2$ and $p\text{H}_2\text{O}$, and an increase in oxygen content was observed with increased $p\text{H}_2\text{O}$ at roughly constant $p\text{O}_2$. The presence of H-containing species in the structure was confirmed by comparing both inelastic neutron scattering spectra and neutron diffraction data collected for dry and "wet" samples at 10K. The observed vibrational peaks at 104 and 150 MeV and lack of a peak around 420 MeV indicate the absence of hydroxyl groups (hydrogen covalently bonded to oxygen). Electrical conductivities of BCZY were investigated at different temperatures and $p\text{O}_2$ in both dry and wet conditions. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract No. W-31-109-ENG-38.

9:45 AM K1.5

Preparation and Hydrogen Pumping Characteristics of $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_3$ Thin Film.

Tae H. Lee¹, Bryan J. Harder², Chendong Zuo¹, Steve E. Dorris¹ and U. (Balu) Balachandran¹; ¹Energy Technology Division, Argonne National Laboratory, Argonne, Illinois; ²Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois.

High-temperature proton conductors are of great interest for their applications in solid state ionic devices such as solid oxide fuel cells, hydrogen separation membranes, steam electrolyzers, hydrogen pumps, and electrocatalytic membrane reactors. For the applications

using proton conductors as an electrolyte in high current-drain devices, thin film preparation is necessary to reduce electrical losses in the electrolyte. Extensive studies of bulk high-temperature proton conductors have been reported, but not thin-film proton conductors. In this study, we describe a method of preparing thin films of BaCe_{0.8}Y_{0.2}O₃ (BCY) and report its hydrogen pumping characteristics. Thin films of BCY were prepared by the colloidal spray deposition. Dense, crack-free BCY films with thickness of 10 μm and average grain size of 7 μm were successfully deposited on NiO/BCY substrates. Scanning electron microscopy showed that the film is uniform and well-bonded to the substrate. The hydrogen pumping properties of the BCY film were studied at temperatures of 500-900°C. The hydrogen pumping was performed with a galvanostat, and the evolution rate of hydrogen at the cathode side was measured with a gas chromatograph. Platinum was used as the cathode, and Ni/BCY was used as the anode after reduction of the NiO in the substrate. A maximum current density of 3.5 A/cm² was measured at 700°C using wet (3 vol.% of water) 80% H₂ and wet N₂ as the anode and cathode gases, respectively. At higher current density, the rate of hydrogen evolution deviates from Faraday's law due to partial reduction of the BCY film. This work is supported by U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory's Gasification Technologies Program, under Contract W-31-109-Eng-38.

10:30 AM K1.6
Structure-Property Relationships In Mixed-Conducting Hydroxide Ruthenium Oxide. Karen Swider-Lyons¹, Konrad Bussmann¹ and Wojciech Dmowski²; ¹Naval Research Laboratory, Washington, District of Columbia; ²Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee.

Hydrous RuO₂ (or RuO₂·xH₂O) is an attractive material for electrochemical capacitors because of its high specific capacitance (> 720 F/g). Its charge-storage capacity varies as a function of structural water content and is maximized after the as-received RuO₂·2.3H₂O material is heated at 150 °C to yield the composition: RuO₂·0.5H₂O. The high specific capacity of hydrous RuO₂ has been attributed to its high protonic and metallic conductivity that allows the rapid insertion and release of protons and electrons from its structure. This double-insertion mechanism has been supported by the characterization of its local- and medium-range structure. Although hydrous RuO₂ is amorphous to conventional X-ray diffraction (XRD), pair density function (PDF) analysis of high-energy XRD patterns indicates that the material is actually a composite of RuO₂ nanocrystals embedded in a hydrous matrix. The RuO₂ nanocrystals enable metallic conductivity and the hydrous boundaries facilitate protonic conduction. The magnetic properties of hydrous RuO₂ shed more information on its structure-property relationships. Magnetic susceptibility (MS) measurements of samples heated between 25 and 400 C show temperature-independent paramagnetism from room temperature to 100 K. Curie-Weiss behavior dominates below 70K indicating the presence of localized electrons. The concentration of localized electrons is approximately 4% in as-received hydrous RuO₂ (RuO₂·2.3H₂O) and decreases as the structural water of the RuO₂ is lowered, consistent with an increase in metallic conductivity. The localized spins are attributed to Ru³⁺ ions using corroborating evidence from electron spin resonance spectroscopy. The trends in the temperature-independent paramagnetism also suggest that the itinerancy of the electrons increases with decreasing water content in hydrous RuO₂. These findings are consistent with structural data from PDF analysis that show a concurrent increase in the particle size of the RuO₂ nanocrystals.

10:45 AM K1.7
Electron and Proton Conduction Facilitated by Nano-Size Cages in a Complex Oxide. Peter V. Sushko¹, Alexander L. Shluger¹, Katsuro Hayashi², Masahiro Hirano² and Hideo Hosono²; ¹Physics and Astronomy, University College London, London, United Kingdom; ²Materials and Structures Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, Japan.

Development of environmentally friendly hydrogen-based energy conversion devices requires a detailed understanding of properties and behaviour of hydrogenous species in materials. We present the results of a theoretical investigation of the atomic and electronic structure as well as formation and inter-conversion mechanisms of protons, hydride ions, and electrons in a nano-porous complex oxide 12CaO · 7Al₂O₃ (C12A7). Unusual properties of C12A7 are due to its structure formed by a positively charged framework, build from sub-nanometer sized cages, compensated by extra-framework O(2-) ions. It has been recently observed that the hydrogen treatment of the C12A7 results in a high protonic and, at higher temperatures, mixed protonic and electronic conductivity. Moreover, a large number of conduction electrons is formed and retained after the hydrogen-treated C12A7 samples are irradiated with the UV light [1]. We use an embedded cluster approach [2] to reveal the mechanisms of the defect reactions

and optical properties of the hydrogenous species. It is demonstrated that the formation of the protons and the hydride ions is due to dissociation of H₂ molecules into H-/H pairs in the nano-cages of C12A7. The H- ions occupy sites at the cage centers, where they are stabilized by the lattice relaxation, while the H ions bind to the cage-wall oxygen ions. The formation of the conduction electrons can be induced by the photo-ionization of H- ions with 4 - 4.5 eV light. An alternative mechanism of carrier electrons formation involves a thermally activated reaction of the hydride ions with the extra-framework O(2-) ions. We also discuss how the specific crystalline structure of the C12A7 framework can facilitate a high proton and electronic conduction. 1. K. Hayashi, S. Matsuishi, T. Kamiya, M. Hirano, H. Hosono, Nature, v.423, p.626, (2002) 2. P. V. Sushko, A. L. Shluger, K. Hayashi, M. Hirano, H. Hosono, Phys. Rev. Lett., v.91, p.126401, (2003)

11:00 AM K1.8
Effective Energy Landscapes for Mobile Ions in Solid Electrolytes. Stefan N. Adams¹ and Jan Swenson²; ¹GZG, Crystallography, Universitaet Goettingen, Goettingen, Germany; ²Department of Applied Physics, Chalmers University of Technology, Goeteborg, Sweden.

The bond valence (BV) concept is widely used in chemistry, e.g. to judge the plausibility of atom positions in crystal structures from empirical bond-length bond-valence relationships as sites where the BV sum of the atom equals its oxidation state. Our modified BV approach that systematically accounts for the bond softness [1,2] may be effectively used to study the interplay between structure and transport properties of solid electrolytes by identifying energetically favorable transport pathways through the real-space BV mismatch landscape for the mobile type of ions. For crystalline electrolytes, the BV analysis of crystal structures or of local structure models from a combination of crystallographic information with force-field simulations allows to predict the activation energy of the ionic conduction. Accounting for the mass dependence of the conversion from the BV mismatch into an activation energy scale yields a correlation that holds for different types of mobile ions [3]. The H⁺ transfer in proton conductors, however, requires a special treatment, because of its strong coupling to anion motion [4]. Local structure models for disordered systems (such as ion conducting glasses) may be obtained from reverse Monte Carlo (RMC) fits or molecular dynamics (MD) simulations. The RMC method yields static structure models that are in quantitative agreement with experimental diffraction data as well as with constraints based on other types of experimental information (e.g. density, network connectivity). The assumption that the conduction pathways are regions within the structure, where the BV mismatch for a mobile ion remains below a given threshold value, enables us to predict the ionic conductivity of a glass directly from the relative "pathway volume" in a RMC structure model [5,6]. This correlation also holds for mixed alkali glasses [7]. Further insight into the ion transport in glasses results from the analysis of BV mismatch landscapes in terms of the total number of sites for the mobile ions [8] or the reduced local dimensionality of the pathways and their connection to the ion polarizability. A BV analysis of entire MD trajectories allows quantifying the evolution of pathways in time and to investigate the effect of temperature on the extension and dimensionality of the transport pathways. To combine the advantages of RMC and MD structure models we investigate the possibility of an iterative coupling of both techniques. [1] S. Adams; Acta Crystallogr. B 57, 278 (2001). [2] softBV web pages: <http://kristall.uni-mki.gwdg.de/softBV/> [3] S. Adams, J. Swenson, submitted to Solid State Ionics. [4] S. Adams, O. Moretzki, E. Canadell; Solid State Ionics, 168, 281 (2004). [5] S. Adams, J. Swenson; Phys. Rev. Lett. 84, 4144 (2000). [6] S. Adams, J. Swenson; Phys. Chem. Chem. Phys. 4, 3179 (2002). [7] J. Swenson, S. Adams; Phys. Rev. Lett. 90, 155507 (2003). [8] S. Adams, J. Swenson; submitted to J. Phys.: Condens. Matter.

11:15 AM K1.9
A First-Principles Study of Ionic Conductivity in Select Superionic Solids. Brandon Wood and Nicola Marzari; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

First-principles molecular dynamics simulations are well suited to the study of conductivity in superionic solids, thanks to the high frequency of diffusion events observable within reasonable simulation timescales. We carry out extensive Car-Parrinello simulations on supercells comprising between 32 and 112 atoms to investigate two paradigmatic case studies: AgI, a classic example of a superionic solid; and CsHSO₄, an anhydrous superprotonic conductor with promising fuel cell applications. A combination of static, linear-response, and molecular dynamics calculations, as well as a detailed investigation of the maximally localized electronic orbitals, allows us to characterize the structural, dielectric, and vibrational properties of these systems, as well as diffusion coefficients and ionic conductivities. The dynamical simulations offer a unique and unbiased characterization of

the mechanisms of ionic diffusion and the statistics of most-traveled pathways, together with the detailed atomistic processes involved.

11:30 AM **K1.10**

Atomistic Simulation of Oxide Ion Transport in Stabilized Zirconia. Ram Devanathan¹, William J. Weber¹ and Subhash C. Singhal²; ¹Fundamental Science Directorate, Pacific Northwest National Laboratory, Richland, Washington; ²Energy Science and Technology Directorate, Pacific Northwest National Laboratory, Richland, Washington.

A fundamental understanding of ionic transport in oxides is needed to advance fuel cell technology. In an effort to understand oxide ion transport at the atomic level in solid oxide fuel cell electrolytes, we have performed molecular dynamics simulations, using reliable potentials, to study ionic transport in Y_2O_3 and Sc_2O_3 stabilized zirconia for a range of compositions and several temperatures. Our results reproduce the peak in ionic conductivity of yttria-stabilized zirconia as a function of composition, and show that the activation energy for oxide ion diffusion can vary from 0.6 to 1.1 eV depending on the composition. Our results are in excellent agreement with experimental observations and provide insights into defect-dopant interactions. These interactions have important implications for not only the ionic conductivity but also the degradation of fuel cell materials.

11:45 AM **K1.11**

Ab Initio Analysis of Defect Chemistry in Doped LaGaO₃. Akihide Kuwabara and Isao Tanaka; Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan.

First principles calculations with projector augmented wave method has been carried out for Sr and/or Mg-doped rhombohedral LaGaO₃. The formation energies of 10 kinds of defects have been systematically computed in consideration of temperature and oxygen partial pressure. Sr²⁺ ion is found to be stable at La site rather than Ga site, whereas Mg²⁺ ion is stable at Ga site. The solution of dopants accompanied with the formation of oxygen vacancies shows the lowest energy at temperatures of 500 to 1600 K and oxygen partial pressures of 10⁻²¹ to 1 atm. Defects resulting in n- or p-type conductivity are energetically unfavorable under these conditions. The present theoretical results are consistent with experimental results of doped LaGaO₃ in the literature regarding both site preference of dopants and the dependence of ionic conductivity on oxygen partial pressure.

SESSION K2: Oxide Ion Conductors/Oxygen Permeation Membranes

Chairs: Werner Sitte and Yasutake Teraoka
Monday Afternoon, November 29, 2004
Republic B (Sheraton)

1:30 PM ***K2.1**

Novel Ceria Solid Solutions: Unusual Behavior Under Oxidizing Conditions. Harry L. Tuller and Todd Stefanik; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Acceptor like dopants such as Gd, Sm, Y, etc. are typically added to CeO₂ to generate high levels of oxygen deficiency and thereby high levels of ionic conductivity via the motion of oxygen vacancies. Pr like Ce exhibits a +4 oxidation state under highly oxidizing conditions but reduces much more readily than Ce towards the +3 oxidation state even under intermediate oxygen partial pressures. This leads to unusual behavior in the Ce_{1-x}Pr_xO_{2-y} (PCO) system under oxidizing conditions which we have investigated in some detail. Examples include oxygen partial pressure dependent ionic conductivity, electronic conduction via a Pr impurity band (at elevated Pr levels) and exceptionally high deviations from stoichiometry. Electrical conductivity and coulometric titration data are presented for the PCO system for x between 0 and 0.2 as functions of PO₂ and temperature. Defect and transport models are presented which provide insight into this unusual behavior. These results are contrasted with another unusual ceria solid solution studied by our group in the past, Ce_{1-x}U_xO_{2+y}.

2:00 PM **K2.2**

Segregation of Gd at the interfaces of Gd-doped ZrO₂-CeO₂ Hetero-Multi-Layer Films Grown on Sapphire.

Chongmin Wang, S. Azad, L. Saraf, V. Shutthanandan, M. H. Engelhard, D. E. McCready, O. Marina, S. Thevuthasan and M. Watanabe; Pacific Northwest National Laboratory, Richland, Washington.

Multi-phase materials such as composites and thin films are widely used as electrolytes in electronic devices, fuel cells, sensors and catalysts. Development of electrolyte materials with high oxygen ion

conductance at low temperatures is essential to increase the efficiency and lifetime of these devices. Ionic conductivity is critically influenced by defect chemistry. One way to control defect chemistry is by doping of the material with one or more dopants. In this study, multi-layer films of Gd-doped ZrO₂ and Gd-doped CeO₂ were grown on Al₂O₃ using molecular beam epitaxy. The microstructures of the film were characterized using x-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), conventional and high-resolution transmission electron microscopy (HRTEM), electron energy-loss spectroscopy (EELS), energy dispersive x-ray (EDX) elemental mapping, and selected area electron diffraction. The films incorporate high-density internal defects, such as domain boundaries and volumetric and interfacial dislocations. High spatial resolution EDX mapping reveals segregation of Gd at the interfaces between ZrO₂ and CeO₂. It has been noticed that the Gd interface segregation is related to the double layer formation, thus discussion will be placed on the correlation of the segregation behavior with respect to the thickness of the heterolayer film.

2:15 PM **K2.3**

Structural, electrical and mechanical properties of self-supported membranes of Gd-doped ceria. Mark Greenberg¹, Igor Lubomirsky¹, Juergen Fleig² and Joachim Maier²; ¹Materials & Interfaces, Weizmann Institute of Science, Rehovot, Israel; ²Max Planck Institute for Solid State Research, Stuttgart, Germany.

Gadolinium-doped ceria has attracted a lot of attention because it exhibits noticeable ionic conductivity already at 300 °C. In addition, the slow rate of the chemical reaction between ceria and Si promises integration of ceria-based solid electrolyte membranes in Si-based micro-electro-mechanical systems (MEMS). We have investigated structural, mechanical and electrical properties of nanocrystalline membranes of 20% Gd-doped ceria with 20-50 nm grain size, 300-1000 nm thickness and 150-300 μm lateral dimensions. The substrate-supported films were prepared by RF magnetron sputtering and annealed after deposition at 600 °C in air. It was found that despite a complete relaxation of the mechanical stress, this treatment produces films with a unit cell, which is 0.3-0.4% larger than that of the stoichiometric material. The self-supported membranes prepared from these films show detectable differences of electrical conductivity in vacuum (10⁻⁵ mbar) and in air. Increase of the conductivity with increasing oxygen pressure suggests electronic rather than ionic conductivity, which is in agreement with the very low values of the activation energy (80-150 meV). To elucidate the nature of the observed behavior, the substrate supported films were oxidized by low energy, high density oxygen plasma and annealed again at 600 °C. After this treatment, the films adopt a unit cell which is characteristic for stoichiometric material. The self-supported membranes prepared from these films do not exhibit any differences in electrical conductivities measured in vacuum and in air. The activation energy in these films is significantly higher (>400 meV). The observed behavior can be explained by the hypothesis of stress-induced vacancy formation and suggests that this effect has to be taken into account for practical implementation of ceria-based microscopic devices.

2:30 PM **K2.4**

Oxide Ion Conduction in Oxygen Rich Doped Ba₂In₂O_{5+δ} Brownmillerite. Aurelie Rolle, Nambi Venkatesan Giridharan, Pascal Roussel, Francis Abraham and Rose-Noelle Yannier; Laboratoire de Cristallographie et Physicochimie du Solide, Université des Sciences et Technologies de Lille, CNRS UMR 8012, ENSCL, Villeneuve d'Ascq, France.

The Brownmillerite Ba₂In₂O₅ is well known for its fast oxide ion conduction above 925°C [1]. It also exhibits protonic conduction under 300°C. TGA combined with DTA performed under humid air atmosphere confirmed an uptake of water starting at 100°C followed by a dehydration at 300°C. To stabilise Ba₂In₂O₅ fast oxide ion properties at lower temperature, partial substitution for Ba and In sites were performed with cations of higher valence than two for Ba and three for In. Vanadium, niobium, tantalum, molybdenum and tungsten were introduced in the indium site. High oxide ion conduction have been reported when barium was partially substituted by lanthanum [2-4]. In this study bismuth which exhibits a radius close to lanthanum was considered. Solid solutions were evidenced in all the cases. They were characterised by high temperature X-ray diffraction, TGA-TDA, impedance spectroscopy. To characterise the oxygen migration in these materials neutron diffraction data were collected at variable temperature and combined with high temperature X-ray data. References [1] J.B. Goodenough, J.E. Ruiz-Diaz, Y.S. Zhen, Solid State Ionics 44 (1990) 21 [2] K. Kakinuma, H. Yamamura, H. Haneda, T. Atake, J. of Thermal Analysis and Calorimetry 57 (1999) 737 [3] Y. Uchimoto, T. Yao, H. Takagi, T. Inagaki, H. Yoshida, Electrochemistry 68 (2000) 531 [4] K. Kakinuma, H. Yamamura, H. Haneda, T. Atake, Solid State Ionics 140 (2001) 301

2:45 PM **K2.5**

Synthesis, Characterization and Properties of New Vanadia-Alumina and Vanadia-Silica Composites Prepared by Interpenetrating Polymer Network Approach.

Herenilton Paulino Oliveira¹, Elaine Cabrini Zampronio¹, Glauciane Nascimento Barbosa¹, Carlos Frederico Graeff² and Tania Faria Lassali³; ¹Química, Sao Paulo University/FFCLRP, Ribeirao Preto, Sao Paulo, Brazil; ²Fisica-Matemática, Sao Paulo University/FFCLRP, Ribeirao Preto, Sao Paulo, Brazil; ³Lab Resíduos Químicos, Sao Paulo University/PCARP, Ribeirao Preto, Sao Paulo, Brazil.

The synthesis of novel multicomponent materials composed of transition metals in inorganic matrices has received growing attention over the past 10 years, in particular because they are attractive candidates in many fields of modern technologies. In this study, we incorporated vanadium pentoxide xerogel into an alumina matrix and into a silica matrix. The idea behind this study is to incorporate vanadium pentoxide xerogel into an inorganic matrix retaining its lamellar structure and electrochemical properties as well. Herein, we present the synthesis, characterization and electrochemical properties of new multicomponent materials obtained from the polymerization of vanadium pentoxide in inorganic matrix (alumina and silica) forming an interpenetrating polymer network using soft chemistry approach. The novel materials were characterized by X-ray diffraction, infrared spectroscopy, thermogravimetric analysis, electron microscopy, energy dispersive X-ray spectrometry, cyclic voltammetry and impedance spectroscopy. V2O5/SiO2 and V2O5/Al2O3 xerogel composites prepared by soft chemistry present conductivity almost five orders of magnitude higher than other related systems. Moreover, the electrochemical behavior is quite similar to that found for V2O5 xerogel. Finally, this investigation revealed the dependence between electrochemical properties (investigated by cyclic voltammetry and impedance spectroscopy) and precursors of silica matrix as well as the synthetic conditions. It should be noted that the electrochemical response is dependent on support electrolyte solution varying the cation species, i.e., with increasing the cation size as has been observed, the insertion process becomes more difficult resulting in a low rate of electronic transfer. Overall, the synthetic approach applied in this study is extremely attractive due to its simplicity and can provide new strategies for tailoring new materials and future family members for electrochromic devices, batteries and chemical sensing. Acknowledgement: FAPESP and CAPES.

3:30 PM ***K2.6**

Fe/Mn-Based Perovskite-Type Oxides with Excellent Oxygen Permeability and Reduction Tolerance. Yasutake Teraoka, Hironobu Shimokawa, Hajime Kusaba and Kazunari Sasaki; Department of Materials Sciences, Kyushu University, Kasuga, Fukuoka, Japan.

Dense membranes of mixed ionic-electronic conductive (MIEC) materials with oxygen semi-permeability at elevated temperatures can be applied not only to oxygen separator but also to membrane reactors, for example, of the partial oxidation of methane to synthesis gas (POM). Although La-Sr-Co-Fe (LSCF) perovskites with Sr/Co-rich compositions are inherently excellent oxygen-permeable materials, the lack of the stability against thermal and chemical reduction of LSCFs makes it difficult to construct stable membrane reactors of POM and even oxygen separation. Therefore, development of oxygen-permeable and reduction-tolerant materials is important in the field of MIEC science and technology. This study has revealed that Fe/Mn-based perovskites are excellent oxygen permeable materials with exceeding reduction tolerance which can be successfully applied to the POM membrane reactor. A series of (A, Sr)-(Fe, Mn)-O (A=La, Ba, Ca) perovskites in the Sr/Fe-rich composition region were prepared, and the oxygen permeability was evaluated with the [air/membrane/He] cell construction using 1 mm-thick membrane sintered at 1300-1450 oC. Among oxides investigated in this study, Ba-substituted oxide (Ba_{0.3}Sr_{0.7}FeO_{3-x}, BSF37) exhibited the highest oxygen permeability of 3.0 cm³(STP)cm⁻²min⁻¹ at 900 oC, which is higher than that of any of LSCFs. The substitution of La and Ca for Sr and that of Mn for Fe caused a decrease in the oxygen permeability. TG analysis in 5%H₂/N₂ stream up to 1000 oC showed that Fe/Mn-based perovskites were quite stable against the reduction. The substitution of adequate amounts of Ba and Mn for Sr and Fe, respectively, into SrFeO_{3-x} improved the reduction tolerance, and BSFM3791 (Ba_{0.3}Sr_{0.7}Fe_{0.9}Mn_{0.1}O_{3-x}) was the most stable against the reduction. The stable working of the POM membrane reactor, [air/membrane/20vol%CH₄-Ar], at 900 oC was confirmed with the BSFM3791 membrane but not with LSCF1991. In conclusion, Fe/Mn-based perovskites, especially BSFMs, are promising materials for application to oxygen separation and membrane reactor with excellent oxygen permeability and reduction tolerance.

4:00 PM **K2.7**

Oxygen Permeable Properties of Ce_{0.8}Gd_{0.2}O_{1.9}-MFe₂O₄

Composite Thin Films Prepared by a Chemical Solution Deposition Method. Isao Kagomiya^{1,2}, Takashi Iijima⁴ and Hitoshi

Takamura³; ¹AIST, Tsukuba, Japan; ²Core Research for Evolutional Science, Japan Science and Technology, Tokyo, Japan; ³Material Science, Tohoku University, Sendai, Japan.

Recently, interest has increased on electric- and ionic- conductive (mixed conductive) oxides since it is possible to separate only oxygen gas from air. Ce_{0.8}Gd_{0.2}O_{1.9}(CGO) - spinel-type ferrite MFe₂O₄ (M=divalent cation) is a composite-type mixed conductor. In this system, MFe₂O₄ phases are including in the ionic conductive CGO so as to enhance the electric conduction. O₂ permeable flux density of the system is as high as that of mixed conductive perovskite-type like La-Sr-Co-Fe oxides. In addition, this composite system has good stability under both reduction- and oxidation- atmospheres. In fact, the O₂ permeable flux density of the CGO - CoFe₂O₄ ceramics with 1-mm thickness is 0.21 mmol cm⁻² min⁻¹ at 1000°C under a O₂ partial pressure difference between air and He (20 sccm). Previously, we have achieved high O₂ flux density at 1000°C by preparing a CGO-15mol%CoFe₂O₄ thin film on a porous CGO substrate with a chemical solution deposition method. The density exceeds that obtainable using a bulk material. In this study, we try to increase O₂ flux density below 1000°C based on the CGO-M₂O₄ thin film preparation technique in order to find a possibility of low temperature- O₂ separation. Some studies have reported nano-scale effect on an ionic-conductor CGO. This effect is usage to increase ionic- or electric- conduction at lower temperature. We control both microstructures and morphologies of CGO-MFe₂O₄ thin films and investigate O₂ permeable flux density below 1000°C.

4:15 PM **K2.8**

Heterogeneity of Transport Properties in Operating Perovskite Oxide Membranes Revealed by Quenched Isotopic Transients. Charles Arthur Mims, Peter M. Brodersen, Stefan Gruber and Linjie Hu; Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada.

Tubular oxygen separation membranes of dense La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ} and La_{0.2}Sr_{0.8}Fe_{0.8}Cr_{0.2}O_{3-δ} were investigated using ¹⁶O₂ -¹⁸O₂ isotopic transients to reveal the transport properties (surface and bulk) under steady state operation. The internal isotope distributions during particular transient experiments were captured by quick cooling of the membranes, followed by imaging time-of-flight secondary ion mass spectrometric (ToF-SIMS) analysis of exposed cross- sections. A La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ} membrane quenched under a mild oxygen activity gradient (pO₂' = 0.2, pO₂" = 0.015) at 1073K showed heterogeneity in the isotope distribution as a function of radial direction. This heterogeneity was associated with incipient cracks in the material. However, at a radial direction not associated with the cracks, the isotope distribution as a function of radius could be fit with a single value of the oxygen diffusion coefficient, consistent with the relatively mild oxygen potential gradient across the membrane. A La_{0.2}Sr_{0.8}Fe_{0.8}Cr_{0.2}O_{3-δ} membrane was investigated under a high oxygen activity gradient (pO₂' = 0.2, pO₂" = 3 x 10⁻¹⁵ in CO/CO₂) at 1173K. In this case, the quenched oxygen profile was consistent with a higher oxygen diffusion coefficient near the surface in contact with the CO/CO₂atmosphere. This variation was consistent with the expected increase of oxygen vacancy concentration under low oxygen activity.

4:30 PM **K2.9**

Intermediate Temperature Electrochemical Ceramic Oxygen Generators. Agusti Sin¹, Evgeny Kopnin¹, Yuri Dubitsky¹, Antonio Zaopo¹, Antonino S. Arico², Laura R. Gullo², Daniela La Rosa² and Vincenzo Antonucci²; ¹Pirelli Labs, Milano, Italy; ²ITAE-CNR, Messina, Italy.

Today there is a large number of commercial processes that need pure oxygen, oxygen-enriched or oxygen-depleted streams. Examples of industrial uses of oxygen enriched atmospheres include glass making, the petrochemical industry, bleaching for the pulp of paper in the paper making industry, and for cutting and welding in the metallurgical industry. Oxygen is also consumed in small quantities for critical tasks of life support for military, aerospace and medical applications. Oxygen is separated from air by one of the three conventional processes: the cryogenic distillation of air (for large scale production), pressure swing adsorption and vacuum swing adsorption. The cost of the process depends on the purity required and the production scale. In the present work, a separation process based on an electrochemical ceramic oxygen generation (ECOG) device is adopted. The method of operation is similar to an electrolysis cell and more properly to an electrochemically driven-oxygen pump in which air and electrical power are used to generate pure oxygen. The flux of oxygen produced by an ECOG is directly proportional to the current passing through the cell upon application of a certain voltage. The

objective is to achieve maximum current (oxygen generation) with the minimum applied voltage at temperatures as low as possible (> 800°C). This approach has distinct advantages with respect to the conventional technologies mentioned before. The ECOG devices produce high purity of oxygen (i.e. 100%) in a single operation unit and, as a consequence, the production costs may be significantly decreased as well as small and light weight devices for portable uses are envisaged

4:45 PM K2.10

Oxide-Ion Transport in Gadolinium Zirconate - Titanates under High Pressure. Hitoshi Takamura^{1,3}, Hirofumi Kakuta^{2,3}, Atsunori Kamegawa^{1,3}, Masuo Okada^{1,3} and Harry L. Tuller⁴;
¹Department of Materials Science, Tohoku Univ., Sendai, Japan;
²Institute for Materials Research, Tohoku Univ., Sendai, Japan;
³CREST, Japan Science and Technology Agency, JST, Japan;
⁴Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Pyrochlore compounds, $A_2B_2O_7$, are of interest both as electrodes and as electrolytes in solid oxide fuel cells. From a scientific viewpoint, the high oxide-ion conductivity originating from structural disorder is also of great interest. Gadolinium zirconate ($Gd_2Zr_2O_7$; GZ), for example, exhibits a high oxide-ion conductivity of 10^{-2} S/cm at 1000 °C without acceptor dopants; Frenkel-type defects on the oxygen sub-lattice are responsible for the high oxide-ion conductivity. On the other hand, ordered gadolinium titanate ($Gd_2Ti_2O_7$; GT) exhibits a higher oxide-ion conductivity of 10^{-1} S/cm at the same temperature with acceptor dopants such as Ca. To further understand the nature of the formation of mobile defects and oxide-ion transport in the gadolinium zirconate-titanates (GTZ), we performed conductivity measurements under high pressure in the range of 2 to 6 GPa. Activation volumes for defect formation, ΔV_f , and oxide-ion migration, ΔV_m , may be extracted from the pressure dependence of the conductivity. A cubic-anvil-type apparatus was used to achieve pseudo hydrostatic pressures. The electrical conductivities of Ca-doped GT and GTZ were evaluated as functions of pressure and temperature. The activation volume, ΔV , the sum of ΔV_f and ΔV_m , of Ca-doped GT and GZ was found to be 0.9 and 2.0 cm³/mol at 750 °C, respectively. In addition, ΔV for GZ strongly depended on temperature, while that for Ca-doped GT was only weakly temperature dependent. The difference in the magnitude of ΔV and the deconvolution of ΔV into ΔV_f and ΔV_m were examined by means of atomistic computer simulations.

SESSION K3: Poster Session: Fuel Cells
Chairs: Philippe Knauth, Christian Masquelier, Enrico Traversa and Eric D. Wachsman
Monday Evening, November 29, 2004
8:00 PM
Exhibition Hall D (Hynes)

K3.1

Co-Sintering of Dense Electrophoretically Deposited YSZ Films on Porous NiO-YSZ Substrates for SOFC Applications. Giuseppe Savo, Alberto Rainer, Alessandra D'Epifanio and Enrico Traversa; Dept. of Chemical Science and Technology, University of Rome Tor Vergata, Rome, Italy.

One of the main problems in the fabrication of anode supported solid oxide fuel cells is related to the sintering of electrolyte layer on anodic substrate, because differential densification of the layers may result in cracks during thermal process. Co-firing approach consists of simultaneous sintering of both electrolyte and anode. In this way, shrinkage of porous layer is compatible with the densification of electrolyte film. In this work co-firing technique was used for the sintering of YSZ thick films deposited on green NiO-YSZ layers by electrophoretic deposition (EPD). EPD is a colloidal process based on the motion of charged particles in the electric field in the direction of the electrode with opposite charge, thus forming a compact layer. With respect to other techniques, EPD has several advantages: short formation times, little restriction in the shape of substrates, simple deposition apparatus, possibility to have a mass production, low cost, easy control of the thickness of the deposited film through simple regulation of applied potential and deposition time. The technological feasibility of applying the technique to solid oxide fuel cells was investigated in different conditions and on different substrates. A slurry was prepared starting from a commercial NiO-YSZ anodic powder (Praxair), polyvinylidene fluoride (PVDF binder SOLEF 6020, Solvay), a nanometric carbon powder (super P, Carbon Belgium), dispersed in N-methyl-2-pyrrolidone. The slurry was poured in a mould and a green membrane was obtained after evaporation of the solvent. A suspension of YSZ powder was prepared starting from commercial YSZ (TZ8Y Tosoh) 1wt%, $d_{50} \approx 2 \mu\text{m}$ in pure methanol and deposited by EPD on green NiO-YSZ membranes using a planar EPD cell setup. Sintering conditions were assessed from the results of

TG-DTA analysis performed on green bodies. Green and fired samples were characterized in terms of morphology and porosity by scanning electron microscopy (FE SEM).

K3.2

Electrical and Hydrogen Permeation Properties of SrCe_{0.8}Yb_{0.2}O_{3-δ} / Ni Cermet Membranes. Sun-Ju Song, Tae H. Lee, C. Zuo, L. Chen, S. E. Dorris and U. Balachandran; Ceramics Session, Argonne National Lab., Argonne, Illinois.

Research on hydrogen separation membranes is motivated by the increasing demand for an environmentally benign, inexpensive technology for separating hydrogen from gas mixtures. Although most studies of hydrogen separation membranes have focused on proton-conducting oxides by themselves, the addition of metal to these oxides increases their hydrogen permeability and improves their mechanical stability. In this presentation, the electrical and hydrogen permeation properties of SrCe_{0.8}Yb_{0.2}O_{3-d} (SCYb) will be presented. The results show that the hydrogen permeation rate is limited by electron flow at the investigated temperatures (600 – 900°C). To further enhance hydrogen permeability, a cermet (i.e., ceramic-metal composite) membrane was made by adding Ni to SCYb. The cermet showed no phase change after sintering in reducing atmosphere. At 900°C, with 20% H₂ /balance He as a feed gas (pH₂O = 0.03 atm), the hydrogen permeation rate was 0.113 cm³/min-cm² for Ni/SCYb and 0.008 cm³/min-cm² for SCYb. The dependence of hydrogen permeability on temperature, thickness, and hydrogen partial pressure gradients will be discussed. This presentation will demonstrate that adding Ni to SCYb considerably increases its hydrogen permeability by increasing its electron conductivity. *Work supported by U. S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory's Gassification Technologies Program, under Contract W-31-109-Eng-38.

K3.3

Proton Conduction and Fuel Cell Performance of Sintered SiO₂ Solid Electrolyte. Akihiko Yamaji, Atsushi Segawa, Tadaharu Adachi and Wakako Araki; Dept. of Mechanical Sciences and Engineering, Tokyo Inst. of Tech., Tokyo, Japan.

In this research, the conductivity of sintered SiO₂ (polycrystalline (Cristobalite) and amorphous phases) has been studied by dc measurement and ac-impedance measurement at high temperatures in various controlled atmosphere, and also the performance of Al-doped SiO₂ (Cristobalite phase) electrolyte fuel cell was tested. Each sintered SiO₂ (Cristobalite and amorphous phases) was found to be a proton conductor at high temperatures, and the conductivity of the Cristobalite and the amorphous phases were 2.13×10^{-5} and 4.13×10^{-6} S/m respectively at 900 °C. The conductivity of the crystalline phase was about 10 times larger than that of the amorphous phase. To improve the proton conductivity of the sintered SiO₂ solid electrolyte, various kinds of dopants were examined. Dopants such as Al₂O₃ and Sc₂O₃ show a remarkable influence on protonic conduction of sintered SiO₂. The conductivity of the sintered SiO₂ (Cristobalite) doped with 0.5 mol. % Al₂O₃ increased to 3.94×10^{-5} S/m and this value was about 2 times larger than that of nondoped one. The performance of 0.5 % Al₂O₃ doped SiO₂ (Cristobalite) electrolyte fuel cell with porous platinum electrodes was tested. The open circuit voltage of 1.85 mm thick electrolyte single-cell was 1.03 V at 900 °C and the maximum power density was 90 μW/cm² at 900 °C.

K3.4

NMR and impedance study of H⁺-ion irradiated TiH₂PO₄.

Se-Hun Kim¹, Kyu-Won Lee¹, Cheol-Eui Lee¹ and S. J. Noh;

¹Department of Physics, Korea University, Seoul, South Korea;

²Department of Applied Physics, Dankook University, Seoul, 140-714, South Korea.

The H⁺-ion treatment effect on TiH₂PO₄, a KH₂PO₄ (KDP)-type ferroelectrics, was studied by nuclear magnetic resonance (NMR) and AC conductivity measurements. A sample of TiH₂PO₄ was irradiated by 1-MeV H⁺ ion beams to a dose of 10^{15} ions/cm². After the irradiation, the hydrogen-bond geometry was changed, which may affect the order-disorder proton dynamics. And the PO₄ tetrahedra were deformed, which was identified by the isotropic chemical shift and the full width at half maximum (FWHM) of the high-resolution ³¹P NMR spectra. From the impedance spectra, two types of charge transport were observed above the ferroelastic phase transition temperature. After the irradiation, the change in the dielectric loss indicated that in the domain wall motion. The macroscopic and microscopic changes due to the irradiation were discussed in the light of the proton dynamics.

K3.5

Structure, Phase Transitions and Protonic Conductivity of Compounds in the Cs_xRb_{1-x}H₂PO₄ System. Sossina M. Haile

and Lisa A. Cowan; Materials Science, Chemical Engineering, California Institute of Technology, Pasadena, California.

Superprotonic phase transitions, polymorphic transformations at which protonic conductivity increases by several orders of magnitude, appear to be facilitated by large cations, such as Cs and Rb. In particular, the compounds CsH_2PO_4 and RbH_2PO_4 exhibit superprotonic conductivity, with transition temperatures of 230 and 280 °C, respectively. Furthermore, the compounds crystallize in different structures at room temperature (CsH_2PO_4 is monoclinic whereas RbH_2PO_4 is tetragonal), and only the high temperature structure of the Cs compound is known (cubic, CsCl structure-type). A study of the intermediate system, $\text{Cs}_{1-x}\text{Rb}_x\text{H}_2\text{PO}_4$, has been undertaken with the aim of elucidating the precise connection between (average) cation size and superprotonic behavior. Compounds in the CsH_2PO_4 - RbH_2PO_4 system were synthesized in increments of $x = 0.1$ by aqueous methods. Stoichiometric amounts of CsH_2PO_4 and RbH_2PO_4 were placed in a thermal bomb along with 1-2 mL H_2O to prevent dehydration, and then held at 350 °C for three hours. Intermediates with composition from CsH_2PO_4 through $\text{Cs}_{0.2}\text{Rb}_{0.8}\text{H}_2\text{PO}_4$ crystallize in the CsH_2PO_4 structure, with the RbH_2PO_4 structure appearing only for $\text{Cs}_{0.2}\text{Rb}_{0.8}\text{H}_2\text{PO}_4$ and the end-member Rb compound itself. Room temperature magic angle spinning (MAS) NMR studies revealed a linear dependence of ^{133}Cs , ^{87}Rb and ^1H -NMR chemical shifts on Rb content throughout the entire composition range. Transition temperatures were measured by differential scanning calorimetry carried out in closed volume containers so as to minimize the influence of thermal dehydration. The transition temperature remained relatively constant at 225 °C for compositions between CsH_2PO_4 and $\text{Cs}_{0.5}\text{Rb}_{0.5}\text{H}_2\text{PO}_4$. Beyond this range it increased monotonically with rubidium content. Impedance measurements carried out under appropriate water partial pressures (0.3 - 0.7 atm) confirmed these results and demonstrated the transitions to be superprotonic in nature. The absence of a correlation between room temperature structure type and transition temperature indicates the greater importance of chemistry, possibly via cation radius size effects, over crystalline structure on superprotonic phase transitions in this system.

K3.6

Specificity of the Local Structure of Nanocrystalline Doped Ceria Solid Electrolytes. Vladislav A. Sadykov¹, Yulia V. Frolova¹,

Vladimir V. Kriventsov¹, Dmitrii I. Kochubei¹, Ella M. Moroz¹, Dmitrii A. Zyuzin¹, Yulia V. Potapova¹, Vitalii S. Muzykantov¹, Vladimir I. Zaikovskii¹, Elena B. Burgina¹, Holger Borchert¹, Stylianos Neophytides², Erhard Kemnitz³ and Kerstin Scheurell³; ¹Heterogeneous catalysis, Borekov Institute of Catalysis, Novosibirsk, Russian Federation; ²Institute of High Temperature Processes & Chemical Engineering, Patras, Greece; ³Institute for Chemistry, Humboldt University, Berlin, Germany.

Nanocrystalline ceria solid solutions are now of a great interest due to their easy sintering into mechanically strong dense submicron ceramics as well as specific defect/transport properties associated with high surface/grain boundary areas. However, still little is known about specificity of their real/defect structure due to difficulties of their characterization by traditional diffraction methods. This work presents results of studies of the structural features of nanocrystalline doped $\text{Ce}_{1-x}\text{Me}_x\text{O}_{2-y}$ samples (Me= Sm, Bi, Gd; $x = 0-0.5$) prepared via the polymerised precursor (Pechini) route by using a combination of diffraction (XRD, TEM, WAXS on SR) and spectroscopic (EXAFS, Raman, FTIRS of lattice modes, XPS, SIMS) methods. According to X-ray diffraction data, all these samples are single-phase fluorite-like solid solutions, their lattice constants linearly increasing with the dopant content, while domain sizes declining. High-resolution TEM data confirm a good nanodomains crystallinity. However, the local structure around Ce and dopant cations studied by EXAFS and WAXS on synchrotron radiation was found to be strongly distorted even in pure nanocrystalline ceria depending upon the type and content of a dopant as well. Progressive disordering of the lattice with the dopant content is also reflected in decline of the intensity of EXAFS peaks. At a high dopant content, a local rearrangement of the structure into that of a lower symmetry is reflected in appearance of new EXAFS peaks and splitting of the Raman and IR bands. Analysis of the amplitudes of peaks assigned to different coordination spheres and corresponding distances revealed the most uniform distribution in the ceria lattice for smallest Gd cations. In addition, for Gd doped ceria, anion vacancies appear to be preferentially located in the coordination sphere of Ce cations, while they are mainly associated with bigger dopants. Comparison with the published data on the local structure of dense coarse-grained ceria-based electrolytes with the same composition revealed a higher flexibility of the nanocrystalline systems structure, which can be assigned to the effects of domain boundaries and free surfaces. Segregation of dopants at the surface/domain boundaries revealed by SIMS and XPS could play here some role. However, the lattice oxygen mobility estimated by dynamic isotope exchange appears to correlate with the density of free

anion vacancies located in the coordination sphere of Ce cations and not with the density of domain boundaries. This work is in part supported by INTAS 01-2162 and ISTC 2529 Projects. DAAD postdoctoral research scholarship to H.B. is acknowledged.

K3.7

The effect of lattice vacancies on mechanical properties of cerium oxide. Yanli Wang, Keith Duncan, Eric Wachsmann and Fereshteh Ebrahimi; University of Florida, Gainesville, Florida.

Electrolytes used in solid oxide fuel cells (SOFC) experience mechanical property degradation under the operation environments of elevated temperature and low oxygen partial pressure. Theoretical modeling predicts that the mechanical degradation is related to the reduction in the elastic modulus due to an increase in the vacancy concentration. Pure cerium oxide was selected in this work to investigate this correlation because a strong dependency of mechanical properties on the oxygen partial pressure is anticipated. Different levels of oxygen lattice vacancies were created by holding the as-sintered CeO_2 samples at elevated temperatures and under different oxygen partial pressures for a long time until equilibrium was reached. The vacancy concentration was conserved to room temperature by fast cooling. X-ray diffraction (XRD) results showed that the nonstoichiometric cerium oxide samples kept the fluorite crystal structure after annealing treatments. As expected, the lattice parameter decreased as the vacancy concentration was increased. The intrinsic mechanical properties of the samples were evaluated using nanoindentation technique. Since the indents are contained within single grains, the effect of grain boundaries is excluded. All the samples were carefully polished prior to indentation to remove any surface effects. The results indicated that the mechanical properties were dependent on the lattice vacancy concentration as well as the presence of processing defects such as pores. Both the elastic modulus and the hardness decreased as the oxygen vacancy concentration was increased. Interestingly, the amount of reduction in the elastic modulus was consistently the same for a given environment and independent of the presence of processing defects. Therefore, the effects of vacancy concentration and pores are additive. This paper discusses the effect of temperature and oxygen partial pressure on mechanical properties of oxide electrolytes for SOFC.

K3.8

Mesopore Size Dependence of Protonic and Lithium Ionic Conductivity of Porous Alumina. Hideki Maekawa^{1,2,3}, HangYan Shen^{2,3}, Yutaka Fujimaki¹, Kotaro Kawata¹ and Tsutomu Yamamura¹; ¹Department of Metallurgy, Tohoku University, Sendai, Japan; ²Center for Interdisciplinary Research, Tohoku University, Sendai, Japan; ³PRESTO, JST, Kawaguchi, Japan.

Mesoporous Al_2O_3 was synthesized by the sol-gel method and the pore size was controlled over the range of 3-15nm. Proton conductivity of these samples was examined, which was as high as 0.004 Scm^{-1} at 25 °C. A systematic dependence of conductivity upon pore size was observed, in which the conductivity increased with increasing the pore size.

K3.9

Abstract Withdrawn

K3.10

Electrical and Dielectric Anomalies in Nanocrystalline SrTiO_3 . Palani Balaya, Juergen Fleig, Martin Ahrens, Janez Jamnik and Joachim Maier; Max Planck Institute for Solid State Research, Stuttgart, Germany.

Enhanced surface to volume ratio and increased number of interfaces in nanomaterials lead to exciting phenomena [1-3] both at high as well as low temperatures. In this presentation, we show some of our recent findings in nanocrystalline SrTiO_3 . Unlike microcrystalline SrTiO_3 having both bulk as well as semi-infinite interfacial contributions to conduction, in nominally pure SrTiO_3 nanoceramics (dave = 80 nm with 93% density) the bulk contribution disappears and space charge effects are observed throughout. Based on the analysis of the impedance spectra of above samples, it is found that the effective dielectric constant of nanocrystalline SrTiO_3 is the same as that of the bulk of microcrystalline sample. The pO_2 exponent of the conductivity for nanoceramics is estimated to be +0.21, indicating a hole dominated conduction process. The Debye length is deduced to be larger than the grain size, thus confirming the appearance of a mesoscopic phenomenon (space charge overlap). Another exciting effect refers to the size dependence of dielectric properties in SrTiO_3 at low temperatures [4]. We will discuss this striking phenomenon in more detail in the presentation. References: 1. N. Sata, K Eberman, K. Eberl and J. Maier, Nature 408 (2000) 946 2. S. Kim and J. Maier, J. Electrochem. Soc. 149 (2002) J73 3. J. Maier, Z. Phys. Chem. 217 (2003) 415 4. P. Balaya et al., in preparation.

K3.11

Metastable Phase Evolution in the $\text{YO}_{3/2}\text{-TiO}_2\text{-ZrO}_2$ System.

Tobias Schaedler¹, Wesley Francillon², Ashutosh Gandhi¹, Sanjay Sampath², Clare P. Grey³ and Carlos G. Levi¹; ¹Materials Department, University of California, Santa Barbara, California; ²Department of Materials Science and Engineering, State University of New York, Stony Brook, New York; ³Department of Chemistry, State University of New York, Stony Brook, New York.

The metastable phase evolution of a wide range of compositions centered about the pyrochlore phase in the $\text{YO}_{3/2}\text{-TiO}_2\text{-ZrO}_2$ system was studied. The competing phases in this system all have similarities with the fluorite structure. The fluorite and pyrochlore structures in this ternary are technologically interesting due to the potential for controlling the degree of ionic and electronic conductivity. Insight into the thermodynamics and kinetics governing phase selection was obtained. Powders of various compositions were synthesized by precursor routes. After pyrolysis an amorphous oxide was obtained for most compositions, which was subsequently heat-treated in a stepwise manner at progressively higher temperatures to explore the sequence of phase evolution. When substituting Zr for Ti in $\text{Y}_2\text{Ti}_2\text{O}_7$ the first crystallization product was a defective fluorite-like structure. Pyrochlore formed at temperatures increasing from 900°C to 1400°C with increasing amount of Zr up to 30% Zr. When substituting Zr for Y, keeping the Ti content constant at 50%, the first crystallization product was also a defect fluorite but after further heat treatments rutile and pyrochlore phases appeared. A two-phase microstructure of pyrochlore and orthorhombic ZrTiO_4 developed at 1300°C, which is believed to be the equilibrium structure. The ionic conductivities of selected compositions were correlated with their metastable microstructures.

K3.12

Doped LaGaO_3 : Fast Oxygen-Ion Conductors Investigated by ^{17}O and ^{71}Ga MAS NMR and X-Ray Diffraction.

John L Palumbo¹, Jonathan C. Hanson² and Clare P. Grey¹;
¹Chemistry, SUNY at Stony Brook, Stony Brook, New York;
²Chemistry, Brookhaven National Laboratory, Brookhaven, New York.

LaGaO_3 when doped with 10% Sr on the La site and 10% Mg on the Ga site (LSGM), shows very high oxygen-ion conductivity applicable to Solid Oxide Fuel Cell (SOFC) electrolytes, as well as many other applications. In this study, pure lanthanum gallate, as well as combinations of the doped varieties, are investigated to understand oxygen motion through the crystalline lattice of this perovskite, in an attempt to design future materials that exploit this mechanism. Comparisons of the long range order, as determined by X-ray diffraction, to the short range order, as determined by ^{17}O and ^{71}Ga MAS NMR offer insight to the nature of crystalline defects which are believed responsible for such high oxygen conductivity. Variable temperature (VT) experiments performed from room temperature to 1000°C at the National Synchrotron Light Source at Brookhaven National Laboratory make evident the phase changes in lanthanum gallate. Simulations of the VT MAS NMR spectra show changes in the quadrupole coupling constant (QCC) about the local environments inhabited by oxygen in the various species examined. Distortions of the GaO_6 octahedra sublattice near operating temperature as well as vacancies created by Mg in the Ga site and Sr on the La site are investigated with respect to the mechanism of oxygen conduction.

K3.13

The Structure Related Properties of Ion Conducting Lanthanum Gallate-Based Perovskites. Ekaterina Politova¹, G. M. Kaleva¹, Alexander Mosunov¹, Sergey Stefanovich¹ and Elena Proskuryakova²; ¹L.Ya.Karpov Institute of Physical Chemistry, Moscow, Russian Federation; ²Moscow Academy of Fine Technology, Moscow, Russian Federation.

Lanthanum gallate based oxides attract much attention due to wide prospects of their possible applications as catalysts and solid electrolytes in electrochemical devices. Partial aliovalent substitution of strontium and magnesium for lanthanum and gallium respectively plays essential role in the enhancement of oxygen conductivity in perovskite structure solid solutions. In this work, properties of ceramic solid solutions $(\text{La}_{1-x}\text{Sr}_x)[(\text{Ga}_{1-x}\text{M}_x)_{1-y}\text{Mg}_y]\text{O}_{3-\delta}$ with $\text{M}=\text{Fe, Ni, Cr, Mn}$; $0 \leq x \leq 1$, $0 \leq y, z \leq 0.2$ were studied by means of the X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), dielectric and IR-spectroscopy methods. Ceramic samples were prepared by the multi-step solid state reactions at temperatures 1000-1500°C. The distinctive feature of solid solutions studied is the monotonous increase of the average unit cell parameter with strontium and magnesium content increasing, while the nonmonotonous unit cell parameter changes are observed along with the transition element content increasing. The contraction of the unit cell is observed for all compositions with $x < 0.3$. This allows us to assume the realization of cation substitutions with M species in 3+ or higher valence state. The substitution of the high spin configuration

Fe^{3+} for Ga^{3+} should be assumed in order to explain the observed increasing of the unit cell volume at $x > 0.4$. The IR-spectra collected for the Fe-containing powders revealed splitting of broad absorption bands located near 600 cm^{-1} which mark stretching vibrational modes, to two or three bands. This indicates the formation of microregions with the symmetry lower than recorded by the X-Ray diffraction and points to inhomogeneity of the compositions on the nanoscale level. The SEM and TEM studies of some compositions confirmed the conclusion. The observed shift of vibration frequencies along with the x increasing is consistent with the unit cell volume changes and testifies the changes in the B-O bond energy provided by the B-ion substitutions. The influence of chemical composition and the structure related properties on electric and mass transport will be discussed. The work was supported by the Russian Foundation for Basic Research, grant 04-03-32094.

K3.14

Transport in $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-\delta}$ Membranes Under Low and High Oxygen Activity Gradients. Charles Arthur Mims and Linjie Hu; Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada.

Dense membranes of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-\delta}$ were investigated at 1073K - 1173K under conditions relevant to air separation (low oxygen activity gradient, i.e. air on one side, inert sweep on the other) as well as under conditions relevant to syngas production (high oxygen activity gradient - air on one side, CO/CO_2 mixtures on the other). Isotopic transients ($^{16}\text{O}_2$ - $^{18}\text{O}_2$) were performed at these operating conditions in order to evaluate, under steady state operation, the separate contributions of bulk and surface processes to the membrane performance. In low gradient experiments, the oxygen activation rates and oxygen diffusion coefficients under steady state were consistent with those measured by the isotope exchange depth profiling (IEDP) techniques under gradientless conditions. Under "high oxygen gradient" conditions, two operating modes were found. At low CO partial pressures (< 0.05 atm at 1173K), a mode was observed where oxygen recombination on the "fuel" side was competitive with CO oxidation. This was accompanied by a small oxygen potential gradient across the membrane, with the fuel side surface at a high oxygen potential, molecular oxygen in the "fuel" side gas and a low oxygen flux. Isotope transients showed that under these conditions, oxygen activation on the air side was largely reversible and CO oxidation on the "fuel" side was irreversible. At higher CO partial pressures, CO oxidation became sufficiently rapid to greatly reduce the oxygen activity on the fuel side surface. This was accompanied by quenching of oxygen recombination on the "fuel" side and a large increase in oxygen flux. Isotope transients under these conditions showed irreversible oxygen activation on the air side and partial reversibility of CO oxidation on the "fuel" side. The implications for surface oxidation kinetics and the role of multiple steady states will be discussed.

K3.15

Electrochemical Behaviour of Co-Doped LSGM Perovskites Prepared by Sol-Gel Synthesis. Riccardo Polini¹, Alessia Falsetti¹, Enrico Traversa¹, Oliver Schaefer² and Philippe Knauth²;
¹University of Rome Tor Vergata, Rome, Italy; ²MADIREL, University of Provence, Marseille, France.

Solid oxide fuel cells (SOFCs) offer a highly efficient power generation system. One of the major requirements for the development and commercialization of low-cost SOFCs is the reduction in the operating temperature. One of the methods to reach this aim is the use of solid electrolytes which exhibit superior ionic conductivity at intermediate temperatures ($T < 800$ C). Among these ionic conductors, doped Lanthanum Gallate materials show high oxide ionic conductivity in the 600-800 C range. These perovskites are usually prepared by time- and energy-consuming solid state reaction. In this paper, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2-x}\text{Co}_x\text{O}_{3-y}$ (LSGMC) powders containing different amounts of Co ($x = 0.05, 0.085$ and 0.10) were prepared from precursors synthesised by citrate sol-gel method. The decomposition of the amorphous precursors was studied by TG/DTA. Crystalline powders were obtained by firing at 1000 C (10 h) and dense high-purity pellets were prepared by pressing (300 MPa) and sintering in air at 1475 C (5, 10 and 20 h). The sintered pellets of LSGMC were characterized by X-Ray Diffraction (XRD) Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and X-Ray Photoelectron Spectroscopy (XPS). The conductivity of LSGMC sintered pellets containing different amounts of Co ions in the B sites of the perovskite lattice was assessed by electrochemical impedance spectroscopy (EIS) in the 300-800 C temperature range.

K3.16

Development and Characterization of Thin-Film Perovskite Membranes with Oxygen Permeability. Ruslan Muydinov¹, Maria Popova², Anna Parfenova², Andrey Kaul¹, Dirk Stiens³ and Georg Wahl³; ¹Chemistry, Lomonosov Moscow State University,

Moscow, Russian Federation; ²Material Science, Lomonosov Moscow State University, Moscow, Russian Federation; ³Institute of Surface Technology, Technical University, Braunschweig, Germany.

Selective oxygen permeability is known for perovskites with mixed O^{2-} - electronic conductivity. Diminishing of the thickness is thought to be a way to increase the oxygen flux through perovskite layer. The films of $Ba_{0.5}Sr_{0.5}Co_{1-x}Fe_xO_{3-d}$ - BSCF (3-5 μ m thick) were deposited by MOCVD technique on the different porous substrates (YSZ, Al_2O_3 , CSZ, BSCF). Gas tightness, selective oxygen flux at 750-950°C and stability of the asymmetric membrane in working conditions were investigated. It was shown that sufficiently gas tight films could be obtained directly on the substrates if the pores in the later are of submicron size. However, such substrates may limit gas diffusion and finally oxygen permeation through asymmetric membrane. The criteria for substrate microstructure based on the gas leakage and diffusion measurements were proposed and a new approach to modification of large-pore substrates for obtaining gas-tight but oxygen selectively permeable membranes was developed. Chemical interaction on the film/substrate interface was investigated and the membrane stability was improved by introducing an intermediate layer ($BaZrO_3$ or $BaAl_2O_4$). The ways to accelerate the heterogeneous oxygen exchange at the surface of perovskite layer were considered.

SESSION K4/A3: Joint Session: Solid State Ionics-based Sensors

Chairs: Johannes Schwank and Enrico Traversa
Tuesday Morning, November 30, 2004
Republic B (Sheraton)

8:30 AM *K4.1/A3.1

A Titania Nanotube-Array Room-Temperature Sensor for Selective Detection of Hydrogen at Low Concentrations.

Craig A. Grimes^{2,1}, Oomman K. Varghese^{2,1} and Gopal K. Mor^{2,1};
¹Penn State University, University Park, Pennsylvania; ²Penn State University, University Park, Pennsylvania.

A tremendous variation in electrical resistance, from the semiconductor to metallic range, has been observed in titania nanotube arrays at room temperature, approximately 25°C, at ppm levels of hydrogen gas. The titania nanotube arrays are fabricated by anodizing a titanium foil or thin film in, typically, a hydrofluoric acid electrolyte with the diameter of the resulting nanotubes dependent upon the anodization voltage. For example, using a HF electrolyte a 10 V anodization voltage results in nanotubes of 22 nm inner diameter, while a 20 V anodization voltage results in 76 nm diameter tubes. Initially amorphous, the crystallinity of the nanotubes can be controlled by the temperature, time and atmosphere of a subsequent anneal. The crystalline nanotube arrays are coated with a 10 nm layer of palladium by evaporation, with Pt electrical contacts made by sputtering through a mask atop the Pd sensitized nanotube-array. At 25°C these sensors exhibit a resistance variation of the order of 104 in the presence of 100 ppm hydrogen, and a resistance variation of 106 to 1000 ppm hydrogen. Sensor resistance changes linearly from the lowest level we have been able to test, 20 ppm, to 1000 ppm, and then non-linearly to the explosive limit. The sensors demonstrate complete reversibility, repeatability, negligible drift, no hysteresis, and wide dynamic range. The sensors have a room temperature 90% response time of several tens of seconds, depending upon details of the fabrication process. The nanoscale geometry of the nanotubes, in particular the points of tube-to-tube contact, is believed to be responsible for the outstanding hydrogen gas sensitivity. Furthermore, while reduction of nanotube diameter from 76 nm to 22 nm increases the surface area by a factor of two the hydrogen sensitivity is increased by approximately a factor of 200, hence the material architecture, not just surface area, plays a key role in determining the resultant properties. Cross-sensitivity testing on the titania nanotube sensors shows no response to CO, CO₂, and NH₃.

9:00 AM K4.2/A3.2

Resistive Oxygen Gas Sensors Using Cerium Oxide Nanosized Powder. Norimitsu Murayama, Noriya Izu, Woosuck Shin and Ichiro Matsubara; National Institute of Advanced Industrial Science and Technology, Nagoya, Aichi, Japan.

Resistive oxygen gas sensors operate based on the electrical conductivity of oxide semiconductor changing with the amounts of oxygen deficiency. The sensors are essentially suitable for low-cost production because of their small size and simple structure. The resistive oxygen gas sensors are promising candidates for electrical fuel injection control of two-wheel vehicles, which is necessary for responding to tightening two-wheel emission control regulations. Cerium oxide (CeO₂) is suitable material for the sensors, since it has large diffusion coefficient for oxygen. The response time of the sensor

decreases with decreasing the powder size. Therefore, CeO₂ nanosized powder is necessary for fast response sensors. Cerium oxide nanosized powder was synthesized by modified precipitation method. The precipitate, which was formed from the addition of NH₄OH to Ce(NO₃)₃ aqueous solution, and was filtered. The obtained gel was mixed with carbon powder with a particle size of about 20 nm by a mechanically rotating mixer. The mixture was dried at 70 °C in air. The carbon powder was burned out by heat treatment at 900 °C in air for 4 h, resulting in the formation of granules of aggregated CeO₂ nanosized powder. The CeO₂ nanosized powder was easily disaggregated by ultrasonic vibration. Finally, the CeO₂ powder with a size of 50 nm was obtained. Using the powder, thick films were screen-printed on alumina substrates, and were fired at 1100 °C. The grain size was about 120 nm. The response time was about 20 ms at 800 °C.

9:15 AM K4.3/A3.3

Thermodynamic and Kinetic Principles for Electrochemical Gas Sensors based on Solid Ionic Conductors.

Evangelos D. Tsagarakis¹ and Werner Weppner²; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Faculty of Engineering, Christian Albrechts University, Kiel, Germany.

Several concepts can be applied for gas detection using solid ionic conductors. The fundamental characteristics and the essential variables for proper design of electrochemical cells are analyzed in terms of the sensing principle applied. The principal properties for materials as components of electrochemical devices are being illustrated. Employment of dynamic method allows implementation of the Fourier coefficients to generate a complex plane plot representation. This can be particularly useful for extracting information regarding the selectivity of an electrochemical cell to multiple gas species. Moreover, modeling the system response upon a periodical perturbation can be beneficial on understanding the individual processes and optimizing the overall performance.

9:30 AM *K4.4/A3.4

Non-Nernstian Planar YSZ-based Electrochemical Sensors with One Semiconducting Oxide Electrode.

Elisabetta Di Bartolomeo and Maria Luisa Grilli; Dept of Chemical Science and Technology, University of Rome Tor Vergata, Rome, Italy.

At present, non-Nernstian solid electrolyte electrochemical sensors seems to be the most promising devices for high temperature applications. Solid oxide electrochemical O₂ sensors are inexpensive and have successfully shown to work in harsh combustion exhaust environment. If modified to selectivity measure NO_x or CO /hydrocarbons concentrations, this type of sensors can be used to improve the combustion as a feed-back elements in engine control systems and thus comply with the always much more strict automotive emission regulations. Coating or undercoating one Pt electrode with semiconducting oxide powder with high catalytic properties in gas reduction/oxidation, it is possible to design devices with good selectivity and fast response time. Planar sensors based on tape-cast YSZ layers (150 μ m of thickness) were fabricated. Two Pt finger electrodes were deposited on one side of the layers. One of the electrodes was covered with an oxide thick film. The oxide tested included WO₃, La_{0.8}Sr_{0.2}FeO₃ and In₂O₃. All the oxides were prepared using different chemical methods. The oxide powders were mixed with a screen-printing oil and thus painted on one metallic electrode. The sensors were tested in potentiometric devices at various concentrations of NO₂ and CO (200-1000 ppm in synthetic air), at different temperatures. Amperometric and electrochemical impedance spectroscopy (EIS) measurements were performed to understand the sensing mechanism. Long-term measurements were carried out to investigate the stability of the sensors. Some field tests were also performed. Planar sensors were located close to a commercial oxygen sensor, downstream the three-way catalytic converter of a FIAT fire 1242 c.c. spark ignition engine coupled to a dynamometer. The gas sensor packaging used was like a commercial lambda probe provided with heating facility. Another commercial oxygen sensor was located upstream the catalytic converter to control the air/fuel ratio (A/F) of the engine. EMF response of gas and oxygen sensors both located downstream the catalytic converter were recorded simultaneously. The performance of the gas sensors was measured at the stoichiometric point (A/F=14) at different engine regimes (RPM and torque) and thus at different operating temperatures. To increase the NO_x concentration in the exhausts, some measurements at lean-fuel conditions (A/F>14) were also performed. The response of gas sensors was compared with the response of the commercial lambda probe. Moreover the EMF measurements were related to the exhaust gas concentrations measured by spectroscopic analytical equipment at the engine exhaust end: non-dispersive infrared spectrometer (NDIR) for CO and CO₂, chemiluminescence spectrometer for NO_x, and flame ionised detector (FID) for unburned hydrocarbons. Preliminary measurements showed promising results in terms of sensitivity, stability and reproducibility, even though the response time should be

improved.

10:30 AM *K4.5/A3.5

Chemical Sensors for Automotive Applications.

Richard E. Soltis, Physical & Environmental Sciences, Ford Motor Company, Dearborn, Michigan.

Chemical sensors have become an essential part of the control system for vehicles powered by internal combustion engines (ICE). These sensors currently are used for feedback control of the air-to-fuel ratio (A/F) for improved vehicle performance and reduced emission levels. In addition, they also have been widely employed for monitoring the conversion efficiency, or 'health' of the catalyst as part of the on-board diagnostics (OBD) requirements. In the future, stricter emission standards and alternative powertrains (e.g. H2ICE, fuel cells, lean burn, and hybrids) will undoubtedly require additional sensors for control and monitoring. At present, the oxygen sensor, which has been used universally for over 20 years, is the only exhaust gas sensor used on vehicles. It is one of the few sensors that can meet the stringent demands imposed by the extreme range of operating temperatures and harsh chemical environment of the automotive exhaust. This type of sensor is essentially a Nernst cell comprised of yttria-stabilized zirconia (YSZ) as the electrolyte (oxygen-ion conductor) with porous platinum electrodes. These sensors typically have an internal heater for rapid warm-up and to provide a more stable output signal. Recently, solid state electrochemical sensors for measuring NOx have been developed for automotive applications. These sensors, also based on YSZ, consist of multiple oxygen pumping cells, with an integral heating element. Other materials for chemical sensing, including metal oxide resistors and SiC-based devices are also candidates for exhaust gas sensors. However, long term stability and durability concerns have resulted in limited implementation. Chemical sensors for other less-demanding applications, such as hydrogen leak detection or cabin air quality, are also of interest and are currently under development by several manufacturers. After a brief introduction to the basic operating principles of oxygen sensors, recent developments in electrochemical sensors, including planar sensor fabrication technology, will be described. The status of other zirconia-based sensors designed to measure gases such as NH₃, NO_x, HC, H₂O, and CO₂ will also be reviewed. Finally, chemical sensors based on other technologies will be discussed in light of current trends in emerging emission standards and alternative powertrains.

11:00 AM K4.6/A3.6

Humidity Sensing with Manganese Oxide Ambigel

Nanoarchitectures. Michael Scott Doescher, Jeremy J. Pietron, Jeffrey W. Long and Debra R. Rolison; Code 6171 Surface Chemistry Branch, NRL, Washington, District of Columbia.

Architecture is an essential element of sensor performance. Mesoporous electrically conducting birnessite manganese oxide is synthesized via sol-gel chemistry followed by evaporation of a nonpolar low surface tension liquid to prevent pore collapse. Ambigel nanoarchitectures have bicontinuous pore and solid networks that permit facile diffusion of analytes throughout the high-surface-area architecture. This combination of active nanoscale surface and full accessibility to analyte is especially appealing for gas-phase, temperature, and humidity sensors. The effects of electrode architecture were explored by characterizing both manganese oxide monoliths and sintered powder films (formed by drop casting ground ambigel on interdigitated array electrodes) to determine their pore-size distribution (analysis of nitrogen physisorption data), thermal response, and the electrical response (impedance spectroscopy) under temperature and atmospheric control. Monolithic mesoporous manganese oxide nanoarchitectures exhibit a conductimetric humidity response at equilibrium that is 17 times more sensitive than the sintered particulate film derived from the same material. As relative humidity increases, water condensation in the monolith creates an electrically wired pore-solid nanoarchitecture. Long-range continuity of the pore network in the ambigel permits proton conduction over macroscopic distances between measurement electrodes. The flux of protons in sintered powder samples of the same material is limited due to the disruption of proton conduction pathways at interparticle connections, thus limiting the sensitivity of the device to humidity.

11:15 AM K4.7/A3.7

Sr(Ti,Fe)O_{3-δ} exhaust gas sensors. Thomas Schneider, Christoph Peters, Stefan Wagner, Wolfgang Menesklou and Ellen Ivers-Tiffée; Institute of Materials for Electrical and Electronics Engineering, Universitaet Karlsruhe (TH), Karlsruhe, Germany.

In automotive applications oxygen sensors control the air-fuel ratio in order to reduce fuel consumption. Direct injection engines or lean burn engines operating with air excess ($\lambda > 1$) require more advanced sensor concepts [1]. Acceptor doped Sr(Ti,Fe)O_{3-δ} has been qualified as a resistive type oxygen sensor material [2], its electrical

conductivity reflects the equilibrium between the oxygen partial pressure pO₂ in the atmosphere and the bulk stoichiometry at temperatures typically above 700 °C. SrTi_{1-x}Fe_xO_{3-δ} solid solutions were found to change their temperature coefficient of resistance (TCR) from negative to positive as iron increasingly substitutes for titanium, with the TCR tending towards zero at x = 0.35. This composition, Sr(Ti_{0.65}Fe_{0.35})O_{3-δ}, thus shows a temperature independent and, in contrast to donor doped compounds, a long term stable characteristic [3,4]. For the development of a planar type sensing element, Sr(Ti_{0.65}Fe_{0.35})O_{3-δ} has to be applied as a thick film on a zirconia substrate which has integrated Pt heating elements as well as Pt contacts [5]. Temperature independence (at T = 750...900 °C, pO₂ = 10⁻⁴...1 bar) and fast response times (t₉₀ = 6.5 ms at 900 °C), both key issues of Sr(Ti_{0.65}Fe_{0.35})O_{3-δ}, have to be maintained over the entire lifetime of the sensing element. In this work, financially supported by the Federal Ministry for Education and Research (Germany, BMBF PTJ-NMT 03N3102), the structural and electrical properties of the sensor are investigated with regard to the chemical stability of the sensing element. [1] E. Ivers-Tiffée et al., *Electrochimica Acta* 47 (2001), 807-814 [2] R. Moos et al., *Sensors and Actuators B* 67 (2000), 178-183 [3] W. Menesklou et al., *Sensors and Actuators B* 59 (1999), 184-189 [4] W. Menesklou et al., *MRS Symp. Proc.* 604 (2000), 305-310 [5] J. Riegel et al., *Solid State Ionics* 152-153 (2002), 783-800

11:30 AM K4.8/A3.8

A Study of the Electrical Properties and Stability of Sr(Ti,Fe)O₃ Thin Films for Oxygen Sensing Applications.

Scott J. Litzelman, Avner Rothschild and Harry L. Tuller; Crystal Physics and Electroceramics Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts.

In recent years, SrTi_{0.65}Fe_{0.35}O₃ (STF-35) has been studied in bulk ceramic and thick film form due to its unique temperature independent resistance above 700 C and pO₂ > 10⁻⁴ bar while retaining sensitivity to variations in pO₂ [1,2]. As a consequence of its unique properties, STF-35 has become a prime resistive oxygen sensor candidate for automotive exhaust systems. Recently, sensors fabricated from thick films were discovered to suffer from instabilities due to reaction between STF-35 and the alumina substrate upon which it had been deposited [3]. In this study, thin films of STF-35 are deposited on alumina and magnesia substrates and interaction products, if any, are investigated in detail in an attempt to identify a stable sensor-substrate combination. Preliminary measurements of the electrical properties of the film are also reported and compared with data obtained on bulk or thick film STF-35. To study the stability of STF-35 with respect to the substrate, thin films were deposited via pulsed laser deposition (PLD) onto alumina and magnesia substrates. X-ray diffraction analysis demonstrates that STF-35 reacts with alumina to form an intermediate reaction product, SrAl₁₂O₁₉. No such reaction was found when MgO substrates were utilized. Analysis by Rutherford Backscattering Spectrometry (RBS) does indicate, however, some depletion of strontium and iron near the substrate-film interface. The electrical properties of the films were studied using lithographically-designed microelectrodes in a newly-constructed microprobe chamber which allows for measurements in controlled atmospheres, up to temperatures of 1000 C. The thermal activation energies and response to changes in pO₂ are presented and discussed. REFERENCES [1] Menesklou, W., et al., High temperature oxygen sensors based on doped SrTiO₃. *Sensors and Actuators B*, 1999. 59: p. 184-189. [2] Moos, R., et al., Materials for temperature independent resistive oxygen sensors for combustion exhaust control. *Sensors and Actuators B*, 2000. 67: p. 178-183. [3] Moos, R., et al., Temperature-independent resistive oxygen exhaust gas sensor for lean-burn engines in thick-film technology. *Sensors and Actuators B*, 2003. 93(1-3): p. 43-50.

11:45 AM K4.9/A3.9

High Temperature Operation and Stability of Langasite Resonators.

Holger Fritze¹, Michal Schulz¹, Huankiat Seh² and Harry Tuller²; ¹Department of Physics, Metallurgy and Materials Science, TU Clausthal, Clausthal-Zellerfeld, Germany; ²Department of Materials Science & Engineering, MIT, Cambridge, Massachusetts.

High temperature stable piezoelectric materials such as langasite (La₃Ga₅SiO₁₄) and gallium orthophosphate (GaPO₄) are attractive as the basis of gas phase chemical sensing at elevated temperatures. Specific surface affinity layers cause gas atmosphere dependent mass changes and, thereby, shifts in resonance frequency of piezoelectric resonators coated with such films. High sensitivity is expected since the mass sensitivity of e. g. langasite resonators at 800 °C has been shown to be on the same order of magnitude as that of quartz resonators at room temperature [1]. Factors limiting potential use of langasite as a gas sensor platform at elevated temperatures include excessive conductive and viscous damping, deviations from stoichiometry and chemical instability. We begin by summarizing the

results of atmosphere dependent electrical conductivity and temperature dependent oxygen and gallium diffusivity data. A defect model consistent with these results points to oxygen ion transport dominant under oxidizing conditions shifting to electronic conduction under reducing conditions. Intentional doping of langasite single crystals is performed to modify the high temperature conductivity and piezoelectric properties of langasite. Based on a one-dimensional description of the resonator device, the material constants of the resonator are determined as a function of the temperature by fitting the calculated complex impedance to the experimental data in the vicinity of the resonance frequency. The effective viscosity of the resonator material and the bulk conductivity are found to control the resonator quality. The intentional doping suggests the possibility of lowering the damping by choosing the appropriate dopant concentrations. Based on the defect model, improvement of the resonance properties, i. e. lowering of damping at high temperatures, seems to be feasible. The rate of gallium loss from the surface at intermediate temperatures (750 °C), calculated based on the gallium diffusion data, is not believed to be of major concern regarding resonator performance. Conductivity degradation in hydrogen containing atmospheres is observed and the potential creation of reaction products is under investigation. [1] H. Fritze, O. Schneider, H. Seh, H. L. Tuller, G. Borchardt, High Temperature Bulk Acoustic Wave Properties of Langasite, Phys. Chem. Chem. Phys. 5, pp. 5207-5214, 2003.

SESSION K5/FF5: Joint Session: Solid State Chemistry
of Ionic Conductors
Chairs: Nathaniel Brese and Harry Tuller
Tuesday Afternoon, November 30, 2004
Republic B (Sheraton)

1:30 PM *K5.1/FF5.1

NMR Investigations of Ionic Conduction Mechanisms in Oxides and Fluorides: Applications to Pyrochlores, Perovskites, Aurivillius Phases and Fluorites. Namjoo Kim, John L. Palumbo, Stephen A. Boyd and Clare P. Grey; Chemistry, SUNY Stony Brook, Stony Brook, New York.

Solid state NMR may be used to correlate local structure with the dynamics that occur in ionic conductors. For example, in studies of $\alpha\text{-Bi}_4\text{V}_2\text{O}_{11}$, we have shown that ^{17}O MAS NMR may be used to (i) distinguish between oxygen ions in the $[\text{Bi}_2\text{O}_2]^{2+}$ and vanadium oxide (perovskite) layers, and (ii) detect the mobility of the ions in the perovskite layers. $^{17}\text{O}/^{51}\text{V}$ double resonance NMR experiments, which probe proximity between different nuclei, were used to confirm the assignments of the resonances and as an additional probe of oxygen mobility. Two-dimensional NMR may be used to detect much slower motion, allowing a wider range of oxide-ion conductors to be studied with ^{17}O NMR. Applications of this approach to study motion in Nb^{5+} -doped Bi_2WO_6 and Ca^{2+} -doped $\text{Y}_2\text{Tl}_2\text{O}_7$ will be shown. In more recent work, we are investigating the effect that particle size has on local structure and conductivity of doped fluorides.

2:00 PM K5.2/FF5.2

Structure Specificity of Nanocrystalline Praseodymia Doped Ceria. Vladislav A. Sadykov¹, Vladimir I. Voronin², Alexander N. Petrov³, Yulia V. Frolova¹, Vladimir I. Zaikovskii¹, Holger Borchert¹ and Stylianou Neophytides⁴; ¹Heterogeneous catalysis, Boreosc Institute of Catalysis, Novosibirsk, Russian Federation; ²Institute of Metals Physics, Ural Branch of RAS, Ekaterinburg, Russian Federation; ³Chemical Department, Ural State University, Ekaterinburg, Russian Federation; ⁴Institute of Chemical Engineering & High Temperature Processes, Patras, Greece.

Praseodymia doped ceria possessing a high mixed conductivity is of a great interest for such application as fuel cell electrodes, oxygen separation membranes, sensors etc. However, up to day neutron diffraction studies of this system have not been available. In this work, nanocrystalline samples of praseodymia doped ceria ($x\text{Pr} = 0.5$) prepared by Pechini route and calcined under air at 500-1300 °C were studied by using TEM and neutron diffraction methods. The neutron diffraction studies were performed at room temperatures with the use of a D7a neutron diffractometer installed at the horizontal channel of an IVV-2M reactor. The structural parameters were refined by the Rietveld full-profile method with the Fullprof program package. The charge state of Pr in samples was characterized by XPS. TEM revealed a good crystallinity of nanodomains (typical sizes 50-100 Å) disorderly stacked into platelets. Within studied doping range, all samples were found to be single-phase fluorites. The lattice constant goes through the maximum at $x = 0.3$. This trend correlates with variation of the diffraction peaks half-width and intensity of diffraction background corresponding to an admixture with a high non-elastic thermal neutron scattering cross-section (such as

hydroxyls, water etc). This behavior was explained by existence of both Pr^{3+} and Pr^{4+} cations in samples as revealed by XPS. At higher Pr content $\text{Pr}^{4+}/\text{Pr}^{3+}$ ratio increases which explains decreasing of the lattice constant due to smaller size of Pr^{4+} cation. The surface layer hydroxylation leading to the increase of O/Me ratio up to 2.2 was demonstrated by XPS, while the lattice hydroxyls were detected by FTIRS. Domain boundaries could be hydroxylated as well due to their loose structure. For all nanocrystalline samples, Rietveld structure refinement has not revealed any substantial deviations of the O/Me occupation factors ratio from 2, though it does not exclude simultaneous presence of both cation and anion vacancies in the lattice. Decline of a mean Pr-O distance with Pr content approaching that of $\text{Ce}^{4+}\text{-O}$ was revealed correlating with the increase of Pr^{4+} content for heavily-doped samples. For a given Pr content, the lattice constant declines with calcination temperature reaching at 1300 °C values typical for dense coarse-grained systems due to oxidation of Pr^{3+} to Pr^{4+} and dehydroxylation of a sample. Based upon all these results, the structural model for the nanocrystalline praseodymium doped ceria is suggested. This includes existence of both cation and anion vacancies in the lattice filled in part by dissociated water species. The relative stability of this defect structure is ensured by a high value of the free surface and developed domain boundaries network. This work is in part supported by INTAS 01-2162 and ISTC 2529 Projects. DAAD postdoctoral research scholarship to H.B. is acknowledged.

2:15 PM K5.3/FF5.3

Measurement of the Transport Mechanism of YSZ and CGO Thin Films with Nanometer-Sized Grain Structure. Joshua L. Hertz, Anja Bieberle and Harry L. Tuller; Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Micro-solid oxide fuel cells hold promise as portable power sources with energy densities considerably above that exhibited by batteries. However, the use of thin film processing schemes often produces films with nanometer-scale grain sizes. Others have reported transport mechanism changes in zirconia and ceria-based materials at these size scales, often leading to decreases in activation energy^{1,2}. In this work, thin film yttria-stabilized zirconia [YSZ] and cerium gadolinium oxide [CGO] solid electrolytes were sputtered onto insulating substrates over a range of temperatures. Films were produced with a range of grain sizes, ranging from as small as 10-20 nm for those sputtered at room temperature. For reference, polished samples of single crystal and bulk, poly-crystalline YSZ were also used. Platinum, platinum-YSZ cermet and gold film electrodes were then sputtered on top and lithographically patterned to give interdigitated electrodes with well-controlled geometry. Electrode patterns with variable separation distances and triple phase boundary lengths, ranging over nearly two orders of magnitude, were used. Impedance spectroscopy was carried out on these samples at controlled temperatures, DC bias and oxygen partial pressures. The microstructure and chemistry of the films were characterized by XRD, TEM, AFM, WDS and RBS. Correlating the measured electrochemical performance data with sample morphology, geometry, composition and measurement environment provided insight into the transport mechanism of the films as well as the reaction pathways at the electrodes. This work was supported by the DoD Multidisciplinary University Research Initiative (MURI) program administered by the Army Research Office under Grant DAAD19-01-1-0566. 1. P. Mondal, A. Klein, W. Jaegermann and H. Hahn, Solid State Ionics, 118, 331 (1999). 2. Y. Li, M. Liu, J. Gong, Y. Chen, Z. Tang and Z. Zhang, Mat. Sci. and Eng. B, 103, 108 (2003).

2:30 PM *K5.4/FF5.4

Ion Conduction - Bulk vs. Interface. Joachim Maier, Solid State Chemistry I, Max Planck Institute for Solid State Research, Stuttgart, Germany.

The first part of the talk gives a brief overview on fundamentals of ion conduction in the bulk of solids, in particular on the dependence of charge carrier concentrations on materials and control parameters. The second part highlights the modifications in charge carrier concentrations that are due to the presence of interfaces, and discusses in how far the purposeful introduction of interfaces can be used as a materials design parameter. The third part discusses true size effects, i. e. effects in which neighboring interfaces perceive each other. It is shown that nano-ionics is of similar perspective for Solid State Ionics as nano-electronics is for the field of electronics. Size reduction leads to a variety of anomalies in terms of ion conduction, mixed conduction, and charge storage that can be understood in terms of defect chemistry and can be used in terms of electrochemical devices.

3:30 PM *K5.5/FF5.5

Ionic Transport Properties of Mixed Conducting Perovskite Oxides. Werner Sitte and Edith Bucher; Department of General, Analytical and Physical Chemistry, University of Leoben, Leoben, Austria.

Mixed ionic-electronic conducting oxides are of interest as potential candidates for solid oxide fuel cell cathodes, oxygen permeable membranes, or sensors. At high temperatures and low oxygen partial pressures these transition metal oxides exhibit large concentrations of vacant oxygen sites, inducing high ionic conductivity and high oxygen diffusivity. However, with increasing oxygen deficit, vacancy association in microdomains within the disordered matrix is assumed. The degree of ordering in the oxygen sublattice controls the number and mobility of ionic charge carriers available for oxygen transport. Experimental evidence for order-disorder transitions has been reported for a number of compounds in the $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ system. Measurements of the oxygen transport properties, i.e. the temperature and $p\text{O}_2$ -dependences of the ionic conductivity and the kinetic parameters for oxygen exchange (chemical diffusion coefficient, surface oxygen exchange coefficient) are used to gain insight into oxygen vacancy ordering and formation of defect clusters in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($x=0.4, 0.6$) and $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ($x=0.6$) [1]. Additionally, selected samples quenched from the T- and $p\text{O}_2$ -conditions of interest are studied on the nanometer scale by transmission electron microscopy in order to elucidate the microstructure [2]. It is concluded that ordering leads to progressive immobilization of oxygen vacancies and consequently to a decrease of the ionic conductivity with increasing oxygen nonstoichiometry in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($x=0.4, 0.6$). Similar effects are believed to be responsible for the decrease of the chemical diffusion coefficient of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($x=0.6$) with decreasing oxygen partial pressure. Microdomains with vacancy ordered structures could be detected by analytical electron microscopy in highly oxygen-deficient samples of $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$. High resolution transmission electron microscopy revealed a superstructure within the oxygen sublattice in domains of about 100 nm in size. References 1. E. Bucher, A. Benisek, W. Sitte, Solid State Ionics 157 (2003) 39-44. 2. E. Bucher, W. Sitte, I. Rom, I. Papst, W. Grogger, F. Hofer, Solid State Ionics 152-153 (2002) 417-421.

4:00 PM K5.6/FF5.6

Defect Chemical Role of Mn in Gd-Doped CeO_2 (GDC).
Sang-Hyun Park and Han-Il Yoo; School of Materials Science and Engineering, Seoul National University, Seoul, South Korea.

It has been known that addition of a small amount of Mn remarkably accelerates sintering of Gd-doped CeO_2 , that is, rendering the sintering possible at much lower temperature than otherwise. This phenomenon is generally understood as being due to Mn acting as acceptors to increase the concentration of charge compensating oxygen vacancies and hence to enhance the mass transport. In this case, one would even expect that the electrolytic domain of GDC may be enlarged towards the reducing atmosphere because Mn tends to be more effective as acceptors due to its ever reducing valence down to +2 (or MnCe^{2+}) with decreasing oxygen activity. In order to elucidate the defect chemical role of Mn in GDC, we examined the electrical conductivity on 5 m/o Mn-doped GDC in association with XRD and EPMA analyses. It has been found that Mn addition does neither enhance the ionic conductivity nor enlarge the electrolytic domain width towards reducing atmosphere, indicating that Mn is by no means so effective an acceptor as expected. Furthermore, despite that the specimens are X-ray-wise pure, rastered EPMA results revealed at grain boundaries the isolated packets with Mn enriched. It is, thus, suggested that the solubility limit of Mn in GDC is likely no more than 1 m/o and the sintering enhancement is likely due to a liquid phase at grain boundaries due to the enriched Mn.

4:15 PM K5.7/FF5.7

Growth and Characterization of Highly Oriented Pure and Gd 2O_3 Doped $\text{CeO}_2(111)$ on $\text{ZrO}_2(111)/\text{Al}_2\text{O}_3(0001)$ System. Debasis Bera^{1,2}, S. Seal¹, S. Azad², C. M. Wang², V. Shutthanandan², D. E. McCready², M. H. Engelhard² and S. Thevuthasan²; ¹MMAE, University of Central Florida, Orlando, Florida; ²Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington.

Epitaxial growth of ceria on insulator substrates has been the focus of materials research in the recent years due to its applications in technological devices such as sensors, solid oxide fuel cells, batteries and three-way catalysts of automobiles. Highly oriented pure and Gd 2O_3 doped ceria films have been grown on pure and $\text{ZrO}_2(111)$ buffered $\text{Al}_2\text{O}_3(0001)$ substrates using oxygen plasma-assisted molecular beam epitaxy (OPA-MBE). These films were characterized by several surface and bulk sensitive capabilities. The Ceria films grown on pure $\text{Al}_2\text{O}_3(0001)$ substrate show polycrystalline features due to structural deformations resulting from the large lattice mismatch between the $\text{Al}_2\text{O}_3(0001)$ substrate and the ceria film. However, the ceria films grown on a thin layer of $\text{ZrO}_2(111)$, which is grown as a buffer layer on top of $\text{Al}_2\text{O}_3(0001)$, appears to be epitaxial and highly oriented. This is presumably due to the much smaller lattice mismatch between cubic zirconia and ceria compared to the substantial differences between the lattice parameters of $\text{Al}_2\text{O}_3(0001)$

and ceria. Oxygen ionic conductivity in Gd 2O_3 doped ceria films has been measured as a function of Gd concentration and these results will be compared with the ion conductance of the polycrystalline ceria films. Inter-diffusion of elements at the $\text{CeO}_2/\text{ZrO}_2$ interface has been studied using high resolution transmission electron microscopy (HRTEM) and x-ray photoelectron spectroscopy (XPS) depth profiling. Detailed discussion of these results, along with the Rutherford backscattering spectrometry results will be presented.

4:30 PM K5.8/FF5.8

Morphology and Electrochemistry of Hydrothermally Synthesized Olivine Phosphates. Brian L. Ellis, Subramanya P. Herle, Young-Ho Rho, William R. M. Makahnouk and Linda F. Nazar; Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

Among the many positive electrode materials being studied for rechargeable lithium batteries, LiFePO_4 is a promising material based on its low environmental impact and low cost of the raw materials. However, the material has a low inherent electrical conductivity, limiting its electrochemical performance thus far. Two of the most critical solutions in producing LiFePO_4 that exhibits close to theoretical capacity at high rates have been found to be coating the crystallites with carbon (or another conductive coating) and reduction of the particle size to reduce the transport path length. We report here novel synthetic methods based on hydrothermal synthesis in the presence of solution additives, which result in very small crystallite, single-phase LiFePO_4 . The LiFePO_4 products are produced either directly by hydrothermal synthesis, or by coating the precursor crystallites with various agents, followed by heat treatment at 600°C-800 °C under reducing atmospheres. The morphology of the end product can be controlled by the manipulation of the concentration of precursors, pH, hydrothermal pressure and the nature of the additive. Control of these factors results in crystallites with an average size of between 500 - 700nm, and a narrow particle size distribution. Morphology and particle size distribution of the hydrothermal product are maintained during heat treatment at higher temperatures, as the additive remains on the surface of the crystallite and hence limits particle sintering. The effects of morphology and particle size on electrochemical performance will be described.

4:45 PM K5.9/FF5.9

Vibrational Features of Polyphosphates used as Lithium Intercalation Materials. Christian M. Julien¹, Pavel Jozwiak^{2,1}, Jerzy Garbacz² and Michel Massot³; ¹LMDH, University P et M Curie, Paris, France; ²Faculty of Physics, University of Technology, Warsaw, Poland; ³LPMC, University P et M Curie, Paris, France.

Among the huge family of compounds constituted by phospho-oxide polyanions, the polyphosphates can be sub-classified into orthophosphates characterized by $(\text{PO}_4)^{3-}$ isolated units, pyro- and diphosphates in which P_2O_7 groups are formed by two shared corner $(\text{PO}_4)^{3-}$ units, and triphosphates ($n=3$) where three $(\text{PO}_4)^{3-}$ units form $(\text{P}_3\text{O}_{10})^{5-}$ anions. The adaptability of PO_4 tetrahedra and P_2O_7 groups of interest possess an open framework that houses interstitial lithium ions. Thus, lithium transition-metal phosphates built from MeO_6 octahedra linked to PO_4 tetrahedra are candidates as positive electrodes for Li-ion batteries. We present here the results obtained from structural characterisation using X-ray diffractometry and local probe such as Raman and FTIR spectroscopy. Vibrational features and local cationic environments in different structures including both crystalline and glassy form of phospho-olivines LiMePO_4 , pyrophosphates $\text{LiMe}_{1.5}\text{P}_2\text{O}_7$, and Nasicon-like $\text{Li}_3\text{Me}_2(\text{PO}_4)_3$ frameworks are presented. The infrared and Raman spectra of these materials are interpreted using factor group analysis and molecular model. Spectroscopic data show the fingerprint of the various frameworks and the possibility of obtaining direct information about the configuration of $(\text{PO}_4)^{3-}$ polyanions and of P-O-P bridges.

SESSION K6: Poster Session: Lithium Batteries
Chairs: P. Knauth, Christian Masquelier, Enrico Traversa and Eric D. Wachsman
Tuesday Evening, November 30, 2004
8:00 PM
Exhibition Hall D (Hynes)

K6.1

Coating of Spinel LiMn_2O_4 and its Electrochemical Properties. Hanxing Liu, Xiaoyan Gan, Xianjun Zhu, Chen Hu, Jian Zhou and Shixi Ouyang; State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, Hubei Province, China.

LiMn_2O_4 is one of important cathode in secondary battery. Some of problem of the cathode materials blocked its application in industry.

One of those problem is that the cycles in high temperature. The purpose of present study is trying to get better in cycles of battery by coating Ni compound on LiMn2O4 with sol-gel method. High quality LiMn2O4 grain can be obtained which can greatly decrease Mn dissolution and consequently improve cycle performance of cathode. The processing of the method includes: (1) the LiMn2O4 grains are capped by nickel-doped gel with a content of X=0.1 (X=Ni/(Ni+Mn)); (2) heated at 7500C for 20 hours. XRD, SEM, and XPS were employed to detect the microstructure and valence of products obtained by modification process shown above. The results shown the compounds belong to the spinel type with a molecular formula of LiNixMn2-xO4. Chemical properties were tested, which showed that Mn dissolution were low. In correspondence to great resistance to erosion of electrolyte, the cycle performance is good and capacity retain can reach 103mAh/g after 60 cycle at 600C, higher than the LiMn2O4 which were not coated.

K6.2

Theoretical Analysis on the Structure and Properties of LiFePO4. Hanxing Liu, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, Hubei Province, China.

According the request of Li-ion secondary battery, peoples try to find high performance cathode materials. LiFePO4-based compounds attract us due to their high energy density, low raw materials cost, environmental friendliness and safety. Their key limitation has been extremely low electronic conductivity, until now believed to be intrinsic to this family of compounds. In present research work we did some basic problem including the influence of composition on the electronic structure, and conductivity etc. The experimental data including XRD, XPS were used to confirm the information of electronic structures. Quantum mechanism calculation method was also employed to calculate bonding order, fermi energy.

K6.3

Ab-initio Calculation for Intercalation Voltage in Layered LiMO2 (M= Zr, Nb, Rh, Mo, and Ru). S. P. Singh¹, M. S.

Tomar¹ and A. F. Van Der Ven²; ¹Department of Physics, University of Puerto Rico, Mayaguez, Mayaguez, Puerto Rico; ²Material Science and Engineering, MIT, Cambridge, Boston, Massachusetts.

Average intercalation voltages were calculated by inserting lithium ions into Vth group transition-metal oxides. The effect on the intercalation voltage of metal substitution was systematically studied by altering the Vth group transition metals M (M = Mo, Zr, Nb, Rh, Ru) in LiMO2 in the γ -NaFeO2 structure. In addition, the effect of crystal structure on intercalation voltage was studied in different structures. The intercalation voltages evaluated in LDA and GGA approximations using VASP are given in Table. LiZrO2 in layered structure has very low intercalation voltage and can be considered as an anode material. Lattice parameters in the layered γ -NaFeO2 structure computed in both LDA and GGA approximations are in agreement with experimentally reported work. A minor cation substitution like Mo and Rh could improve the capacity fading and other electrochemical properties of the existing materials such as LiNiMnO2. Initials experimental results will be presented.

K6.4

Insulator-Metal Transition in Li_xCoO₂: Combined TEM and AFM Studies. Anne Clemenccon, Sundeep Kumar and Yang Shao-Horn; Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Layered lithium cobalt dioxide, LiCoO2, is the most widely used positive electrode material in lithium rechargeable batteries. Menetrier et al. have reported the existence of a first-order phase transition between insulating Li0.94CoO2 and metallic Li0.75CoO2 using nuclear magnetic resonance analyses. Both phases have a rhombohedral crystal structure having space group R-3m with slightly different cell parameters. Our study is aimed at understanding the effect of this insulator-metal phase transition on the microstructure and transport properties of charged Li_xCoO2 samples. X-ray powder diffraction and electron diffraction techniques were used to probe structural changes while ex-situ and in-situ atomic force microscopy was employed to study the surface changes and modification in the electronic conductivity of Li_xCoO2 as a function of the lithium concentration.

K6.5

Abstract Withdrawn

K6.6

Discussion about Influence of B-Site Ion Valence for Perovskite-Type Li Ion Conductor, (La_{2/3-1/3p}Li_p)(Mg_{1/2}W_{1/2})O₃ (p=0.05, 0.11 and 0.14). Tetsuhiro Katsumata, Megumi Takahata, Nobuko Mochizuki and Yoshiyuki Inaguma; Faculty of Sci., Gakushuin Univ., Tokyo, Japan.

The perovskite-type Li ion conductors have been well known as high Li ion conductor and many fundamental researches have been carried out. For these compounds, it was revealed that the activation energy increases with the lattice contraction and its dependence is influenced by the valence of the B-site ion, i.e. the activation energy of the compound having tetravalent cation at B-site is smaller than that of the compound having the octavalent cation at the B-site when the lattice parameters are the same. In the case of complex B-site perovskite-type Li ion conductors, this dependence is dominated by the valence of B-site ion having higher valence. In this study, we synthesized perovskite-type Li conductors, (La_{2/3-1/3p}Li_p)(Mg_{1/2}W_{1/2})O₃ (p=0.05, 0.11 and 0.14), which are called LLMW, and investigated the influence of the valence of B-site ions in complex B-site perovskites. Furthermore, the static potential of A-site and the bottleneck for the Li ion was calculated from the coulomb potential and short-range repulsion for the perovskite-type structure with different valence B-site ion, and discussed the influence of the lattice parameter and valence of B-site ion on the activation energy from the variation of the difference between the potentials at the A-site and bottleneck with lattice parameter. LLMW have the ordered perovskite-type structure, i.e. NaCl-type ordering of W⁶⁺ and Mg²⁺ ions at the B-site and the alternative arrangement of La and Li ions and vacancies along the c-axis. In these compounds, the Li ions are considered to migrate in La-poor-layer and the highest ionic conductivity, 1.2×10⁻⁵ S/cm, is obtained for p=0.14. It is noted that the activation energy of these compound decreased with Li content, even though the lattice parameter did not vary. According to the structure refinement of LLMW, it was found that the covalent character of the W-O bond is enhanced with the increase in the Li content. These results indicates that the activation energy of LLMW is primarily influenced by the Coulomb repulsion between Li and W ions and the decrease in the activation energy is responsible for the decrease in the effective charge of the W ion due to increase in the covalent character of the W-O bond. The potential calculation also supports this idea. This calculation could qualitatively reproduce the variation of the activation energy with the lattice parameter and the valence of B-site ion obtained by the experiments. Furthermore, it is suggested that the Coulomb repulsion between Li and B-site ion at the bottleneck dominates the activation energy for the Li ion migration.

K6.7

A Vacuum Plasma Counter-Electrode Technique for Evaluating Secondary Battery Electrode Materials. Anne Takesian¹, Fernando Vereda¹, Rebecca Swartz², Peter Zerigian¹, Terry E. Haas³ and Ronald B. Goldner¹; ¹Electrical and Computer Engineering, Tufts University, Medford, Massachusetts; ²Mechanical Engineering, Tufts University, Medford, Massachusetts; ³Chemistry, Tufts University, Medford, Massachusetts.

In this paper we shall describe a recently developed vacuum plasma counter-electrode technique for evaluating secondary battery electrode materials in thin film form. Two motivations for developing the technique were: (i) to by-pass the electrochemical stability window limitations associated with liquid electrolytes; and (ii) to allow one to study electrode materials in essentially isolated half cells that employ a solid electrolyte (which, in turn, avoids the need to separate out any electrochemical, or other, effects arising from a second solid-solid interface, as well as eliminating problems associated with fabricating a high integrity entire solid-state cell). We shall present quantitative results obtained from using the technique to carry out electrochemical cycling studies on half cells composed of a polycrystalline rf sputter deposited tungsten oxide film electrode overcoated with either a thermally evaporated lithium orthophosphate or a thermally evaporated ion beam assist deposited lithium phosphorous oxynitride electrolyte [1]. The plasma counter electrode was generated by rf sputtering a five-inch diameter lithium orthophosphate target, at 13.56 MHz and low power (< 10W). A strip of lithium foil was used as a reference electrode in a side by side arrangement with the half cells (with the lithium foil place in intimate contact with the same lithium ion electrolyte that covered the electrode under test, but laterally displaced by approximately 1 mm from the electrode). Corroborating data was also obtained from electrochemical cycling experiments on the same half cells that employed a lithium metal counterelectrode, a lithium metal reference electrode, and a liquid electrolyte (lithium perchlorate in propylene carbonate) in an argon filled glove box. Similar data will be presented for half cells that used either a polyphenylene electrode or a lithium cobalt oxide electrode. The electrochemical cycling results provide strong evidence for the utility of the vacuum plasma counterelectrode technique for electrochemically characterizing secondary battery electrode materials, especially over a large voltage window. Some of this work was supported by Frank and Eleanor Pao and by NASA.

K6.8

Abstract Withdrawn

K6.9

Structural and Electrochemical Characterization of $\text{LiNi}_0.425\text{Mn}_0.425\text{Co}_0.15\text{O}_2$ Materials Synthesized by Different Synthesis Routes. Nicolas Tran¹, Laurence Croguennec¹, Christian Jordy², Philippe Biensan² and Claude Delmas¹; ¹Institut de Chimie de la Matière Condensée de Bordeaux-CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, Université Bordeaux I, PESSAC, France; ²SAFT - Direction de la Recherche, Bordeaux, France.

Cobalt partial substitution for nickel and manganese in $\text{LiNi}_0.5\text{Mn}_0.5\text{O}_2$ has been suggested as a way to enhance the cyclability and to decrease the polarisation of the Li // Li(Ni,Mn)O₂ batteries. To this purpose, $\text{LiNi}_0.425\text{Mn}_0.425\text{Co}_0.15\text{O}_2$ has been prepared by three different synthesis methods and has been studied from a structural, microstructural and electrochemical point of view. Chemical and redox analyses, X-ray diffraction patterns refinements and magnetic measurements will be discussed: they led us to propose for $\text{LiNi}_0.425\text{Mn}_0.425\text{Co}_0.15\text{O}_2$ an alpha-NaFeO₂-type long range structure and a cationic distribution with 7% of Ni²⁺ ions in the interslab space and the same amount of Li⁺ ions in the slab. The cycling tests of these materials were performed between 2 V and 4.5 V with a constant C/20 rate. The reversible capacity, the capacity retention and the polarisation obtained for each material were quite different. As such differences in electrochemical behaviour could not only be attributed to the structure of the materials, scanning electron microscopy, particle size and surface area measurements were carried out. The microstructure of $\text{LiNi}_0.425\text{Mn}_0.425\text{Co}_0.15\text{O}_2$ is believed to be a key point for its electrochemical behaviour in lithium-ion batteries.

K6.10

Profiling of Anode Surface Cycled in LiBOB-based Electrolyte of Li Ion Batteries. Unchul Lee, Kang Xu, Sheng S. Zhang and Richard Jow; AMSRD-SE-EI, Army Research Laboratory, Adelphi, Maryland.

As the youngest battery chemistry, Li ion technology was made possible by the formation of stable electrode/electrolyte interfaces. The correlation between the electrochemistry and the surface profile of the graphitic anode was studied in this work with a new salt lithium bis(oxalate)borate (LiBOB). In an attempt to depict a dynamic picture of the formation of graphite/electrolyte interface during the initial forming cycle, we employed X-ray photoelectron spectroscopy in combination with the pre-formation technique to establish the dependence of the surface chemistry on the forming potential of the anode. A progressive transition in the 1s electron binding energies of the major elements was observed as the lithiation proceeds; however, the surface chemical species as well as their abundances seemed to stabilize around 0.55 V and remained constant during the subsequent delithiation process, indicating that a stable solid electrolyte interface (SEI) exists thereafter. Integrating the information revealed by different analyses, we believe that the reductive decomposition of BOB-anion starts at ca. 1.00 V, while the effective protection of graphene surface by SEI is available after the anode is lithiated below the potential of 0.55 V. As the youngest battery chemistry, Li ion technology was made possible by the formation of stable electrode/electrolyte interfaces. The correlation between the electrochemistry and the surface profile of the graphitic anode was studied in this work with a new salt lithium bis(oxalate)borate (LiBOB). In an attempt to depict a dynamic picture of the formation of graphite/electrolyte interface during the initial forming cycle, we employed X-ray photoelectron spectroscopy in combination with the pre-formation technique to establish the dependence of the surface chemistry on the forming potential of the anode. A progressive transition in the 1s electron binding energies of the major elements was observed as the lithiation proceeds; however, the surface chemical species as well as their abundances seemed to stabilize around 0.55 V and remained constant during the subsequent delithiation process, indicating that a stable solid electrolyte interface (SEI) exists thereafter. Integrating the information revealed by different analyses, we believe that the reductive decomposition of BOB-anion starts at ca. 1.00 V, while the effective protection of graphene surface by SEI is available after the anode is lithiated below the potential of 0.55 V.

K6.11

Electrical Conductivity of LiMPO_4 (M = Fe, Mn, Co) Olivines. C. Delacourt¹, C. Wurm¹, F. Sauvage¹, J.-B. Leriche¹, R. Bouchet², M. Morcrette¹, J.-M. Tarascon¹ and C. Masquelier¹; ¹Laboratoire de Reactivité et Chimie des Solides, Université de Picardie Jules Verne, UMR CNRS 6007, Amiens, France; ²Laboratoire Matériaux Divisés, Revêtements, Electroceramiques, CNRS-Université de Provence, Centre Saint Jerome, Marseille, France.

Recent optimization studies of LiFePO_4 as a positive electrode in lithium batteries were mainly focused in lowering the particles' size, so as to minimize electronic and ionic (Li^+) paths within LiFePO_4

grains, and in creating an efficient carbon coating around the particles, thus improving electronic transport properties in the overall LiFePO_4/C composite [1]. Doping with supervalent elements, such as Nb, Zr, Mg..., was proposed by Chiang's group [2] as an alternative that led to much controversy [3]: an increase of 8 orders of magnitude of the intrinsic electronic conductivity of the triphylite particles was claimed. The optimization of the performances of LiMnPO_4 has been much less successful so far: low temperature preparation techniques and/or chemical carbon coating were not sufficient to counterbalance the very low electronic/ionic transport properties of this particular phase [4]. We undertook a very detailed investigation of electrical and electrochemical measurements of various LiMPO_4 samples. Carbon-coated LiFePO_4/C samples were prepared as published elsewhere [1]. Tentatives to dope LiMPO_4 with Nb was unsuccessful and systematically led to carbon-coated particles if the Nb- or Fe-precursors contained carbon. An isostatic press was used to obtain dense pellets that were subsequently sintered in inert atmosphere. Electrical properties were measured as a function of temperature by means of impedance spectroscopy and dc-measurements. The electrical conductivity of C-free pure LiFePO_4 is close to $10^{-9} \text{ S.cm}^{-1}$ at 300K ($E_a \approx 0.6 \text{ eV}$). On the other hand, conductivity values as high as $10^{-3} - 10^{-1} \text{ S.cm}^{-1}$ at 300K ($E_a \approx 0.08 \text{ eV}$) were measured on numerous carbon-coated samples (including those that had been tentatively "doped" with Nb). These results suggest that the overall conductivity of optimized LiFePO_4/C composite powders is extremely sensitive to the conductive carbon network coated at the surface of LiFePO_4 , even for very low carbon contents (around 1 to 2 wt. %). Similar conductivity measurements carried out on pure LiMnPO_4 , show an insulator behaviour for this compound, with electrical conductivities of several orders of magnitude below LiFePO_4 , thus strongly limiting its full utilization as a positive electrode material in lithium-ion batteries. 1. A. Audemer, C. Wurm, M. Morcrette, S. Gwizdala and C. Masquelier, **WO2004/001881 A2** 2. S.-Y. Chung, J. T. Bloking and Y.-M. Chiang, *Nature Mater.*, **1**, 123 (2002) 3. N. Ravet, A. Abouimrane and M. Armand, *Nature Mater.*, **2**, 702 (2003) 4. C. Delacourt, P. Poizot, M. Morcrette, J.-M. Tarascon, et C. Masquelier, *Chem. Mater.*, **16**, 93 (2004)

K6.12

Thermal Degradation Mechanisms of Lithium Nickel Oxide Derivatives. Laurence Croguennec¹, Marianne Guilmar¹, Nicolas Tran¹, Gwenaëlle Rousse^{2,3} and Claude Delmas¹; ¹Institut de Chimie de la Matière Condensée de Bordeaux-CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, Université Bordeaux I, Pessac, France; ²Institut Laue Langevin, Grenoble, France; ³Université Pierre et Marie Curie, Paris, France.

In the scope of our general studies on lithium nickel oxide derivatives as positive electrode materials in lithium-ion batteries, we have tried to understand mechanisms involved upon thermal degradation of the electrode. In situ X-ray diffraction correlated with Thermal Gravimetric Analyses coupled with Mass Spectrometry, and in situ neutron diffraction were used to characterize in details the thermal degradation mechanisms of $\text{Li}_x\text{Ni}_{1.02}\text{O}_2$, $\text{Li}_x\text{Ni}_{0.89}\text{Al}_{0.16}\text{O}_2$, $\text{Li}_x\text{Ni}_{0.70}\text{Co}_{0.15}\text{Al}_{0.15}\text{O}_2$ and $\text{Li}_x\text{Ni}_{0.90}\text{Mn}_{0.10}\text{O}_2$ materials ($x = 0.50$ and 0.30). The irreversible chemical and structural modifications occurring during the thermal treatment of these $\text{Li}_x(\text{Ni,M})\text{O}_2$ phases are very similar whatever the composition of the starting material: in all cases two phase transitions are observed, the main differences being the transition temperatures, the reaction energies and the reaction kinetics. The effects of aluminum, cobalt and manganese on the stability of deintercalated substituted lithium nickel oxides will be discussed by considering (i) the stability of the structure, (ii) the stability of the cation oxidation states in relation with their environments and (iii) the ability for a cation to move from an octahedral site to another one.

K6.13

Growth and Characterization of Lithium Pyrophosphates as Positive Electrodes for Lithium Batteries. Atmane Aitsalah¹, Khalil Benkhrouja², Michel Massot³, Francois Gendron¹ and Christian M. Julien¹; ¹LMDH, University P et M Curie, Paris, France; ²LMCM, University Chouaib Doukkali, EL Jadida, Morocco; ³LPMC, University P et M Curie, Paris, France.

Pyrophosphates $\text{AMe}_1.5\text{P}_2\text{O}_7$ form cage structures where the framework is built of PO_4 tetrahedra linked by bridging oxygen to give P_2O_7 groups. They can be classified in two groups according to the configuration of the P-O-P bridges into the P_2O_7 units. They exhibit either the dichromate-like ($\text{K}_2\text{Cr}_2\text{O}_7$) framework or the thortveitite-like ($\text{Sc}_2\text{Si}_2\text{O}_7$) lattice. The P_2O_7 groups are connected to the MeO_6 octahedron by sharing two oxygen corners, each belonging to a PO_4 unit. This induces a 3-D framework in which channel collinear to the [001] direction are formed and where the lithium ions are located. Lithium metal pyrophosphates (with $\text{Me} = \text{Ni, Co, Mn, Cu}$) were grown by solid state reaction while the lithium-iron pyrophosphate was synthesized by wet chemical method.

In this work, we investigate the structural properties of a series of $\text{LiMe}_{1.5}\text{P}_2\text{O}_7$ phases using XRD, Raman and FTIR measurements. The vibrational features of $\text{LiMe}_{1.5}\text{P}_2\text{O}_7$ (Me=Fe, Ni, Co, Mn, Cu) pyrophosphates has been studied by infrared and Raman. A comparison of the Raman and infrared wavenumbers of bands shows that the majority of them are not coincident, this fact confirms that the pyrophosphates possess a centrosymmetric structure. The vibrational spectra display 24 bands in the internal mode region: twelve bands in infrared spectrum and twelve in Raman spectrum; this confirms that the site group C2 for the P_2O_7 anion is adequate, and that the factor group C_2h must be applied. Overall, the spectroscopic fingerprints of pyrophosphate phases are the occurrence of the symmetric and asymmetric stretching modes of P-O-P units.

K6.14

Structural Studies of Phospho-Olivine Compounds

Synthesized by Chimie Douce. Atmane Aitsalah¹, Khalil Benkhoucha², Karim Zaghbi³, Francois Gendron¹ and Christian M. Julien¹; ¹LMDH, University P et M Curie, Paris, France; ²LMDH, University Chouaib Doukkali, El Jadida, Morocco; ³Institut de Recherche Hydro-Quebec, Varennes, Quebec, Canada.

Lithium orthophosphates LiMePO_4 and related materials (Me=Fe, Mn, Co, Ni) have recently received a lot of attention because their very promising use as positive electrodes in rechargeable lithium-ion batteries. They display high redox potentials, fast Li-ion transport, excellent thermal stability, and energy density comparable to that of conventional lithium metal oxides. The aim of this work is to synthesize LiMePO_4 compounds using various 'chimie douce' methods and to characterize and compare the structure of the products by XRD and spectroscopic measurements (Raman and FTIR). The various wet chemical techniques include nitrate, acetate, and succinate precursors. Structural data are compared as a function of the conditions of preparation (temperature, calcinations, reducing atmosphere, etc.). Lithium orthophosphates LiMePO_4 adopt the olivine-related structure built by cross-linked by the PO_4 groups forming a three-dimensional network. As expected, the vibrational spectra are dominated by the fundamental vibrations of the PO_4 polyanions which are split in many components due to the correlation effect induced by the coupling with of Me-O units in the structure. In the region of the internal modes of the phosphate anion, we identify the symmetric stretching mode and triplets in the high-wavenumber region, while the far infrared region displays the external modes. A remarkable aspect of the Raman spectrum is the fact that both bending vibrations show reverse behavior, although usually the symmetric bending is expected to have a higher intensity. The most noticeable feature in vibrational patterns is the highest frequencies of the ν_4 modes for the cobalt phase. The strong covalent bonds within the polyanion complex of LiCoPO_4 explains the difference between redox energies.

K6.15

Electron Spin Resonance Studies of Li-Substituted Manganese Spinel. Monika Kopeć^{1,2}, Jozef R. Dyras¹, Franciszek Krok¹ and Christian M. Julien²; ¹Faculty of Physics, University of Technology, Warsaw, Poland; ²LMDH, Université Pierre et Marie Curie, Paris, France.

Electron Spin Resonance (ESR) is one of the experimental technique which yields information about the immediate environment and the oxidation state of transition metal ions in solids, especially in materials used as positive electrodes in rechargeable lithium batteries. ESR measurements were performed at X-band frequencies in the range of temperature 4-300 K on LiMn_2O_4 and samples with substitution of Li ions for Mn ions. Cationic substitution in LiMn_2O_4 spinel is widely considered such as beneficial for their structural stability because increasing the Mn^{4+} concentration avoids both the dissolution electrode and the onset of the Jahn-Teller effect. Compounds were synthesized using wet-chemical technique from succinate precursors. In this work, we study the evolution of the ESR signal as a function of the average oxidation state of manganese ions from 3.4 to 4. Resonance spectra exhibit only a broad band of 300 mT at room temperature, while two bands are observed at low temperatures with bandwidth of 55 and 3 mT, respectively. All broad bands deviate from the classical lorentzian shape. The occupation of extra Li^+ ions in 16d sites and of the replacement of larger Mn^{3+} ions by smaller Mn^{4+} ions are analyzed and the local structure is discussed according the MnO_6 octahedra distortion in the spinel lattice.

K6.16

Anode Hosts for Lithium Batteries: Revisiting Tin and Aluminum. Quan Fan, Peter Zavalij and M. Stanley Whittingham; Chemistry, SUNY-Binghamton, Binghamton, New York.

Pure tin reacts readily with four lithium atoms, and so is a prime candidate as the host for the anode of lithium batteries. Tin foil and an expanded tin grid (microporous tin) have a capacity of >600

mAh/g over more than 10 deep reaction cycles, indicating the inherent reversibility of tin anode. The microporous tin showed superior chemical capacity retention. Different phases are observed during the intercalation of lithium. Capacity loss was observed after 10 cycles though, consistent with the significant increase of the cell impedance. For comparison aluminum expanded grids were also examined as hosts, where LiAl is formed. Capacities approaching 1 Ah/g were obtained. LiBOB (lithium bis(oxalato)borate) was also studied as the electrolyte salt for comparison with the reactive and high cost LiPF_6 salt. This work is being supported by the US DOE, and is a collaboration with K. Zaghbi of Hydro-Quebec.

K6.17

Reversible Lithium Intercalation in a Li_2MnO_3 Compound: Electrochemical Activity of Short-Range-Order Materials.

Jingsi Yang¹, Gaurav Jain¹, Jun John Xu¹, Mahalingam Balasubramanian², Won-Sub Yoon³ and James McBreen³; ¹Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey; ²Experimental Facilities Division, Argonne National Laboratory, Argonne, Illinois; ³Materials Science Division, Brookhaven National Laboratory, Brookhaven, New York.

Li_2MnO_3 is an interesting compound in the context of the prominent family of lithium intercalation compounds with rock-salt type structures, which has dominated the area of intercalation cathodes for rechargeable lithium or lithium ion batteries. Despite the prominent electrochemical activity of other rock-salt type compounds such as LiCoO_2 , LiNiO_2 and LiMnO_2 , Li_2MnO_3 is known to be electrochemically inactive as a lithium intercalation host. It is believed that lithium cannot be extracted from this compound, as Mn cannot be oxidized beyond $4+$ reversibly. At the same time, lithium cannot be intercalated into this compound either, since all the octahedral sites are occupied and accommodation of incoming lithium ions in the tetrahedral sites is energetically exceedingly unfavorable due to electrostatic repulsion from neighboring cations. Here we report a short-range-order compound with a composition very close to Li_2MnO_3 and bearing structural similarity to the rock-salt Li_2MnO_3 , which exhibits very surprising electrochemical activities. The compound was prepared via a sol-gel synthesis route followed by heat treatment and possesses a largely amorphous structure and consists of ca. 50 nm particles. This short-range-order Li_2MnO_3 when discharged versus a lithium anode yields an intercalation capacity of 163 mAh/g, or 0.71 Li per Li_2MnO_3 , with perfect reversibility. The material also shows excellent capacity retention upon repeated charge/discharge cycling. Under similar conditions, the crystalline Li_2MnO_3 compound shows essentially no discharge capacities and is indeed inactive. X-ray diffraction suggests structural similarity of this short-range-order material to the crystalline rock-salt Li_2MnO_3 . In X-ray absorption spectroscopy studies, both the near edge spectra and the extended x-ray absorption fine structure region show that the local structure of the short-range-order compound is similar to its crystalline counterpart and the difference between these samples appears to be the lack of crystallinity in the short-range-order sample. In-situ XANES shows reduction of the Mn oxidation state during discharge and reversible oxidation during charge, indicating that the discharge and charge indeed entails faradaic lithium insertion and removal. Evidence of such electrochemical activity in a rock-salt Li_2MnO_3 -like compound has never been reported before. The largely amorphous structure and nanostructured morphology of the present material that determine its electrochemical properties will be discussed. This study points towards the unique reaction properties of nanostructured, short-range-order materials, and suggests possibilities for development of new materials of superior intercalation properties and for improvement of existing materials, even ones that are previously thought to be inactive.

K6.18

Novel Lithium Polymer Gel Electrolytes free from Volatile Solvents Prepared by In-Situ Synthesis. Jun John Xu and Hui Ye; Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey.

Search for polymer electrolyte systems that would exhibit high ionic conductivity, Li^+ transport number, chemical, thermal and electrochemical stabilities and mechanical strength, constitutes a very important part in the effort to create a new generation of rechargeable lithium batteries. Here we report novel lithium polymer gel electrolyte films free from volatile solvents prepared via in-situ synthesis. The electrolyte systems are composed of electrolyte solutions based on liquid oligomeric poly(ethylene glycol dimethyl ether) (PEGDME) with negligible vapor pressure, trapped in a cross-linked poly(methyl methacrylate) (PMMA) matrix synthesized and cross-linked in-situ from corresponding monomers, i.e., synthesized from the monomers in the presence of the oligomeric polyether electrolytes. This novel synthesis approach leads to free-standing, highly homogeneous elastic electrolyte films. It also allows precise control and variation of the composition of the resultant electrolyte film for the optimization of

various properties. Room-temperature conductivity of 5×10^{-4} S/cm has been achieved and higher values are expected through further development. The PMMA matrix and the oligomeric polyether electrolyte appear to have molecular level interaction to result in a one-phase system in a wide temperature range extending to at least -50 C, enabling the possibility of using the electrolyte systems for low temperature applications. At the same time, the absence of any solvents with high vapor pressure in the electrolyte films is expected to enable their applications at high temperatures, as well as enhance the stability of the lithium/electrolyte interface. Furthermore, the novel synthesis approach enables in-situ fabrication of rechargeable lithium/lithium-ion cells where the contact between the particles of the active electrode materials and the polymer electrolyte is most intimate. In this presentation, synthesis, characterization, conductivity and interfacial stability of these novel polymer gel electrolyte films synthesized in-situ will be described and their application in lithium polymer batteries discussed.

SESSION K7: Fuel Cells: PEM and SOFC
Chairs: Juergen Fleig and Enrico Traversa
Wednesday Morning, December 1, 2004
Republic B (Sheraton)

8:30 AM *K7.1

Composite Inorganic Filler Based Electrolyte Membranes for Fuel Cells Applications. Antonino S. Arico, Vincenzo Baglio, Alessandra Di Blasi and Antonucci Vincenzo; CNR-ITAE, Messina, Italy.

Composite perfluorosulfonic membranes based on recast Nafion containing ceramic oxides have been operated up to about 150 C both in direct methanol and hydrogen-air polymer electrolyte fuel cells [1,2]. It has been observed that the inorganic oxide inside a membrane enhances the water retention at high temperatures. In the present work, various composite membranes based on recast Nafion containing inorganic nanoparticle fillers (SiO_2 , SiO_2 with adsorbed phosphotungstic acid, ZrO_2 , Al_2O_3) varying by their surface chemistry and acid-base characteristics have been prepared and investigated in DMFC devices. It has been observed that the surface acid-base properties of the inorganic fillers play a fundamental role in determining the conductivity characteristics and fuel cell performance at high temperatures [3-5]. The conductivity of the membranes and the maximum power density at 145 C of Direct Methanol Fuel Cells (DMFCs) increase with the filler surface acidity. The surface acidity of the fillers influences the bending and stretching vibrational frequencies of the water physically adsorbed on the filler surface. Accordingly, the more acidic is the filler surface, the larger is the capability to undergo a strong interaction with water through the formation of hydrogen bonds. This latter effect produces a decrease of the O-H stretching and bending frequencies in the physically adsorbed water. The maximum DMFC power density at 145 C is related to the characteristics of the water adsorbed on the filler particles. The obtained results indicate that the acid-base behaviour of the oxide filler plays a key role in determining the cell performance. These oxide materials do not possess elevated intrinsic protonic activity at 145 C as well as their low weight content (3%) does not allow to justify a significant contribution as proton conductors. Their effect is mainly due to the hygroscopic characteristics and the large surface area which enable suitable water adsorption on the surface enhancing the water retention properties of the membranes. References [1] A. S. Arico, P. Creti, P. L. Antonucci, V. Antonucci, *Electrochem. Solid-State Lett.*, 1 (1998) 66. [2] V. Antonucci, A. S. Arico, *Europ. Patent*, EP 0 926 754 A1, 1-5 (1999). [3] A. S. Arico, V. Baglio, A. Di Blasi, E. Modica, P. L. Antonucci, V. Antonucci *J. Power Sources*, 128 (2004) 113. [4] A. S. Arico, V. Baglio, A. Di Blasi, V. Antonucci, *Electrochem. Commun.*, 161 (2003) 251. [5] A. S. Arico, V. Baglio, A. Di Blasi, P. Creti, P. L. Antonucci and V. Antonucci, *Solid State Ionics*, 161 (2003) 251.

9:00 AM K7.2

Studies of Polymeric Proton-Conducting Materials Using High-Resolution Solid-State NMR. Gang Ye, Nathan Janzen, S. Rahima Benhabbour and Gillian R. Goward; Chemistry, McMaster University, Hamilton, Ontario, Canada.

It has been reported that heterocycles, such as imidazole, benzimidazole or pyrazole may act as proton solvents in ionomers resulting in conductivities comparable to those of hydrated polymers. Imidazole has been used as proton solvent, to enable fast proton transport within a hydrogen-bond network which mimics that of water. The materials are of interest as potential new proton conducting membranes for fuel cells able to function at temperatures above 130°C . We have studied the transport properties of model materials consisting of short oligo-ethyleneoxide chains terminated by imidazole groups (Imi-nEO). With the goal of improving the

mechanical properties of these materials, we have also characterized materials in which imidazole is covalently linked to a polymer backbone such as polysiloxane; or immobilized on the surface of siloxane-based nanoparticles. We demonstrate the utility of high-resolution solid-state ^1H NMR for investigating proton-conducting electrolytes. The comparison of a single-pulse spectrum with a double-quantum filtered spectrum gives a direct assessment of the mobility of the protons. Good resolution of resonances in the hydrogen-bonding region is achieved. Moreover, homonuclear double quantum NMR spectra, acquired using the back-to-back sequence, provide information concerning the relative proton mobilities. The study provides insight into the mechanism of proton-mobility in these materials relative to the Imi-nEO materials and shows a single type of H-bonding consistent with an amorphous structure but lacking sufficient density of imidazole rings to facilitate fast proton conductivity. We have extended this approach to characterize more traditional proton-conductors, such as poly(ether-ether)ketone, and NafionTM. We show that the correlation between macroscopic and microscopic proton mobility is observed in such aqueous systems as well, and have established an activation energy of 8 kJ/mol for NafionTM, based on ^1H NMR relaxation studies.

9:15 AM K7.3

Free-Standing Hydrogen Bonded Layer-by-Layer Thin Films for Ion Conduction. Jodie L. Lutkenhaus and Paula T. Hammond; Chemical Engineering, MIT, Cambridge, Massachusetts.

Polyelectrolyte multilayer thin films have shown promise as new functional materials for fuel cells, batteries, solar cells, and electrochromic displays. We have recently shown that alternating layers of hydrogen bonded polyethylene oxide and polyacrylic acid films can be tuned to exhibit high ionic conductivities in a stable, solid state. Polyethylene oxide in its pure form is semicrystalline, leading to a poor ionic conductivity; the use of plasticizers like ethylene carbonate can suppress crystallization, but at the cost of mechanical stability. Instead of plasticizers we turn to hydrogen bonded multilayer assemblies, a process that allows for the deposition of conformal thin films of tunable thickness. Properties like ionic conductivity, mechanical stability, and effective crosslink density of these hydrogen bonded films are directly related to the final structure of these films. Recently, we have developed a new method for isolating hydrogen bonded multilayers like polyethylene oxide (PEO) and polyacrylic acid (PAA) in ambient, bench top conditions without the use of any aqueous post-processing. In this talk, "peelable" free-standing multilayer films are discussed and characterized with differential scanning calorimetry, thermal gravimetric analysis, and tensile testing. The structure and crystallinity of these films are analyzed and compared to an alternative, electrostatically bonded system of polyacrylic acid and linear polyethylene imine (PEI), the nitrogen analog of PEO. With the isolation of controllable thin films of micron scale thickness, we can now directly incorporate multilayer membranes in electrochemical devices without a bulky substrate.

9:30 AM K7.4

Nanostructured PEFC Electrode Catalysts Prepared via In-situ Colloidal Impregnation. Kazunari Sasaki^{1,2}, Shuhei Tanaka¹, Kenji Shinya¹, Yuudai Kawazoe¹, Takashi Kuroki¹, Kouhei Takata¹, Hajime Kusaba¹ and Yasutake Teraoka¹; ¹Interdisciplinary Graduate School of Engineering Science, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan; ²Hydrogen Technology Research Center, Kyushu University, Fukuoka, Japan.

Nanostructured Platinum-based electrode catalysts were prepared via in-situ colloidal impregnation for polymer electrolyte fuel cells. Crystallite size, grain size, and distribution of Pt nanoparticles on carbon support materials were characterized by XRD, TEM, high-resolution FESEM, and STEM. Effective surface area and kinetically-controlled current density of Pt electrode catalysts were analyzed by cyclic and hydrodynamic voltammetry using rotating disk electrodes. PEFCs with these electrode catalysts were also prepared and their I-V characteristics were examined at 80°C . We have succeeded to develop Pt electrode catalysts with a diameter of a few nm, supported on carbon nanofibers with different structures (including herringbone-type fibers, platelet-type fibers, and highly-conductive vapor-grown fibers), carbon nanotubes, as well as carbon black. The dependencies of nanostructure and electrochemical properties on crystallographic structure of carbon support materials and preparation conditions of electrode catalysts are analyzed and discussed. Nanostructural design of PEFC electrode catalyst layers using carbon nanofibers as catalyst supports and electrode fillers is also discussed.

10:15 AM *K7.5

Factors Influencing Transport in Polymer Electrolytes: The Relative Importance of Nano- and Microscale Processes. Thomas A. Zawodzinski, Derek Lebzelter, Hayley Every, Berryinne

The search for improved proton conductors operating at temperatures exceeding 100°C has focused on several classes of materials. The most common approach has been the use of sulfonated aromatic polymers, based on the expectation of high thermal stability. However, such polymers often exhibit substantially slower transport of water or ions under conditions of decreased water content. We will describe recent NMR studies of water transport that explicitly compare local (nano-scale) and long range (micron scale) influences on transport in a series of sulfonated polymers with varying morphology but similar acid strength. This study allows us to assess the relative importance of fundamental chemical interactions and morphology in determining the behavior of these materials. Based on these findings, other avenues toward improved transport in polymers under investigation in our labs, including the development of phase-separated multiblock copolymers, composite electrolytes and more highly acidic polymers, will be analyzed.

10:45 AM K7.6

Structure, Thermal Behavior, and Superprotonic Conductivity of the New Solid Acid $\text{Cs}_6(\text{H}_2\text{SO}_4)_3(\text{H}_{1.5}\text{PO}_4)_4$. Sossina M. Haile and Calum R.I. Chisholm; Materials Science, Chemical Engineering, California Institute of Technology, Pasadena, California.

Investigations into the CsHSO_4 - CsH_2PO_4 system have yielded a new solid acid, $\text{Cs}_6(\text{H}_2\text{SO}_4)_3(\text{H}_{1.5}\text{PO}_4)_4$, which undergoes a superprotonic transition over the temperature range 95-120 °C. Room temperature single crystal X-ray diffraction revealed $\text{Cs}_6(\text{H}_2\text{SO}_4)_3(\text{H}_{1.5}\text{PO}_4)_4$ to crystallize in the space group I-43d with a lattice constant of $a = 14.539(6)$ Å. The compound has a unit-cell volume of $3073(2)$ Å³ and 16 formula units per cell, giving a calculated density of 3.976 g cm⁻³. Refinement of all 2719 independent reflections yielded weighted residuals of 0.0339 and 0.0164 based on F^2 and F values, respectively. The structure contains only one crystallographically unique site for the Cs, S, P, and H atoms, leading to a highly unusual three-dimensional network of hydrogen-bonded tetrahedra. Thermal analysis of the superprotonic transition showed it to be accompanied by a large heat of transformation, $\Delta H = 66 \pm 3$ J g⁻¹, and to exhibit considerable hysteresis. The onset of thermal decomposition in $\text{Cs}_6(\text{H}_2\text{SO}_4)_3(\text{H}_{1.5}\text{PO}_4)_4$ takes place at approximately 200 °C. Both high temperature X-ray and neutron powder diffraction established that the structure of the superprotonic phase is cubic, with $a = 4.991(1)$ Å, and most likely takes on a CsCl structure, with Cs atoms at the corners of a simple cubic unit cell and an XO₄ group (X = S or P) at its center. The conductivity of the high temperature phase at 140 °C is 6×10^{-3} ohm⁻¹ cm⁻¹, with an activation energy for proton transport of 0.40(1) eV. The high temperature phase of $\text{Cs}_6(\text{H}_2\text{SO}_4)_3(\text{H}_{1.5}\text{PO}_4)_4$ also exhibits the unusual behavior of negative thermal expansion. This is attributed to the fact that the Cs:XO₄ ratio is 6:7, as opposed to the ideal value of 1:1 for the CsCl structure type.

11:00 AM *K7.7

Preparation of $\text{La}_{1.61}\text{GeO}_{5-\delta}$ Based Oxide Ion Conducting Film by Pulsed Laser Deposition Method and its Application for SOFC. Tatsumi Ishihara and Jingwang Yan; Department of Applied Chemistry, Kyushu University, Higashi-ku, Japan.

From preventing the global warming issues, the development of highly efficient power generating systems is urgent and an important subject. Many interests are focused on fuel cell technology. Solid oxide fuel cell (SOFC) has many advantages such as high stability, high efficiency (>50%), and flexibility of fuels. However, the operating temperature of the current SOFC is expecting higher than 1073 K. Therefore, start up requires a large energy input as well as a long period. Therefore, SOFC operating at temperatures lower than 773 K is expecting as the ideal fuel cell among the various types of fuel cells. Fast oxide ion conductor is a key material for intermediate temperature SOFC and in order to develop SOFC operating at temperatures lower than 773 K, achievement of high oxide ion conductivity is essentially required. In this study, preparation of $\text{La}_{1.61}\text{GeO}_{5-\delta}$ based oxide film was studied with pulsed laser deposition methods. $\text{La}_{1.61}\text{GeO}_{5-\delta}$ is the new fast oxide ion conductor, of which oxide ion conductivity is close to LaGaO_3 based oxide at high temperature. La_2GeO_5 based oxide film with nano level thickness was successfully prepared on the dense Al_2O_3 substrate and on the porous $\text{NiO-Ce}_{0.85}\text{Sm}_{0.15}\text{O}_2$ substrate by pulsed laser ablation method. It was found that oxide ion conductivity increases with decreasing the thickness of film. Therefore, oxide ion conductivity in this material seems to be improved by decreasing thickness of film by space charge theory. In accordance with improved oxide ion conductivity, the extremely large power density of the cell (400 mW/cm²) is achieved on the cell using La_2GeO_5 electrolyte film at 873K.

11:30 AM K7.8

Design and Characterization of Integrated On-Plane Micro-SOFC. Woo Sik Kim¹, Sun Hee Choi¹, Hyoungchul Kim¹, Joosun Kim¹, Hae-Weon Lee¹, Huesup Song¹, Jong-Ho Lee¹ and Hyung-Ho Park²; ¹Nano-Material Research Center, Korea Institute of Science and Technology, Seoul, South Korea; ²Ceramic Engineering, Yonsei University, Seoul, South Korea.

As the portable electrical commercial goods such as mobile phones, digital cameras and notebook become popularized in normal life; micro-SOFC is widely viewed as a promising powder source. Moreover, micro-SOFC is also expected as one of the most proper power sources for the Microsystems such as sensors and actuators. However, there are several matters to be attended, such as the design of cell structure, and the comprehension about thin film properties of the components (electrolyte, cathode, anode), and so on. Therefore, in this work, thorough investigation about the changes of electrical and physical properties of electrolyte and electrode attendant upon the shift from bulk to thin film will be presented. And we will report the fabrication procedure of novel designed micro-SOFC integrated via silicon-based micro-fabrication techniques and its cell performance as well.

11:45 AM K7.9

Influence of the Grain Boundaries on Conductivity of Nanocrystalline Zirconia and Ceria. Vladimir Petrovsky, Piotr Jasinski, Harlan U. Anderson and Tatiana Petrovsky; EMARC, University Missouri-Rolla, Rolla, Missouri.

There is a tendency in many practical applications of lowering processing temperature for solid electrolyte layer deposition which in particular leads to nanocrystalline structure of the material. Several features of solid oxide fuel cells (SOFCs) can be considered as the examples. Processing temperature needs to be lowered for cathode supported cells to prevent chemical reactions between electrolyte and cathode materials. Nanocrystalline structure of the materials is of special importance for anode and cathode reaction interlayers to ensure high effective surface area and to decrease electrode overpotentials. Application of MEMS technology for micro-SOFCs suggests low thickness of the electrolyte and, consequently, nanocrystalline structure of the material. Electrical behavior of nanocrystalline materials could be significantly influenced by the grain boundaries which can effect the final characteristics of the devices. The influence of the grain boundaries on ionic conductivity of yttria stabilized zirconia (YSZ) and samarium doped ceria (SDC) were investigated. Three different technologies were used to prepare nanocrystalline electrolytes: colloidal suspensions, polymeric precursors and combination of colloidal suspensions with polymeric precursors (so called net shape processing). As a result initial nanocrystalline samples with the different structure were prepared. The samples were annealed at different temperatures in the range from 400 to 1400°C to overlap the grain size from 20nm to 10³µm and investigated using impedance spectroscopy. Significant differences were found in the behavior of nanocrystalline zirconia and ceria. Two distinct semicircles were found on all zirconia samples corresponding to grain and grain boundary impacts in the resistance. Activation energies for both resistances are very close (1.00 and 1.05eV correspondingly). The grain resistance does not change at the annealing process, but grain boundary resistance decreases after high temperature annealing which courses decrease in overall resistance of the material. The calculations show that decrease in the grain boundary resistance is connected only with increase in the grain size and specific grain boundary resistance (per unit surface area of grain boundary) does not change at the annealing process. Contrary, SDC samples have only one distinct semicircle and do not show significant impact of grain boundaries on the sample resistance. Activation energy of the overall conductivity (0.91eV) and the value of the conductivity do not change after high temperature annealing in the grain size range from 50nm to 10³µm. This difference between YSZ and SDC is most likely connected with different electronic conductivity of the materials, which suggests that grain boundary resistance is due to the exchange reaction on the surface of the grains.

SESSION K8: Solid-Oxide Fuel Cells
Chairs: Ludwig Gauckler and Eric D. Wachsman
Wednesday Afternoon, December 1, 2004
Republic B (Sheraton)

1:30 PM *K8.1

Single Gas Chamber Solid Oxide Fuel Cells. Ludwig J. Gauckler, B. E. Buegler and M. E. Siegrist; Department Materials, Nonmetallic Inorganic Materials, ETH Zurich, Zurich, Switzerland.

Single Chamber Solid Oxide Fuel Cells (SC-SOFC) can be understood as fuel cells with only one gas compartment operating in a non-equilibrium gas mixture of fuel and oxygen. In conventional fuel

cells, the oxidant and the fuel are usually separated by a gas tight electrolyte, thus the cell has two gas chambers. The operation of a SC-SOFC relies on the selectivity of the cathode and the anode exposed both to the same gas mixture of fuel and air. In 1990 Dyer was able to generate electric power from a device with two electrodes made of platinum separated by a thin, ion conducting and porous film [1]. Hibino et al. have been working on Single Chamber Solid Oxide Fuel Cells and produced first cells with similar power densities than conventional SOFCs using electrolytes like $\text{SrCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$, $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ and $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ [2,3,4] and in recent years $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_2$ [5]. Riess et al. rationalized the operating principle of such cells on the bases of selective electrodes [6]. SC-SOFC offer the possibility to simplify SOFC designs because only one gas compartment is necessary. After this effect was almost neglected for two decades, today rather impressive power densities of more than 300 mW/cm^2 at low operating temperatures of 600°C had been demonstrated. We review the today's understanding and experimental results of SC-Solid Oxide fuel Cells and report about model experiments. Our results are based on a Single Chamber SOFC using $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ as cathode, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ as electrolyte and $\text{Ni-Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.90}$ as anode. In order to achieve low overpotentials, integrated current collectors (Pt) were embedded in the electrodes. The cells generated 350 mW/cm^2 at 500°C and 480 mW/cm^2 at 600°C on a gas mixture of methane and moistened air. Power density and OCV depend on temperature and the air/fuel flow rate ratio. These results are in good agreement with earlier work of Hibino [5] and are encouraging. Future work aims at new fuel cell designs that are possible with the "Single Chamber"-approach and evaluating their fuel utilization. [1] Dyer, C.K., Nature, 1990. 343. [2] Hibino, T., K. Ushiki, and Y. Kuwahara, Solid State Ionics, 1996. 91: p. 69-74. [3] Hibino, T., K. Asano, and H. Iwahara, Chemistry Letters, 1994: p. 485-488. [4] Asano, K., T. Hibino, and H. Iwahara, Journal of the Electrochemical Society, 1995. 142(10): p. 3241-3245. [5] Hibino, T., et al., Journal of Electrochemical Society, 2002. 149(2): p. A133-A136. [6] I. Riess, P.J. van der Put, J. Schoonman, Solid State Ionics, 1995, 82, 1-4.

2:00 PM **K8.2**

Exploration of Electrophoretic Deposition of YSZ Electrolyte for Solid Oxide Fuel Cells. Zhigang Xu, Rajaram Gukan, Devdas Pai and Jag Sankar; North Carolina A&T State University, Greensboro, North Carolina.

Electrophoretic deposition is widely used to prepare ceramic laminates. It was recently introduced to the area of fuel cell manufacturing. This will be a low-cost and efficient method to process electrolyte coatings on porous electrodes of fuel cells. The research in our center includes two aspects, one of which is to make porous anode substrates using slip casting, the other of which is to coat the anodes with YSZ electrolyte by electrophoretic deposition. By studying of various combinations of composition of the starting materials, ball milling time, and sintering temperature, homogenous porous anode was obtained. Two different charging methods of the YSZ particles in the suspension were used for electrophoretic deposition. Processing parameters, such as particle size in the suspension, deposition current density, deposition time, and sintering temperature were investigated. Experiments tuned out optimized deposition conditions for dense and thin YSZ coating on the anode substrates for intermediate-temperature solid oxide fuel cells.

2:15 PM **K8.3**

Effect of Orientation and Density of Interfaces on Oxygen Transport Across Doped Ceria-Zirconia Electrolytes. Laxmikant Saraf¹, V. Shutthanandan¹, S. Azad¹, C. Wang¹, D. W. Matson², O. Marina³, Y. Zhang¹, A. Dirkes¹ and S. Thevuthasan¹; ¹EMSL, Pacific Northwest National Laboratory, Richland, Washington; ²Materials Chemistry & Surface Research, Pacific Northwest National Laboratory, Richland, Washington; ³Energy Materials Division, Pacific Northwest National Laboratory, Richland, Washington.

Fundamental understanding of oxygen transport behavior in solid oxide fuel cells (SOFC) has been interest of research community for decades due to the need for development in efficient alternative energy technology. Recent developments in new techniques made it possible to investigate oxygen transport behavior in SOFCs in great details. Efforts are underway to enable an effective oxygen ion transport in solid electrolytes at intermediate temperatures (700-1000 K), where the electronic conduction at low partial pressures of oxygen is expected to be suppressed compared to high temperature (1050-1300 K) region. Glancing angle sputter deposition (GLAD) is one of those recently developed techniques that allows creation of vertical interfaces with respect to the substrate. Such columnar structures also provide desired porosity in oxides for the impingement of second oxide electrolyte eventually creating high density vertical interfaces. Yttria-stabilized zirconia and doped cerium oxide are well known candidates for electrolytes in SOFCs that can be grown with

techniques like GLAD. In this study, we investigate changes in oxygen transport behavior in case of YSZ/CeO₂ films where ceria-zirconia interfaces are lying parallel and perpendicular to the sapphire substrate. Parallel interfaces on sapphire were created by growing alternate ceria and zirconia multilayers using dc magnetron sputtering in a mixture of argon and oxygen ambient. High density vertical interfaces were created by impinging sol-gel grown ceria solution into vertical YSZ columns that are grown by GLAD. Direct and indirect oxygen transport measurements were made by ac impedance spectroscopy and 18O oxygen uptake measurements. Oxygen transport using parallel and perpendicular electrolyte interfaces and its relationship with structural properties will be discussed in details. Finally, we conclude the discussion with potential use of creating such interfaces with its advantages and disadvantages.

2:30 PM **K8.4**

Bi-Layer Interconnections for Solid Oxide Fuel Cells. Wenhua Huang and Srikanth Gopalan; Manufacturing Engineering, Boston University, Boston, Massachusetts.

Solid oxide fuel cells (SOFCs) are currently being investigated intensively for applications in distributed power generation. SOFCs are environmentally clean, have very high power generation efficiencies, emit very little acid-rain causing NO_x and SO_x pollutants, and are noiseless and modular. Presently, one of the principal goals of research in this area is to reduce the stack operating temperature from a nominal value of 1000°C to between 600 and 800°C. Several barriers need to be overcome before the stack operating temperature can be lowered without compromising the performance of the cell. These include availability of a low-cost high conductivity electrolyte, newer cathode and anode materials with polarization losses comparable to those that are currently employed at 1000°C and new interconnection (IC) materials with minimal ohmic losses. State-of-the-art IC materials from the doped-lanthanum chromite family have very poor conductivity at lower operating temperatures especially on the fuel side, and thus result in unacceptably high cell-to-cell resistance. The approach being pursued most actively for the lower operating temperature SOFC IC is the use of oxidation resistant chromium based alloys. However, progress in the development of such alloys has been limited due to the formation of resistive scales which are also prone to spalling. In this paper we present an alternate approach for lower operating temperature SOFC ICs consisting of a bi-layer structure. The bi-layer structure consists of a p-type layer exposed to cathodic gas (air/oxygen) and an n-type layer exposed to anodic gas (fuel). By careful design of the composition and thicknesses of the two layers, one can in principle obtain an IC with a low cell-to-cell resistance. The requirements for the bi-layer IC is high conductivity and excellent stability in a high oxygen partial pressure gradient. In this paper, it is theoretically shown that the interfacial oxygen partial pressure which is an important design variable, is dependent primarily on the oxygen partial pressure gradient across the IC, the low level oxygen conductivities of the two layers and is largely independent of their electronic conductivities and the total current density through the IC material. Further, it is also shown that for a given pair of p-type and n-type materials, by carefully choosing the thicknesses of the two layers, one can in principle ensure that the interfacial oxygen partial pressure remains higher than the decomposition partial pressure for the p-type layer. Preliminary experimental results on a model bi-layer IC are also presented along with the technical challenges to be addressed.

2:45 PM **K8.5**

Multi-fuel Capability of SOFCs: Degradation phenomena by carbon deposition and sulfur poisoning. Kazunori Sasaki^{1,2}, Keisuke Shiosaki¹, Katsushi Susuki¹, Masanobu Uchimura¹, Naofumi Imamura¹, Akira Iyoshi¹, Hajime Kusaba¹ and Yasutake Teraoka¹; ¹Interdisciplinary Graduate School of Engineering Science, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan; ²Hydrogen Technology Research Center, Kyushu University, Fukuoka, Japan.

While the multi-fuel capability is one of the relevant features of solid oxide fuel cells (SOFCs), the use of hydrocarbon-based fuels as well as practical fuels containing sulfur impurities could cause degradation of their electrochemical performance. The former may lead to carbon deposition, while the latter results in sulfur poisoning of SOFC anodes. Using SOFCs consisting of ZrO₂-based electrolytes, cell voltage was measured at a given current density operated with higher hydrocarbons such as C₈H₁₈, C₁₀H₂₂, C₁₂H₂₆, synthetic GTL kerosene, as well as with mixed H₂ and CO gases containing H₂S up to 100ppm. Degradation phenomena were analyzed as a function of operational conditions with or without Ru-based external reforming catalysts. Gradual decrease in cell voltage was observed for higher hydrocarbon-based fuels. On the other hand, sulfur poisoning causes a rapid decrease in cell voltage within a few minutes to a lower but constant value. However, sulfur poisoning became serious with decreasing operational temperature and/or at a higher CO/H₂ ratio of the fuels. We have succeeded to develop H₂S-tolerant SOFCs based

on Sc₂O₃-doped ZrO₂ electrolyte materials. Nanostructural change on Ni catalyst surfaces was examined by XRD, ESCA, SEM-EDX, AFM, and local I-V characteristics measurements by an AFM probe, revealing carbon deposition on Ni surfaces, especially around grain boundaries. The stability of electrode materials with carbon and sulfur is discussed and compared with that in thermodynamic equilibrium.

3:30 PM ***K8.6**

Electrochemistry at Oxygen Electrodes: Novel Kinetic Considerations and Their Application to SOFC Cathodes and NEMCA. Juergen Fleig, Max-Planck-Institute for Solid State Research, Stuttgart, Germany.

The electrochemical reduction of oxygen and the inverse oxidation of oxide ions play a prominent role in many applications of solid state ionics such as solid oxides fuel cells (SOFCs), oxygen pumps, amperometric sensors and non-Faradaic electrochemical modification of catalytic activity (NEMCA). In mechanistic studies of the corresponding electrochemical gas-solid reactions, concepts well-proven in aqueous electrochemistry are often adopted without critically discussing their validity in solid state electrochemistry. In this contribution a quantitative approach is presented which demonstrates that some basic assumptions valid in aqueous electrochemistry do no longer hold when considering oxygen electrochemistry at solid electrolytes. The model is applied to the oxygen reduction reaction at mixed conducting SOFC cathodes yielding severe deviations from a Butler-Volmer kinetics for ionic as well as electronic charge transfer reactions. Experiments with well-defined La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-x} thin film microelectrodes are discussed in the light of this model. Similar considerations can also be applied to quantitatively relate the overpotential of an electrode to its work function change upon polarization. This work function change is assumed to play an important role in understanding the NEMCA effect. It is shown that only in some special (though not unrealistic) cases the often assumed identity of overpotential and work function change results.

4:00 PM **K8.7**

Investigation of Oxygen Reduction Reaction Mechanisms on SOFC Cathode Material La_{0.8}Sr_{0.2}MnO_{3-d} Using Thin-film Microelectrodes. Gerardo Jose Cordova la O¹, Bilge Yildiz² and Yang Shao-Horn³, ¹Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The oxygen reduction reaction (ORR) on La_{0.8}Sr_{0.2}MnO_{3-d} (LSM) cathode is of interest from both a fundamental and applied point of view. ORR on LSM has been extensively studied for over two decades, however to date, there is still no agreement on the exact reaction pathway and rate limiting step (rls) for ORR on LSM under different conditions, particularly at the molecular level. The ORR on LSM is currently the principal contributor to performance losses in solid oxide fuel cell (SOFC) devices limiting efficient operation to temperatures above 800°C. It has been generally viewed that oxygen reduction in LSM cathodes using Y₂O₃-doped ZrO₂ (YSZ) electrolyte takes place at the three-phase boundary (TPB) sites. However, recent studies using dense electrodes have shown the important contribution of the bulk ionic pathway. In order to understand the role of surface and bulk ORR pathways on LSM, it is essential to have electrodes of known composition, microstructure, and dimensions for precise correlation to the obtained electrochemical behavior and performance. Specifically, microstructural features such as electrode surface area, TPB length, and electrode/electrolyte interfacial area are critical to identify the dominant ORR pathway and the rls in LSM. In this study, we report on the electrode fabrication, microstructural characterization, chemical analysis, and electrochemical performance of thin-film LSM microelectrodes. The geometrically well-defined LSM microelectrodes were fabricated using RF-sputtering and subsequent photolithography. Techniques such as atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) were used to analyze the microelectrode surface, internal microstructure, and cathode/electrolyte interface structure. Chemical composition was determined using techniques such as energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). Electrochemical characterization was performed via AC impedance spectroscopy techniques. The relationship between microstructure and oxygen reduction kinetics will be discussed in detail.

4:15 PM **K8.8**

Characterization of Solid Oxide Fuel Cell (SOFC) Materials with Electron Stimulated Desorption and Charge Trapping (ESD-CT). Haiyan Chen¹, Yenfeng Chen¹, Alex Aleksandrov¹, Jian Dong², Meilin Liu² and Thomas M. Orlando¹, ¹School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, Georgia;

²School of Materials Science & Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Lowering the operating temperature of solid oxide fuel cells (SOFCs) is critical to the commercialization of this highly efficient energy-conversion device. As the operating temperature is reduced, however, the interfacial polarization resistances increase rapidly, severely limiting fuel cell performance. When hydrogen is used as the fuel, the resistance to oxygen reduction at the cathode plays a dominant role. To fully understand the mechanisms of defect mediated oxygen reduction, it is critical to understand the roles of surface defects in these processes. Electron stimulated desorption and charge trapping (ESD-CT) are surface analysis techniques that can probe defects and electronic properties of surfaces. Since defects or local disorder on a surface act as the trapping sites of electronic excitations, they can thus serve as preferential sites for ion desorption. This makes ESD a powerful technique for exploring defects and their role in surface reactions critical to electrochemical performances of SOFCs. Our ESD characterization of polycrystalline Ce_{0.9}Gd_{0.1}O_(2-δ) (GDC), a promising electrolyte for intermediate-temperature (500 - 600°C) SOFCs, represents the first application of this technique to fuel cell materials. Electron beam induced charging and stimulated desorption studies indicate that the main cationic products resulting from electron bombardment are H⁺, H₃O⁺ and O⁺. The dependence of the H⁺ and H₃O⁺ ion kinetic energies and yields on the surface potentials have been systematically investigated. The charging of GDC by electron beam bombardment is dependent on the incident electron energy, negative at lower energy and positive at higher energy. The positive charging is caused by hole-trapping at sites close to Gd³⁺, and the negative charging is caused by effective electron trapping at oxygen vacancy rich grain boundaries. The ESD thresholds for H⁺, O⁺, and H₃O⁺ from polycrystalline GDC surfaces were also measured at room temperatures. All three cations have a 22 eV threshold and a yield change at 40 eV, with an additional yield change at 150 eV for O⁺. The 22 eV threshold is associated with the ionization of O 2s, Ce 5p or Gd 5p levels and the 40 eV yield change is close to that of Ce 5s or Gd 5s levels. Cation desorption is stimulated by Auger decay of these levels. Two-hole one-electron mixed final states of water also have thresholds at 22 and 40 eV and may also be involved. The yield change at 150 eV for O⁺ desorption points to bond breaking of Gd-O as the origin of O⁺ desorption. The temperature dependence of O⁺ and H₃O⁺ desorption under 50 and 400 eV electron beam bombardment suggests the involvement of free oxygen vacancies in O⁺ production and also demonstrates the influence of water adsorption on surface oxygen vacancy density.

4:30 PM **K8.9**

Cathodes for Intermediate Temperature SOFCs.

Allan J. Jacobson and Guntae Kim; Chemistry, University of Houston, Houston, Texas.

Mixed ionic-electronic conductors are used as electrodes in solid oxide fuel cells (SOFCs), sensors, and as oxygen ion transport membranes for oxygen separation. The perovskite related oxide, La₂NiO_{4+x} (LNO), is currently of interest for SOFC cathodes due to the high diffusivity of the oxygen ion interstitials. The structure of LNO is related to that of K₂NiF₄ and can be described as consisting of perovskite layers alternating with LaO rock salt layers. The oxygen excess in LNO is associated with the incorporation of interstitial oxygen anions into the rock salt layers. Loss of interstitial oxygen ions as O₂ occurs above 650 K with a corresponding decrease in conductivity. In this paper, the electrical conductivity relaxation (ECR) technique has been used to separately determine the oxygen ion diffusion coefficient and the surface reaction rate for Ln₂NiO_{4+x} (Ln = La, Pr). The AC impedance response of La₂NiO_{4+x} in LNO/CGO/LNO symmetric cells will also be described. The results are compared with previous data for LNO and other compositions.

4:45 PM **K8.10**

Preparation and characterization of lead ruthenate based composite cathodes for SOFC application. Vincenzo Esposito^{1,2},

Enrico Traversa¹ and Eric Wachsman²; ¹Department of Chemical Science and Technology, University of Rome, Rome, Italy;

²Department of Materials Science and Engineering, University of Florida, Gainesville, Florida.

Ruthenium based pyrochlores are known for their electrical properties and remarkable performances of this material have been investigated in catalysis and in electrochemical application. Particularly, lead ruthenate (Pb₂Ru₂O_{6.5}) has been evaluated as possible candidate for SOFCs cathodic applications because of its low polarization in the oxygen reduction process. In this work, pure composition of Pb₂Ru₂O_{6.5} obtained by a new co-precipitation method was used to fabricate composite ceramic electrodes. Nanometric pyrochlore powders were mixed to YSZ or ESB to fabricate porous the composite electrodes deposited on YSZ or ESB electrolyte. Powders phase and morphology were studied, respectively, by XRD and FE-SEM.

Reactivity between Pb2Ru2O6.5 and the materials was studied by XRD, EDS and FE-SEM. Electrochemical features of the composites were performed by electrochemical impedance spectroscopy (EIS) at different temperatures in symmetric cells configuration of the electrodes and electrolytes. Low and intermediate temperature (200 C-550 C) allowed to separate and study each cell component contribution and relative reactivity of the composites. Electrode polarization of the cells in air was studied at higher temperature (600 C-750 C). The composite pyrochlore electrodes properties were also compared to single Pb2Ru2O6.5 phase electrodes in symmetric cells in way to evaluate the effect of the pure ionic conductor phase in the composite electrodes polarization.

SESSION K9: Poster Session
Chairs: P. Knauth, Christian Masquelier, Enrico Traversa and Eric D. Wachsman
Wednesday Evening, December 1, 2004
8:00 PM
Exhibition Hall D (Hynes)

K9.1

Advance in Nanostructural Electrochemical Reactors for NOx Treatment in the Presence of Oxygen. Masanobu Awano, Kouichi Hamamoto, Yoshinobu Fujishiro, Shingo Katayama and Sergei Bredikhin; Advanced Manufacturing Research Institute, Natl.Inst. of Advanced Industrial Science and Technology, Nagoya, Japan.

Dramatic improvements in the selective separation and purification of NOx in exhaust gases by an electrochemical reactor have been achieved. The novel electrochemical cells for NOx decomposition were developed by nano-scale control of penetrating pores from the catalytic electrode surface to the bottom of the catalytic electrode layer, and by distribution at the interfaces of ionic and electronically conducting grains through the electro-catalytic electrode of the cell. Dramatic improvement in current efficiency and suppression of the working voltage of the cells enabled their application as a novel reactor for NOx decomposition of gases from gasoline and diesel engine vehicles, gas engines and other industrial equipments with the advantage of less energy consumption in comparison with "the fuel penalty" for presently used catalytic systems. The cells are able to work as a deNOx reactor even under excess oxygen contents up to 10% because of the selective separation to NOx molecules by the nano-space reaction. For the first time such nano-reaction has been shown to realize sufficiently applicable yielding rates. Enlarged cells revealed high performance similar to small experimental cells.

K9.2

A Novel Superstructure of Cation Defect-Ordered and Oxygen-Disordered Barium Tungsten Oxide. Seung-Tae Hong and Yun-Ho Roh; LG Chem Research Park, Daejeon, South Korea.

Superstructures of a simple perovskite ABO₃ can be induced by orderings of A-site, B-site cations, or defects. The title compound, Ba_{2.75}WO_{5.75}, is a novel example of A-site defect-ordered structures that has never been conceived previously for a long time after the discovery of the compound. It has been believed to be the cryolite (Na₃AlF₆) type, but still the crystal structure is not clearly understood. In this study, the structure was solved for the first time by the powder X-ray and neutron techniques. This presentation describes synthesis and the novel crystal structure that would be the first example of A-site defect-ordered perovskite with 4x4x4 superstructure, and quite unusual oxygen disordering. In-situ high temperature XRD study on the phase transformation and ionic transport properties will be discussed.

K9.3

Further Evidence for Trapped Diatomic Nitrogen in IBAD LiPON Films. Fernando Vereda¹, Phillip E. Stallworth², Steve G. Greenbaum³, Terry E. Haas⁴, Anne E. Takesian¹, Peter Zerigian¹ and Ronald B. Goldner¹; ¹Electrical and Computer Engineering, Tufts University, Medford, Massachusetts; ²Division of Science, City College of New York, New York, New York; ³Physics Department, Hunter College of CUNY, New York, New York; ⁴Department of Chemistry, Tufts University, Medford, Massachusetts.

Previous work has shown that the ion beam assisted deposition (IBAD) of lithium phosphorus oxynitride (LiPON) is a promising method for the production of this thin film solid electrolyte [1]. A summary of recent nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy studies of thermally evaporated Li₃PO₄ and IBAD LiPON films will be presented. The NMR study of the LiPON films confirmed the presence of phosphorus in PO₄ tetrahedra, either in orthophosphate (PO₄³⁻) or pyrophosphate (PO₃O_{1/2}²⁻) units, and the additional presence PO₃N tetrahedra in which the nitrogen atom was doubly coordinated to two phosphorus atoms [2]. The NMR spectra also suggested the

presence of a form of trapped diatomic nitrogen. In this paper we will present further evidence for the presence of this form of diatomic nitrogen – namely, IR absorptions in the 2030-2200 cm⁻¹ spectral range that exhibited ¹⁴N/¹⁵N isotopic shifts. 1 F.Vereda, R B.Goldner, T.E.Haas and P. Zerigian. "Rapidly grown IBAD LiPON films with high Li-Ion conductivity and electrochemical stability," Electrochemical and Solid-State Letters, 5(11), A239-A241 (2002). 2 "Solid state NMR studies of lithium phosphorus oxynitride electrolyte prepared by nitrogen ion beam assisted deposition," P.E. Stallworth, F. Vereda, S.G. Greenbaum, T.E. Haas, P. Zerigian, R. Goldner. 14th International Conference on Solid State Ionics. Monterrey, CA. June 2003

K9.4

3D Microbatteries with C-MEMS/CNFs and C-MEMS/CNTs Electrode Arrays. Chunlei Wang¹, Rabih Zaouk¹, Lili Taherabadi¹, Marc Madou¹, Vijaya Kayastha² and Yoke Khin Yap²; ¹Mechanical and Aerospace Engineering, University of California, Irvine, Irvine, California; ²Physics, Michigan Technological University, Houghton, Michigan.

Advanced materials and novel battery designs are the two essential areas that will determine future advances in miniature batteries. In this work, we are incorporating carbon nanofibers (CNFs) and carbon nanotubes (CNTs) into carbon microelectromechanical systems (C-MEMS) to form arrays of electrodes for the formation of three-dimensional (3D) microbatteries. Our C-MEMS technique is based on the pyrolysis of patterned photoresists. This technique is used for the formation of carbon post with high aspect ratios >10. We have demonstrated that Li ions can be charged and discharged in these carbon posts. The obtained capacity is 220 mAh g⁻¹, which is within the range of reversible capacities reported for coke. Upon miniaturization of the active battery material in an array of posts, an increased Li capacity is important. This is very desirable so that besides increasing power density and decreasing battery charge/discharge rates, we also can maintain a high overall battery capacity. Since it has been shown that single-walled carbon nanotubes reversibly intercalate Li up to a rate of Li_{2.7}C₆ after applying an appropriate ball-milling treatment, we are now combining C-MEMS structures with CNTs and CNFs. The use of CNTs and CNFs in microbatteries has not been demonstrated. Further, the issue of the contact interface between these nanomaterials and current collectors has not been addressed. We have integrated CNFs into C-MEMS posts for achieving higher electrode surface areas and higher Li intercalation rates. We have successfully embedded CNFs at the surface of the C-MEMS post arrays. Further, we have also been able to grow very high-density vertically-aligned CNTs by thermal chemical vapor deposition. These CNTs can be patterned into arrays of microtowers. The application of these C-MEMS/CNTs and C-MEMS/CNFs electrode arrays for 3D Li ions microbatteries will be discussed in the conference.

K9.5

Single Ion Conducting Polymer Electrolytes with Fast Ion Conduction Pathways. Sundeep Kumar¹, Sang-Woog Ryu², Anne M. Mayes² and Yang Shao-Horn¹; ¹Mechanical Engineering, MIT, Cambridge, Massachusetts; ²Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

The conductivity of dry polymer electrolytes based on amorphous polyethylene oxide (PEO) is intrinsically limited by the coupling between ion motion and the slower segmental motion of the polymer chain. Recently, Wright and coworkers reported decoupled lithium ion conduction in amphiphilic PEO-based copolymer electrolytes doped with LiClO₄ or LiBF₄. Fast ion conduction pathways were generated in these copolymers by self assembly upon thermal cycling, resulting in ambient conductivities of 10-3 S/cm. To create single-ion conducting polymer electrolytes having fast ion conduction pathways, we synthesized a self-assembling amphiphilic polyelectrolyte copolymer of lithium methacrylate and a methacrylate macromonomer of oligo(ethylene oxide)₅ end-capped with octadecane. Some samples were doped with BF₃ to enhance ion dissociation. Impedance spectroscopy was used to measure ionic conductivity as a function of temperature. Ambient conductivities up to 6x10⁻⁵ S/cm were achieved after thermal cycling, a three order of magnitude enhancement over uncycled materials. The thermally cycled samples along with uncycled samples were characterized using wide angle and small angle X-ray scattering and differential scanning calorimetry. The correlation between microstructure and lithium conductivity will be discussed.

K9.6

Ion Transport Studies on PMMA with NH₄SCN as Solid Polymer Electrolytes Using DMSO+EC as Solvent. S. L. Agrawal and Shilpa Pandey; Department of Physics, A. P. S. University, REWA, M. P., India.

The present work reports the ion conducting properties of NH₄SCN

doped with PMMA using DMSO as solvent. Thermal characterization of PMMA with NH_4SCN complexes through DSC analysis indicating complexation of salt with Polymer, XRD pattern of solid polymer electrolytes at different composition is measured. The X-ray pattern reveals that the crystallinity of the studied electrolyte decreases with increasing ammonia salt. Samples containing more than 25 weight ratio added salt are X-ray amorphous. Polarization studies showed the ionic transport behavior as indicated by large value of transference number ($t_i > .92$). The ionic conductivity was found to increase continuously with the salt concentration. Further, the temperature dependency of ionic conductivity seems to obey the VTF relation. The values of the polymer complexes are present and discussed.

K9.7
Sonochemical Synthesis of Nanostructured Manganese Oxide Electrodes for Supercapacitors. Itaru Honma, Mitsuhiro Hibino and Hao-Shen Zhou; EEI, AIST, Tsukuba, Ibaraki, Japan.

For the system in which not only high-energy but also high-power operation is required, such as pure and hybrid electric vehicles, it is crucial to develop auxiliary power sources for rapid discharge and charge. If lithium ion battery is applied to this use, its electrode materials should possess low-price, low-toxicity in terms of widespread diffusion as well as high electrode performance. Many manganese oxides have attracted the attentions as electrode materials of lithium ion battery because they can intercalate lithium and have above natures. With a view to rapid discharge and charge, an active material should be prepared in the form of microparticle and contact preferably with conducting additives. The nanostructures of many materials has been prepared conveniently by sonochemical method, in which ultrasound is irradiated to a synthetic solution. It was previously found that the synthesis in an aqueous system lead inevitably to the presence of structural water in product. Without careful removal, residual water degrades cyclability of discharge and charge [1]. In this study, manganese oxides are synthesized sonochemically in non-aqueous system and examined as high-rate electrode materials.

K9.8
Abstract Withdrawn

K9.9
Electrophoretic Fabrication of "Separator-less" Rechargeable Lithium Ion Batteries. Dong-Wan Kim, Steven M. Tobias, Jennifer Giocondi, Yukinori Koyama and Yet-Ming Chiang; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

In situ two- and three-dimensional batteries without the use of physical separators by electrophoretic assembly are described in this work. Electrophoresis, the motion of charged particles towards an electrode under an applied field, is widely used to characterize the behavior of solutions and suspensions, and has also been used to deposit materials in the form of thin films, coatings, and even bulk products. By carrying out electrophoresis of charged-particle systems within a confined volume, it is possible to separate and organize cathode-active and anode-active materials into a variety of device constructions. The direction of electrophoretic migration was controlled for several particle-solvent systems useful in batteries by adjusting suspension chemistry. The electrophoretic mobility was directly observed using a two-dimensional metal electrode configuration. By applying the suspension to the microelectrodes and imaging particle migration under an applied potential difference, systems having selective deposition of cathodes and anodes were developed. The active materials studied to date include LiCoO_2 , LiFePO_4 and various carbon anodes. The two-dimensional electrophoretic separation of materials results in separator-less 2D batteries. We subsequently investigated the fabrication of three-dimensional battery architectures using electrophoretic assembly. Due to improved volumetric utilization of active material and reduced ion transport distances, three-dimensional battery designs may provide improved energy and power density compared to conventional laminated designs. A fundamental advantage of the electrophoretic approach is that physical separation can be produced between the two active electrode materials without requiring the insertion or deposition of a discrete separator film or electrolyte layer. One model system for electrophoretically assembled 3D batteries uses reticulated vitreous carbon foams as the anode. To create the 3D battery, the pore space within the carbon foam was infiltrated with a cathode active mixture of LiCoO_2 and Super P suspended in a solvent-solid polymer electrolyte solution. An electric potential was applied to electrophoretically separate the cathode from the carbon structure and densify the cathode network. Details of the process and resulting electrochemical properties will be presented in the talk.

K9.10
Application of CuBr Ion Conductor Thin-Films for Ammonia Gas Detection. Pascal Lauque¹, Marc Bendahan¹, Jean-Luc Seguin¹ and Philippe Knauth²; ¹L2MP, University Aix-Marseille III, Marseille,

France; ²MADIREL, University of Provence, Marseille, France.

Thin-films of the well-known solid ion conductor CuBr can be prepared by chemical reaction between metallic copper and an aqueous copper(II) bromide solution. These films are used for sensitive and selective ammonia gas detection at room temperature, based on the large electrical resistance change when exposed to low ammonia concentrations (< 100 ppm). The sensor is operating at ambient temperature and allows highly specific ammonia detection without cross-effect in particular of other reducing gases. The sensor fabrication is a simple process, allowing low cost device production. The sensor properties are compared with commercial tin dioxide-based systems with clear advantages in terms of sensitivity and especially selectivity. The probable detection mechanism is discussed: it is based on gas adsorption and formation of ionic space charge regions. The only disadvantage of the CuBr sensor, relatively long response and recovery times, is related to the quite low mobility of the ionic carriers at room temperature.

K9.11
Synthesis, spectroscopic and electrochemical characterization of hybrid membranes for Polymer Electrolyte Membrane Fuel Cells. Maria-Luisa Di Vona¹, Debora Marani^{1,4}, Alessandra d'Epifanio¹, Enrico Traversa¹, Marcella Trombetta², Silvia Licoccia¹, Stefano Caldarelli³ and Philippe Knauth⁴; ¹Dept. Chem. Science and Technology, Univ. Rome Tor Vergata, Roma, Italy; ²Interdisciplinary Center for Biomedical Research (CIR), Univ. "Campus Bio-Medico", Roma, Italy; ³TRACES, Univ. Provence, Marseille, France; ⁴MADIREL, University of Provence, Marseille, France.

Proton electrolytes are key components of Polymer Electrolyte Membrane Fuel Cells (PEMFCs). Requirements to be met are: high proton conductivity, high hydrolytic stability and, when their use is foreseen in DMFCs, low permeability to methanol to avoid alcohol crossover. Proper mechanical properties must also be achieved. Both mechanical and electrical properties are related to the ratio between hydrophilic and hydrophobic groups in the membranes: the polymer backbone confers proper mechanical and thermal properties while conductivity is usually inferred by hydrophilic acidic side chain groups. Much research efforts are devoted to the development of new electrolytes to overcome the problems connected with the use of Nafion, the most widespread polymeric system for PEMFCs. The main drawbacks of Nafion are operation below 100 °C, high cost, need of humidification, high methanol cross-over. The possibility of using composite membranes where inorganic fillers are dispersed in a polymeric matrix has been investigated and quite satisfactory performances have been reported. Given the difficulty to achieve homogeneous samples, we are now studying the development of organic/inorganic hybrid membranes where the inorganic component is covalently bound to the organic one. The properties of such covalent hybrids can be modulated by modifying the ratio between organic and inorganic groups and the nature of the chemical components. Totally aromatic polymers bearing carbonyl, ether or sulfone groups, were selected as the organic backbone, functionalized with sulfonic groups to achieve proton conductivity. However, the mechanical properties show a parallel progressive deterioration with the degree of sulfonation. The formation of covalent bonds between the polymeric chain and Si(OR)₃ groups was identified as a mean to introduce an inorganic component that can undergo further sol/gel reactions. Organic/inorganic hybrids were synthesized by reaction of sulfonated polymers with silicon tetrachloride, followed by hydrolysis. Further amounts of inorganic component can be added by sol/gel reaction with tetraethylorthosilicate (TEOS) to modulate mechanical properties and the electrical performance. The materials were characterized by means of multinuclear Nuclear Magnetic Resonance spectroscopy (¹H, ¹³C, ²⁹Si), Thermogravimetric and Differential Thermal Analysis, Differential Scanning Calorimetry, Fourier Transform Infra-red Spectroscopy and Electrochemical Impedance Spectroscopy.

K9.12
Investigations of Imidazole-Based Lithium Conducting Materials. Agata R. Czardybon, U. Sivasubramaniam and Gillian R. Goward; Chemistry, McMaster University, Hamilton, Ontario, Canada.

This study focuses on the development of novel polyelectrolytes that include lithiated imidazole heterocycles for use in lithium ion rechargeable batteries. Materials are characterized on the basis of their macroscopic ionic conductivity, measured by impedance spectroscopy, and the local mobility of the lithium ions, characterized by ⁷Li solid-state NMR. By comparing these two measures of lithium ion transport, we develop a picture of the ionic conductivity at the microscopic level. Multinuclear solid state NMR (⁷Li, ¹³C) provides information on microscopic interactions including ionic mobility and ring reorientations which govern the efficiency of conductivity. Our research includes ⁷Li variable MAS NMR studies at intermediate spinning speeds, and relaxation investigations to determine

spin-lattice relaxation times (T_1) of lithium ion hopping. A very long T_1 (135 s at ambient temperature) and low value of activation energy $E_a = 0.25$ kJ/mol suggests rigid molecule structure and the absence of the ring reorientation of the model compound, lithium imidazolium. This data is contrasted with related studies of both imidazole and imidazole methylsulfonate, which are of interest as model compounds for related proton-conducting materials. With the goal of creating new polyelectrolytes, we have synthesized electrolytes incorporating lithiated imidazole rings, where lithium transport may be independent of polymer-backbone flexibility, and thus polymers with high glass transition temperatures may be viable. Such materials are highly desirable for secondary lithium polymer battery applications.

K9.13

Modeling and Experimental Study of Interaction between Poly (3-hexylthiophene) Conducting Polymer and Hydrazine Vapor. Hong Yang and Bryan A. Chin; Materials Engineering, Auburn University, Auburn, Alabama.

Conducting polymers are one of the most promising sensing materials for gas detection. Compared with metal oxide and organic crystal materials, conducting polymers have the advantages of superior processability, higher sensitivity, and lower operational temperature. A number of studies have been done to investigate the response of different conducting polymers to odors, organic vapors, and reactive gases. However, the exact interaction mechanism between the gas molecules and conducting polymer thin film is not clear. In this research, a microelectronic-fabricated miniature device combined with gas sensitive poly (3-hexylthiophene) (P3HT) thin film has been developed for the detection of extremely toxic and flammable hydrazine vapor. The interaction mechanism between the hydrazine molecules and the oxidized P3HT thin film has been investigated experimentally and these data have been used to develop a theoretical model. Previous investigators have proposed six theoretical mechanisms to describe the behavior observed in conductive polymer gas sensors. These mechanisms are: pure diffusion, slow diffusion, unsaturated linear reaction, saturated reaction, saturated nonlinear reaction, and moving boundary process. A numerical approach using the finite volume method was used to evaluate the observed experimental phenomenon under different hydrazine concentrations, environment temperatures, and film thicknesses. The authors determined that a mechanism of slow diffusion and fast reaction could be used to explain the observed experimental data. Based upon the modeling result, the authors concluded that hydrazine molecules diffuse into the P3HT thin film, and react with charge carriers; the depleting of charge carriers leads to a reduction in P3HT thin film's conductivity.

K9.14

Thin Films of $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ for Hydrogen Gas Sensors. Seungwan Song, L. Peter Martin and Robert S. Glass; Energy and Environment Directorate, Lawrence Livermore National Laboratory, Livermore, California.

Thin films of $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ have been evaluated as electrolytes for amperometric hydrogen gas sensors. The films were deposited on dense substrates by spin-coating a viscous metal-citrate sol followed by annealing at 850°C for 1 hour and 1500°C for 5 hours. The sol-gel derived thin films required lower annealing temperature and time, compared to coatings prepared using commercial $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ oxide powder slurries. X-ray diffraction data indicated that the sol-gel process yields a crystalline film with orthorhombic (*Pnma*) structure consistent with the $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ perovskite. The films were a few tens of nanometers thick, appeared smooth, and covered the substrate completely. To complete the hydrogen sensor fabrication, two porous Pt electrodes were attached to the top of the film. Amperometric detection of hydrogen in the temperature range of 400 - 650°C was evaluated by, applying a constant voltage between the electrodes and measuring the resultant current. At all H_2 concentrations investigated, linear I-V behavior was observed for all applied potentials between 0.0-0.3V. For use as an amperometric sensor, it was found that an applied voltage of 250 mV yielded currents that correlated well to the H_2 concentration in the range of 4 - 100%. Further analysis of sensor dependence on film thickness and morphology as well as the sensor performance using films deposited on different substrates and tested under different conditions will be presented.

K9.15

Abstract Withdrawn

K9.16

FTIR Features of Lithium Iron Phosphates used as Positive Electrodes in Rechargeable Lithium Batteries. Atmane Aitsalah¹, Pavel Jozwiak^{2,1}, Jerzy Garbacz² and Christian M. Julien¹; ¹LMDH, University P et M Curie, Paris, France; ²Faculty of Physics, University of Technology, Warsaw, Poland.

There has been considerable interest in lithiated phosphates as a positive electrode materials in Li-ion cells because of their superior cost, safety, stability and low toxicity. Despite the extensive studies of the phospho-olivine LiFePO_4 and nasicon-like $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ structures, there few reports on their vibrational properties. The main objective of this work is to investigate the structural properties and lattice dynamics of several lithium-iron phosphates using Fourier transform infrared (FTIR) spectroscopy in a wide range of frequencies, from 100 to 2000 cm^{-1} . Samples include LiFePO_4 diphosphate, $\text{LiFe}_1.5\text{P}_2\text{O}_7$ pyrophosphate, and $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ nasicon-like structure grown by wet chemical techniques. As these polyphosphates display a strongly condensed framework, FTIR spectroscopy is a powerful local probe for their structural characterisation. The crystallinity of the specimens was assessed from both the XRD and FTIR patterns. By assuming the separation of the vibrations into internal modes of PO_4 (or P_2O_7) units and external modes, the vibrational analysis of phosphate-based compounds was made using the correlation method. A comparison of the spectral fingerprints of lithium metal phosphates shows as follows. For phospho-olivine structures, in the region of the internal modes of the phosphate anion, we identify the symmetric stretching modes with appearance of triplets in the high-wavenumber region and doublet in the far-infrared region due to the site-symmetry effect and the correlation effect. The appearance of the symmetric and antisymmetric P-O-P stretching vibration constitutes the specific spectral fingerprints of pyrophosphates. For nasicon-like framework, internal modes involving the displacement of oxygen atoms of the pseudo-tetrahedral anions present frequencies closely related to those of the free molecule. Lantern units present in the nasicon phases give rise to infrared bands in the high-wavenumber range which are attributed to the stretching vibrations of terminal PO_3 units.

SESSION K10: Lithium Batteries I
Chairs: Ryoji Kanno and Christian Masquelier
Thursday Morning, December 2, 2004
Republic B (Sheraton)

8:30 AM *K10.1

Characterization of Li Insertion Mechanisms in Lithium-ion Battery Electrode Materials by Mossbauer Spectroscopy and First-principles Calculations. Pierre-Emmanuel Lippens, Josette Olivier-Fourcade and Jean-Claude Jumas; LAMMI-UMR 5072 CNRS, Universite Montpellier II, Montpellier, France.

The microscopic analysis of Li insertion mechanisms in electrode materials of lithium-ion batteries is often difficult and requires the use of different experimental techniques. For example, x-ray diffraction method fails in the accurate identification of nanocrystalline or amorphous phases occurring during lithium insertion-deinsertion. The Mossbauer spectroscopy provides information on the local electronic density of different isotopes such as ^{57}Fe , ^{119}Sn or ^{121}Sb . It is therefore a suitable tool to study changes in the oxidation state and electronic population, formation of crystalline or amorphous phases, etc... during charge and discharge. Results are presented for iron, tin and antimony based materials and for other negative electrode materials containing ^{57}Fe or ^{119}Sn dopants used as probe isotopes. Mossbauer experimental data are combined with results of first-principles calculations in order to relate the electrochemical reactions in the electrode materials to the local electronic and structural changes.

9:00 AM K10.2

Tailored Nanostructured Materials for Advanced Rechargeable Energy Storage Devices. Amit Singhal¹, Ganesh Skandan¹, Glenn Amatucci² and A. Manthiram³; ¹NEI Corporation, Piscataway, New Jersey; ²Rutgers University, Piscataway, New Jersey; ³University of Texas, Austin, Texas.

The use of nanomaterials as electrodes in both rechargeable bulk and thin film Li-ion based batteries presents new opportunities for energy density, exceptionally high rates of charge and discharge, higher cyclability, and lower cost. Furthermore, there is increasing evidence that the small feature size in nanostructured materials may allow reversible intercalation of polyvalent ions, leading to practical devices not possible until now. The presentation will describe our efforts in producing engineered nanostructures for use as electrode materials in a variety of rechargeable rocking chair cells. Electrochemical results on a variety of nanocrystalline cathode materials, including lithium manganese oxide and lithium metal phosphates that are commercially important because of their low-cost and non-toxicity, will be discussed. For example, we have demonstrated that in Li-ion prototype cells, nanostructured $\text{LiMn}_x\text{MxO}_2$ exhibits an energy density of 550 Wh/kg, which is comparable to state-of-the-art LiCoO_2 cathodes, along with 100 % coulombic efficiency and good cyclability. On cycling, nanostructured layered $\text{LiMn}_x\text{MxO}_2$ transformed to the spinel phase, but the transformation did not significantly affect the cyclability of the material. Further, we have

also developed nanostructured anode materials for a novel asymmetric hybrid device, which charges and discharges in a few minutes like a supercapacitor, and displays an order of magnitude higher energy density than a supercapacitor. This work has been sponsored in part by Missile Defense Agency, Office of Naval Research, National Aeronautics Space Administration and US Department of Energy.

9:15 AM **K10.3**

Improved Composite Electrode and Lithium Battery Performance from Smart Use of the Polymers and their Properties. Vincent Gaudefroy¹, Delphine Guy¹, Bernard Lestriez¹, Renaud Bouchet² and Dominique Guyomard¹; ¹Institut des Matériaux Jean Rouxel, UMR CNRS 6502, Nantes, France; ²Laboratoire MADIREL, Marseille, France.

Most studies in the field of rechargeable batteries deal with the search for new formulations and structures of active electrode materials. But the active material of a battery cannot function by itself as an electrode. The electrode is in fact a very complex medium which needs to bring efficiently the ionic reactants and the electrons to the surface of the active material (AM) particles. Such a complex medium is generally obtained by mixing together the AM grains with non-electroactive additives such as a very fine powder of carbon black (CB) and a polymeric binder. It seems quite obvious that the organization of the CB and polymeric binder dispersion and/or morphology within the composite electrode should have an influence on the electrode performance. However, such an issue is a research area, which has never been carefully studied yet. While polymers have been thoroughly investigated for a while for their use as a component of the electrolyte, their utilization as the electrode binder has not been studied. As a matter of fact, for room temperature lithium batteries, the usual binders remain among the two polymer families, PTFE, and PVdF and derivatives. This study focuses on the preparation of a new polymeric binder combination that was used for lithium trivanadate (Li_{1.2}V₃O₈) based composite electrodes (solvent-cast). Li_{1.2}V₃O₈ that offers a theoretical capacity of 360 mAh/g, was investigated as a very promising positive electrode material during the past two decades. However, the experimental capacity generally remains much lower than the theoretical value. The maximum obtained constant cycling capacity is actually of 150 mAh/g (3.3-2 V range) at room temperature when a classical binder (PVDF) is used. Here, the surrounding of the AM was changed by playing with the nature of the polymer binder, its plasticization and using mixed polymers with complementary properties. In each case the electrochemical response was followed, the electronic conductivity was measured, and SEM investigations were performed. New polymeric combination allowed reaching a specific capacity of 280 mAh/g. Well performing composite electrode material with efficient electronic conduction network was achieved from a more homogeneous CB distribution due to good binder-CB interactions and from optimum ratios between plasticized binder and CB. 1 - D. Guy, B. Lestriez and D. Guyomard, Adv. Mater., 16, 553 (2004). 2 - D. Guy, B. Lestriez, R. Bouchet, V. Gaudefroy, D. Guyomard, accepted for publication in Electrochem. Solid-State Lett.

9:30 AM **K10.4**

Strategy Towards Solid State Li-Ion Batteries Assembled From Interpenetrating Nanostructured Battery Materials. Justin C. Lytle¹, Kyu T. Lee², Nicholas S. Ergang¹, Seung M. Oh²

and Andreas Stein¹; ¹Department of Chemistry, University of Minnesota, Minneapolis, Minnesota; ²School of Chemical Engineering and Research Center for Energy Conversion & Storage, Seoul National University, Seoul, South Korea.

We report a strategy towards the fabrication of solid-state Li-ion batteries assembled from interpenetrating nanostructured battery materials based on a three-dimensionally ordered macroporous (3DOM) geometry. 3DOM solids possess continuous nanoscale skeletons (wall thicknesses ca. tens of nm) that encase three-dimensionally interconnected, close-packed spherical voids hundreds of nm in diameter. Carbon electrode battery materials with this ordered macroporous structure demonstrate rapid electrochemical cycling compared to their bulk counterparts, overcoming rate-limiting factors via nanometer scale ion-diffusion pathlengths and relatively large electrode/electrolyte interfacial areas. Cell assembly began with the synthesis of 3DOM carbon monolith anodes, which were prepared by infiltration of poly(methyl methacrylate) (PMMA) colloidal crystal templates with a resorcinol-formaldehyde (RF) sol, followed by subsequent thermal processing to depolymerize the PMMA template and carbonize the RF gel. Poly(phenylene oxide)-based polymer electrolyte was electrodeposited on 3DOM carbon to ensure electronic insulation of the anode. Anode/electrolyte composites were immersed in Li-ion liquid electrolyte and dried under vacuum to induce solid-state ionic conductivity through the polymer electrolyte. Vanadia ambigel cathode material was formed in the remaining macropore void space by infiltration with a vanadium alkoxide sol. Cathode ambigels were electrochemically charged with Li-ions, and cells were

galvanostatically cycled to investigate their rate performance.

10:15 AM ***K10.5**

Electrochemical Extrusion of Copper by Lithium. Role of the Initial Structure on the Habitus of the Metallic Copper. Morcrette Mathieu¹, Leriche Jean-Bernard¹, Rozier Patrick², Dupont Loic¹, Poizot Philippe¹, Masquelier Christian¹ and Tarascon Jean-Marie¹; ¹LRCS/CNRS, Amiens, France; ²CEMES/CNRS, Toulouse, France.

New concepts are needed for alternative materials in lithium batteries. Alternative to classical insertion, displacement reactions induced by lithium insertion were demonstrated by several groups on different intermetallic systems. Thus, it was tempting to determine whether such displacements reactions could also occur with other classes of materials. Guided by earlier studies dealing with the Li reactivity of copper or Ag-based ternary oxides or sulphides, for which the authors did observe a non-or partially reversible Li insertion/Cu extrusion process, we decided to revisit the electrochemical reactivity of Cu-based vanadate phases towards Li, hoping that such materials could present some benefits if we could master the reversibility of the 2e⁻ of the Cu²⁺/Cu(0) redox process. In this presentation, we will focus on the complex mechanism of extrusion of copper out of a vanadium oxide : Cu_{2.33}V₄O₁₁. This copper vanadate electrochemically reacts with Li in an unusual and spectacular way, which entails a reversible Li insertion/extrusion process leading to the growth/disappearance of Cu dendrites with a concomitant reversible decomposition /crystallization of the initial electrode material. We extended our investigations on this peculiar phenomenon to several families of Cu-containing materials. Through an arsenal of techniques (In Situ X-ray diffraction, HRTEM, in situ SEM) we determined that several key parameters affect the potential of the Cuⁿ⁺/Cu(0) couple, and the morphology of the metallic copper extruded (particles versus dendrites). The character of the ionic conductivity within the structure of the host material (insulating compound vs lamellar structure vs 3D conductor) appears to play a major role.

10:45 AM **K10.6**

Structure and Electrochemical Performances of the Li_{1+x}(Ni_{0.425}Mn_{0.425}Co_{0.15})_{1-x}O₂ Materials. Nicolas Tran¹, Laurence Croguennec¹, Francois Weill¹, Christian Jordy², Philippe Biensan² and Claude Delmas¹; ¹Institut de Chimie de la Matière Condensée de Bordeaux-CNRS, Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, Université Bordeaux I, Pessac, France; ²SAFT, Direction de la recherche, Bordeaux, France.

In the present work, well crystallized Li_{1+x}(Ni_{0.425}Mn_{0.425}Co_{0.15})_{1-x}O₂ materials were prepared by a coprecipitation method. For x = 0 in the Li_{1+x}(Ni_{0.425}Mn_{0.425}Co_{0.15})_{1-x}O₂ phases, the nickel, cobalt and manganese ions are expected to be at the divalent, trivalent and tetravalent state respectively. The presence of an excess of lithium ions in the structure leads thus to the formation of trivalent nickel ions. As tetravalent nickel ions were never found in layered materials synthesized at high temperature, it was expected that the solid solution limit would correspond to x_{max} = 0.175. Therefore, this study was carried out in the 0 < x < 0.25 range. Chemical and redox analyses, X-ray and neutron diffraction experiments and magnetic measurements will be discussed. The proposed long range structure is of an alpha-NaFeO₂-type with (i) a Li⁺/Ni²⁺ exchange between the interlayer space and the slab and (ii) the lithium excess in the slab. It should be noted that an increasing lithium excess in the material leads to a decrease in the amount of transition metal ions in the interlayer space. Moreover, an electron diffraction study has also shown that a short range ordering occurs in these materials. Diffraction lines were observed for x=0 and extra spots for x=0.12, which was in good agreement with a sqrt(3)ahex*sqrt(3)*ahex ordering in the slab. The cycling tests of these overlithiated materials were performed between 2 V and 4.3 V with a constant C/20 rate. The reversible capacity obtained for the first cycle was good (155 mAh/g) for the material synthesized without lithium excess and decreased as the lithium content in the material increased, which is consistent with the increasing average oxidation state of the metal ions when the lithium concentration in the material increases.

11:00 AM **K10.7**

A DFT+U Study of Electron Correlation Effects on Total Energy Calculation of Transition-Metal Compounds. Fei Zhou, Matteo Cococcioni, Dane Morgan and Gerbrand Ceder; MIT, Cambridge, Massachusetts.

A large number of properties of solid state materials can now be predicted with standard first-principles methods such as the Local Density (LDA) or Generalized Gradient Approximation (GGA). Even though known problems exist when using these methods for predicting the electronic structure of transition metal oxides, they are usually credited with good accuracy in total energy calculations. However, it

has been recently pointed out that the lack of appropriate treatment of electronic correlation in these materials, and the ensuing electron delocalization leads to considerable errors in predicting redox reactions. Notably for Li insertion oxides, the lithium intercalation voltage is underestimated by 0.5 -1 eV in LDA and GGA. More dramatically the Li_2FeO_4 system is known experimentally to phase separate but LDA/GGA predicts stable intermediate compounds, resulting in a qualitative error. Both examples are related to LDA/GGA errors in total energy differences between transition metal compounds. We show that all these errors are caused by the spurious self-energy interaction in LDA and GGA. While this error cancels when looking at many properties, the electron transfer between different elements, that is common to redox reactions, reduces the error cancellation, thereby leading to poor ab-initio predictions for redox systems. We demonstrate that the DFT+U method, in which transition metal states are treated with a more appropriate many-body model, gives considerably better predictions on lithium insertion reactions than standard LDA and GGA. Using linear response theory, the effective Coulomb interaction parameter U at transition-metal sites can be self-consistently calculated for a material, making this a fully ab-initio technique. In all but one material, the experimental average lithium intercalation voltage is reproduced within 0.1- 0.2 V. DFT+U also corrects the qualitative error in Li_2FeO_4 and gives intermediate Li_2FeO_4 to be unstable with respect to the lithiated and delithiated phases. We believe that the more accurate treatment of electron correlation on the transition metal sites will greatly enhance the predictive character of ab-initio methods for these materials.

11:15 AM K10.8

Formation of O6 Stacking upon Cycling and Thermal Treatment of T#2-Li2/3Co2/3Mn1/3O2. Laurence Croguennec¹,

Frederic Tournadre¹, Shinichi Komaba^{1,2}, Mathieu Morcrette³, Patrick Willmann⁴ and Claude Delmas¹; ¹Institut de Chimie de la Matière Condensée de Bordeaux-CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, Université Bordeaux I, Pessac, France; ²Department of Chemical Engineering, Iwate University, Iwate, Japan; ³Laboratoire de Réactivité et Chimie des Solides, Université Picardie Jules Verne, Amiens, France; ⁴Centre National d'Etudes Spatiales, Toulouse, France.

Layered LiMO₂ materials obtained by lithium ion exchange in P2 sodium containing phases demonstrated interesting properties as positive electrode materials for Li-ion batteries. Recently the crystal structure analysis, the electrochemical and physico-chemical properties of T#2-Li₂/3Co₂/3Mn₁/3O₂ obtained by Li/Na ionic exchange in molten salts were studied. From neutron diffraction data and nuclear density Fourier difference map calculations, lithium ions were found distributed among two distorted tetrahedral sites of the interslab space. Good electrochemical performances were obtained for T#2-Li₂/3Co₂/3Mn₁/3O₂ in lithium batteries, with an efficient capacity of 155 mAh.g⁻¹. The redox processes were studied using XANES, NMR and conductivity measurements. Phase transitions observed upon cycling and thermal treatment of T#2-Li₂/3Co₂/3Mn₁/3O₂, and especially their reversibility, will be discussed on the basis of thermal analyses and X-ray diffraction. Indeed, several phase transitions occur upon cycling, with especially transformation of T#2 stacking into O6 in two lithium composition ranges. T#2 is also transformed into O6 upon thermal treatment, before decomposition into Li₂MnO₃ and Co₃O₄. The O6 phase thus formed shows good reversible capacity in lithium batteries.

11:30 AM K10.9

Structural Characterization of Lithium Intercalation in Nanostructured Ferric Oxides. Gaurav Jain¹, Jun John Xu¹, Mahalingam Balasubramanian² and James McBreen³; ¹Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey; ²Experimental Facilities Division, Argonne National Laboratory, Argonne, Illinois; ³Materials Science Division, Brookhaven National Laboratory, Brookhaven, New York.

Hematite or $\alpha\text{-Fe}_2\text{O}_3$ is one of the most stable and naturally abundant transition metal compounds. It possesses a hexagonal R-3C structure with oxygen atoms in HCP arrangement and Fe occupying 2/3rd of the octahedral sites. Lithium intercalation in $\alpha\text{-Fe}_2\text{O}_3$ has been studied by a number of groups. The face-sharing of [Fe-O₆] octahedra in the crystallographic c direction renders occupation of the vacant octahedra by Li⁺ energetically unfavorable. It has been reported that the compound shears to a cubic packing upon intercalation of a very small amount of Li. The overall electrochemical properties reported for micro-crystalline $\alpha\text{-Fe}_2\text{O}_3$ as a lithium intercalation cathode are extremely unpromising, with capacities not more than a few tens of mAh/g. Recently, Larcher et al.¹⁻² contrasted the behavior of a nano-metric $\alpha\text{-Fe}_2\text{O}_3$ versus a micro-metric $\alpha\text{-Fe}_2\text{O}_3$. They reported that the hexagonal to cubic phase transformation is much delayed in the nano-metric sample, which showed much superior electrochemical performance over the

micro-metric sample. We have reported a nanocrystalline ferric oxide that exhibits excellent electrochemical properties³. At C/50 the material delivers a discharge capacity of 249 mAh/g, corresponding to reaction with 1.48 Li per Fe₂O₃, with > 99% reversibility. At C/5, the material yields a capacity of 195 mAh/g with nearly perfect capacity retention upon repeated cycling. These properties are in drastic contrast with those of the microcrystalline $\alpha\text{-Fe}_2\text{O}_3$. Here we report detailed XRD and XAS characterization of this nanocrystalline ferric oxide, along with other $\alpha\text{-Fe}_2\text{O}_3$ samples with systematically varied particle size or morphology, crystallinity, and defect concentration, to illustrate structure-electrochemical property relationships. The investigations have concluded: 1) The nanostructured morphology and nano-metric particle size, disorder, defects and vacancies in the crystal structure are all important factors determining the electrochemical properties of the nanocrystalline ferric oxide, 2) There is a clear reduction in the reversible intercalation capacity with an increase in the crystallinity and particle size of the $\alpha\text{-Fe}_2\text{O}_3$ samples, 3) Presence of a small number of Fe vacancies, charge compensated by the presence of H⁺ in the structure, appears to have a favorable impact on the electrochemical properties of the $\alpha\text{-Fe}_2\text{O}_3$ samples. These investigations point to the advantages of structural amorphosity and disorder including Fe vacancies, as well as nano-metric particle size, in rendering superior electrochemical properties of ferric oxides. 1. D. Larcher, C. Masquelier, D. Bonnin, Y. Chabre, V. Masson, J.-B. Leriche and J.-M. Tarascon, J. Electrochem. Soc., 150, A133 (2003). 2. D. Larcher, D. Bonnin, R. Cortes, I. Rivals, L. Personnaz and J.-M. Tarascon, J. Electrochem. Soc., 150, A1643 (2003). 3. J. J. Xu and G. Jain, Electrochem. & Solid State Lett., 6, A190 (2003).

11:45 AM K10.10

Recent Advances in Three-Dimensional (3D) Thin Film Microbatteries. Menachem Nathan¹, Diana Golodnitsky², Vladimir Yuft^{1,2}, Inna Shekhtman², Tanya Ripenbein^{1,2}, Ella Strauss², Svetlana Menkin² and Emanuel Peled²; ¹Department of Physical Electronics, Tel Aviv University, Tel Aviv, Israel; ²School of Chemistry, Tel Aviv University, Tel Aviv, Israel.

We present recent advances in the development of three-dimensional (3D) rechargeable Li thin film micro-batteries on silicon and on glass microchannel plates (MCP). In such 3D microbatteries, the battery sandwich-like structure, which comprises electrodes (anode and cathode), a solid electrolyte separator and optional current collectors, is deposited conformally on all available surfaces. These include internal surfaces of holes formed in the substrate. Such 3D microbatteries thus utilize the dead volume of a substrate, the result being more than an order of magnitude increase in capacity and enhancement of other figures of merit. The talk discusses materials and processing issues as well as characterization of half and full cells. We present the first operating full-cell (current collector/cathode/polymer electrolyte/anode) 3D microbattery built in a glass microchannel plate (MCP). The MCP is in the form of a plate with a thickness of 0.5 mm, and consists of a matrix of regular hexagonal channels with a diameter of ca. 50 micrometer spaced about 10 micrometer apart. The first prototype included an electrochemically deposited molybdenum sulfide cathode of about 1 micrometer thickness formed on a nickel current collector, a polymer separator of a few micrometer thickness, and a lithiated graphite anode. This prototype provided a capacity of about 1.5-2 mAh/cm², which represents an enhancement of ca. 30 times over the capacity of a similar footprint full-cell built on a planar substrate. 3D microbatteries based on perforated substrates thus become real candidates for applications that require battery sizes compatible with MEMS devices

SESSION K11: Lithium Batteries II

Chairs: Pierre-Emmanuel Lippens and Mathieu Morcrette

Thursday Afternoon, December 2, 2004
Republic B (Sheraton)

1:30 PM *K11.1

All Solid-State Battery Using Super Ionic Conductor, Thio-Lisicon - Electrode/Electrolyte Interfacial Design Concept. Ryoji Kanno, Takeshi Kobayashi, Taro Inada, Noriyuki Sonoyama and Atsuo Yamada; Department of Electronic Chemistry, Tokyo Institute of Technology, Yokohama, Japan.

Thio-LISICON (Lithium SuperIonic CONductor) is one of the best lithium ion conductive solids ever found in inorganic materials. The room-temperature conductivity exceeds 10⁻³ Scm⁻¹ with negligibly small electronic conductivity and a high decomposition potential. It is of great interest to investigate the ion transport mechanism as well as an application to all solid-state batteries. The material would be installed in place of flammable liquid electrolytes in conventional lithium-ion rechargeable batteries. Based on the relationships between

the structures and ionic conduction of the thio-LISICON family, $\text{Li}_{4-x}\text{M}_{1-y}\text{M}'_y\text{S}_4$ with $M = \text{Si, Ge, and } M' = \text{P, Al, Zn, Ga, Sb,}$ we discuss the conduction mechanism and its material-design concept. The all solid-state batteries with the thio-LISICON electrolyte was studied and fast charge-transfer at the self-assembled solid electrolyte interface (SEI) was clarified. The SEI phase was formed between the Li-Al anode and the thio-LISICON ($\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$) solid-electrolyte by applying current through the cell. After the spontaneous formation of the SEI phase, the interfacial resistance vibrated and decreased to constant values with the charge-and-discharge process. The "breathing" interface effectively makes a close contact at the electrolyte/electrode boundary and promotes fast charge-transfer at the solid-interface.

2:00 PM K11.2

A Nanosilicon Electrode with Superior Cyclability for Lithium-Ion Batteries. Michael Holzappel¹, Hilmi Buqa¹, Werner Scheifele¹, Petr Novak¹ and Frank-Martin Petrat²; ¹Paul Scherrer Institut, 5232 Villigen PSI, Switzerland; ²Degussa AG, Creavis Technology and Innovation, 45764 Marl, Germany.

A large volume change generally occurs during the lithium insertion and de-insertion into/from silicon as electroactive material for lithium-ion batteries. By reducing the particle size, the high mechanical stress resulting from this process is diminished. Newly developed nano-sized silicon has shown superior cycling behaviour, with respect to reversible charge capacity and cycle life. The silicon material used in this study was prepared by thermal decomposition of a silicon-containing precursor in a reducing atmosphere. Standard electrochemical cycling of bulk electrodes containing 80% of silicon active material yielded over 1300 mA/g for more than 60 cycles. A second way to reduce the high mechanical stress upon electrochemical cycling is to deliberately limit the charge capacity. With a limitation to 700 mAh/g, the material was cycled for over 250 cycles. In electrodes containing 20% of silicon, more than 900 mAh/g were attained for more than 100 charge/discharge cycles with a capacity fading of less than 0.1% per cycle by the standard and more than 200 cycles were obtained by a capacity limited cycling procedure.

2:15 PM K11.3

Structural and electrochemical properties of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$. Miaomiao Ma, Natasha A. Chernova, Peter Y. Zavalij and Stanley M. Whittingham; Institute for Materials, Binghamton University, Binghamton, New York.

The layered oxide $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ was synthesized by heating the mixed hydroxide precursor. This 442 composition was found to show the highest capacity of these mixed transition metal oxides. It has the optimum cobalt concentration to both substantially order the lattice, yet leave enough nickel on the lithium sites to minimize conversion to the 1T structure of CoO_2 on deep charging. A combined x-ray and neutron diffraction study showed conclusively that only nickel, not manganese or cobalt is found on the lithium sites. Magnetic measurements also confirmed the presence of nickel on the lithium sites, and showed the effectiveness of cobalt at minimizing nickel disorder. Heating above 800°C always leads to nickel disorder. The structural and thermal stability of reduced lithium content materials was studied; the structure remains rhombohedral except for $x \leq 0.05$, and cobalt substitution improves the thermal stability of the layered compound, but not the chemical stability. The kinetic/rate characteristics of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ electrodes in lithium cells were determined by the galvanostatic intermittent titration technique (GITT). This work was supported by DOE through the BATT program.

2:30 PM K11.4

A Study of the Li/Electrolyte Interface in Lithium Metal/Gel Polymer Symmetric Cells. Anna Teyssot¹, Michel Rosso¹, Lucas Sannier² and Stephane Lascaud³; ¹LPMC, UMR 7643, Ecole Polytechnique, Palaiseau, France; ²LRCS, Université de Picardie Jules Verne, Amiens, France; ³R&D, EDF, site des Renardieres, Moret sur Loing, France.

The increasing diffusion of modern portable devices has prompted considerable efforts to decrease the operating temperature of Li batteries, with the consequent development of new gel polymer membranes (GPE)^[1]. Due to the crucial role of lithium metal/gel membrane interface for battery performance, many studies have been devoted to the subject^[2]. In this work we present the study of a PVdF/PEO/EC/PC based gel membrane, charged with LiTFSI lithium salt. We focus on the Li/electrolyte interface by means of symmetric Li/electrolyte/Li cells, well adapted to this study^[3]. Some of these cells were assembled with an internal reference electrode to separate the contributions of both surfaces, with a special interest to the negative electrode (acting as working electrode - WE), equivalent to the negative pole of a Li metal battery during charge. The

evolution of impedance spectra upon aging (2 months) was studied. An equivalent circuit is proposed to describe the whole spectra (50 kHz to 0.1 Hz), and particularly the contribution of the interface. We identify a native passivation layer that does not vary with aging, and a second passivation layer whose surface resistance grows with the square root of time^[3]. We then polarised the cells under galvanostatic conditions at different current densities ranging from 0.03 to 0.3 mA.cm⁻²: for all current densities we obtained a characteristic evolution of the internal potential, consisting first in an increase of the potential to a maximum, followed by a decrease to a stabilized lower potential. We also recorded impedance spectra on the WE in dynamical mode during polarisation. Our measurements on a three electrode cell show that the decrease of the potential is mainly due to the decrease of the interface contribution at the WE. We think this decrease is due to the porous morphology of deposited lithium, and to the resulting increase of the specific surface. Our hypothesis is confirmed by SEM on symmetric cell's WE after polarisation. Different degrees of porosity appear for cells polarised at 0.06, 0.12, 0.3 mA.cm⁻². Impedance measurements on the WE enable to separate the potential into two terms: an ohmic contribution mainly due to the passivation layer and a non-ohmic contribution. This non-ohmic potential varies as the square root of polarisation time and is proportional to the current density imposed on the cell. This suggests the existence of a Nernst diffusion process. Its characteristic relaxation time is longer than the time needed to establish a stationary concentration profile in the bulk, so we attribute this effect to the creation of a concentration gradient in the passivation layer during polarisation. **References:** [1] L. Sannier, R. Bouchet, L. Santinacci, S. Grugeon, J.-M. Tarascon, J. Electrochem. Soc., 151, A873-879 (2004). [2] N. Munichandraiah, M.J. Scanlon, R.A. March, J. Power Sources, 72, 203 (1998). [3] R. Bouchet, S. Lascaud, M. Rosso, J. Electrochem. Soc., 150, A1385-1389 (2003).

2:45 PM K11.5

High Energy Density, All-Solid-State Batteries: A Challenging New Concept towards 3-D Integration. Peter H.L. Notten, Fred Roozeboom and Loic Baggetto; Philips Research Laboratories, Eindhoven, Netherlands.

Portable energy plays a crucial role in our modern-day society. The use of wireless electronic equipment, such as laptop computers, mobile phones, PDA's and electrical shavers has been rapidly growing during the last two decades and this growth will become even more pronounced in the near future. In addition, there is a strong tendency that "portability" will broaden towards very small applications, e.g. wireless Autonomous Devices. It is anticipated by the electronic industry that smart Autonomous Devices, enabling future Ambient Intelligence inside offices and houses, will play a dominant role in our future life [1]. Characteristic of these Autonomous Devices is that they have to operate independently, meaning that the energy supply must be guaranteed wirelessly. This implies that both energy scavenging and electrochemical energy storage are of crucial importance for these devices. It has been reported that all-solid-state Li-based rechargeable batteries can be frequently charged and discharged [2]. These thin-film batteries were, however, planar structured and include a dynamic metallic lithium anode and a LiCoO_2 intercalation cathode. The thin film geometries were grown, by making use of physical deposition techniques [2,3]. However, the geometric energy density of these devices is unfortunately relatively low due to its planar structure. Interestingly, Takamura et al. [4] recently discovered that the amount of Li which could be reversibly intercalated and de-intercalated in thin film silicon electrodes is about 10 times higher than in conventional graphite electrodes, making these anodes much more energy dense and, compared to metallic Li, mechanically more robust. Silicon is a well-known substrate material nowadays widely applied in the electronic IC-industry, allowing a high degree of component integration. One of the latest developments is the integration of capacitors into Si wafers; 3-D structured high surface area substrates are obtained by either physical or wet-chemical etching, enabling the beneficial deposition of high surface area electrode structures [5]. Based on the various above-mentioned developments a new battery concept is proposed to come to fully 3-D integrated, all-solid-state, rechargeable batteries, revealing a high energy density. This concept will be based on the Li-intercalation chemistry of Silicon and LiMeOx . In the present presentation the details of this challenging 3-D integrated battery concept will be disclosed, including the etching process and the subsequent deposition of active electrode and electrolyte thin-film layers. **References** [1] W. Verhaegh, et al., "Algorithms in ambient intelligence", Kluwer, Dordrecht, ISBN 1-4020-1757-X (2003). [2] Bates, et al., Sol. State Ionics 43-44 (1993) 103. [3] P.J. Bouwman, et al, Sol. State Ionics, 152 (2002) 181. [4] T. Takamura, et al., J. Power Sources, in press (2004). [5] F. Roozeboom, et al., Int. J. Microcircuits and Electronic Packaging, 24 (3) (2001) pp. 182-196.

3:30 PM **K11.6**

Tin oxides with hollandite structure as anodes for lithium ion batteries. N. Sharma, G.V. Subba Rao and B.V.R. Chowdari; Physics Department, National University of Singapore, Singapore, Singapore.

Tin oxides have been extensively studied as alternate materials to the commercially employed graphite as anodes for lithium ion batteries. The reversible capacity arises as a result of de-alloying/alloying reaction of $\text{Li}_{4.4}\text{Sn}$ at voltages ≈ 1.0 V vs Li. Studies on amorphous tin composite oxides, binary and ternary crystalline oxides have shown that the key factors influencing the electrochemical response are the nature and amount of counter (matrix) atoms/ions which are electrochemically-inactive, the crystal structure and oxygen coordination of Sn in the compound, particle size and morphology and the operating voltage range. Calcium counter ion, 3D-structure and octahedral O-coordination have been shown to be favorable in yielding high and stable capacities. Presently we have synthesized tin oxides with the hollandite structure, $\text{K}_2(\text{Li}_2/3\text{Sn}_{22/3})\text{O}_{16}$, $\text{K}_2(\text{MgSn}_7)\text{O}_{16}$, $\text{K}_2(\text{M}_2\text{Sn}_6)\text{O}_{16}$, $\text{M}=\text{Fe}$, Mn containing SnO_6 octahedra. They were characterized by X-ray diffraction, X-ray photoelectron spectroscopy and SEM techniques and their electrochemical properties were studied in the range, 0.005-1.0 V vs Li at 60 mA/g up to 50 cycles. Reversible capacities ≈ 400 mAh/g with coulombic efficiency $\approx 98\%$ were found for $\text{M}=\text{Li}$, Mg and Fe . For $\text{M}=\text{Li}$, the 5th cycle capacity is as high as 596 mAh/g (3.6 moles of recyclable Li). At the end of the 50th cycle, 85% of the 5th cycle capacity is retained. Complimentary cyclic voltammetry and impedance spectral studies were carried out and results will be discussed. *Corresponding author. Tel.: (65) 6874 2956; Fax.: (65) 6777 6126 e-mail: phychowd@nus.edu.sg

3:45 PM **K11.7**

Solution synthesis and electrochemical properties of V2O5 nanostructures. Guozhong Cao, Materials Science and Engineering, University of Washington, Seattle, Washington.

Single crystal V2O5 nanorod arrays and Ni - V2O5 core-shell nanocable arrays have been synthesized using various solution methods and their electrochemical properties have been studied for electrochemical pseudocapacitor applications. V2O5 oxide nanorod arrays were grown in polycarbonate membranes by electrochemical deposition, surface condensation induced by a pH change as a result of H2O electrolysis, and sol electrophoretic deposition. Uniformly sized V2O5 nanorods with a length of 10 micrometers and diameters of 100 or 200 nm were grown over large area with near unidirectional alignment. TEM micrographs and electron diffraction patterns of V2O5 nanorods clearly show the single-crystalline nature of nanorods from all three growth routes and all have a growth direction of [010]. The growth mechanisms of single crystal V2O5 nanorods are attributed to evolution selection growth and homoepitaxial aggregation. Ni - V2O5 nanocable structures were formed by first growth of Ni nanorod arrays (200 nm in diameter and 10 micrometer long) using electrochemical deposition and followed with coating of V2O5 (30 nm in thickness with uniform coverage) on the surface of Ni nanorods by sol electrophoretic deposition. Electrochemical analysis revealed that V2O5 nanostructures possess significantly improved Li+ storage capacity and intercalation and discharge rate, due to enhanced surface area and transport kinetics. For example, in comparison with sol-gel derived V2O5 films, single crystal V2O5 nanorod array electrodes have approximately 5 times higher intercalation and discharge rate for a given storage capacity, and achieve 5 times higher storage concentration of Li+ using the same charge current density. Ni - V2O5 nanocable arrays have demonstrated a Li+ storage capacity more than one order of magnitude higher than that of single crystal V2O5 nanorod arrays. The relationships between electrochemical properties, nano- and microstructures, and growth processes have been discussed.

4:00 PM **K11.8**

Templated nanocomposite electrodes for solid-state rechargeable lithium batteries. Jong Hak Kim, Elsa Olivetti, Donald R. Sadoway and Anne M. Mayes; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Templated nanocomposite electrodes for lithium rechargeable batteries were fabricated by in situ growth of active cathode materials within the continuous ion conducting domains of a microphase-separated graft copolymer. Small angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) reveal the spatially-selective incorporation of the inorganic component, which was prepared from vanadium triisopropoxide and silver salt by sol-gel synthesis with poly((oxyethylene)₉ methacrylate)-graft-poly(dimethyl siloxane), POEM-g-PDMS. The formation of silver doped vanadium oxide (e.g. AgxV2O5) as an active component was confirmed by wide angle x-ray scattering (WAXS). The domain periodicity of graft copolymer increased from 21 to 35nm upon the incorporation of silver

doped vanadium oxide. The selective interaction of the active components with POEM was further verified by differential scanning calorimetry (DSC) and FT-IR spectroscopy. Solid-state, rechargeable lithium batteries consisting of the templated nanocomposite cathode, an electrolyte of POEM-g-PDMS doped with lithium salt and a lithium metal anode were constructed and tested for battery performance.

4:15 PM **K11.9**

Novel Non-aqueous Sol-Gel Synthesis of Carbon-Coated LiMPO₄ (M = Fe, Mn, Co) for Lithium Ion Batteries. Jingsi Yang and Jun John Xu; Department of Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey.

The olivine-type LiMPO_4 ($\text{M} = \text{Fe}$, Mn , Co , etc.), especially LiFePO_4 , has attracted great attention in recent years as promising cathode materials for rechargeable lithium-ion batteries. One approach to achieving desirable rate performance of these materials of low electronic conductivity is to synthesize nanocomposites consisting of submicron particles of LiMPO_4 and an electronic conductive phase, typically carbon, in intimate contact with each other. Here we report a simple, versatile sol-gel method using ethylene glycol as the solvent for the synthesis of carbon-coated phase-pure LiMPO_4 with submicron particle size and uniform size distribution. The method consists of two simple steps, namely, formation of a monolithic organo-gel by dissolving lithium acetate, iron(II) acetate and phosphoric acid in ethylene glycol and pyrolysis of the gel at 700 °C under flowing nitrogen. With this method, phase purity of LiFePO_4 is easily attained owing to the homogeneous mixing of precursors at the molecular level in the precursor gel. Surface carbon coatings of 1-3 wt% on LiFePO_4 particles was formed in-situ through pyrolysis of the precursor gel. The surface carbon coatings help prevent irregular particle growths and ensure submicron size and uniform size distribution of the LiFePO_4 particles formed. The favorable physical characteristics of the synthesized LiFePO_4 particles lead to excellent electrochemical properties. Slow rate charge at C/100 gives an apparent specific capacity of 165 mAh/g when charged to 4.0 V, corresponding to 0.99 Li per Fe, with nearly perfect reversibility. Specific discharge capacities of ca. 150 mAh/g, corresponding to more than 0.88 Li per Fe, achieved at both C/5 and 2C rates demonstrate the excellent rate capabilities of the synthesized LiFePO_4 . The synthesis method offers a simple route to high-performance LiFePO_4 , and is versatile in that other LiMPO_4 ($\text{M} = \text{Mn}$, Co) with similar physical characteristics and surface carbon coating can be synthesized in the same way as well. The electrochemical performance of the synthesized LiMPO_4 ($\text{M} = \text{Fe}$, Mn , Co) will be presented and discussed and the advantages of the novel synthesis route demonstrated.

4:30 PM **K11.10**

Neutron diffraction and electrochemical studies of $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. Shih-Chieh Yin¹, Young-Ho Rho¹, Ian Swainson² and Linda F. Nazar¹; ¹Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada; ²Chalk River Laboratories, Chalk River, Ontario, Canada.

LiCoO_2 has remained the cathode choice in Li-ion batteries for the last decade despite many drawbacks. Most recently, however, interests have shifted to partially, or completely replace the Co^{3+} with ($\text{Ni}^{2+} + \text{Mn}^{4+}$) to reduce the cost and improve safety. Amongst solid solutions of the Li-Ni-Mn-Co-O series, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ has received particular attention owing to its high capacity and thermal stability. A major issue in these ordered rock salt structures is the problem of irreversibility on the first cycle, and degree of $\text{Li}^+/\text{Ni}^{2+}$ cation disorder which inhibits the rate capability. To examine these factors, a variety of different synthesis methods were employed which led to $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ materials that exhibited varying degrees of cation disorder. Neutron diffraction studies were then carried out on a series of samples ($\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, $x = 1.00 \rightarrow 0.05$) prepared by chemical oxidation, and these were coupled to XRD and electrochemistry investigations. Our studies reveal that control of the precursor chemistry can lead to $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ materials exhibiting as little as 2.7% Li/Ni disorder. Even at this low degree of disorder, no long range ordering of the transition metal cations was apparent, and the extent of metal cation/ Li^+ disorder between the 3b and 3a sites was preserved on Li extraction and re-insertion. Of primary interest is that lithium extraction and reinsertion is dependent on subtleties of cation ordering, and particle morphology. Very highly ordered materials that could be readily and fully delithiated (0.05Li) cleanly converted to a pure O1 phase via gliding of the metal oxide slabs. These showed decreased reversibility, however: namely re-conversion of O1 \rightarrow O3 phase is hindered on re-insertion. In contrast, materials that exhibited slightly higher degrees of disorder and incomplete Li extraction on full oxidation ($< 0.25\text{Li}$) retained a large fraction of the original O3 stacking, and better reversibility. The relationship of these factors to electrochemical performance will be discussed.

4:45 PM **K11.11**

Factors Influencing the Lithium Extraction Rate in Layered Oxide Cathodes of Lithium Ion Cells. Arumugam Manthiram

and Jehwon Choi; Materials Science and Engineering, University of Texas at Austin, Austin, Texas.

Lithium ion cells currently use the layered LiCoO_2 cathode, but only 50 % of its theoretical capacity corresponding to a reversible extraction of 0.5 lithium ions per Co could be practically utilized (140 mAh/g). Also, Co is expensive and relatively toxic. In this regard, layered $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ (LNMC0) oxides are appealing as they offer higher capacity (180 mAh/g) with a lower cost. One of the major issues with the nickel-rich layered oxide compositions is the low rate capability. With an aim to understand the factors that influence the rate capability, we present here a systematic investigation of the rate of lithium extraction from the layered LNMC0 compositions with various Mn and Co contents using both a chemical lithium extraction technique and electrochemical charge-discharge methods. The chemical lithium extraction was carried out by stirring the layered oxide powders with an acetonitrile solution of nitronium tetrafluoroborate under argon atmosphere. An analysis of the lithium content by atomic absorption spectroscopy indicates that the residual lithium content remaining in the chemically delithiated LNMC0 samples after 15 min of chemical lithium extraction time decreases with increasing Co content. The data suggest a faster lithium extraction rate in the cobalt-rich layered oxide compositions. With the electrochemical method, we have evaluated the rate capabilities of the LNMC0 samples at various C rates. The data show that the rate capability increases monotonically with increasing Co content in LNMC0, confirming a faster lithium extraction rate in the cobalt-rich compositions as found with the chemical method. With an aim to understand the origin of the variation in rate capability with Co content, we have compared the electrical conductivity, particle size and morphology, and degree of cation disorder between the lithium and transition metal planes. The results show that there is no clear dependence of the electrical conductivity and particle size on the Co content, indicating that the differences in the observed rate capabilities are not due to the differences in electrical conductivity or particle size. Rietveld analysis of the X-ray data reveals that the observed difference in the lithium extraction rate correlates well with the degree of cation disorder in the layered lattice. Recognizing that cation disorder is the dominant factor in controlling the rate capabilities of layered oxide cathodes, various synthesis and processing strategies to suppress the cation disorder would be presented.