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E-MRS Spring Meeting 2004  
May 24-28, 2004

## SYMPOSIUM K

Solid state ionics: high temperature vs. low  
temperature defect chemistry

Symposium Organizers:

Werner Sitte, University of Leoben, Austria

Jürgen Fleig, Max-Planck-Institut, Stuttgart, Germany

Janez Jamnik, National Institute of Chemistry, Ljubljana, Slovenia

Hans-Dieter Wiemhöfer, University of Münster, Germany

Papers will be published in Solid State Ionics

# E-MRS 2004 SPRING MEETING

## SYMPOSIUM K

Tuesday, May 25, 2004

Morning

Session I: Modelling and mechanisms

Session chair: Werner Sitte

- K-I.1** 9:00 -Invited- HIGH TEMPERATURE DEFECT CHEMISTRY VS. LOW TEMPERATURE DEFECT CHEMISTRY  
**Joachim Maier**, Max-Planck-Institut für Festkörperforschung, Heisenbergstr.1, 70569 Stuttgart, Germany  
A major challenge in materials research is the understanding of the point defect concentrations under operation conditions of electronic or electro-chemical devices.  
After a short presentation of general defect thermodynamical and defect kinetic principles, cases are discussed in which severe differences between the high temperature equilibrium situation and the low temperature quenched situation occur. Emphasis is laid on the treatment of partial equilibria, in which certain ensembles can be considered to be in equilibrium while others can be considered as frozen. Even under ideal quenching conditions, the quenched state is not a 1:1 mapping of the defect chemical situation at quenching temperature. This is primarily a consequence of the different rate constants of ionic and electronic processes. Such phenomena are in particular relevant for electroceramics whose operation temperature strongly deviates from the preparation temperature. The contribution shows how relevant materials must be processed in order to achieve a reproducible low temperature defect chemistry and how such a low temperature defect chemistry can be rationalised. The description requires detailed knowledge of the high temperature defect chemistry and rough knowledge of the defect chemical kinetics. Examples considered specifically include superconductors, ion conductors and proton conductors (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>, SrTiO<sub>3</sub>(Fe<sub>2</sub>O<sub>3</sub>), ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>), BaCeO<sub>3</sub>(H<sub>2</sub>O) and SrZrO<sub>3</sub>(H<sub>2</sub>O)).
- K-I.2** 9:30 -Invited- FROM PEROVSKITES TO APATITES: THE ATOMISTIC MODELLING OF DEFECTS, PROTONS AND ION TRANSPORT IN OXIDE MATERIALS  
**M. Saiful Islam**, Chemistry Division, University of Surrey, Guildford, U.K.  
Oxide materials based on perovskite and apatite structures are attracting considerable attention owing to their fundamental scientific interest and to their promising electrochemical applications (solid oxide fuel cells, ceramic membranes). This presentation on these complex oxides will highlight recent computer modelling studies, which are now well established techniques for probing the properties of solid state ionics on the electronic, atomic and nano-scale. Contemporary work will be illustrated by studies on oxygen ion-mixed conductors (e.g. LaGaO<sub>3</sub>, LaCoO<sub>3</sub> perovskites, La<sub>9.33</sub>Si<sub>6</sub>O<sub>26</sub> apatite) and proton conductors (e.g. CaZrO<sub>3</sub>). The key defect-related properties include ion transport mechanisms, defect-dopant clustering (high vs low T), site-selectivity of cation dopants, and, finally, surface structures. In every case, our simulation results are closely correlated with the available experimental work (e.g. diffraction, EXAFS, conductivity).  
Islam MS et al, Chem.Comm., 1486 (2003); J. Mater.Chem., 14, 65 (2004)
- K-I.3** 10:00 DEFECT CHEMISTRY OF (La,Sr)<sub>1-x</sub>Mn<sub>1-y</sub>O<sub>3-z</sub> PEROVSKITES MODELLED USING THE CALPHAD APPROACH  
**A.N. Grundy**, L.J. Gauckler, Nonmetallic Materials, ETH Zurich, Switzerland, B. Hallstedt, RWTH Aachen, Germany  
The defect chemistry of (La, Sr)MnO<sub>3</sub> (LSM) perovskites is quite complex but also very important for applications as diverse as solid oxide fuel cell cathodes or giant magnetoresistive materials.  
We model this phase using the compound energy formalism and applying the CALPHAD methodology. It is shown, that the CALPHAD method is not only suitable for the calculation of phase equilibria, but is also capable of modelling the complex defect chemistry encountered in the LSM perovskites. Particularly interesting results are obtained, when the oxygen nonstoichiometry of the perovskites (La, Sr)<sub>1-x</sub>MnO<sub>3</sub> and (La, Sr)Mn<sub>1-y</sub>O<sub>3</sub> i.e. perovskites with cation nonstoichiometry are modelled. It is shown, that some of the defect models proposed in literature cannot be brought into agreement with the thermodynamic considerations presented here.

**K-I.4** 10:20 HYDROGEN EFFECTS IN ZIRCONIA AND HAFNIA  
Jacob Gavartin and Alexander Shluger, Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, U.K.  
Hydrogen is ubiquitously present in both natural and artificially grown oxides, and it affects strongly their electrical and mechanical properties. Depending on the industrial application, high hydrogen concentrations may be desirable (as a likely dopant or as a working agent in fuel cells) or adverse (as in the toughening ceramic films). However, the control of hydrogen presence is hard to achieve because of a great variety of energetically close and easily interchangeable forms it may accept, and because of a difficulty of experimental identification of some of these forms. In the present paper we use ab initio molecular dynamics simulations to study hydrogen forms in high-k oxides. In particular, we consider, protons, hydrogen atoms, hydroxide ions and water molecules in various polymorphs of Zirconia and Hafnia in the context of microelectronic and engineering applications. We discuss the stability, reactivity and diffusivity of the above defects, and their effects on mechanical and electrical degradation. The calculations suggest a mechanism for the tetragonal-to-monoclinic phase transformation and the role of proton diffusion on the relative stability of these phases. We also discuss the conditions under which various charge states of hydrogen are realised and how they affect the dielectric response. Based on our calculations, we discuss general and oxide specific properties of hydrogen.

10:40

**BREAK**

## Session II: Modelling and mechanisms

Session chair: M. Saiful Islam

**K-II.1** 11:10 -Invited- FORMATION AND MOBILITY OF PROTONIC DEFECTS IN LOW- AND HIGH TEMPERATURE SEPARATOR MATERIALS FOR FUEL CELL APPLICATION  
**Klaus-Dieter Kreuer**, Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany  
Hydrated acidic polymers (e.g. Nafion) and systems based on phosphoric acid, phosphonic acid and heterocycles (e.g. imidazole) are currently used or considered as separator materials for low temperature (20-200°C) fuel cells, while proton conducting oxides have an interesting potential for high temperature (>500°C) fuel cell applications. Although all materials are good proton conductors the involved protonic defects and the conduction mechanisms show distinct differences, which are discussed in this presentation. These are mainly the consequence of the structural and dynamical properties of soft extended hydrogen bond networks (at low temperature) and rigid oxide lattices (at high temperature).

**K-II.2** 11:40 PROTONIC DEFECT IN TRIFLUOROMETHANESULFONIC ACID MONOHYDRATE DETERMINED BY AB INITIO MOLECULAR DYNAMICS  
Stephen J. Paddison, Lawrence R. Pratt, Theoretical Chemistry and Molecular Physics Group, Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545, USA  
High proton conductivity in solid polymer electrolyte membranes (PEMs) with minimal water is an important research and development goal for efficient operation of fuel cells at temperatures above 90 °C. Trifluoromethanesulfonic acid monohydrate solid provides a model system for studying proton conduction in the archetypical PEM Nafion® at low degrees of hydration. We use ab initio molecular dynamics to investigate the structure and proton dynamics in the solid at 300 K employing the PW91 functional. Calculations performed on five uncorrelated and distinct systems for a total simulation time of 40 ps established the stability of the experimental monoclinic crystal structure consisting of layers where each hydronium ion is hydrogen-bonded to three sulfonate groups. Through the removal and subsequent return of a single proton from the unit cell, a stable (> 30 ps) defect was created consisting of two delocalized protons: one proton is shuffled between two CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> groups, and the other as a Zundel (H<sub>5</sub>O<sub>2</sub>) ion. The Helmholtz free energy of formation of this defect was calculated to be 0.25 eV from a quasi-harmonic model based upon statistical determination of normal modes; corresponding well to the experimentally measured activation energy for proton transport in hydrated Nafion® of 0.36 eV. These results provide the first molecular insight in the mechanisms of proton conduction in minimally hydrated sulfonic acid based polymer electrolytes.

**K-II.3** 12:00 STOCHASTIC MODELING OF ION DYNAMICS IN GLASSES  
T. Höhr(a), W. Dieterich(a) and P. Maass(b), (a)Fachbereich Physik, Universität Konstanz, 78457 Konstanz, Germany, (b)Institut für Physik, Technische Universität Ilmenau, 98648 Ilmenau, Germany  
Network glasses doped with alkali ions show interesting dc-transport and dynamic properties detected in diffusion and conductivity studies, nuclear spin relaxation, quasielastic neutron scattering and ultrasonic experiments. Prominent features are a sensitive dependence of the dc-conduction on composition in single-ion glasses, mixed alkali effects and “quasi-universal” behaviour in various ac-measurements. Recently, a “nearly constant loss” (NCL) in dielectric relaxation spectroscopy was found as a second universal feature in the dynamic response of ionic glasses.  
Such features are well described by many-particle stochastic lattice gas models based on site-energy disorder and Coulomb interactions among the migrating ions. By means of extended Monte Carlo simulations we will discuss ion motion subjected to Coulombic traps, which are randomly distributed in space. In particular, we will show that this counterion model bears a mechanism for an NCL-type response, which in this way is interpreted as a result of correlated dipolar reorientation processes.

**K-II.4** 12:20

#### NEARLY CONSTANT LOSS BEHAVIOUR IN Na- $\beta$ -ALUMINA

Radha D. Banhatti and K. Funke, University of Muenster, Institute for Physical Chemistry and Sonderforschungsbereich 458, Correnstrasse 30, 48149 Muenster, Germany

Structurally disordered crystalline fast-ion conductors and glasses exhibit conductivities which, at high frequencies and low temperatures, show a linear dependence with frequency and, therefore, a frequency-independent dielectric loss. The origin of this phenomenon, widely known as Nearly Constant Loss, or NCL [1, 2], is still under debate. We model the low-temperature frequency-dependent conductivity spectra of Na- $\beta$ '-alumina, using the MIGRATION concept (an acronym for Mismatch Generated Relaxation for the Accommodation and Transport of IONs), as described in Ref. [3]. We show that both the low-frequency dispersive regime and the NCL regime can be additively combined to describe the total experimental spectra. Remarkably, the onset angular frequency of the NCL regime,  $\omega_1$ , is the same as the elementary hopping rate,  $\Gamma_0$ , of the mobile ions. From this, we conclude that the NCL effect in crystalline materials is caused by localised hopping into well-defined sites, since the barrier heights are the same as for those hops that eventually result in translational motion. This is different for glasses where we find  $\Gamma_0 < \omega_1$ .

1. A. S. Nowick, B. S. Lim, and A. V. Vaysleyb, *J. Non-Cryst. Solids* **172-174** (1994)1243.
2. X. Lu and H. Jain, *J. Phys. Chem. Solids* **55** (1994) 1433.
3. K. Funke, R. D. Banhatti, I. Ross and D. Wilmer, *Z. Phys. Chem.* **217** (2003) 1245.

**K-II.5** 12:40

#### IONIC TRANSPORT IN SODIUM-RUBIDIUM BORATE MIXED- AND SINGLE-ALKALI GLASSES

Á.W. Imre, S. Voss, F. Berkemeier and H. Mehrer, Institut für Materialphysik, Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany

Measurements of the electrical conductivity using an ac complex impedance technique have been performed in a series of sodium-rubidium borate single- and mixed-alkali glasses. Furthermore, the diffusion of sodium-22 and rubidium-86 isotopes was investigated in the mixed-alkali glasses by means of radiotracer experiments. Both, the conductivity and radiotracer experiments show the main features of a mixed-alkali effect: i) the ionic conductivity has a minimum with composition, ii) the activation enthalpy of the dc conductivity times temperature has a maximum, iii) the diffusivities of sodium-22 and rubidium-86 reveal a crossover. The diffusivity crossover is found to be temperature independent in the investigated temperature range. The diffusivity of rubidium-86 decreases exponentially with rubidium content at a constant temperature. The sodium-22 diffusivity behaves similar for sodium-rich compositions, however in the rubidium-rich side it is nearly composition independent. In contrast to pure sodium-borate glass with 20% alkali content, the Haven ratio in the rubidium-borate glass depends on temperature. The conductivities of the mixed-alkali glasses are compared with the sum of the conductivities of the corresponding single-alkali glasses in which the concentration of the given alkali ions is the same as in the mixed-alkali glass. In the investigated sodium-rubidium borate glasses the conductivity of the mixed-alkali glasses is always larger, than the conductivity sum of the single-alkali glasses.

13:00

**LUNCH**

Tuesday, May 25, 2004

Afternoon

Session III: Transport in nanostructured materials

Session chair: Joachim Maier

- K-III.1** 14:30 -Invited- DEFECT CHEMISTRY IN NANOCRYSTALLINE ANATASE (TiO<sub>2</sub>)  
A. Weibel, R. Bouchet, **Philippe Knauth**, MADIREL, Université de Provence-CNRS, Centre St Jérôme, 13397 Marseille Cedex 20, France  
Nanocrystalline ceramics have a mean grain size below 100 nm and are theoretically expected to present significantly modified properties, especially regarding the electrical conductivity. First experimental studies revealing important property changes have been performed recently on typically ionic conducting refractory oxides: CeO<sub>2</sub> and partially stabilized tetragonal ZrO<sub>2</sub>. We have investigated another oxide, conventionally assumed to be an n-type semiconductor with low conductivity: anatase TiO<sub>2</sub>. Nanocrystalline and nanoporous anatase is widely investigated, given its exciting new applications, including photoelectrochemical cells and photocatalysis.  
The first challenge was the preparation of dense nanocrystalline anatase ceramics, because a phase transition into the thermodynamically stable rutile modification occurs at higher temperatures, so that conventional sintering can not be used. We succeeded for the first time by using hot-pressing typically at 600°C and 6 kbar. Under these conditions, TiO<sub>2</sub> remained phase-pure anatase. The electrical properties of the resulting nanoceramics were then investigated as function of temperature (300-900 K), oxygen partial pressure, dopants (including Zn, Al, Si, Nb) and mean grain size (30-100 nm). The properties are discussed considering defect thermodynamics. Dopant segregation at boundaries is especially addressed in the framework of space charge theory.
- K-III.2** 15:00 ION TRANSPORT AT INTERFACES: AN AC CONDUCTIVITY STUDY ON GLASS CERAMICS CONTAINING NANOCRYSTALLITES  
**Bernhard Roling**, Sevi Murugavel, Institute of Physical Chemistry and Collaborative Research Center 458, University of Muenster, Corrensstr. 30, 48149 Muenster, Germany  
Nanostructuring of solid electrolytes often leads to an enhanced ionic conductivity. For instance, the conductivity of nanocrystalline ionic conductors can be increased by adding nanocrystalline insulators. In the case of glasses, a conductivity enhancement can be achieved by the formation of nanocrystallites during partial crystallisation. Furthermore, the ionic conductivity of polymer electrolytes can be improved considerably by incorporating nanoparticles, such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>, into the polymer matrix. In many cases, the origin of the conductivity enhancement effects is not understood. In order to obtain more information about ionic diffusion mechanisms in nanostructured electrolytes, we have carried out an AC conductivity study on 4 AgI \* Ag<sub>4</sub>V<sub>2</sub>O<sub>7</sub> and Li<sub>2</sub>O \* Al<sub>2</sub>O<sub>3</sub> \* 2 SiO<sub>2</sub> glasses and glass ceramics at different stages of the crystallisation process. In the early stages of this process, the formation of nanocrystallites leads to an enhancement of the ionic conductivity, which is related to the large interface area between nanocrystallites and glassy phase. We use a brick layer model in order to separate and compare the bulk and the interfacial contributions to the ac conductivity spectra of the glass ceramics, and we find that the ionic dc conductivity at the interfaces is about two to three orders of magnitude higher than in the bulk. Furthermore, a comparison of the frequency dependence of interfacial and bulk conductivity indicates a larger number of empty ionic sites in the interfacial regions as compared to the bulk.
- K-III.3** 15:20 CONDUCTIVITY OF FREESTANDING THIN FILMS OF NANOCRYSTALLINE Gd-DOPED CERIA  
Mark Greenberg and **Igor Lubomirsky**, Weizmann Institute of Science, Rehovot, 76100, Israel, Juergen Fleig, Sangtae Kim and Joachim Maier, Max Planck Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany  
Cerium oxide is a promising material for a number of applications ranging from high dielectric constant layers to fuel cells. The slow chemical reaction between CeO<sub>2</sub> and Si may also permit applications of CeO<sub>2</sub> based membranes integrated in Si-based microelectromechanical systems (MEMS).  
We have investigated electrical properties of freestanding nanocrystalline membranes of 20% Gd-doped CeO<sub>2</sub> with 20-50 nm grain size, 300-1000 nm thickness and 150-300 µm lateral dimensions. Impedance spectroscopy performed in air and in vacuum (10<sup>-5</sup> mbar) has been used to separate different conductivity contributions. Interesting features such a changing membrane shape upon current flows and very low activation energies will be discussed in terms of defect chemistry.
- K-III.4** 15:40 CONDUCTIVITY OF NANOCRYSTALLINE AND MICROCRYSTALLINE SrTiO<sub>3</sub>  
**P. Balaya**, J. Fleig and J. Maier, Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany  
We present results of conductivity measurements using impedance spectroscopy on undoped SrTiO<sub>3</sub> nanocrystalline (average grain size of 80 nm with 93% of theoretical density; Sr/Ti = 1.004 and Fe impurity less than 60 ppm) and microcrystalline samples in the temperature range 350 - 500°C, equilibrated over the oxygen partial pressure (pO<sub>2</sub>) of 10<sup>-5</sup> to 1 bar. While the impedance plot of microcrystalline SrTiO<sub>3</sub> exhibits two semicircles, one at low frequency and the other at high frequency corresponding to the grain boundary and bulk contributions respectively, the nanocrystalline SrTiO<sub>3</sub> shows only one semicircle, the effective dielectric constant of which coincides with the bulk of the microcrystalline sample. The total conductivity of nanocrystalline SrTiO<sub>3</sub> is found to be less than that of microcrystalline with an activation energy of 0.95 eV at 1 bar. The pO<sub>2</sub> dependence of conductivity for the nanoceramic is estimated to be .24, suggesting a hole dominated conduction process. These results are analyzed on the basis of both brick layer as well as space charge models, in order to infer the interfacial properties. It is concluded that in the case of nanocrystalline SrTiO<sub>3</sub>, the space charge regions overlap in these nanograins leading to a strongly depressed p-type interfacial conduction.

- K-III.5** 16:00 HYDROGEN AS A SOURCE OF PROTONIC AND ELECTRONIC CONDUCTION IN A NANO-POROUS COMPLEX OXIDE  
**P.V. Sushko**, A.L. Shluger, Department of Physics and Astronomy, University College London, Gower St., London WC1E 6BT, U.K. and K. Hayashi, M. Hirano, H. Hosono, Transparent Electro-Active Materials Project, ERATO, JST, KSP C-1232, 3-2-1 Sakado, Takatsu-ku, Kawasaki 213-0012, 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 structure and formation and inter-conversion mechanisms of protons, hydrate ions, and electrons in a nano-porous complex oxide  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  (C12A7). 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 hydrate ions is due to dissociation of  $\text{H}_2$  molecules in the nano-cages of C12A7. The formation of the conduction electrons due to a thermal and photo-activated mechanisms as well as high proton and electronic conduction are facilitated by the specific crystalline structure of the C12A7.  
 1. K. Hayashi, S. Matsuishi, T. Kamiya, M. Hirano, and H. Hosono, *Nature*, 423, 626, (2002) 2. P. V. Sushko, A. L. Shluger, K. Hayashi, M. Hirano, and H. Hosono, *Phys. Rev. Lett.*, 91, 126401, (2003)

16:20

**BREAK**

## Session IV: Ionic and mixed ionic-electronic conductors I

Session chair: Ilan Riess

- K-IV.1** 16:50 -Invited- DEFECT CHEMISTRY OF MIXED-CONDUCTING PEROVKITE OXIDE MEMBRANES  
**Henny J.M. Bouwmeester**, University of Twente, Department of Science and Technology, Inorganic Materials Science Group, MESA+ Institute for Nanotechnology, P.O. Box 217, 7500 AE Enschede, The Netherlands  
 This paper reviews the defect chemistry of mixed-conducting perovskites oxides such as  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-d}$ . Membranes made of these materials are capable of selective oxygen permeation. They can be integrated in advanced concepts for the production of oxygen and syngas. Crucial to the performance as membrane is that the materials are capable of rapid oxygen exchange at the gas-solid interface and oxygen diffusion within the bulk. Results from both thermodynamic and kinetic studies of oxygen and electronic defects in  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-d}$  and related materials are presented. The role of point defect chemistry governing oxygen transport kinetics, but also the time-dependent degradation is discussed.
- K-IV.2** 17:20 -Invited- SOFTWARE FOR DEFECT CHEMISTRY ANALYSIS  
**João.C.C. Abrantes**(a), J.R. Frade(b), (a)ESTG, Instituto Politécnico de Viana do Castelo, 4900 Viana do Castelo, Portugal, (b)Ceramics and Glass Engineering Dep. (CICECO), University of Aveiro, 3810 Aveiro, Portugal  
 The defect chemistry methodology is commonly used to interpret the transport properties of materials and to predict effects of variable working conditions on the electrical properties and processes which depend on mass transport. Analysis of defect diagrams might be far from trivial, even for materials with simple defect structure, and classical methods are thus based on approximate electroneutrality conditions for different regions of the defect diagrams. Those conditions must be carefully selected, and relevant trends of the defect diagrams require time consuming algebraic re-arrangements of those neutrality conditions with the relevant mass action constants. The transitions between different regions of the defect diagram are poorly described. The present work proposes an alternative numerical method to solve the overall system without any kind of mathematical simplification. The method has been mainly designed for defect chemistry calculations in oxide materials, using temperature, oxygen partial pressure and concentrations of additives as independent variables. It is easily extended to include other variables such as the water vapor partial pressure. The method also allows simulations of non equilibrium effects. Mass action constants are combined with the overall neutrality condition and/or mass conservation relations to obtain the concentration of a selected defect versus working conditions. A software package DefChem was developed for this purpose. Its applicability is demonstrated for selected case studies. DefChem is also used to interpret results obtained with different experimental techniques, such as conductivity versus the partial pressure of relevant gases (e.g. oxygen or water vapour), ion blocking, thermogravimetry, coulometric titration, etc.

**K-IV.3** 17:50

KINETICS OF OXYGEN STOICHIOMETRY CHANGES: MECHANISTIC INTERPRETATION AND  $k^*$ - $D^*$  CORRELATION

Rotraut Merkle and Joachim Maier, Max-Planck-Institute for Solid State Research, Heisenbergstr. 1, 70563 Stuttgart, Germany

The oxygen incorporation comprises surface reaction and subsequent oxygen diffusion in the bulk (and across grain boundaries), and each of these processes can limit the overall rate. For many large bandgap oxides, the effective chemical rate constant  $k^*$  of the surface reaction has a larger activation energy than the bulk chemical diffusion coefficient  $D^*$ . Consequently, the oxygen incorporation switches from surface limitation at lower temperatures to diffusion limitation at high T. The mechanistic details of the surface reaction were studied in-situ on a model system, Fe-doped SrTiO<sub>3</sub> single crystals. From the observed pO<sub>2</sub> dependence and the selective acceleration of the forward reaction by UV irradiation, we can conclude that molecular oxygen species appear in the rate determining step rds, and that one conduction electron is involved before or in the rds [1].

For oxygen tracer exchange of electron-rich perovskites such as (La,Sr)(Mn,Fe,Co)O<sub>3-z</sub>, log  $k^*$  and log  $D^*$  were found to be linearly related not only in the case of a temperature variation, but also in the case of a variation of the compound [2]. We show that this can be interpreted by a linear relation between the  $k^*$  activation energy and the overall reaction enthalpy of the oxygen incorporation. This is a first clear example of such a linear free energy relation (which are more widely established in organic chemistry, cf. Hammett equation) for gas-solid reactions. [1] R. Merkle, J. Maier; Phys. Chem. Chem. Phys. 4 (2002) 4140. [2] R. A. De Souza, J. Kilner; Solid State Ionics 126 (1999) 153

**K-IV.4** 18:10

DEFECTS IN HYDROGEN CONTAINING OXIDES UNDER REDUCING CONDITIONS

Marius Widerøe, Truls Norby, Centre for Materials Science, University of Oslo, Gaustadalleen 21, 0349 Oslo, Norway

Apparent hydride ion conductivity under reducing conditions and high temperatures has been observed in some oxides in our group while measuring the total, oxygen ion and hydrogen ion conductivity. Experimental results will be discussed in light of theory of different hydrogen defects in oxides, especially under reducing conditions and in the temperature range of 350°C - 1050°C. In known cases of thermodynamics for the equilibrium between protons (as metal hydroxides) and hydride ions (as metal hydrides), the hydride ions are not stable under the conditions used in the present investigation (H<sub>2</sub>/H<sub>2</sub>O/Ar mixtures at elevated temperatures). The expected dependencies of hydride ion concentrations as a function of oxygen partial pressure and temperature will be discussed along with possible diffusion mechanisms for hydride ions in oxides.

Wednesday, May 26, 2004

Afternoon

Session V: Defects and transport in grain boundaries

Session chair: Philippe Knauth

- K-V.1** 14:00 -Invited- STRUCTURES AND PROPERTIES OF GRAIN BOUNDARIES IN SEMICONDUCTING ELECTROCERAMICS  
**Robert Freer**, Materials Science Centre, University of Manchester/UMIST, Manchester M1 7HS, U.K.  
ZnO-based varistors and BaTiO<sub>3</sub>-based thermistors exhibit important variations in microstructure and chemistry in the vicinity of the grain boundaries. The resulting electrical interface barriers give rise to valuable electrical properties, which are sensitive to ceramic formulation and processing conditions. Most models to describe the properties are based on the defect states, or assemblages of shallow and deep traps. Traditional measurement techniques yield only bulk or averaged properties, such as resistivities of grains and grain boundaries. Greater understanding of the microstructural control of properties at the grain to grain level has come through the utilisation of a variety of local investigative techniques. These include SEM/AFM based procedures including electron beam induced contrast (EBIC), scanning surface potential microscopy (SSPM) and local nano-impedance microscopy/spectroscopy (NIM). Quantitative information on trap states can be obtained via deep level transient spectroscopy (DLTS) and microcathodoluminescence spectroscopy. The presentation will highlight the achievements of a number of a number of techniques and include the changes in defect states with temperature.
- K-V.2** 14:30 TRANSPORT ACROSS INTERNAL AND EXTERNAL INTERFACES IN Fe-DOPED SrTiO<sub>3</sub>  
**R.A. De Souza**, Institut für Physikalische Chemie I, RWTH Aachen, 52056 Aachen. Germany, J. Maier, Max-Planck-Institut für Festkörperforschung, 70509 Stuttgart. Germany  
We present the results of experiments on various bicrystals of Fe-doped SrTiO<sub>3</sub>, a model system in which the internal interfaces are known to block the transport of charge and mass. Three symmetrical low-angle grain boundaries were studied, with misorientation angles of 2.3°, 5.4° and 7.8°. Charge transport across the boundaries was investigated by means of a.c. impedance spectroscopy as a function of temperature and oxygen partial pressure. Spatially resolved optical absorption spectroscopy was employed to monitor in situ oxygen chemical diffusion across the 7.8° interface. All results are consistent with the existence of space charge regions at the interfaces that are depleted of mobile charge carriers (electron holes and oxygen vacancies).  
In this contribution we present the results of experiments on various low-angle tilt grain boundaries in Fe-doped SrTiO<sub>3</sub>, from which we extract conclusions concerning the relationship between interfacial structure and transport properties, and thus the origin of the grain boundary resistance.
- K-V.3** 14:50 BULK AND GRAIN BOUNDARY RESISTIVITIES OF DONOR DOPED BARIUM TITANATE CERAMICS  
**W. Preis**, A. Bürgermeister, W. Sitte, Department für Allgemeine, Analytische und Physikalische Chemie, Montanuniversität Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria, P. Supancic, Institut für Struktur- und Funktionskeramik, Montanuniversität Leoben, Peter-Tunner-Strasse 5, 8700 Leoben, Austria  
The electrical properties of both the bulk and the grain boundaries of PTC ceramics have been determined as a function of temperature ranging from 25 to 400°C by application of impedance spectroscopy. The resistances of the bulk and the grain boundaries as well as the capacitance of the grain boundary regions of n-conducting (Ba,Pb)TiO<sub>3</sub> have been obtained by fitting an appropriate equivalent circuit to the impedance spectra. Samples of equal dimensions and compositions but different grain sizes have been investigated. Whereas the bulk resistance remains almost constant throughout the whole temperature range, the grain boundary resistance shows a steep increase of several orders of magnitude (positive temperature coefficient of resistance) above the Curie temperature, which was confirmed by differential scanning calorimetry to be around 115°C. The grain boundary resistances varied typically between 35 ohm and 30 megaohm and the bulk resistances were found to be approximately 5 ohm. The variation of the grain boundary capacitance with temperature, depending remarkably on the grain size of the samples, follows the Curie-Weiss law. Both the steep increase of the grain boundary resistance and the Curie-Weiss behaviour of the grain boundary capacitance are described theoretically by application of an extended Heywang model. The defect chemistry in the grain boundary regions is modelled by assuming Schottky type space charge depletion layers. Optimized values for the temperature dependent energy level and the density of the acceptor type grain boundary states are given.

- K-V.4** 15:10 THE GRAIN BOUNDARY EFFECT IN HEAVILY DOPED CERIUM OXIDE  
A. Tschöpe, S. Kilassonia, R. Birringer, Universität des Saarlandes, Technische Physik, Gebäude 43, Postfach 15 11 50, 66041 Saarbrücken, Germany  
 Recent studies on the grain size-dependent conductivity and thermopower of polycrystalline cerium oxide ceramics revealed an intrinsic grain boundary effect, which could be described by the space charge model. While these investigations were performed on ceria ceramics with low concentrations of lower-valent impurities, the present study focussed on the development of this intrinsic grain boundary effect when the concentration of trivalent dopants (Gd, Y, La) was increased up to 15 at.-%. At low temperatures and ambient atmosphere, the grain boundary contribution to the total resistance of microcrystalline cerium oxide decreased dramatically at concentrations above 1 at.-% for all dopants. In order to analyze the experimental results, the space charge model was extended to take into account the high defect concentrations expected in these materials and the non-equilibrium "quenched" distribution of dopant ions, obtained during the cooling of the polycrystalline ceramic after sintering. By consideration of the sample history, an excellent agreement between experimental results and the space charge model was achieved. Further results on the grain size-dependent conductivity of heavily doped cerium oxide suggested, that a significant contribution to conductivity stemming from enhanced oxygen ion diffusion along grain boundaries can be ruled out.
- K-V.5** 15:30 NONLINEAR ELECTRICAL PROPERTIES OF GRAIN BOUNDARIES IN OXYGEN ION CONDUCTORS: CASE OF ACCEPTOR DOPED CERIA  
Xin Guo and Rainer Waser, Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany  
 Owing to the positively charged grain boundary cores in acceptor-doped ZrO<sub>2</sub> and CeO<sub>2</sub>, oxygen vacancies are depleted in the space charge layers. In this work, the validity of the space charge depletion concept was checked for Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> ceramic of high purity. Up to 14 volts dc bias voltages were applied to the sample at 400 °C in air, and the grain boundary properties were separated by means of impedance spectroscopy. It was discovered that the current-voltage relation for individual grain boundary was nonlinear, and that the effective grain boundary thickness increased with increasing bias. Both phenomena unambiguously prove the space charge depletion concept.

15:50

**BREAK**

## Session VI: Ionic and mixed ionic-electronic conductors II

Session chair: Henny J.M. Bouwmeester

- K-VI.1** 16:20 -Invited- SIMULATION OF DIFFUSION PROCESSES AND CHARGE TRANSPORT IN MIXED IONIC/ELECTRONIC CONDUCTORS  
**Rene Meyer**, Xin Guo, Rainer Waser, Institut fuer Festkoerperforschung Forschungszentrum Juelich, 52425 Juelich, Germany  
 We report on numerical simulations of diffusion and charge transport in mixed ionic/ electronic conductors in the mesoscopic scale. The utilized model allows calculating thermodynamic and kinetic processes in the bulk and at grain boundaries of mixed conductors even for significant changes in the defect concentrations and under large potential gradients. The model also includes the derivation of experimentally accessible data such as tracer diffusion profiles and of electrical quantities such as dc conductivity or complex impedance spectra. The excellent applicability of the proposed model for diffusion processes is demonstrated on the re-oxidation of donor-doped SrTiO<sub>3</sub> (STO) in combination with <sup>18</sup>O tracer diffusion experiments [1]. A numerical estimation of the ionic ac conductivity in Y-doped CeO<sub>2</sub> ceramics under dc voltage bias is performed as an example of a charge transport process.  
 [1] R. Meyer, R. Waser, J. Helmbold, G. Borhardt, Phys. Rev. Lett. 90 105901/ 1-4
- K-VI.2** 16:50 -Invited- HYDROGEN DEFECTS IN OXIDIC SOLIDS  
**Truls Norby**, University of Oslo, Centre for Materials Science, Gaustadalleen 21, 0349 Oslo, Norway  
 Oxides contain nominally no hydrogen species, but dissolve them from ambient hydrogen or water vapour as defects, most typically interstitial protons trapped on oxygen ions to form hydroxide defects. At sufficiently high temperatures these protons become mobile and jump from oxygen to oxygen, giving proton conductivity in the oxide. The concentration of such protonic defects are well described by simple defect chemistry and thermodynamics, which will be discussed in some detail in the talk. Hydroxides and acid oxysalts also contain protons residing on oxygen ions, but in this case they occupy crystallographic sites and in stoichiometric amounts. Only in a few cases do these proton sublattices become sufficiently dynamic to give high proton conduction at elevated temperatures before the compound decomposes or melts. One example is cesium hydrogen sulphate, CsHSO<sub>4</sub>, in which each proton becomes distributed on a total of 4 equivalent sites in a disorder-type phase change at around 140°C. This partial occupancy represents defects, and the talk focuses in general terms on defects in compounds with nominally stoichiometric proton contents. These defects may be formed by intrinsic disorder (as in CsHSO<sub>4</sub>), by doping, or by non-stoichiometry. It is stressed that many of these materials exhibit uptake of liquid or semi-liquid water, and that apparent proton conduction may sometimes be caused by this water phase.

- K-VI.3** 17:20 IONIC AND ELECTRONIC CONDUCTIVITY IN LEAD-ZIRCONATE-TITANATE STUDIED BY IMPEDANCE SPECTROSCOPY  
Bernard A. Boukamp, Mai T.N. Pham, Dave H.A. Blank and Henny J.M. Bouwmeester, Inorganic Materials Science, Fac. Science and Technology and MESA+ Institute for Nanotechnology, Twente University P.O.Box 217, 7500 AE Enschede, The Netherlands  
Lead-zirconate-titanate (PbZr<sub>0.53</sub>Ti<sub>0.47</sub>O<sub>3</sub>) is a ferroelectric material with a high dielectric constant. The ionic conductivity above the Curie transition temperature (~400 °C) is controlled by the lead vacancy concentration. This vacancy concentration is determined by the process conditions during sintering of the ceramic pellets. In the para-electric phase the electronic conductivity shows a (pO<sub>2</sub>)<sup>0.25</sup> dependence, indicating p-type conduction, while the ionic conductivity remains virtually constant. Through careful measurement and analysis of the sample impedances, the ionic and electronic conductivities can be separated in the ferro-electric phase. Below the Curie transition temperature both ionic and electronic conductivities are strongly dependent on the ambient and on the cooling (and heating) history of the samples. In the ferro-electric phase the ionic conductivity is most likely controlled by clustering of oxygen- and lead vacancies, forming neutral and immobile complexes.
- K-VI.4** 17:40 DEFECT CHEMICAL ANALYSIS OF THE ELECTRONIC CONDUCTIVITY OF STRONTIUM-DOPED LANTHANUM FERRITE  
E. Bucher, W. Sitte, Department of General, Analytical and Physical Chemistry, University of Leoben, 8700 Leoben, Austria  
La<sub>0.4</sub>Sr<sub>0.6</sub>FeO<sub>3-d</sub> is a mixed ionic-electronic conducting perovskite-type oxide with various applications (cathodes for SOFCs, oxygen permeable membranes, sensors). The oxygen non-stoichiometry has a major influence on the electronic conductivity. Therefore, defect chemical analysis is an essential tool for interpreting the electronic transport properties. Electronic conductivities were studied as a function of oxygen non-stoichiometry in the range 1E-5 < pO<sub>2</sub> /atm < 1 at temperatures 100 < T /°C < 900. At constant pO<sub>2</sub> the electronic conductivity is thermally activated at T < 300°C, but decreases with further increase of temperature due to desorption of oxygen from the lattice. This effect is especially pronounced in the intermediate pO<sub>2</sub>-range 1E-4 < pO<sub>2</sub> /atm < 1E-2 where significant oxygen deficit occurs. The temperature dependence of the oxygen non-stoichiometry of La<sub>0.4</sub>Sr<sub>0.6</sub>FeO<sub>3-d</sub> was combined with results of the temperature dependence of the electronic conductivity. Thus, activation energies for electronic conduction at constant oxygen stoichiometries were obtained for the high temperature range (T > 300°C) which are in agreement with activation energies of the thermally activated conductivity at low temperatures (T < 300°C). The oxygen partial pressure dependence of the electronic conductivity in the pO<sub>2</sub>-range under investigation indicates a predominantly p-type character. Concentrations of electronic defects can be calculated from experimental data of the oxygen non-stoichiometry. Therefore, the mobility and the Seebeck coefficient of holes can be estimated from the electronic conductivity and charge carrier concentration at a defined oxygen partial pressure.

Thursday, May 27, 2004

Morning

Session VII: Methods and characterization

Session chair: Bernard A. Boukamp

- K-VII.1** 8:30 -Invited- TRAPPING EFFECTS DURING CHARGE AND MASS TRANSPORT IN OXIDES  
**Manfred Martin**, Institute of Physical Chemistry, RWTH Aachen University, Templergraben 59, 52056 Aachen, Germany  
Defect association and trapping of defects have a strong influence on charge and mass transport in oxides. It will be shown that both the Onsager transport coefficients and the thermodynamic driving forces depend on association and trapping of defects. Special emphasis will be laid on the association and dissociation dynamics during trapping and the consequences for the transport coefficients. For dilute systems, specific and analytical results can be obtained using well-known models from diffusion theory and transposing them to the transport problem under consideration. The results will be applied to the electronic conductivity in pure and doped oxides, the diffusivities in oxides with cation and oxygen disorder, and chemical diffusion phenomena such as demixing in external potential gradients.
- K-VII.2** 9:00 -Invited- OXYGEN IN HIGH TEMPERATURE SUPERCONDUCTORS: OXYGEN DIFFUSION AND OXYGEN MICROSTRUCTURE PROBED BY TRANSPORT AND MAGNETIC MEASUREMENTS  
**Andreas Erb**, Walther-Meissner-Institut, Bayerische Akademie der Wissenschaften, Walther-Meissner-Str. 8, 85748 Garching, Germany  
With the development of the novel crucible material BaZrO<sub>3</sub> [1] a new class of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  single crystals (YBCO) has become available, the purity of which reaches semiconductor grade (> 99.995 %). This purity has given way to a set of new findings and basic understanding of the physics and the microstructure of the oxygen sub lattice in high T<sub>c</sub> superconductors. On well oxygenated samples it is possible to observe the vortex lattice by STM and MFM without additional surface conditioning and to study the influence of pinning centers such as twin boundaries and oxygen vacancies on vortices. By controlling the oxygen content [2] and distribution of the vacancies it has been shown that the so-called fishtail effect, an anomaly in the magnetization curves of high temperature superconductors, which over a long period has been considered being an intrinsic property of the YBCO system, is intrinsically absent in pure samples with homogeneous oxygen distribution [3]. Specific heat measurements yielded the direct observation of a first order like melting of the vortex lattice in fully oxygenated YBCO up to 26 T, questioning different proposed vortex phase diagrams. This observation of vortex lattice melting has also been observed in Dy-123 and Eu-123 single crystals, where additional disorder mechanisms occur. The effect of different types of disorder on the pinning properties in high temperature superconductors will be discussed.  
[1] A. Erb et al., Physica C 258 (1996) 9 [2] A. Erb et al., Physica C 259 (1996) 83 [3] A. Erb et al., Solid State Communications 112 (1999) 245
- K-VII.3** 9:30 CATION DIFFUSION IN SOLID SOLUTIONS OF SODIUM ORTHOPHOSPHATE AND SODIUM SODIUM SULFATE - A DETAILED STUDY BY QUASIELASTIC NEUTRON SCATTERING AND CONDUCTIVITY SPECTROSCOPY  
**D. Wilmer**, H.W. Meyer, Institute of Physical Chemistry, Corrensstr. 30, 48149 Münster, Germany and J. Combet, Institut Laue-Langevin, 6 rue Jules Horowitz, 38042 Grenoble Cedex 9, France.  
Solid solutions of sodium orthophosphate and sodium sulfate in their cubic modification are both fast cation conductors and plastic phases, i.e., their tetrahedral anions are rotationally disordered. The addition of sodium sulfate to sodium orthophosphate stabilises the cubic phase down to lower temperatures and creates vacancies in the cation sublattice. The spatial and temporal details of the cation jump diffusion in these materials were examined by impedance spectroscopy and quasielastic neutron scattering.  
Since the sodium ions are distributed on an FCC lattice, the variation of the neutron scattering linewidths with scattering vector Q has to be analysed in terms of a model for ion hopping on a non-Bravais lattice. The data analysis allows to evaluate the residence times on the different sublattices. The sodium motion is found to be dominated by jumps between neighbouring tetrahedrally co-ordinated sites, the jump distance being half the FCC lattice constant. The sodium self diffusivities follow an Arrhenius law with activation energies ranging from 0.64 eV for pure sodium orthophosphate to 0.30 eV for the 1:1 solution. While the activation energies from the solid solutions agree well with those from impedance measurements, pure sodium orthophosphate exhibits a considerably lower activation energy for charge transport, viz., 0.42 eV, indicating a different mechanism when compared to the solid solutions. This behaviour is probably related to the lack of vacancies in the "undoped" samples.

- K-VII.4** 9:50 RADIOTRACER DIFFUSION AND ION CONDUCTION IN THE POLYMER ELECTROLYTE PEO30NaI  
Sh. Obeidi, B. Zazoum and N.A. Stolwijk, Institute of Materials Physics, University of Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany  
 We studied ion transport in a polymer electrolyte consisting of poly(ethylene oxide) (PEO) and sodium iodide in a Na-to-O ratio of 30. Depth profiles of <sup>22</sup>Na and <sup>125</sup>I were measured by means of microtome sectioning after diffusion annealing in the temperature range from 67 to 180 °C, in which PEO30NaI is fully amorphous. Tracer diffusion coefficients of Na and I were obtained from Gaussian or erfc fits to the measured profiles. We found that I diffuses faster than Na by a factor of 2 to 5 upon going from high to low temperatures. Additional information was obtained by measurements of the dc electrical conductivity using impedance spectroscopy. To this aim the frequency-dependent impedance of PEO30NaI was recorded as a function of temperature. In contrast to both tracer diffusivities, the dc conductivity exhibits a pronounced Vogel-Tamann-Fulcher behaviour reflected by a downward curvature in the Arrhenius plot. As a consequence, the overall ion diffusivity as calculated from the dc conductivity via the Nernst-Einstein equation increasingly falls below the sum of the Na and I tracer diffusivity with increasing temperature. This phenomenon can be explained by the formation of neutral Na-I ion pairs which contribute to mass transport but not to charge transport. Evaluating simultaneously the different types of experimental data within a combined single-ion/ion-pair diffusion model yields not only the diffusivities of all individual species but also the ion-pairing reaction constant as a function of temperature.
- K-VII.5** 10:10 BOND VALENCE ANALYSIS OF AMORPHOUS AND CRYSTALLINE SOLID ELECTROLYTES  
S. Adams, GZG, Kristallographie, Universitaet Goettingen, Germany and J. Swenson, Condensed Matter Physics, Chalmers University of Technology, Goeteborg, Sweden  
 A modified bond valence (BV) approach may be effectively used to study the interplay between microscopic structure and transport properties of solid electrolytes. Combining this approach with reverse Monte Carlo (RMC) modelling or molecular dynamics (MD) simulations provides a deeper understanding of ion transport mechanisms, especially in highly disordered or amorphous solids.  
 For crystalline electrolytes local structure models are derived from a combination of crystallographic information and simulations. For glasses RMC structure models are BV-analysed to assess the total number of equilibrium sites and to identify transport pathways for the mobile ions. The observed correlation between the pathway volume fraction and the transport properties permits to predict both absolute value and activation energy of the dc ionic conductivities of unordered solids (including mixed alkali glasses) directly from their structural models. A corresponding BV analysis of MD trajectories allows to quantify the evolution of pathways in time. The BV model suggests that the rapid increase in conductivity with temperature is linked to the change in extension and dimensionality of the conduction pathways as well as of the number of equilibrium sites for mobile ions.
- 10:30 **BREAK**

Session VIII: Ionic and mixed ionic-electronic conductors III  
 Session chair: Truls Norby

- K-VIII.1** 11:00 -Invited- PO<sub>2</sub> DEPENDENCE OF VALENCE NUMBER OF Co IN LaGaO<sub>3</sub> AND ITS INFLUENCE ON PARTIAL ELECTRONIC AND OXIDE IONIC CONDUCTIVITY  
**Tatsumi Ishihara**(b), S. Ishikawa(a), H. Nishiguchi(a) and Y. Takita(a), (a)Department of Applied Chemistry, Faculty of Engineering, Oita University, Dannoharu 700, Oita 870-1192, Japan, (b)Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-Ku, Fukuoka, 812-8581, Japan  
 Co doped LaGaO<sub>3</sub> exhibits high oxide ion conductivity at intermediate temperature and this material is expected as the electrolyte of intermediate temperature solid oxide fuel cells. Doping small amount of Co is effective for increasing oxide ion conductivity, however, mechanisms for improved ion conductivity by doping Co is not clear. In this study, we investigated PO<sub>2</sub> dependence of average number of Co cation in LaGaO<sub>3</sub> lattice by the conventional redox titration method. It was seen that average number of Co is intermediate value between 2 and 3 and PO<sub>2</sub> dependence of Co valence number was deviated from Wagner theory, i.e. 1/4 slope and close to 1/10. In good agreement with this decreased PO<sub>2</sub> dependence, PO<sub>2</sub> dependence of the estimated partial electronic conduction by polarisation method decreased from 1/4 to 1/10 slope with decreasing temperature. Considering the estimated amount of oxygen vacancy, improvement of oxide ion conductivity by doping Co can not be explained by increasing the amount of oxygen vacancy. Therefore, it is considered that mobility of oxygen vacancy may increase by doping Co to LaGaO<sub>3</sub> based oxide. Improvement in mobility of oxygen vacancy was measured by using Hole effects. In agreement with major charge carrier of oxygen vacancy, positive Hole signal is observed and it was seen that the estimated mobility of charge carrier was much improved by doping Co.

**K-VIII.2** 11:30 -Invited-

#### COMPARISON BETWEEN LIQUID STATE AND SOLID STATE ELECTROCHEMISTRY

**Ilan Riess**, Physics Department, Technion-Israel Institute of Technology, Haifa 32000, Israel

We discuss the similarities and differences between liquid state electrochemistry (LSE), and solid state electrochemistry (SSE). Though based on the same thermodynamic principles the properties of these cells are quite distinct. Differences exist in the bulk conduction mechanism, partially in electrode reaction, and in cell construction and morphology. This lead also to differences in applications.

Differences that come immediately to mind are: The lack of electronic (electron/hole) conduction in most liquid electrolytes (LEs) while electronic conduction exists, to some extent, in all solid electrolytes (SEs). In LEs both cations and anions are mobile while in SEs only one kind of ions is usually mobile. In liquid state cells one has the option to stir and replenish the LE. This is not possible, of course, when using SEs. A reference electrode is not introduced into the SE but onto the SE surface. Contrary to SSE where the electrode can have a complex composition in LSE it is usually the LE that has a complicated composition, containing many different kinds of ions. These differences and others will be discussed in more detail in the talk. We shall review the geometry of liquid and solid electrochemical cells, materials properties, in particular, charge carriers, their nature, concentration and conduction mechanism, the theoretical current-voltage relations in the bulk and the relevant boundary conditions, the experimental methods for characterizing materials properties and over potentials and electrode processes. This talk is based on a chapter with the same name published by the speaker in: Encyclopedia of Electrochemistry, Vol 1, E. Gileadi and M. Urbakh (eds.), Wiley, VCH, 2002.

**K-VIII.3** 12:00

#### OXYGEN PERMEATION AND SURFACE PROPERTIES OF Pr-Fe-BASED PEROVSKITE-TYPE MIXED CONDUCTORS

**H. Itoigawa**, H. Takamura, A. Kamegawa and M. Okada, CREST, Japan Science and Technology Agency, Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-yama 02, Sendai 980-8579, Japan

Mixed ionic and electronic conductors with a perovskite-type structure consisting of rare-earth and transition metals are of considerable interest as materials for oxygen separation and partial oxidation of hydrocarbons. Oxygen ion and electronic conductivities and the exchange kinetics of oxygen on membrane surfaces are key properties to determine an oxygen flux density. In this work, the electrical conductivity and surface properties of perovskite-type oxide,  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{Fe}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$  (PCFM), were investigated. The total electrical conductivity of PCFM ( $x = 0 \sim 0.2$ ) decreased by a slope of 1/4 with reducing oxygen partial pressure, suggesting that hole conductivity was a dominant carrier. For  $x = 0.2$ , 0.36 mm-thick sample showed an oxygen flux density,  $j_{\text{O}_2}$ , of 4.6 micro-mol/cm<sup>2</sup>/s at 1273 K.  $j_{\text{O}_2}$  was evaluated as a function of membrane thickness,  $L$ , and found to be limited by surface exchange kinetics below 0.5 mm. The surface properties of PCFM were studied by means of impedance spectroscopy (IS) and electro-motive force (EMF) measurements. The IS measurements revealed that surface polarizations and resistances strongly depend on the membrane thickness, in other words,  $j_{\text{O}_2}$ . Furthermore, EMF also showed a membrane thickness dependency in the case of  $L < 0.5$  mm.  $j_{\text{O}_2}$  and surface exchange kinetics of PCFM will be discussed in conjunction with results on these electrochemical analyses.

**K-VIII.4** 12:20

#### HIGH-TEMPERATURE CONDUCTIVITY IN STRAINED EPITAXIAL $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ THIN FILMS

J.A. Pardo, **J. Santiso**, C. Solis, G. Garcia and A. Figueras Crystal Growth Laboratory. Institut de Ciència de Materials de Barcelona, ICMAB-CSIC. Campus UAB, 08193 Bellaterra. Spain

In the search for new functional materials with relevant MIEC conductivities and enhanced stability for the application in different types of electrochemical devices, recent studies have pointed towards some Sr-Fe-O complex oxide materials with perovskite-related intergrowth structure, such as  $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ . Very little is known about the intrinsic transport properties of this compound. The best approach for studying such complex materials is to prepare high quality crystalline films.

In this work we present our results in the preparation of  $\text{Sr}_4\text{Fe}_6\text{O}_{13}$  epitaxial films with b-axis orientation on different perovskite substrates by means of pulsed laser deposition. The films were characterised by X-ray diffraction and electron microscopy. The planar conductivity of the films at high temperatures was measured by ac impedance spectroscopy under different atmospheres. In the films the epitaxial strain caused by the substrate mismatch induced subtle changes in the cell parameters and microstructure of the films which are correlated with the measured transport properties.

12:40

**LUNCH**

14:00

## POSTER SESSION

- K/P01** EFFECT OF Mo DOPING ON STRUCTURE AND PROPERTIES OF NANOSIZED INVERSE SPINEL  $\text{LiCoVO}_4$   
 W. Chen, L.Q. Mai, Q. Xu, Q.Y. Zhu, Institute of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China  
 Pure and Mo-doped nanosized  $\text{LiCoVO}_4$  were prepared by using citrate as chelating reagent and investigated by XRD, XPS, ESR and impedance spectroscopy. The results show that substitution of vanadium by molybdenum tends to regularize the atomic stacking and reduce octahedral distortion, which results in the increase of electrical and electrochemical properties.
- K/P02** SOLID STATES DETECTORS FOR MEASUREMENTS LOW AND HIGH RADIATION DOSES  
I.Kh. Abdukadirova, Institute of Nuclear Physics, Solid State Physics, p.Ulugbek, 702132 Tashkent, Uzbekistan  
 The spectroscopic characteristics of the irradiated on the reactor and gamma-course of the solid states oxides was investigated. The aim-their used at studied ecological investigations of surrounding, measurements low and high radiation doses. The silica glasses of some types ( I - IV ).  
 The diapason of gamma-radiation doses ( 100 - 105 Gy ) was found, where a linear slope of the wavelength 284 and 396 nm photoluminescence intensity was observed in the silica glasses of type I, II. The short waves luminescence of band appears in the glasses of type III at the dose D &#61502; 5.105 Gy at the irradiation temperature T &#61619;300K, intensity which increases fastly till 5.106Gy ( it can be used in the dose relay). The bands of visual colour ( 540 nm ) been used in health monitoring of low gamma doses (102 - 105 Gy) was concluded. Generation of neutron irradiation of the non-bridge oxygen ( red luminescence ) was revealed in glasses of type I, IV on the interval doses of 106-3.108 Gy. The radiation defects role in the structure changes was concluded, with it is concentration been used at measurements of high neutron radiation doses.
- K/P03** HIGH TEMPERATURE ELECTRICAL CONDUCTIVITY IN  $\text{ZnS:Al}$  AND IN  $\text{CdSe:Al}$   
K. Lott, T. Nirk, S. Shinkarenko Tallinn Technical University, Ehitajate tee 5, 19086 Tallinn, Estonia  
 High temperature electrical conductivity (HTEC) as a function of temperature and component (Zn, Cd or Se) vapour pressure has been studied in  $\text{ZnS:Al}$  and in  $\text{CdSe:Al}$  single crystals at high temperature. HTEC measurements were carried out using a two-zone resistance furnace and a vacuum sealed quartz ampoule with four tungsten or graphite electrodes. Dopants of group III act as donors in II-VI compounds. We determined the activation energies from HTEC isobars and slope values from HTEC isotherms in the large temperature region (500 - 12000C) and component vapour pressures. Near-zero activation energy of electron concentration with the  $\sim T^{-3/2}$  dependence of mobility of electrons was observed in HTEC isobars of Al-doped CdSe at Cd vapour pressure. The equilibrium constant of the association of aluminium with the metal component vacancies has been determined. It was shown that the onefold ionized substitutional Al (at Zn or at Cd place) were the dominating defects in  $\text{ZnS:Al}$  and in  $\text{CdSe:Al}$  at high metallic component vapour pressure. Here we publish HTEC isotherms of  $\text{ZnS:Al}$  and  $\text{CdSe:Al}$  to construct the high temperature defect equilibrium models of these systems.
- K/P04** ZINC NON-STOICHIOMETRY IN ZnO  
K. Lott, S. Shinkarenko Tallinn Technical University, Ehitajate tee 5, 19086 Tallinn, Estonia, E. Gorohova, S.I. Vavilov State Optical Institute, St.Petersburg, Russia, A. Grebennik, Y. Silkov, A. Vishnjakov, D.I. Mendelejev University of Chemical Technology of Russia, Miusskaya sq.9, 125190 Moscow, Russia  
 Excess Zn in polycrystalline, ceramic and monocrystalline ZnO is determined. The ZnO samples tested were prepared by heat treatment of ZnO different samples at temperature 9000C and at fixed Zn pressures from 0,1 to 0,6 of saturated pZn at given treatment temperature. To determine the excess zinc, the atomic absorption photometry of zinc vapour is used in the conditions of solid-vapour equilibrium. The vapour-crystal equilibrium in  $\text{ZnO:Zn}$  crystal was established in 20-40 min which is several orders of magnitude shorter than the time of self-diffusion at the same conditions. Optical absorbance, proportional to the concentration of zinc atoms in the vapour phase, was registered photoelectrically on Zn resonance line. The analysis of temperature dependence of zinc pressure indicated that the value of zinc excess lies in the concentration interval of  $10^{18} - 10^{19} \text{ cm}^{-3}$  and depends on the sample biography and the conditions of preliminary heat treatment. The experimental results are used for preliminary high temperature defect equilibrium calculations for ZnO.
- K/P05** DEFECT ASSOCIATION IN Fe-DOPED  $\text{SrTiO}_3$ : A QUANTITATIVE IN-SITU EPR STUDY  
Rotraut Merkle and Joachim Maier, Max-Planck-Institute for Solid State Research, Heisenbergstr. 1, 70563 Stuttgart, Germany  
 The knowledge of bulk defect concentrations is an indispensable basis for further studies of transport properties. While at sufficiently high temperatures isolated point defect dominate, the association of defects becomes increasingly important at lower temperatures, and can lower the concentrations of mobile charge carriers significantly. Qualitatively the associates of oxygen vacancies with transition metal acceptor dopants in  $\text{SrTiO}_3$  are well known since the 1960's [1].  
 Our quantitative in-situ EPR measurements of the Fe<sup>3+</sup> center allow to observe directly the temperature-dependent association of oxygen vacancies with Fe<sup>3+</sup> in single crystalline  $\text{SrTiO}_3$  samples [2]. A large fraction of the oxygen vacancies is bound in associates at 25°C. As expected, the associate concentration decreases with increasing temperature, and almost vanishes at 300°C. The measured effective association enthalpy is about -26 kJ/mol for low Fe concentrations and decreases with increasing dopant concentration, while the association entropy remains unaltered. This observation is discussed in the light of cube-root expressions for activity coefficients. [1] E. S. Kirkpatrick, K. A. Müller, R. S. Rubins; Phys. Rev. A 135 (1964) 86 [2] R. Merkle, J. Maier; Phys. Chem. Chem. Phys. 5 (2003) 2297

- K/P06** INVESTIGATION OF THE PHASE DIAGRAM AND THE DEFECT STRUCTURE OF NONSTOICHIOMETRIC Li-Mn-O SPINEL  
Ch.H. Luo, M. Martin, Institute of Physical Chemistry, RWTH Aachen (Aachen University of Technology), Germany  
 Lithium manganese oxide has been studied extensively as a potential cathode material for lithium rechargeable batteries, due to its low cost, limited environmental impact and excellent voltage profile characteristics. In our work the phase diagram and the defect structure of nonstoichiometric Li-Mn-O spinel were investigated. A series of Li-Mn oxide samples were prepared by the Pechini method and the composition was determined using ICP-OES. The single phase conditions of the samples were determined by in situ X-ray diffraction (XRD) and by thermogravimetry (TG). The diffraction patterns and the mass changes were measured as a function of increasing and decreasing temperature (TG: 1 degree Celsius/min, in situ XRD: 50 degree Celsius intervals) and of partial pressure of oxygen. It was found that the Li-Mn oxide forms a spinel structure in a certain temperature and partial pressure of oxygen region, even for the oxide with lithium deficiency. In the single spinel phase region determined in this work the changes of the oxygen nonstoichiometry, for the spinel investigated were carried out as a function of partial pressure of oxygen for different temperatures by TG. The experimental results are discussed in terms of possible defect chemical models of the Li-Mn-O spinel. The temperature and the correspondent partial pressure of oxygen are estimated for a stoichiometric Li-Mn-O spinel.
- K/P07** CONDUCTIVITY STUDIES ON PMMA BASED PROTON CONDUCTING GEL ELECTROLYTES  
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 Over the years Polymeric gel electrolytes have been attracted scientist for active research on account of their increasing application in various electrochemical Device. Within the framework of polymer electrolytes, importance of proton conducting electrolytes in ECD applications highlights the need for search of non-aqueous proton conducting polymeric gel electrolytes as these electrolytes offer an approach to attain high conductivity nearing that of liquid electrolytes along with elastomeric and adhesive property. Thus, in present work, an attempt has been made to synthesize PMMA based proton conducting gel electrolytes and characterize them electrically. these electrolytes have been prepared by conventional technique in different stoichiometric ratios. Two types of salts namely NH<sub>4</sub>SCN and (NH<sub>4</sub>CH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub> are used with DMF as casting solvent in the synthesis. The synthesized electrolyte were subsequently electrically characterized over a temperature range (303-383)K using complex impedance spectroscopy in the frequency in the frequency range 40Hz-100KHz. The ionic conductivity of as synthesized gels were assessed from cole-cole plot as a function of PMMA concentration as well as temperature. The maximum conductivity of liquid electrolyte [2.78X10<sup>-2</sup> scm<sup>-1</sup> for NH<sub>4</sub>SCN and 7.7X10<sup>-3</sup> scm<sup>-1</sup> for (NH<sub>4</sub>CH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>] dropped on addition of PMMA in the matrix with the salt system. The temperature dependence of gel electrolytes revealed VTF behaviour. All the results have been explained on the basis of existing models. Small variation in the conductivity with temperature and long term mechanical stability suggested the possible usage of these electrolytes in ECD and Smart Windows.
- K/P08** ELECTRONIC CONDUCTIVITIES OF La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>(3-δ)</sub> WITH CONSTANT OXYGEN NON-STOICHIOMETRIES BETWEEN 15 AND 1200 K  
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 The electronic conductivity of La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>(3-δ)</sub> with a well defined defect chemistry was determined in the temperature range from 15 to 1200 K. At temperatures lower than 700 K in air, the material tends to form a stoichiometric compound (δ = 0). To adjust nonstoichiometries with δ > 0 at temperatures below 700 K, the material was equilibrated at different temperatures T > 700 K under an oxygen partial pressure of pO<sub>2</sub> = 10<sup>-4</sup> atm and subsequently cooled down in closed ampoules so that the equilibrated nonstoichiometry was frozen in. Electronic conductivity measurements were performed on these samples with different but constant δ-values between 15 and 1200 K. Other authors [1] performed resistance measurements at T < 300 K on La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub> (0 < x < 0.5) with different defect electron concentrations varied by changing the Sr-content. Our results can be compared well with these results [1], indicating that the defect electron concentrations can be influenced by a variation of the strontium or the oxygen content. The conductivities of La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>2.85</sub> are comparable with those of La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3</sub>. Both samples exhibit low defect electron concentrations and show semiconductive behavior below 500 K, whereas samples with high defect electron concentrations (like La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3</sub>) were metallic throughout the investigated temperature range. Samples in-between show strongly varying conductivity-temperature dependences.  
 [1] M. A. Senaris-Rodriguez, J. B. Goodenough, J. Solid State Chem. 118 (1995) 323-336.
- K/P09** GETTERING BY HEAT THERMAL PROCESSING-APPLICATION IN CRYSTALLINE SILICON SOLAR CELLS  
N. Khehdher, A. Ben Jaballah, M. Hassen, M. Hajji, M.F. Boujmil, B. Bessaïs, H. Ezzaouia, R. Bennaceur, INRS, Hammam-Lif, Tunisia  
 Rapid thermal processing (RTP) originally developed for processing microelectronic devices has been investigated in the recent decade for its potential in the production of silicon solar cells. New directions in photovoltaics depend very often on financial possibilities and new equipment. The aim of this study is to present the improvement by gettering treatments by using an infrared lamps heating furnace for removal of metal impurities. Before annealing, the Si substrates is exposing to acid vapors issued from a mixture of HNO<sub>3</sub> and HF. This technique surname Chemical Vapor Etching (CVE) method. This technique enables us to groove the Si wafers on the both surface and to realize side buried and rear buried contacts (RBC). This findings show that the CVE process leads to an anisotropic groove which enables us to groove locally and in depth Si wafers using an adequate anti-acid mask. The grooved areas have a sufficient resolution to be applied in Si solar cells. The first step consists in making heat treatment of the sample using a Porous Silicon sacrificial layer on both sides at temperature 1000°C during 60 min annealed time in SiCl<sub>4</sub> ambient. The second stage, simultaneous diffusion of phosphorus from a POCl<sub>3</sub> source and aluminum layer is used to realize emitter and back surface field in a single high-temperature step, with optimized gettering effect. This CVE - based grooving technique was used to achieve buried grid metallic contacts in order to improve the current collection in Si solar cells, without altering the illuminated surface. A significant enhancement of the current density and the spectral response of the Si cells were observed. The improvements prove the gettering of impurities through the wafer

- K/P10** ON OPTIMUM THERMODYNAMIC CONDITIONS FOR PREPARATION OF HIGH QUALITY GSO:Ce scintillators  
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 With the aim of improving the reliability of preparation technology of high-quality GSO:Ce crystals, studies were carried out of optimum conditions for single-phase crystallization with stoichiometric matching of clusters of the crystal-forming components with the growth surface structure, including the absence of crystallization centers with orientation not coinciding with the crystallographic direction of growth.  
 Thermodynamic conditions of growth have been chosen, ensuring overheating of the initial melt (viscosity) to the optimum level and a well-balanced (as for the energy release and convective heat transfer) scattering to the environment of the extra energy conducted to the melt for its overheating. Optimum axial position of the growth crucible has been determined, in which its upper edge stretches out from the inductor by several millimeters to the region of the inductor edge effect, where the density of the heating electromagnetic flux is sharply falling. Data are presented on design features and growth regimes that allow production with high reproducibility level of GSO:Ce scintillation crystals up to 50 mm in diameter and up to 150 mm long with high spectrometric quality (energy resolution - 8.5-10.4 %,  $\epsilon = 662$  keV, 137Cs). The authors gratefully acknowledge financial support of this work by STCU under Project Gr-48(j).
- K/P11** PROPERTIES OF SOFC UNIT CELL USING SYNTHESIZED  $(La_{1-x}Sr_x)Mn_{1+y}O_3$ -CATHODE BY GLYCINE NITRATE PROCESS AND DIFFERENT ELECTROLYTE  
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 The  $(La_{1-x}Sr_x)Mn_{1+y}O_3$  (LSM) cathode prepared using glycine nitrate process were investigated with different electrolyte,  $(La_{1-x}Sr_x)(Ga_{1-y}Mg_y)O_3$  (LSGM) or YSZ. A precursor was prepared by combining glycine according with Sr contents, and was heated to evaporate excess water. The  $(La_{1-x}Sr_x)Mn_{1+y}O_3$  cathode by glycine nitrate process has a single phase when Sr contents were from 0.1mole to 0.3mole, and average particle size was about 40-13210. The  $(La_{1-x}Sr_x)Mn_{1+y}O_3$  cathode with heat treatment at 1200-8451; showed a plot of electrical conductivity versus temperature for different Sr contents. Unit cell prepared from the LSM cathode and the LSGM or YSZ electrolyte, after the unit cell was fired at 1200-8451; for 2h in air. Interface reaction of between the LSM cathode and the LSGM or YSZ electrolyte were no reaction. The manufactured unit cell measure LSGM electrolyte against YSZ electrolyte using a Solatron 1260 analyzer.
- K/P12** POLY (2-VINYL PYRIDINIUM FLUOROBORATE) AS IONICS AND ADHESIVE  
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 Polymer electrolyte usually consists of polymer and a salt and is considered to be solid solutions in which the polymer functions as solvent. The most widely studied systems in this field are on conducting polymer electrolytes based on polyethylene oxide (PEO) complexes with alkali metals salts, silver salts and lithium salts. Since pyridine is a good electron donor as well as a strong ligand capable of forming co-ordination bond, poly (2-vinyl pyridine) (P-2VP) forms complex with strong electron acceptors. They have been studied from the viewpoint of electronic conductivity behavior and as semiconductors.  
 Here we are reporting the electrical conductivity, conduction behaviour and adhesive strength of poly (2-vinyl pyridine) and its fluoroborate salt in solid state. 2-vinyl pyridine is polymerized thermally and its HBF<sub>4</sub> salt is prepared by acidification. The polymer electrolyte is characterized by IR, 1H NMR, TGA and DSC techniques. The electrical conductivity of the salt is found to be in the range of 10<sup>-3</sup> to 10<sup>-5</sup> S cm<sup>-1</sup> in different temperature range. There is about 102 to 103 fold increase in conductivity for the new polymer salt. The material is shown to be predominantly ionic conduction with  $t_{ion} \gg 0.81$ . Apparent activation energies are found 0.0375 and 0.143 eV for the polymer and the salt respectively. The polymer electrolyte shows a moderate adhesive strength and the tensile and lap-shear tests are performed to characterize. The novelty of this work is that the polymer electrolyte functions both as adhesive and ionics in the virgin state and unlike PEO complexes with alkali metals or other salts, there is no need of external salt to be added.
- K/P13** Sn-Mn BASED INTERMETALLIC COMPOUND AS ANODE FOR LITHIUM ION BATTERIES  
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 Lithium alloys have been proposed as an alternative to substitute graphite as the negative electrode in lithium-ion batteries. However, despite their high lithium ion storage capacity, they have poor capacity retention during cycle life. This is due to the drastic volume changes that destroy the crystal structure of the active alloy during the insertion and extraction reaction of lithium ions into the alloy lattice. Intermetallic compounds have been studied to hinder the volume changes. Sn-Mn based compound prepared by the sol-gel method was examined as an alternative anode material. The intermetallic compound was tested using lithium metal as the counter electrode and a capacity of more than 150 mAh/g was achieved. Electrochemical agglomeration and irreversible trapping of inserted ions by host lattice are highlighted in this study.
- K/P14** CONDUCTIVE PROPERTIES OF SILICON NITRIDE THIN FILMS WITH EMBEDDED NANOPARTICLES  
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 Silicon Nitride (SiN) thin films with embedded crystalline nanoparticles have been produced by plasma enhanced chemical vapour deposition at low substrate temperatures. The incorporation of nanoparticles in an amorphous matrix has converted the film from dielectric to ion (H) conducting thanks to the enhanced porosity of the material. Ion conductivity has been proved by impedance spectroscopy (0.01Hz-1MHz) and also in liquid environment by cyclic voltammetry measurements. The deposited films have been imaged with transmission electron microscopy and this showed films 100-200 nm thick with nanoparticles of controlled and uniform grain size depending on deposition conditions. Highest conductivities were obtained for nanoparticles of small grain size (~10 nm). Optically the thin films are highly transparent (T>90%) and the chemical characterization showed that nanostructured films oxidized in time due to their porous microstructure.

**K/P15**

**THERMODYNAMIC STUDIES ON TRANSITION METAL OXIDE BRONZES**

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Transition metal oxide bronzes with the general formula  $A_xM_oO_3$  ( $A$  = alkali or alkaline earth metal,  $M$  = transition metal,  $0 \leq x \leq 1$ ) are known for quite some time. They possess some interesting properties caused by their special structure. Inter alia they show high chemical resistance and electrochemical activity. So by way of example these compounds are used as material for ion sensitive electrodes or electrochemical reference electrodes [1, 2]. The chemical and physical properties of these materials have been studied intensively in the recent years. However, mostly in a temperature range between 5 and 300 K [3]. Now we present first results of thermodynamic and electrochemical studies of various tungsten and molybdenum oxide bronzes in a temperature range from 280 to 900 K. Therefore solid state impedance spectroscopy in inert atmosphere have been carried out. The impedance spectra show multifaceted behaviour of the various oxide bronzes. The activation energy of the electrical conductivity differs from 5 up to 35 kJ/mol. Some of the bronzes show hysteresis effects or transition from ionic conductor to metallic conductor depending on temperature. Further DTA studies in air and under inert conditions have been carried out. The temperature resistance is heavily depending on the composition, too. In air the pyrolysis starts mostly at temperatures above 600 K. Under inert conditions the temperature resistance is significantly improved. [1] P. Shuk, U. Guth, M. Greenblatt; *J. Solid State Electrochem.* 6 (2002) 374-383 [2] J. Gabel, W. Vonau, U. Guth; *Ionic.* 9 (2003) 176 - 181 [3] M. Greenblatt; *Chem. Rev.* 88 (1988) 31 - 53

**K/P16**

**ELECTRONIC SURFACE PROPERTIES OF RF MAGNETRON SPUTTERED  $In_2O_3$  AND  $In_2O_3:Sn$**

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Transparent conducting oxides (TCOs) are widely used as electrodes in thin film solar cells and other optoelectronic devices. ITO ( $In_2O_3:Sn$ ) and  $SnO_2$  are used in CdTe and a-Si:H solar cells, while ITO is also used as a contact material to organic LEDs. In order to optimise contact properties it is necessary to understand TCO surface and interface properties where the Fermi level position with respect to the conduction band is of particular importance. The Fermi level position is strongly affected by the oxygen vacancy concentration. Therefore it is necessary to investigate in situ prepared and thus contaminant free TCO films and interfaces between different contact materials. Here we present a systematic study of the electronic properties of undoped and Sn-doped  $In_2O_3$  films prepared by rf magnetron sputtering. For this purpose different  $O_2:Ar$  gas mixtures and sample temperatures were used during film deposition. The deposition chamber is directly connected to a photoelectron spectrometer system avoiding exposure to ambient air between preparation and analysis of the freshly prepared films. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) results show that the surface Fermi level position with respect to the valence band differs from 2 to 3 eV depending on the preparation conditions.

**K/P17**

**THE ELECTRONIC STRUCTURE OF PEROVSKITE MANGANATES**

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Rare earth manganates of a general formula  $La_{1-x}A_xMnO_3$  are of great interest due to CMR effect and as cathode for oxide fuel cells. The cooperative Jahn-Teller effect induces a local lattice distortion and the electron localization in the charge-ordered state. As a continuation of our previous studies [1,2], we performed the first-principles DFT calculations of the atomic and electronic structure of pure  $LaMnO_3$  and  $SrMnO_3$  and their solid solutions.

We discuss the band structure, density of states, and the electronic density distribution. Special attention is paid to the structure optimization, covalency effects in the chemical bonding and the local lattice distortion. These calculations serve as a first step to the development of thermodynamics of these solid solutions and, in particular, an analysis of the Sr impurity spatial distribution in the host  $LaMnO_3$  matrix. [1] Evarestov R.A., Kotomin E.A., Heifets E., Maier J., and Borstel G. *Solid State Comm.* 127 (2003) 367 [2] Heifets E., Evarestov R.A., Kotomin E.A., Dorfman S., and Maier J. *Sensors and Actuators B*, 2004, in press.

**K/P18**

**NEW CURRENT COLLECTOR DESIGN AND MATERIALS FOR SOLID-OXIDE FUEL CELLS**

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Although the operating concept of high temperature solid oxide fuel cells (SOFCs) is well known, the details of the electrochemical reactions as well as the selection of materials for the individual components presents serious challenges. An elemental unit of the cell consists of an anode, a cathode and a solid electrolyte in between, which in SOFCs is an oxide. In addition a current collector or two current collectors, one for each electrode, must be provided. The reason is that the electrode materials to date have improved catalytic properties but limited electrical conductivity (of the order of 100 S/cm). A current collector (CC) would have a conductivity 2-4 orders of magnitude higher. Unfortunately, the materials for CC that can operate at elevated temperatures (600-1000°C) are refractory. Thus their preparation is difficult and expensive. The design, so far, uses either plates or stripes of the refractory materials as CC. This significantly limits the cell design.

We suggest to use refractory powders to prepare the CC. (\*) This allows for more flexibility in the cell design. However, the apparent conductivity of the powder is low, many orders of magnitude lower than the conductivity of the bulk. The reason can be traced back to the poor contact between the refractory grains and between the grains and the electrodes. We show that this problem is solved by allowing a second phase to be generated, e.g. by in-situ oxidation of the CC power grains which "heals" the weak contacts points. A dramatic decrease in the apparent resistivity of the powder is observed. We present also, possible new materials for the CC as well as possible new cell designs facilitated by in situ preparation of the CC from refractory powders. \*Patent applied for.

- K/P19**      **PREMELTING EFFECT IN AgBr: MD SIMULATION**  
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 AgBr is known to exhibit anomalous increase of ionic conductivity on approach to the melting point ( $T_m=701\text{K}$ ) at the temperatures of 100-150K below  $T_m$ . Various experimental data suggest that incipient premelting of the phase occurs in the temperature range. Although structural features and diffusion coefficients in the melted AgBr were shown to resemble the ones observed in superionic state, it is still unclear whether the “diffuse phase transition” model gives adequate description of the phenomenon.  
 The premelting effect has been investigated by molecular dynamics simulation. The calculations were performed using MOLDY code. A constant pressure (NPT) ensemble was represented by 1000 ions positioned in such a way that to create a rock salt-like crystal structure. The effective potential was used in a functional form originally proposed by Vashishta and Rahman. The thermodynamic, structural and kinetic properties have been studied in the temperature range covering the melting point. The premelting was observed as a sudden increase in mobility of silver-cation sublattice. The calculated values of diffusion coefficients for Ag in the “premelting temperature range” ( $\sim 2 \cdot 10^{-6} \text{ cm}^2/\text{s}$ ) were comparable to the ones of superionic conductors. The structural characteristics of the system in a melted state were in good agreement with experimental data.
- K/P20**      **COMPLETE REVERSIBILITY OF HETEROGENEOUS Li-STORAGE IN RuO<sub>2</sub> ELECTRODE**  
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 We present here the performance of RuO<sub>2</sub> as an active electrode material for rechargeable lithium batteries. RuO<sub>2</sub> shows a high Li-storage capacity of 1120 mAh/g on uptake of 5.6 Li, with 98% Columbic efficiency at the first discharge/charge cycle. Based on XRD, Raman spectroscopy and HRTEM measurements performed on RuO<sub>2</sub> at various stages of discharge/charge processes, it is observed that full Li-uptake transforms polycrystalline RuO<sub>2</sub> into nanocrystalline composite of Ru and Li<sub>2</sub>O with a grain size of 2-5 nm covered by a 5-10 nm surface solid/electrolyte interphase (SEI) layer. In the fully Li-extraction state, nanocrystalline RuO<sub>2</sub> formed again and the SEI layer disappeared completely. The overall reaction can be written as:  $\text{RuO}_2 + 4 \text{Li} + 4 \text{e}^- \rightarrow \text{Ru} + \text{Li}_2\text{O}$ , which is analogous to the heterogeneous reaction observed in other transition metal oxides and fluorides. When the cycling is limited between 1.2-0.05 V, a reversible capacity of 150 mAh/g with a good cyclability is observed. We believe that this reversible Li-storage is caused by a heterogeneous interfacial storage process. Among the materials studied so far, it is worth mentioning that only RuO<sub>2</sub>, allowed complete extraction of Li (nearly 100 % Columbic efficiency) in the first cycle, while in other materials only 75 % or less Li can be extracted. We discuss in detail the cause for the complete extraction of Li in case of RuO<sub>2</sub> in comparison with few other materials such as CoO and TiF<sub>3</sub> in terms of the microstructure of nanocomposite M/LiX (X = O, F) and the mass ( $\text{e}^-$ , Li and O<sub>2</sub>/F<sup>-</sup>) transport.
- K/P21**      **OXYGEN PERMEATION AND MECHANICAL PROPERTIES OF Ba-La-In-BASED PEROVSKITE-TYPE OXIDES**  
Y. Aizumi, H. Takamura, A. Kamegawa and M. Okada, CREST, Japan Science and Technology Agency, Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-yama 02, Sendai 980-8579, Japan  
 Mixed ionic and electronic conductors are of interest in view of promising applications such as oxygen separation and partial oxidation of hydrocarbons. In this study, oxygen permeation and mechanical properties of (Ba<sub>0.5-x</sub>Sr<sub>x</sub>La<sub>0.5</sub>)(In<sub>1-y</sub>Fe<sub>y</sub>)O<sub>3- $\delta$</sub>  (x = 0.05 ~ 0.25; y = 0 ~ 0.9) with a perovskite-type structure have been investigated. The oxygen flux density of (Ba<sub>0.5-x</sub>Sr<sub>x</sub>La<sub>0.5</sub>)(In<sub>0.4</sub>Fe<sub>0.6</sub>)O<sub>3- $\delta$</sub>  (x = 0.05 ~ 0.25) strongly depended on Sr content; the highest value of 10.8 micromol/cm<sup>2</sup>/s was attained for x = 0.2 at 1273 K under air / Ar-10%CH<sub>4</sub> gradients. This suggests that the electrical conductivity, especially oxide-ion conductivity of these oxides depends on the unit-cell free volume, which can be controlled by Sr content. The electrical conductivity of these oxides was measured as functions of temperature and partial oxygen pressure. In addition to oxygen flux density, mechanical properties are also essential in view of membrane applications. The Young's modulus and fracture toughness of (Ba<sub>0.3</sub>Sr<sub>0.2</sub>La<sub>0.5</sub>)(In<sub>1-y</sub>Fe<sub>y</sub>)O<sub>3- $\delta$</sub>  (y = 0 ~ 0.9) was also evaluated. Regardless of Fe content, the Young's modulus and fracture toughness of these oxides were almost constant in the range of 80 ~ 100 GPa and 0.8 ~ 1.0 MPa/m<sup>1/2</sup>, respectively.
- K/P22**      **HIGH MIXED ELECTRONIC-PROTONIC CONDUCTIVITY IN NANOPOROUS CRYSTAL, 12CaO-7Al<sub>2</sub>O<sub>3</sub>**  
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 12CaO·7Al<sub>2</sub>O<sub>3</sub>·O<sub>3</sub> (C12A7) has a positively-charged nanoporous lattice framework. Oxide ions partially occupy cages of the lattice, and are apparently responsible for the fast oxide ionic conduction in an oxidizing atmosphere. We have reported that hydride ( $\text{H}^-$ ) ions are incorporated in the cages by a hydrogen-annealing. The resultant C12A7 undergoes an ultraviolet light-induced insulator to electronic conductor transition at room temperature. In this presentation, we will report that the C12A7 exhibits a fast mixed electronic-protonic conduction in a hydrogen atmosphere at elevated temperatures. Total electrical conductivity in equilibrium with 0.2 atm  $\text{H}_2$  atmosphere at 800-1300°C is 2-30 times larger than the oxide ionic conductivity. Transference numbers at 800-1300°C were evaluated both from hydrogen concentration cell and ion-blocking methods. These measurements revealed that the protonic conductivity is fairly large, comparable to those in alkaline-earth cerates, although the main conductive species is electron. High temperature chemical composition is frozen-in when quenched to temperatures below 550°C. Electrons are likely generated from the hydride ions by a thermal excitation process, giving an electronic conductivity several times larger than the oxide ionic conductivity.

- K/P23** OXYGEN INCORPORATION INTO SrTiO<sub>3</sub>: INFLUENCE OF SrO SURFACE COATINGS  
S.F. Wagner, W. Menesklou, L. Merkle, Th. Schneider, E. Ivers-Tiffée, Institut für Werkstoffe der Elektrotechnik, Universität Karlsruhe (TH), Germany  
 Semiconducting metal oxides such as strontium titanate are suitable materials for resistive-type oxygen sensors in dynamic applications provided that their response behaviour to a change in the ambient oxygen partial pressure pO<sub>2</sub> is sufficiently fast. This depends on the kinetics of oxygen incorporation from the gas phase into the solid state – a process which can be separated into two consecutive electrochemical steps: oxygen surface transfer and subsequent bulk diffusion of oxygen vacancies. The latter leads to a change in the sample resistance R giving rise to the characteristic sensor curve R(pO<sub>2</sub>). Since bulk diffusion usually occurs fast, the response behaviour of thin samples (with a large surface-to-volume ratio) is controlled by surface transfer at temperatures below 1000 K.  
 Based on a frequency-domain analysis of the response signal obtained from an electrically contacted SrTiO<sub>3</sub> sample exposed to a modulated pO<sub>2</sub> in a fast kinetic measurement setup, the influence of the surface transfer reaction on the oxygen incorporation kinetics can be assessed from the shape of the frequency response. The effect of thin SrO surface coatings on the kinetics is investigated.
- K/P24** INCREASING OF DEFECTS CONCENTRATION IN GeO<sub>2</sub>-ZrO<sub>2</sub> SYSTEM  
E. Frolova, M. Ivanovskaya, Research Institute for Physical Chemical Problems, BSU, Leningradskaya str. 14, 220080 Minsk, Belarus, V. Petranovskii, S. Fuentes, CCMC, UNAM, Ensenada, B.C. 22800, Mexico  
 The study of Zirconia-based solid solutions has attracted considerable attention because of the variety of its important applications especially as the solid state ionic. Oxygen vacancies created by the aliovalent dopants for charge compensation has been shown to play an important role in stabilizing the cubic and tetragonal structures as well as anionic conductivity. The isovalent dopants do not create anion vacancies, yet they still stabilize tetragonal zirconia against monoclinic distortion. Up to now, the reason of this stabilization is not completely understood.  
 In the present report we provide evidences of an unexpected increase in paramagnetic center concentration with increase in GeO<sub>2</sub> content in GeO<sub>2</sub>-ZrO<sub>2</sub> co-precipitates prepared by ammonia-promoted hydrolysis of the aqueous solutions of ZrO(NO<sub>3</sub>)<sub>2</sub> and GeO<sub>2</sub> (hex) followed by drying and gradual calcinations in the air (600°C). Samples with variable germanium content (5-50 mol %) were characterized by the XRD, DTA, FTIR, ESR and XPS. The possible mechanism of defects formation is proposed. Further exploration of the structure/properties relationship in this system may result in fundamental understanding of a defect formation reason.
- K/P25** EFFECTS OF B AND HEAT TREATMENT IN CARBON AEROGELS FOR ELECTRIC DOUBLE-LAYER CAPACITORS  
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 A novel nanomaterial, carbon aerogels were heated in the absence/presence of B at different temperature. The initial B loading was 1 wt.% and the final B retentivity increased as heat treatment temperature (HTT) increased. Crystallinity and BET surface area of the sample increased and decreased, respectively, as HTT increased and in the presence of B, as expected. The relationship between capacitance and surface area was interesting in the presence of B and different heat treatment temperature.
- K/P26** MICROSTRUCTURE EVOLUTION AND CONDUCTIVITY OF Bi<sub>2</sub>CuO<sub>4</sub>-Bi<sub>2</sub>O<sub>3</sub> COMPOSITES NEARBY THE EUTECTIC POINT  
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 The phenomenon of grain boundaries (GB) wetting may be useful in creating of new generation of ion-conducting materials. This phenomenon is sometimes followed by the formation of so-called grain-boundary liquid channel structures (GBLCS). Formation of GBLCS was found in Bi<sub>2</sub>CuO<sub>4</sub>&#8211;Bi<sub>2</sub>O<sub>3</sub> ceramic composites where GB wetting transition by eutectic liquid occurs. In this system such structures are formed by the grains (possessed the electronic conductivity) and by liquid channels (possessed high ionic conductivity) located on the grain boundaries.  
 Here we carried out the detailed investigation of microstructure evolution in Bi<sub>2</sub>CuO<sub>4</sub>&#8211;Bi<sub>2</sub>O<sub>3</sub> system nearby the eutectic point (770°C) by scanning electron microscopy. For this purpose the Bi<sub>2</sub>CuO<sub>4</sub> wt.%Bi<sub>2</sub>O<sub>3</sub> samples were rapidly heated up to 750, 760, 765, 770, 775 and 780°C and immediately (without hold at this temperature) quenched in air. The microstructure of samples quenched from 750-770°C is characterized by randomly distribution of Bi<sub>2</sub>O<sub>3</sub> over the ceramic bulk. However, the other situation is observed in the samples quenched from temperatures above the eutectic temperature (775 and 780°C). Bi<sub>2</sub>O<sub>3</sub> is localized at three-grain junctions and some GB of Bi<sub>2</sub>CuO<sub>4</sub>. Such drastic evolution in location of Bi<sub>2</sub>O<sub>3</sub> is most likely caused by GB wetting and GBLCS formation. Conductivity investigation of Bi<sub>2</sub>CuO<sub>4</sub>(5-20wt%)Bi<sub>2</sub>O<sub>3</sub> composites was performed by four-point DC technique and two-point AC impedance spectroscopy in the temperature range 660-790°C; in air. It was shown that conductivity dependences exhibit jump near 770°C. The conductivity therewith increased by a factor of 1,2 to 2,2 depending on ceramic composition. The observed conductivity jump once more supports the processes of GB wetting and GBLCS formation.
- K/P27** ELECTRON TRANSPORT AND REDOX STATES IN Gd DOPED CERIA-ZIRCONIA  
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 This contribution focuses on the electronic conductivity of oxygen ion conducting solid electrolytes and derived materials, in particular the doped ceramic CeO<sub>2</sub>-ZrO<sub>2</sub>-system. We prepared monophasic samples with fixed Gd dopant concentration and measured the electronic conductivity with the microcontact technique using Pt or Au.  
 Steady-state current-voltage curves as well as time-dependent voltage relaxation (after polarization) have been used to study conductivity, mobility and concentration of electrons and holes. A considerable change of the electronic conductivities (in the p- and n-type range) was observed as a result of Zr doping in CeO<sub>2</sub>. Clear evidence has been found from an analysis of the polarization curves for the presence of new redox levels in the band gap between the valence band and the Ce-4f states.

- K/P28** ELECTRON TRANSPORT AND ELECTRONIC STATE DENSITIES IN OXYGEN ION CONDUCTING LANTHANUM GALLATES  
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 The electronic conductivity of solid oxide electrolytes usually depends strongly on the temperature and the oxygen activity. Besides that, one often observes a dependence on the concentration of aliovalent cation dopants, which is not well understood. Our investigations focus on the analysis and modelling of the dopant influence on the electronic conduction for the lanthanum gallates doped with Sr<sup>2+</sup> and Mg<sup>2+</sup>.  
 A series of lanthanum gallates (La<sub>1-x</sub>Sr<sub>x</sub>)Ga<sub>1-y</sub>Mg<sub>y</sub>O<sub>3-d</sub> were prepared (x=0.2; D= 0, 0.05; y=0.15,0.20). The electronic conductivity was measured as a function of oxygen partial pressure and temperature for different dopant concentrations x and y. The results show a systematic variation of p-type conductivity with the dopant concentrations. The influence of dopants is analyzed in terms of the electronic structure of the lanthanum gallate. The latter is analyzed in terms of the density of states and the localization character of eigenstates that are located at the top of the valence band, which dominate the electronic transport properties in the p-conducting regime.
- K/P29** STABILITY OF NANOCRYSTALLINE TUNGSTEN OXIDE FILMS AT HIGH TEMPERATURES  
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 Thin films of tungsten oxide have attracted much attention due to many applications of this material in gas sensors, electrochromic and photochromic applications. Thin films of tungsten oxide can be fabricated by evaporation or other vacuum deposition methods. Enhanced gas sensitivity of tungsten oxide films have been reported after annealing at 600 degree C. However, these films have larger cracks and film discontinuities which limited patterning of tungsten oxide films for further miniaturized sensor arrays. Recently we have reported that uniform nanocrystalline films could be fabricated by long time heating at low temperature range of 300 degree C. These films have high adhesion to the substrate and uniform topography which are essential properties to apply in microfabricated gas sensors. In this investigation, we have investigated the stability of such nanocrystalline tungsten oxide films at higher temperature heating. The experiments were carried out to investigate the change of surface morphology and structure of nanocrystalline tungsten oxide films. It is found that after re-crystallization by low temperature annealing, tungsten oxide films are very stable: no large surface cracks or large grains were found. This result encourages that low temperature formed nanocrystalline films can be suitable candidate for miniaturized gas sensor fabrication. In this presentation, greater details of experimental results will be discussed.
- K/P30** IONIC CONDUCTIVITY IN POLY(AMINOPHOSPHAZENE)-SiO<sub>2</sub> COMPOSITE POLYMER ELECTROLYTES  
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 Composite polymer electrolytes from polyphosphazenes have been prepared by incorporation of inorganic nano-particles (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>,...) with the aim of improving mechanical properties and achieving enhanced ionic conductivities. We prepared the polymer electrolytes by mixing poly[bis-(2,2-dimethoxy-ethyl)-amino]-phosphazene] (= MEAP) with varying amounts of LiCF<sub>3</sub>SO<sub>3</sub> and determined the ionic conductivities between 30 and 80°C by impedance spectroscopy. We obtained values in the range between 3.8·10<sup>-8</sup> and 1.7·10<sup>-6</sup> S·cm<sup>-1</sup> (10% wt. LiCF<sub>3</sub>SO<sub>3</sub> <=> Li<sup>+</sup> : (O,N) = 1 : 30).  
 The composite electrolytes, MEAP mixed with SiO<sub>2</sub>-particles, formed *in situ* by sol-gel-process, were characterized by DSC, SEM and EDAX. The effect of the inorganic particles on the ionic conductivity was studied by impedance spectroscopy on samples with variant SiO<sub>2</sub>-contents. We found a maximum conductivity enhancement at 4% wt. SiO<sub>2</sub> (3.0·10<sup>-6</sup> S·cm<sup>-1</sup>, 80°C, 10% wt. LiCF<sub>3</sub>SO<sub>3</sub>). Higher amounts of SiO<sub>2</sub> lead to decreasing conductivities but also to slightly lower T<sub>g</sub> values (-41°C, 2% SiO<sub>2</sub> to -45°C, 10% SiO<sub>2</sub>).
- K/P31** IONIC CONDUCTIVITIES OF POLYPHOSPHAZENE SOLID ELECTROLYTES MIXED WITH DIFFERENT SALTS  
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 Polyphosphazenes are a class of inorganic polymers based on -N=PR<sub>2</sub>- units with a high skeletal flexibility and low T<sub>g</sub> values compared to organic polymers which makes them attractive candidates for low temperature polymer electrolytes.  
 We synthesized poly[bis-(bis-(2-methoxy-ethyl)-amino)-phosphazene] (= BMEAP) as a basic polymer electrolyte material for systems with LiCF<sub>3</sub>SO<sub>3</sub> and NaI. The solvation of the cations is supported by the nitrogen and oxygen of the substituents and the main chain. Impedance spectroscopy on BMEAP with 10% wt. LiCF<sub>3</sub>SO<sub>3</sub> (<=> Li : (O,N) = 1 : 30) gave conductivities up to 3.4·10<sup>-5</sup> S·cm<sup>-1</sup> at 110 °C. DSC-measurements showed that BMEAP is thermally stable up to temperatures of 200 °C. Above 130°C the membranes become very soft. The T<sub>g</sub> values are nearby -50°C and rise only slightly with salt concentration. Compared with 10% wt. LiCF<sub>3</sub>SO<sub>3</sub>, the sample mixed with 10% wt. NaI showed lower ionic conductivities (1.3·10<sup>-5</sup> S·cm<sup>-1</sup> at 110 °C) indicating that the dissociation is less for NaI compared to LiCF<sub>3</sub>SO<sub>3</sub>.
- K/P32** CORRELATION BETWEEN IONIC RADIUS AND DIFFUSION IN STABILISED ZIRCONIA  
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 Multiple diffusion experiments of all stable lanthanides were performed simultaneously in calcia stabilized zirconia (CSZ), yttria stabilized zirconia (YSZ) and scandia stabilized zirconia (ScSZ) at temperatures between 1200 and 1600 °C.  
 For all investigated systems, the bulk diffusivity increases with increasing the lanthanide ionic radius. The experimental activation enthalpy is highest for CSZ and lower for the three-valent systems ScSZ and YSZ. It is not strongly affected by the type of the lanthanide for all systems.

- K/P33** THE EFFECT OF THE DOPANTS AND OXYGEN NONSTOICHIOMETRY ON THE THERMODYNAMIC PROPERTIES OF MICRO AND NANOSTRUCTURED LANTHANUM MANGANITES  
Speranta Tanasescu, Cornelia Marinescu, Florentina Maxim, Institute of Physical Chemistry "I.G.Murgulescu" of the Romanian Academy  
 The thermodynamic properties of the acceptor doped micro- and nanostructured lanthanum perovskites are strongly affected by the nature and the content of the dopant, as well as by the oxygen nonstoichiometry. In the present work the solid electrolyte galvanic cells method have been used in order to make a comparative study of the thermodynamic properties of some micro- and nanostructured substituted lanthanum manganites of general formula  $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{Al}_y\text{O}_3$  ( $x=0.3; 0.33; y=0; 0.05$ ). The relative partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, as well as the equilibrium partial pressures of oxygen have been obtained in the temperature range of 873-1273 K in a reducing atmosphere (10-6 Pa). For the compounds with the same composition, but obtained by different preparation procedures (sol-gel method and solid state reactions) the obtained data evidence the modifications in the thermodynamic properties connected with the nanocrystalline state. The results are discussed being related with the variation of the predominant defects in the oxygen sublattice of the perovskite-type structure.
- K/P34** DEFECT CHEMISTRY AND TRANSPORT PROPERTIES OF LANTHANUM NICKEL OXIDE  
Mirela-Anca Dragan and Michael Schroeder, Institute of Physical Chemistry, RWTH-Aachen, Germany  
 Solid-state oxide materials with high ionic and electronic conductivity has attracted considerable attention for their application in Solid Oxide Fuel Cells, oxygen generators, catalytic membrane reactor, and for their fundamental interest on the defect chemistry and the transport properties.  
 Our study is focused on systematic investigation of oxygen transport on Mixed Ionic Electronics Conductors, MIEC oxides with perovskite-related  $\text{K}_2\text{NiF}_4$  structure.  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ , examined by us has a layered structure. This structure may be described as an intergrowth of rocksalt  $\text{La}_2\text{O}_3$  layers and perovskite  $\text{LaNiO}_3$  layers. The rocksalt layers accommodate interstitial oxygen, whereas the perovskite layers host oxygen vacancies [1]. Experimental data of the deviation of stoichiometry [3],[4], indicate that  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$  may be either oxygen deficient or may exhibit oxygen excess, depending on  $p(\text{O}_2)$  and dopant concentration. In this work, we investigate the contribution of vacancies and oxygen interstitials to the overall oxygen transport process in  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ , by means of oxygen permeation experiments. First experimental results indicate that the permeation process is dominated by an interstitial mechanism, however, model calculation with a defect chemical model suggest that, at low oxygen partial pressure, transport via vacancies becomes significant. References: [1] Licia Minervini, et al.; J. Mater. Chem. (2000) 2349-2354 [3] V. V. Vashook et al.; Solid State Ionics 110 (1998) 245 [4] V. V. Vashook et al.; Solid State Ionics 119 (1999) 23
- K/P35** CHARACTERISATION OF YSZ/CeO<sub>2</sub> SUPERLATTICES PREPARED BY PULSED INJECTION MOCVD  
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 Recent studies have demonstrated that ionic conductivity can be enhanced in nanostructured materials by inducing structure stresses or by introducing interfaces that can cause the redistribution of ions in the space-charge regions. Maier et al. [1] have demonstrated that multilayered films composed of  $\text{CaF}_2$  and  $\text{BaF}_2$  exhibit an increase of several orders of magnitude in the ionic conductivity, which is related to the interface density. Suzuki et al. [2] have assessed, by Molecular Dynamics simulations, that the oxygen diffusion in strained YSZ/CeO<sub>2</sub> superlattices is expected to be larger than that of YSZ, due to a reduction in the activation energy of the ionic diffusion process.  
 In this work, we present the first results in the preparation of such YSZ/CeO<sub>2</sub> superlattices by Pulsed Injection Metal Organic Chemical Vapour Deposition (PIMOCVD). In a first step, we have optimised the experimental parameters in order to prepare epitaxial YSZ and CeO<sub>2</sub> single films. The thickness of the layers in the nanometer scale has been determined by X-ray reflectivity. XRD has been used to determine the film/substrate epitaxial relationship. The surface morphology and roughness have been characterised by AFM. In a second step, YSZ/CeO<sub>2</sub> superlattices have been prepared with a different sequence of YSZ and CeO<sub>2</sub> individual thicknesses. The strain in YSZ layers has been determined by XRD and will be related to the ionic conductivity of such artificial material. [1] K.Suzuki, M.Kubo, Y.Oumi, R.Miura, H.Takaba, A.Fahmi, A.Chatterjee, K.Teraishi, A.Miyamoto, Applied Physics Letters, vol. 73, n°11 (1998) 1502-1504 [2] N.Sata, K.Eberman, K.Eberl, J.Maier, Nature, vol. 408 21/28 (2000) 946-949
- K/P36** DYNAMICS IN FRAGILE IONIC MELTS FROM BROADBAND CONDUCTIVITY SPECTROSCOPY  
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 The dc conductivities of fragile glass-forming ionic melts display marked deviations from the Arrhenius law. Instead of the frequently used Vogel-Fulcher-Tammann relation, we have recently introduced a different equation,  $\sigma_{dc}(T) = \sigma_{hf}(T) \cdot \exp(-\sigma^* / \sigma_{hf}(T))$ , which agrees well with experimental data. Here,  $\sigma_{dc}(T)$  is the non-Arrhenius dc conductivity,  $\sigma^*$  is a constant, and  $\sigma_{hf}(T)$  denotes an Arrhenius-activated high-frequency conductivity, which is experimentally accessible in the THz frequency regime. The above equation is a particular result of the MIGRATION (an acronym for Mismatch Generated Relaxation for the Accommodation and Transport of IONs) concept. With the help of this concept, we model the ion dynamics and explain measured conductivity spectra. In this contribution, we present a set of new conductivity spectra of the fragile melt  $3 \text{KNO}_3 \cdot 2 \text{Ca}(\text{NO}_3)_2$ , covering wide ranges of frequency and temperature. Characteristic changes in shape are detected as the material transforms from the glassy state to a viscous melt and, eventually, to a low-viscosity fluid. The observed solid – fluid transition is described with the help of the MIGRATION concept. Existing conductivity spectra taken from the fragile melts  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$  and  $\text{LiCl} \cdot 7 \text{H}_2\text{O}$  are revisited and also interpreted in terms of the MIGRATION concept.

- K/P37** DEFECT ORDERING IN OXYGEN-DEFICIENT  $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$   
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 At high temperatures and low oxygen partial pressures the transition metal perovskite-type oxides  $\text{La}(1-x)\text{Sr}(x)\text{CoO}(3-d)$  (LSC) and  $\text{La}(1-x)\text{Sr}(x)\text{FeO}(3-d)$  (LSF) exhibit large concentrations of oxygen vacancies which influence the electrical and mechanical properties. Studies of these materials on the nanometer scale in combination with measurements of oxygen transport properties are a valuable contribution to a better understanding of their defect chemistry. Therefore, transmission electron microscopic investigations were performed on LSC and LSF as well as measurements of the ionic conductivities and the chemical diffusion coefficients. Microdomains with vacancy ordered structures could be detected by analytical electron microscopy in highly oxygen-deficient samples of LSC. High resolution transmission electron microscopy revealed a superstructure within the oxygen sublattice in domains of about 100 nm in size. It is assumed that ordering leads to progressive immobilization of oxygen vacancies and consequentially to a decrease of the ionic conductivity with increasing oxygen nonstoichiometry. Similar effects are believed to be responsible for the decrease in the chemical diffusion coefficient of LSC with decreasing oxygen partial pressure.
- K/P38** ELECTROCHEMICAL DEVICE FOR THE PRECISE ADJUSTMENT OF OXYGEN PARTIAL PRESSURES IN A GAS STREAM  
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 The accessibility of an intermediate oxygen partial pressure region (e.g. approx.  $10^{-5}$  to  $10^{-16}$  bar at  $700^\circ\text{C}$ ) is of great importance when investigating the defect chemistry and the transport properties of oxides by conductivity measurements as a function of oxygen partial pressure and temperature. Stable oxygen partial pressures in this region cannot be achieved in a gas stream by simple gas mixing methods. We constructed an electrochemical cell consisting of a tube of platinum-coated yttria stabilised zirconia (YSZ), a miniaturised oxygen sensor positioned close to the sample within the YSZ-tube and an electronic process controller and could demonstrate the realizability of the precise adjustment of oxygen partial pressures stable for more than 24 hours between  $\log(p\text{O}_2/\text{bar}) = 0$  and  $\log(p\text{O}_2/\text{bar}) = -20$ . Measurements were performed at temperatures between  $700^\circ$  and  $1000^\circ\text{C}$ . The applicability of our device at lower temperatures is limited by the oxygen conductivity of YSZ and the working range of the oxygen microsensor. The device was tested by conductivity measurements on the model compound  $\text{SrTiO}_3$  (0.1 mol% Fe).
- K/P39** OXYGEN EXCHANGE MEASUREMENTS ON STRONTIUM-SUBSTITUTED LANTHANUM COBALTITES AND FERRITES  
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 Lanthanum strontium cobaltites or ferrites are mixed ionic-electronic conducting perovskites which are promising materials for oxygen separation membranes or solid oxide fuel cells. Values of the chemical diffusion coefficient and the surface exchange coefficient of oxygen were obtained from the response of disk-shaped samples to stepwise variations of the oxygen partial pressure in the carrier gas. The rate of incorporation / release of oxygen into / from the perovskite was analyzed as a function of time by means of carrier gas titration using a zirconia oxygen pump maintained at  $700^\circ\text{C}$ . In addition, the kinetic parameters for the oxygen exchange between the solid sample and the surrounding gas phase were determined simultaneously by application of conductivity relaxation experiments. Both methods were applied to homogeneous samples of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}(3-x)$  (LSC64),  $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}(3-x)$  (LSC46), and  $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}(3-x)$  (LSF46) as a function of the oxygen partial pressure ranging from 10 to 200 Pa at  $725$  and  $700^\circ\text{C}$ , respectively. Whereas the chemical diffusion coefficients are almost independent of the oxygen partial pressure, the surface exchange coefficients increase with increasing  $p(\text{O}_2)$  in each case. Both kinetic parameters were found to decrease with decreasing strontium content. The substitution of Co by Fe on the B-sites of the perovskite lattice results in a reduction of the surface exchange coefficients.
- K/P40** THERMODYNAMIC AND KINETIC INVESTIGATIONS OF NANOSIZED SILVER STRUCTURES  
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 Thermodynamic and kinetic data of nanomaterials are of great relevance for a further understanding of their physical and chemical properties and possible applications. Electrochemistry is a straight-forward method to gain such information. Three types of experiments are currently under investigation: (I) The morphology of electrodeposited Ag-structures is studied as a function of the control parameters. In particular the question is investigated under what conditions fractal, dendritic or other patterns develop. (II) Emf experiments on such electrodeposited structures as well as nano-crystalline Ag particles are performed and evaluated in terms of excess free enthalpies. (III) The time dependence of the emf is analyzed and relaxation times for the interfacial relaxation processes are extracted.
- K/P41** ELECTRICALLY PROBED NITROGEN PROFILES IN NITROGEN-STABILIZED ZIRCONIA  
 J.-S. Lee, J. Fleig, J. Maier, Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany, T.-J. Chung, School of Materials Science and Engineering, Andong National University, Kyungbuk 760-749 Korea and D.-Y. Kim, School of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea  
 When tetragonal zirconia polycrystals doped with 2 mol% yttria (2Y-TZP) embedded in ZrN are heat-treated at high temperature above  $1500^\circ\text{C}$ , a columnar growth of partially-stabilized zirconia (PSZ) grains occurs driven by nitrogen diffusion. The growth layers consist of a nitrogen-rich cubic phase matrix and nitrogen-poor tetragonal precipitates, similar to conventional PSZ with Ca, Mg, Y, etc., but long (up to  $\sim 10 \mu\text{m}$ ) interconnecting precipitates are characteristic for N-PSZ. Nitrogen diffusion profiles were electrically probed at intervals of  $20 \mu\text{m}$  or  $30 \mu\text{m}$  using microelectrodes of  $10 \mu\text{m}$  diameter. The results clearly showed that the local conductivity in N-PSZ decreases with increasing nitrogen concentration at moderate temperatures below  $400^\circ\text{C}$ , even though the nitrogen incorporation nominally produces additional ionic charge carriers, i.e., oxygen vacancies. This behavior can be attributed to the increasing dopant-vacancy interaction. Compared with zirconia doped with yttrium only, the defect interaction in the nitrated system appears to be much stronger.

K/P42

RECENT PROGRESS IN IONICALLY CONDUCTING CaF<sub>2</sub>-BaF<sub>2</sub> HETEROLAYERS

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Previously, mesoscopic size effects were demonstrated by growing artificial solid ion conductors of CaF<sub>2</sub>-BaF<sub>2</sub> heterolayers using molecular beam epitaxy (MBE) [Sata, et al. Nature 408 (2000) 946] and space-charge dominating interface effects have been supported by microstructural investigations [Jin-Phillipp et al., J. Chem. Phys. in press]. This contribution reports on current systematic studies: 1) Effects of different substrates (sapphire (012), sapphire (006), MgO (111), MgO (110)), leading to the conductivity variation of the substrate/BaF<sub>2</sub> interfaces and to the different crystallographic orientation of the CaF<sub>2</sub>-BaF<sub>2</sub> heterostructure ([111] and [100]), clarify the defect inducing mechanisms at the interfaces. 2) Variation of thickness in one fluoride (with respect to the other) permits the deconvolution of the bulk contributions of the respective fluorides and the boundary effects. 3) Electronic contribution to the conductivity is determined by dc polarization method. 4) Measurements perpendicular to the interface using a conducting Si substrate are expected to introduce a new component to the understanding of the transport mechanism of the heterostructure.

K/P43

REASONABLE k AND D FACTORS FOR MIXED CONDUCTING POROUS SOFC CATHODES

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The electrochemical performance of a solid oxide fuel cell (SOFC) strongly depends on the kinetics of the cathodic oxygen reduction reaction. In mixed ionic and electronic conducting cathodes (MIEC) this reduction reaction not only occurs via the surface of the electrode particles (three phase boundary mechanism) but also via the bulk of the electrode (bulk path). In this contribution numerical two- and three-dimensional simulations are presented which address the effect of materials parameters (oxide ion diffusivity D and oxygen incorporation rate k) on the current distribution in porous MIECs with predominant bulk path. These calculations also yield polarization resistances and reveal which combinations of D- and k-values are appropriate to achieve acceptable cathodic losses. It is, for example, demonstrated that mixed conducting oxides with ionic conductivities as low as 10<sup>-6</sup> S/cm (or oxygen tracer diffusion coefficients D as low as 3·10<sup>-12</sup> cm<sup>2</sup>/s) may still yield acceptable performance of SOFC cathodes.

K/P44

TRANSPORT PROCESSES AND ELECTRODE PROPERTIES OF SOME AN MIXED CONDUCTING COBALTITES AND CHROMITES WITH PEROVSKITE STRUCTURE

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A series of perovskite oxides have been investigated with regard to their electronic conductivity and oxygen transport properties as well as electrode properties on zirconia and Ce<sub>1-x</sub>Gd<sub>x</sub>O<sub>2-δ</sub> electrolytes.

We present results on the systems Gd<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-δ</sub>, Gd<sub>1-x</sub>Sr<sub>x</sub>Co<sub>1-y</sub>Mg<sub>y</sub>O<sub>3-δ</sub>, La<sub>1-x</sub>Ca<sub>x</sub>CrO<sub>3-δ</sub> and Gd<sub>1-x</sub>Sr<sub>x</sub>CrO<sub>3-δ</sub>. The experiments basically consisted of steady-state and time-dependent electrochemical polarisation at microelectrodes made of zirconia or ceria. The contributions due to oxygen ion transfer at the interface and electrode reaction with gaseous oxygen were separated by comparison of microcontacts with and without glass encapsulation.

The perovskites Gd<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-δ</sub> showed a remarkably high surface oxygen exchange and thus a fast oxygen electrode reaction in the temperature range 600 – 800°C, in particular in combination with Gd-doped ceria. We observed for these compounds relatively high oxygen ion conductivities, too. The chromite series La<sub>1-x</sub>Ca<sub>x</sub>CrO<sub>3-δ</sub> yielded low oxygen ion conductivities equal to or lower than 10<sup>-5</sup> Scm<sup>-1</sup> at 700°C. On the other hand, the current-voltage relations at non-encapsulated microcontacts indicated an enhanced oxygen electrode reaction at the three phase boundary.

K/P45

INFLUENCE OF GRAIN SIZE ON THE OXIDATION KINETICS OF NANOCRYSTALLINE CERIA

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Bulk ceramics of oxygen deficient cerium oxide undergo fast oxidation at room temperature [I. Riess et al. J. Appl. Phys. 61, 4931 (1987), Sol. State Ionics 28, 539 (1988)]. Nevertheless, nanocrystalline ceria may remain oxygen deficient for many months at ambient conditions. This fact poses a question related to the reason for the long term stability of nanocrystalline ceria with respect to oxidation.

We investigated oxidation kinetics of nanocrystalline CeO<sub>2-x</sub> by monitoring changes of the lattice parameter in the nanocrystalline (<30 nm) thin films prepared by argon sputtering. The as-deposited films with a stoichiometry of ≈CeO<sub>1.7</sub> remain stable at ambient conditions for many months. Nevertheless, exposure to a high-density low energy oxygen plasma for 1.5 hour results in rapid oxidation of the material. Although, the resulting lattice parameter was significantly larger than that of stoichiometric CeO<sub>2</sub>, no further changes could be induced by exposure to the oxygen plasma or to air. These data indicate that at room temperature, the oxidation rate of nanocrystalline CeO<sub>2-x</sub> is limited by incorporation of atmospheric oxygen at the film surface. It also indicates that at room temperature, the chemical diffusion coefficient of oxygen in nanocrystalline CeO<sub>2-x</sub> is extremely high (>>10<sup>-14</sup> cm<sup>2</sup>/sec). The fact that exposure to the oxygen plasma does not lead to a complete oxidation of the nanocrystalline CeO<sub>2-x</sub>, confirms that the surface energy is a major factor affecting the stoichiometry of CeO<sub>2-x</sub> [J. Maier, Sol. State Ionics 157, 327 (2003); S. Kim et. al. Surf. Sci. 549, 196 (2004)].

16:00

**BREAK**

## Session IX: Anion conductors

Session chair: Harry L. Tuller

**K-IX.1** 16:30 -Invited-

NEW OXIDE ION CONDUCTORS BASED ON  $\text{La}_2\text{Mo}_2\text{O}_9$

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A review of the properties of newly discovered fast oxide-ion conductors  $\text{La}_2\text{Mo}_2\text{O}_9$  and LAMOX family will be presented. In the lanthanum molybdate an order/disorder phase transition at  $580^\circ\text{C}$  is accompanied by an increase of anion conductivity up to values higher than those measured on stabilized zirconias. The room temperature alpha phase is a slight monoclinic distortion with a large superstructure relative to the high temperature cubic beta phase. The transition is suppressed by most of the dopants which, above a certain substitution range, stabilize the highly conducting cubic phase. Substitution by  $\text{R}=\text{Nd}, \text{Gd}, \text{Y}$  on the La site and by W on the Mo site have been studied thoroughly with respect to the optimisation of anion conduction and stability against reduction. Oxygen loss under reducing atmosphere, a drawback in application of molybdates as electrolytes for solid oxide fuel cells, is minimized by tungsten substitution. An efficient control of the samples relative density has been achieved through attrition or ball milling, dilatometric measurements and appropriate sintering, thereby allowing a better characterisation of the transport and oxygen diffusion properties. The electronic transference number is very low, around 0.001 at  $750^\circ\text{C}$ . A specific curvature in the thermal evolution of conductivity suggests the possibility of a VTF-type conduction mechanism above a certain temperature. The high oxygen tracer diffusion coefficient relative to other oxide-ion conductors corresponds to a charge carrier number close to the occupancy of a specific, partially occupied oxygen site with a large anisotropic thermal factor. This is in good agreement with the so-called Lone-Pair Substitution concept proposed as a guiding rule to find new families of such materials.

**K-IX.2** 17:00

OXIDE-ION TRANSPORT IN GADOLINIUM ZIRCONATES UNDER HIGH PRESSURE

H. Takamura, H. Kakuta, A. Kamegawa, M. Okada, CREST, Japan Science and Technology Agency, Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-yama 02, Sendai 980-8579, Japan, and H. L. Tuller, Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

Pyrochlore compounds,  $\text{A}_2\text{B}_2\text{O}_7$ , 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 ( $\text{Gd}_2\text{Zr}_2\text{O}_7$ ; GZ), for example, exhibits a high oxide-ion conductivity of  $10^{-2}$  S/cm at 1273 K without acceptor dopants; Frenkel-type defects on the oxygen sub-lattice are responsible for the high oxide-ion conductivity. To further understand the nature of the formation of Frenkel-type defects and oxide-ion transport in GZ, we performed conductivity measurements under high pressure in the range of 2 ~ 6 GPa. Activation volumes for defect formation,  $\Delta V_f$ , and oxide-ion migration,  $\Delta V_m$  may be extracted from the pressure dependence of the conductivity. A cubic-anvil-type apparatus was used to achieve pseudo hydrostatic pressures. In addition to GZ, the electrical conductivities of Ti-doped GZ and Y-doped zirconia (8YSZ) were evaluated as functions of pressure and temperature. The activation volume,  $\Delta V$ , the sum of  $\Delta V_f$  and  $\Delta V_m$ , of GZ and 8YSZ, was found to be 2.5 and 0.4  $\text{cm}^3/\text{mol}$  at 973 K, respectively. Moreover,  $\Delta V$  decreased rapidly with increasing Ti content; for 10mol%Ti-doped GZ,  $\Delta V$  was 1.5  $\text{cm}^3/\text{mol}$  at 973 K. The deconvolution of  $\Delta V$  into  $\Delta V_f$  and  $\Delta V_m$  was examined.

**K-IX.3** 17:20

HIGH CONCENTRATION OF OXYGEN RADICALS IN  $12\text{CaO}\cdot\text{Al}_2\text{O}_3$ : EFFECTS OF STABILITY AND DIFFUSIVITY OF EXTRA-FRAMEWORK OXYGEN SPECIES

K. Hayashi, M. Hirano and H. Hosono, Japan Science and Technology Agency, KSP C-1232, Kawasaki 213-0012 Japan

$12\text{CaO}\cdot\text{Al}_2\text{O}_3$  ( $\text{C}_{12}\text{A}_7$ ) has positively-charged lattice framework, where various anions can be incorporated in cages. Although only oxide ions occupy one-sixth of cages under the stoichiometric composition, it has been found that high concentration of oxygen radicals,  $\text{O}^{\cdot-}$  and  $\text{O}^{2-}$ , up to  $\sim 2 \times 10^{-3}$   $\text{cm}^{-3}$  (one-third of total cages) can be formed by heat-treatments in oxidizing atmosphere. In the present study, the thermodynamics and kinetics of oxygen radical formation in a dry atmosphere is examined based on isothermal annealing experiment at  $550\text{--}700^\circ\text{C}$  to elucidate the reason why  $\text{C}_{12}\text{A}_7$  stably incorporates such highly reactive species. The formation process of oxygen radicals,  $\text{O}^{\cdot-}$  and  $\text{O}^{2-}$ , is interpreted from the outward diffusion of extra-framework oxide ions, its oxidation by absorbed oxygen molecules to form  $\text{O}^{\cdot-}$  and  $\text{O}^{2-}$  at the surface, and subsequent inward diffusion of the oxygen radicals. The instability of the extra-framework oxide ions is essentially the driving force for this process. The rate-limiting process for the radical formation is not the surface reaction, but the total ionic diffusion process, where the smaller diffusivity of  $\text{O}^{2-}$  likely dominates the process.

OXYGEN MOBILITY AND ELECTRICAL CONDUCTIVITY OF PEROVSKITE-LIKE CUPRATES  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-d}$  AND  $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{3-d}$   
S.N. Savvin, E.V. Mychka, G.N. Mazo, Chemistry Department of Moscow State University, 119899 Moscow, Russia, L.S. Leonova, Yu.A. Dobrovolsky, Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia

Perovskite-like complex oxides that possess enhanced mobility of oxygen have been studied intensively for the last decade ( $\text{LaCoO}_3$ ,  $\text{LaMnO}_3$ ). The compounds are believed to be promising candidates for various technological applications: SOFC electrodes, gas-separating membranes, oxygen sensors. Ability of B-cation to change oxidation state easily on heterovalent doping in A-sublattice results in substantial concentration of vacancies in anion sublattice.

Samples of cuprates  $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{3-d}$  ( $x=0,15; 0,3$ ),  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-d}$  ( $x=0,15; 0,3; 1$ ) were prepared by solid-state route at air. XRD analysis revealed that the samples were single-phase and EDX results confirmed that cationic composition of the samples corresponded to the one initially intended. Electrical conductivity of a sintered polycrystalline ceramics of the cuprates was studied by four-point dc-technique in the atmosphere where oxygen partial pressure was varied from  $10^{-4}$  Pa to 101 kPa. Electrical conductivity measurements for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-d}$  ( $x=0,3; 1$ ) and  $\text{La}_{0,7}\text{Sr}_{0,3}\text{CuO}_{3-d}$  were performed in a temperature range of 300-1170K. Conductivity of  $\text{La}_{1,7}\text{Sr}_{0,3}\text{CuO}_{4-d}$  (750  $\Omega\text{-cm}^{-1}$ , 300K, air) and  $\text{La}_{0,7}\text{Sr}_{0,3}\text{CuO}_{3-d}$  (2260  $\Omega\text{-cm}^{-1}$ , 300K, air) were found to decrease on heating, demonstrating metallic-like temperature dependence. On the contrary, heating of the highly-doped sample  $\text{LaSrCuO}_{4-d}$  (1.76, 300K,  $\Omega\text{-cm}^{-1}$ , air) above 710K lead to the change from semiconductor- to metal-like behavior. Possible mechanisms of the conduction are discussed.

Friday, May 28, 2004

Morning

Session X: Applications

Session chair: Tatsumi Ishihara

- K-X.1** 8:30 -Invited- **LOW TEMPERATURE PREPARATION OF PHOSPHATES FOR LI BATTERY APPLICATIONS**  
**Christian Masquelier**, C. Delacourt, C. Wurm, L. Laffont, P. Poizot, M. Morcrette, J.M. Tarascon LRCS, Université Picardie Jules Verne, Amiens, France  
Much attention has been given recently to the reversible electrochemical insertion of lithium from the olivine-type LiFePO<sub>4</sub> operating on the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple at ~3.5 V vs. Li<sup>+</sup>. When Mn is partly substituted for Fe in the olivine structure, Li<sub>1-x</sub>Fe<sub>1-y</sub>Mn<sub>y</sub>PO<sub>4</sub> compositions operate as well on the Mn<sup>3+</sup>/Mn<sup>2+</sup> redox couple located at ~4 V vs. Li. Recent studies have also demonstrated the reversible electrochemical reaction of lithium with « hydrated » iron phosphates FePO<sub>4</sub>.nH<sub>2</sub>O or Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub>.nH<sub>2</sub>O at interesting average operating voltages of 3.1 V vs. Li. This was demonstrated either for very fine particles (< 100 nm) of amorphous compositions or for highly crystalline forms such as metastrengite FePO<sub>4</sub>.2H<sub>2</sub>O.  
We explored systematically the thermodynamics (temperature, pH, pressure, nature and concentrations of the precursors, ...) and the kinetics (duration, mixing, germs, ...) that govern the precipitation in aqueous solution of three distinct crystalline forms of FePO<sub>4</sub>.2H<sub>2</sub>O and of pure LiMnPO<sub>4</sub>. Our attempts to precipitate LiFePO<sub>4</sub>, on the other hand, failed. In this latter case, optimized electrodes for battery applications were synthesized through a chemical conductive carbon coating at the surface of LiFePO<sub>4</sub> prepared by evaporation of an aqueous solution.
- K-X.2** 9:00 **DEFECT STRUCTURE OF LITHIUM MANGANESE SPINELS (Li:Mn=1:2) CHARACTERISED BY XRD, DSC, TGA AND RAMAN SPECTROSCOPY**  
**M. Molenda**, R. Dziembaj\*, L.M. Proniewicz, E. Podstawka, Faculty of Chemistry, Jagiellonian University, \*Regional Laboratory of Physicochemical Analyses and Structure Researches, ul. Ingardena 3, 30-060 Cracow, Poland  
Lithium manganese spinels are promising cathode materials for 4V lithium ion batteries which may replace more expensive and toxic LiCoO<sub>2</sub>. Stoichiometric LiMn<sub>2</sub>O<sub>4</sub> shows first order phase transition from cubic to orthorhombic structure around 290 K which may impact the performance of cathode material [1]. It is supposed that this transformation is driven by Jahn-Teller distortion of high spin Mn<sup>3+</sup> (t<sub>2g</sub><sup>3</sup>e<sub>g</sub><sup>1</sup>) ions [2]. It is well known that properties of lithium-manganese spinels are strongly depended on method and conditions of preparation.  
A series of lithium-manganese spinels (Li:Mn=1:2) were obtained using sol-gel method. The materials were calcined at various temperatures (300-900°C) in air for 24h and then quenched to freeze the structure. The samples were characterized using X-ray diffraction method with Rietveld analysis, Raman spectroscopy, TGA-MS and DSC compared with results of the electrical conductivity. It was shown that materials calcined at 300-700°C are defect spinel with formula Li<sub>1-x</sub>Mn<sub>2-2x</sub>O<sub>4</sub>, while calcinations above 800°C results in formation of oxygen vacancies according to formula LiMn<sub>2</sub>O<sub>4-y</sub>. Materials with composition close to stoichiometric showed phase transition around room temperature. Measured enthalpy of this transformation correlated well with observed changes in the electrical conductivity of samples, thus it was possible to propose the model of phase transition. Performed Raman spectra confirmed proposed changes in local structure in manganese sublattice. REFERENCES 1. G. Rousse, C. Masquelier, J. Rodriguez-Carvajal, M. Herveu, Electrochem. Solid-State Lett. 2 (1) 6 (1999) 2. A. Yamada, M. Tanaka, K. Tanaka, K. Sekai, J. Power Sources, 81-82 (1999) 73
- K-X.3** 9:20 **ENHANCEMENT OF THE ELECTRONIC CONDUCTIVITY BY MAGNESIUM DOPING OF COBALTITE CATHODES FOR LITHIUM BATTERIES**  
**Fausto Croce**, Dipartimento di Scienze del Farmaco, Università 'G.D. Annunzio', Via dei Vestini 31, 66013 Chieti, Italy, Francesco Nobili, Roberto Marassi, Dipartimento di Scienze Chimiche, Università di Camerino, 62032 Camerino, Italy  
LiCoO<sub>2</sub> is the state of art compound as cathode for Li-ion batteries. It is well known that this oxide undergo a transition in the electronic structure upon Li ion de-intercalation-intercalation process which provoke a dramatic change in the material electronic conductivity. This change reflects in the ionic lithium mobility and can represent a severe limitation of the overall cathodic performances.  
In this presentation we present experimental evidences on the variation of the electronic conductivity of LiCoO<sub>2</sub> cathode upon structural Li electrochemical insertion and de insertion and on how the Mg-doping, by modifying the material electronic structure, enhances its electronic conductivity.

**K-X.4** 9:40

STRESS EFFECTS IN LITHIUM INTERCALATION INTO AMORPHOUS WO<sub>3</sub> THIN FILMS

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Amorphous intercalation materials are potentially useful as electroactive electrodes for energy storage and smart devices such as electrochromic windows. These materials are characterized by a high degree of disorder and show rather distinct properties with respect to their crystalline counterparts.

Lithium intercalation into amorphous thin films was experimentally investigated. The working electrode potential (the chemical potential) and the chemical capacitance (or the thermodynamic factor) dependencies on the insertion level were determined by constant current titration. The chemical diffusion coefficient was measured by means of electrochemical impedance measurements and the jump diffusion coefficient was calculated. As observed both the diffusion coefficients decrease with increasing the insertion level. In order to explain consistently the results for the chemical capacitance, the chemical and jump diffusion coefficients, it is proposed to take into account contribution of the interaction energy of intercalant particles with the host as a power concentration dependence. This contribution takes into account selfstresses that arise in the host due to insertion of guest particles. At the same time the lattice distortion increase the intersite barriers for hopping, causing a decrease of the jump diffusion coefficient with increasing extent of intercalation. Power law dependencies of the diffusion coefficients and the chemical capacitance on the insertion concentration are approved by experimental results. The approach presented indicates that the description of the hopping process of Li in a-WO<sub>3</sub> requires a more complex model in which both the bottom of potential wells and average barrier heights are dependent on the insertion level.

10:00

**BREAK**

Session XI: Applications

Session chair: Christian Masquelier

**K-XI.1** 10:30 -Invited-

THE ROLE OF DEFECT CHEMISTRY IN PREDICTING FEASIBILITY OF HIGH TEMPERATURE RESONANT SENSORS BASED ON La<sub>3</sub>Ga<sub>5</sub>SiO<sub>14</sub>

**Harry L. Tuller** and H. Seh, Department of Materials Science and Engineering, MIT, Cambridge MA 02139, USA, H. Fritze and M. Schulz, Institut für Metallurgie, TU Clausthal, 38678 Clausthal-Zellerfeld, Germany

Langasite (La<sub>3</sub>Ga<sub>5</sub>SiO<sub>14</sub>), a piezoelectric material with no phase transitions to the melting point, is promising as the basis of high temperature resonant sensors. To successfully implement such a device, electrical losses and mass changes brought about by stoichiometry variations need be minimized. The defect and transport properties of nominally undoped and doped langasite are characterized by impedance spectroscopy and oxygen exchange as functions of temperature and oxygen partial pressure. Defect and transport models are used to extract key thermodynamic and kinetic parameters. These are used to predict conditions under which langasite can be effectively utilized as a microbalance platform.

**K-XI.2** 11:00

PARTIAL REDUCTION AND RE-OXIDATION OF IRON- AND COBALT-CONTAINING PEROVSKITES USING CATALYST CHARACTERISATION MEASUREMENTS

[A. Mai](#), F. Tietz, D. Stoever; Forschungszentrum Juelich GmbH, 52425 Juelich, Germany

The oxygen uptake and release of La<sub>1-x-z</sub>Sr<sub>x</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3- $\delta$</sub> ; (x = 0.2, 0.4; y = 0, 0.2, 1) perovskite powders was examined with temperature-programmed techniques. In addition to the commonly used temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO) was used to examine oxygen adsorption on the perovskites that were partially reduced before. While the perovskites' reduction started slowly at an offset temperature of about 300 °C, the reoxidation started already below 100 °C resulting in a distinct reoxidation peak. The measured oxygen stoichiometry changes were in the range of  $\delta$  = 0.03 – 0.18. For the reoxidation process, surface-controlled kinetics were assumed, allowing the use of standard temperature-programmed desorption (TPD) procedures to determine the activation energy of the adsorption process. Simulation of the profiles confirmed the predominant surface kinetics. The determined activation energies were in the range of 0.45 – 0.65 eV. For the presented measurement procedure, the preparative and apparatus demands are much lower than for other surface exchange characterisation procedures and allow a pre-selection of interesting perovskite materials for the use in solid oxide fuel cells or as exhaust catalysts.

- K-XI.3** 11:20 AGING OF NANOSTRUCTURED TETRAGONAL ZIRCONIA ELECTROLYTES FOR INTERMEDIATE TEMPERATURE SOFCs  
Elisabeth Djurado, Laurent Dessemond, Florence Boulc'h, Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces, CNRS 1130, BP 75, 38402 Saint-Martin d'Hères Cedex, France  
 At present, efforts are focused on lowering the operating temperature of solid oxide fuel cells from above 900°C down to 700°C (IT-SOFC). Tetragonal zirconia (TZP) is considered as a promising candidate to be used as electrolyte in IT-SOFC, because of its good mechanical and electrical properties with comparison to cubic zirconia. However, the major drawback of TZP is the low temperature degradation caused by tetragonal to monoclinic phase transition (t-m) accompanied by microcracks. This work presents new experimental data on an aging study of nanostructured and tetragonal single-phased 2.5 mol. % Y2O3-doped ZrO2 ceramics first in the IT-SOFC operating conditions and secondly at 250°C for 1000 hours in steam atmosphere. Excellent results were obtained: at 700°C, only a weak decrease of conductivity was measured due to the appearance of less than 2 mol % of monoclinic zirconia. An excellent stabilization of TZP was obtained contrary to the present literature, probably because of favorable microstructural characteristics of the materials. In-situ impedance and Raman spectroscopies have been coupled to correlate the electrical properties and phase content in order to bring new insight in the mechanism of monoclinic degradation at 250°C. Finally, we can conclude that because of the absence of hydroxide ions signature in Raman spectra neither on the surface nor in the volume, we can assess that no Zr or Y hydroxides interact in the tetragonal-monoclinic transformation mechanism of yttria-doped zirconia as predicted by the literature. Water molecule adsorption on the particle surface and then intergranular diffusion seem to be at the origin of this structural transformation.
- K-XI.4** 11:40 ALUMINA SINGLE CRYSTAL GROWTH BY USING THE Al<sup>3+</sup> CONDUCTING SOLID ELECTROLYTE  
S. Tamura, Y.-W. Kim, T. Masui and N. Imanaka, Department of Applied Chemistry, Faculty of Engineering, Osaka University, Japan  
 Delta(Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>)-Al<sub>2</sub>O<sub>3</sub> single crystals were successfully grown by dc electrolysis of the Al<sup>3+</sup> ion conducting Delta(Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>)-Al<sub>2</sub>O<sub>3</sub> solid electrolyte at 1173 K with 11 V. The Al<sub>2</sub>O<sub>3</sub>-alumina is the intermediate phase in the transformation from Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> to Al<sub>2</sub>O<sub>3</sub> and is generally obtained only in the narrow temperature range between 923 and 1223 K as a polycrystalline phase. Therefore, the Al<sub>2</sub>O<sub>3</sub>-alumina single crystal has not been grown by the conventional methods such as Czochralski (CZ) and floating zone (FZ) methods because it is necessary to melt the starting material over melting point of alumina (2273 K) in order to grow the single crystal and Al<sub>2</sub>O<sub>3</sub> single crystal can only be obtained by those methods. On the other hand, the present dc electrolysis method can be simply applicable at moderate temperatures around 1173 K for the single crystal growth and, therefore, an intermediate phase of Al<sub>2</sub>O<sub>3</sub>-alumina can be artificially grown in a single crystal form. Furthermore, the particle size is also able to be controlled intentionally by adjusting the electrolysis period.  
 Since the dc electrolysis of the solid electrolyte can be carried out in such a temperature region of considerably lower than the melting point of refractory oxides, the present single crystal growth technique is one of the most effective ways to obtain a single crystal of the intermediate oxides such as Al<sub>2</sub>O<sub>3</sub>-alumina which can not be grown by the conventional methods via melt process.
- K-XI.5** 12:00 ELECTROSTATIC SPRAY ASSISTED VAPOUR DEPOSITION OF TiO<sub>2</sub>-BASED FILMS FOR GAS SENSING  
Jing Du and Kwang-Leong Choy, School of Mechanical, Materials, Manufacturing Engineering and Management, University of Nottingham, University Park NG7 2RD, U.K.  
 TiO<sub>2</sub> is one of the best candidates for gas sensing because of its low cost, stable phase even at higher temperature, high gas sensitivity and comparable thermal expansion coefficient to alumina substrate. Further improvement in the performance can be achieved by addition of trivalent or pentavalent dopants. Recently a novel Electrostatic Spray Assisted Vapour Deposition (ESAVD) technique has been used to prepare thin or thick films of various materials. This method offers many advantages over conventional deposition techniques, such as flexibility, inexpensive, high deposition efficiency, use of benign precursor and precise control of the surface morphology and stoichiometry of the deposited films. The ability to control morphology is of particular interest for gas sensor applications because the surface of the film is primarily involved in the initial sensor/gas interaction. This paper reports the relationships of process, structure and stoichiometry of TiO<sub>2</sub> based films incorporated with Cr and Nb doped metal ions deposited by EASVD. Scanning electron microscopy (SEM) was used to characterise the microstructure and surface morphology of the films. Both X-ray diffraction (XRD) and SEM equipped with Energy dispersion X-ray (EDX) were employed to determine the crystal phase and composition of the film. X-ray photoelectron spectroscopy (XPS) was used to analyse the chemical stoichiometry of the deposited films.
- K-XI.6** 12:20 INVESTIGATION OF SURFACE CHEMISTRY OF Sb-DOPED SnO<sub>2</sub> GAS SENSORS BY SYNCHROTRON RADIATION INDUCED XPS AND UPS AND THE EFFECT ON GAS-SENSING CHARACTERISTICS  
A. Panupat, National Metal and Materials Technology Center, Thailand Science Park, Pathumthani 12120, Thailand and U. Korkerd, Department of Material Science, Chulalongkorn University, Bangkok 10400, Thailand  
 Tin oxide is a widely used material for gas sensing applications, its response being a change in conductance on exposure to oxidising or reducing gas. As the function of a gas sensor depends on redox reactions at the surface, the condition of the surface layer is of crucial importance. Surface chemistry of antimony doped tin oxide, prepared by conventional ceramic processing, has been studied by synchrotron radiation induced XPS and UPS. The samples were doped with different concentration of antimony (0.3 - 1.0 wt%) and sintered in different atmosphere, namely in air and in N<sub>2</sub>. The effect of dopant concentration and sintering condition on the surface chemistry and dopant segregation were systematically investigated by XPS, UPS and electron microscopy techniques. Gas sensitivity and response time of antimony doped tin oxide to iso-butane gas were measured at 350 C. The effect of surface chemistry on gas sensing characteristics is discussed.