2014 Spring Meeting Lille, France – May 26th - 30th

SYMPOSIUM C

Solid state ionics: thin films for energy and information applications

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Igor Lubomirsky, Department of Materials and Interfaces, Rehovot , Israel

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PROGRAM VIEW : 2014 Spring
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Solid state ionics: thin films for energy and information applications

26 May 2014 | 27 May 2014 | 28 May 2014 | 29 May 2014 | 30 May 2014

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start at	Subject	Num.
09:00	**INTRODUCTION**	
09:10	**Atomic Scale Verification of Oxide-Ion Vacancy Distribution near a Single Grain Boundary in YSZ** **Authors :** An, J, Park, JS, Koh, AL, Lee, HB, Jung, HJ, Schoonman, J, Sinclair, R, Gur, TM, Prinz, FB **Affiliations :** Stanford University **Resume :** This talk will describe atomic scale structures of grain boundaries in oxide ion conductors. In particular, we report experimental observations of oxide-ion vacancy concentrations near symmetric tilt grain-boundaries of YSZ bi-crystal using aberration-corrected TEM. We observed significant oxygen deficiency due to segregation of oxide-ion vacancies near the grain-boundary core with half-width < 0.6 nm. Electron energy loss spectroscopy measurements with scanning TEM indicated increased oxide-ion vacancy concentration at the grain boundary core. Oxide-ion density distribution near grain boundaries simulated by molecular dynamics corroborated well with experimental results. This talk will summarize a recently published paper in Scientific Reports: Volume: 3, Article Number: 2680, DOI: 10.1038/srep02680, Published: SEP 17 2013 add to my program (close full abstract)	C.0.1
	Strain in Mixed Binary Oxides : Prof. I. Lubomirsky and Prof. B. Yildiz	
09:40	**Anomalous Chemical Expansion of PrxCe1-xO2-δ Nanocrystalline Powders** **Authors :** Y. Kuru1,2,3, S. R. Bishop1,4, D. Marrocchelli1,5, J. -J Kim1, B. Yildiz2, H. L. Tuller1 **Affiliations :** 1Department of Materials Science & Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA ; 2Department of Nuclear Science & Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA; 3Department of Metallurgical & Materials Engineering, Middle East Technical University, Dumlupinar Bulvari No:1, Ankara, 06800, Turkey; 4International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Nishi-ku Fukuoka 819-0395, Japan; 5School of Chemistry, Trinity College Dublin, College Green, Dublin 2, Ireland **Resume :** The chemical expansion behaviour of PrxCe1-xO2-δ nanopowders were investigated between room temperature and 1075 °C in atmospheres having different O2 partial pressures by in situ X-ray diffraction measurements. The variation of crystallite size and microstrain was also determined simultaneously. Microstructures of the powders were monitored by transmission electron microscopy. Anomalous expansion was observed starting from 125 °C and it becomes more evident when Pr concentration increases and O2 partial pressure decreases. The possible mechanisms that may lead to anomalous expansion were discussed and it was confirmed that the influence of small crystallite size and microstrain can be ruled out. The information obtained in this study for PrxCe1-xO2-δ, is expected to be valid and crucial for other technologically important complex oxides. add to my program (close full abstract)	C.1.1
10:00	**Using ellipsometry with lock-in detection to measure activation energy of ion diffusion in ionic and mixed conductors**	C.1.2

Authors : Guy Lazovski1, Ellen Wachtel1, Yoed Tsur2, Igor Lubomirsky1
Affiliations : 1Dept. Materials and Interfaces, Weizmann Institute of Science, Israel 2Dept. Chemical Engineering, Technion, Israel
Resume : We describe a technique for measuring the activation energy of ion diffusion in ionic and mixed ionic/electronic conductors. The technique is based on monitoring small changes in the refractive index through a semitransparent gold contact. Constant bias voltage is applied to the sample to create a depletion layer near this front electrode. The relaxation process induced by bias removal is probed by applying alternating voltage and monitoring by ellipsometry with lock-in detection the changes in the refractive index due to changes in mass density. In this way, the diffusion of ions can be distinguished from that of protons or electrons. Measurements were made on single crystals of 8mol% Y-stabilized zirconia (YSZ8), on ceramic pellets of 20 mol% Gd doped CeO2 (GDC20) and on single crystals of 0.03 mol% Fe-doped SrTiO3 (Fe-STO). In YSZ8, a single moving species with activation energy of 0.84 eV was detected. The "wet" and "dry" states of GDC20 can be clearly distinguished: in the "wet" state there are mobile species other than oxygen vacancies, most likely protons. In Fe-doped SrTiO3, the proposed technique can reliably measure the activation energy of oxygen vacancy diffusion on a background of the much larger electronic conductivity.

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10:20 **BREAK**

10:40 **Isolating the influence of microstructural and strain properties on the oxygen ion transport in YSZ thin films**
Authors : George F. Harrington, Andrea Cavallaro, Stephen J. Skinner, David W. McComb, John A. Kilner
Affiliations : 1) Department of Materials, Imperial College London, London, UK 2) Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio, USA
Resume : Strain effects in YSZ thin films have been a topic of controversy lately with reports of enhancements and reductions in the oxygen ion conductivity compared to bulk ranging over several orders of magnitude [1,2]. Variations in fabrication, processing and measurement techniques employed may be potential causes for this disparity in the literature, as well as an ambiguity in the charge carrier when measuring the transport properties of such systems electrically [3]. We have fabricated highly textured YSZ thin films oriented in the (111) direction onto MgO and sapphire, and the (100) direction onto MgO, LAO and NGO using pulsed laser deposition (PLD). This allows the effect of lattice mismatch to be isolated while keeping the less well defined properties consistent. The films correspond to a range of lattice mismatches from 4.5% tensile to 18% compressive, and have been grown at a number of thicknesses in order to investigate interfacial effects. Impedance spectroscopy combined with isotope tracer diffusion will be shown to directly and unambiguously measure the oxygen ion transport properties in these films. This allows compositional, micro- and nano-structural variations observed in the film interfaces using HR-TEM to be associated with changes in the conduction properties. We will present evidence to show that a regular dislocation network at YSZ/substrate interfaces does not in fact drastically alter the conduction properties despite being linked to enhanced conduction properties previously [1, 4]. 1. Sillassen, M., et al., Adv. Funct. Mater., 2010. 20(13): p. 2071-2076. 2. Gerstl, M., et al., Phys. Chem. Chem. Phys., 2013. 15: p. 1097 - 1107. 3. Kim, H.-R., et al., Phys. Chem. Chem. Phys., 2011. 13(13): p. 6133-6137. 4. Korte, C., et al., Monatsh. Chem., 2009. 140(9): p. 1069-1080.

C.1.3

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11:00 **Growth of Ca3Co4O9 on CGO dense pellet by Pulsed Laser Deposition and thin film characterizations by XRD, TEM, EIS and Ellipsometry.**
Authors : M.-H. Chambrier, I. Kehal, G. Mignardi, X. Flandre, V. Thoréton, A. Rolle ,S. Estradé, J.-F. Blach, C. Pirovano, S. Daviero-Minaud, R. N. Vannier
Affiliations : Univ Lille Nord de France, F-59000 Lille, France ; CNRS, UMR 8181, F-59650 Villeneuve d'Ascq, France; ENSCL, UCCS, F-59652 Villeneuve d'Ascq, France; UArtois, UCCS, F-62300 Lens, France; LENS,MIND-In2UB, Electronics Department, Universitat de Barcelona (UB),Mart'i Franqu's 1, Barcelona 08028, Spain
Resume : In the energetic concern, Solid Oxide Fuel Cells (SOFC) could be an interesting alternative to produce energy. The heart of these electrochemical cells is based upon the assembly of porous electrodes and dense electrolyte. This study was devoted to the promising electrode material Ca3Co4O9 □ (CCO)

C.1.4

and the effect of the shaping of the electrodes and SOFC cells, on the electrochemical properties. To study the effect of a dense CCO layer at the interface between the dense CGO pellet and the CCO porous layer, a dense thin film was deposited on both sides of dense CGO pellets by Pulsed Laser Deposition (PLD). For this purpose, a 1 inch in diameter CCO PLD target, sintered at 900?C was used. As the electrochemical characterizations required symmetrical cells with defined surface-electrode layer, the CGO pellets were packed in a gold sheet fixed to a heat plate using silver on one side, and with a 10 mm in diameter hole, one the other side. Thin film deposition was carried out at temperature of 720?C, under a pressure of 10-1 mbar and with a laser frequency of 2Hz. All films were deposited for 9000 pulses to give more or less the same nominal thickness. The X-ray diffraction characterizations were performed using a 9 kW rotating anode in rasing mode for the precise characterization of thin films. In order to estimate the thickness, ellispometry measurements crossed with TEM observation have been done. TEM samples were prepared by Focused Ion Beam using the lift-out technique. Interestingly, as revealed by impedance spectroscopy the resistance of polarization of the sample with an interfacial dense layer was half that of sample without any interfacial layer.

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11:20 **Rare-earth elements-doped ceria: a correlation between the elastic/inelastic properties, ionic radii and vacancies concentration**

Authors : Roman Korobko1, Chien-Ting Chen2, Sidney Cohen1, Ellen Wachtel1, Sangtae Kim2, Anatoly Frenkel3, Igor Lubomirsky1

Affiliations : 1Weizmann Institute of Science; 2UC Davis; 3Yeshiva University

Resume : Elastic modulus, E, and room temperature creep rate constant, A, were measured by nanoindentation technique in CeO2 doped with Pr3+, Gd3+, Lu3+ and Pr4+ high density ceramics (x=0-20 mol%, Shannon’s radii Pr4+ < Ce4+ < Lu3+<105pm) of Pr3+ and Gd3+, E is independent of dopant concentration, whereas for small ones (<98pm) Pr4+ and Lu3+, E is higher than that of CeO2. All ceramics exhibited viscoplastic primary creep with the displacement ∝A•time^(1/3). A, has a maximum for Pr3+- and Gd3+-doped ceria at 3mol%, then decreases linearly with x, becoming the same for both dopants. For Pr4+- or Lu3+-doped ceria, A is much lower than that for CeO2 and independent of x. Strong inelastic behavior of ceria doped with large ions suggests that a rearrangement of vacancy-related point defects may be a primary source of creep. Similarity in elastic/inelastic behavior of Pr4+- and Lu3+-doped ceria and the dependence of the lattice parameters on x suggests that the contribution of oxygen vacancies to the mechanical properties of doped ceria is minor and questions the accuracy of Shannon’s radius for Lu3+ in octahedral coordination. Measurements of Lu-O bond lengths with EXAFS prove that Lu3+ radius is actually 9% smaller than Shannon’s value, and it is actually smaller than both Pr4+ and Ce4+. C.1.5

add to my program **(close full abstract)**

11:40 **Impact of Strain State and Buckling on the Ionic Transport of Free-Standing Membrane vs. Self-Supported Pt-Gd0.2Ce0.8O1.9-x-Pt Micro-Electrode Structures**

Authors : Yanuo Shi, Sha Li, Markus Kubicek, Jennifer L.M. Rupp

Affiliations : Electrochemical Materials, Department of Materials, ETH Zurich

Resume : Free-standing and ionic conducting metal oxide membranes receive substantial attention for next generation micro-solid oxide fuel cells. It is reported that strain variations can affect the ionic migration and association energies in oxide films based on computational results. However, for free-standing membranes experimental measurements correlating strain to ionic transport are missing. In this work, we connect supported and free-standing Gd0.2Ce0.8O1.9-x membranes to secondary in-plane Pt micro-electrodes and study directly the impact of compressive strain patterns to locally resolve ionic transport. Supported and free standing samples were fabricated and in-situ analyzed in ionic transport changes and optical profilometry. Substrate supported films reveal an activation energy of 0.73 eV for zero-strain. Comparison to the free-standing membranes with same electrode geometry show that a local compressive strain results in an increase of the ionic conductivity activation energy by Δ0.27 eV for 0.42% of local strain (stress of ~1.31 GPa) between the electrodes. Furthermore, electrodes were varied by change in design. We report a measurable impact of strain on ionic conduction for micro-SOFCs and confirm that compressive local strain affects the activation energy of ionic transport. The effective strain of the oxide membrane depends C.1.6

on the electrode area, pattern. This implicates new guidelines for micro-devices in which the oxide membranes are the functional part.

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12:00 **Open circuit potential and Ohmic resistance of micro-SOFC employing a GDC electrolyte**

Authors : Gyeong Man Choi, Younki Lee, Sun Woong Kim

Affiliations : Department of Materials Science and Engineering/ Fuel Cell Research Center, Pohang university of Science and Technology (POSTECH), Pohang, 790-784 Korea

Resume : Micro-SOFC, miniaturized Solid Oxide Fuel Cell for low temperature operation, is being developed for the power source of portable electronic devices. Reducing the thickness of cell components with thin film process, especially the electrolyte of high oxygen-ion conductivity, is needed to avoid the large Ohmic resistance below ~450oC. However, as the cell components are getting thinner into the sub-micrometer scale, the open circuit potential is reduced due to the difficulty of deposition of pore-free film and the oxygen permeation across the film. In this paper, we have discussed the ionic conductivity of Gd-doped ceria thin films measured under “in-plane mode” or “across-plane mode” in addition to the design, the fabrication process and the electrochemical performance of micro-SOFCs. C.1.7

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12:20 LUNCH

Surface Reactivity and Transport of Oxides : Prof. J. Fleig and Prof. W. Sitte

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14:00 **Dynamic Interaction of Surface Point Defects with H2O and CO2 in Cerium Oxide**

Authors : William C. Chueh

Affiliations : Department of Materials Science & Engineering, Stanford University

Resume : Surface electrochemical reactions are ubiquitous in many energy conversion systems. Of immense technological interests are solid-state electrochemical reactions that occur at the solid/gas interface in oxide electro-catalysts, such as those in oxygen-ion-conducting solid-oxide fuel cells and electrolyzers. Unlike their liquid counterparts, these electrochemical reactions involve the simultaneous transfer of ions and electrons between the solid and the gas. In this talk, I will present a complete set of X-ray photoelectron and absorption spectroscopy studies on the surface of nonstoichiometric cerium oxide in H_2/H_2O and CO/CO_2 atmospheres. We directly observed the dynamics of surface oxygen vacancy, polaron, and adsorbate as electrochemical reactions take place. C.2.1

add to my program (close full abstract)

14:30 **Redox activity of surface lattice oxygen in Fe & Co based perovskites revealed by operando spectroscopy**

Authors : David N. Mueller(1), Michael L. Machala(1), Hendrik Bluhm(2), William C. Chueh(1)

Affiliations : (1)Department of Materials Science & Engineering, Stanford University, 496 Lomita Mall, Stanford, CA 94305, USA (2) 2Chemical Sciences Division, Lawrence Berkeley National Laboratory,1 Cyclotron Road, Berkeley, CA 94720, USA

Resume : Oxygen reduction and oxygen evolution reactions limit the efficiency of many electrochemical devices. Great efforts have been made to optimize perovskite-type oxides towards catalyzing these reactions. It is understood that bulk chemistry and stoichiometry of these compounds impacts their electrochemical activity. However, because the reactions take place at the oxide surface, it is imperative to assess the surface electronic structure and chemistry, in order to understand these materials and guide rational design for next generation catalyst materials. We systematically investigated model thin-film electrodes of (La, AE)(TM)O(3-d) where AE = alkaline earth ions and TM = first-row transition metal ions) in operando using surface-sensitive and element-specific X-ray spectroscopies. In all compositions, we found that lattice oxygen near the surface is electrochemically-active during the oxygen reduction and evolution reactions, independent of the cation stoichiometry. That is, the oxygen undergoes oxidation state changes under reaction conditions. This opens up a new vantage point to identify the role of the transition metal in conjunction with the oxygen redox chemistry, leading to a better understanding of the reason behind the superior electrochemical activity of complex perovskite compositions. C.2.2

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15:00

Evidence for the formation of higher order Ruddlesden-Popper phases in thin film air electrodes by HS-LEIS

Authors : Helena Téllez(1,2), Kuan-Ting Wu(2), Mónica Burriel(2), Yan Chen(3), Bilge Yildiz(3), John Kilner(1,2), Stephen Skinner(2), Tatsumi Ishihara(1)

Affiliations : (1) International Institute for Carbon-Neutral Energy Research, Kyushu University, Japan; (2) Department of Materials, Imperial College London, London, UK; (3) Laboratory for Electrochemical Interfaces, Massachusetts Institute of Technology, US

Resume : Ruddlesden-Popper layered oxides (R-P) with the general structure An+1BnO3n+1 show fast oxygen surface exchange kinetics and are promising candidates for intermediate-temperature solid-oxide fuel cells. In contrast to traditional cathodes, such as LSM, the surface exchange process in these mixed ionic-electronic conductors (MIECs) is not limited to the triple phase boundary but to the entire surface exposed to the gas phase. Therefore, it is critical to understand the surface and near-surface chemical composition and microstructure as they will strongly influence the surface exchange properties of these MIECs. Furthermore, the surface composition might be significantly different from the bulk due to the formation of secondary phases, cation and impurity segregation. Additionally, the R-P index (n) can be easily altered due to processing and operating conditions of the ceramic electrodes since these R-P phases are very closely related differing only in the stacking sequence of the perovskite (ABO3)n and rock salt (AO) layers. In this work, we apply high-sensitivity low-energy ion scattering (HS-LEIS) to investigate the dynamic nature of La1-xSrxCoO4 and Lan+1NinO3n+1 thin film cathodes prepared by PLD. The semi-quantitative compositional analysis of the outermost and near-surface reveals the formation of higher index RP secondary phases and other processes that may decrease the active surface area during the deposition and processing of the thin film cathodes.

C.2.3

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15:20

The correlation of cation segregation, film morphology and oxygen reduction reaction of La0.6Sr0.4CoO3-δ thin films

Authors : Rupp G. M., Limbeck A. and Fleig J.

Affiliations : Rupp G. M., Vienna University of Technology; Limbeck A., Vienna University of Technology; Fleig J., Vienna University of Technology

Resume : Many research activities in the field of solid oxide fuel cells focus on lowering operating temperatures to reduce cost and compatibility issues of the cell components. However, it remains a challenge to find suitable intermediate temperature cathode materials. One of the most promising cathode materials is Sr-doped LaCoO3 (LSC), as it offers both mixed ionic-electronic conductivity and acceptable catalytic activity for the oxygen reduction reaction (ORR). Still, degradation of electrochemical kinetics occurs that is most likely correlated to changes of the electrode surface and yet not fully understood. In this contribution, La0.6Sr0.4CoO3-δ thin films (~250 nm) deposited on yttria-stabilized zirconia (100) substrates by pulsed laser deposition were used to perform a systematic study on the inter-relation between surface composition, film morphology and electrochemical performance. Deposition parameters were varied and films of different microstructure were thus obtained. A novel way for analyzing the chemical surface composition by means of in-situ etching procedure with subsequent inductively coupled plasma mass spectrometry (ICP-MS) analysis using different eluents was employed. This allowed identification and quantification of a water-soluble Sr surface phase. Furthermore, the electrochemical kinetics was investigated by electrochemical impedance spectroscopy (EIS) and reveals a performance decrease of the ORR over time which is not solely connected to Sr segregation.

C.2.4

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15:40

Evaluation of Highly Active Perovskites for the Oxygen Reduction Reaction with Single Crystal Thin Films Prepared by Pulsed Laser Deposition

Authors : Dengjie Chen, Chi Chen, Francesco Ciucci

Affiliations : Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Hong Kong, SAR China.

Resume : Solid oxide fuel cells (SOFCs) are devices that can convert chemical energy to electricity directly with advantages are efficient, distributable and environmental-friendly. Here, we fabricate perovskite single crystal thin films as cathodes with the composition of Ba0.6Sr0.4Nb0.1Co0.9O3-δ (BSNC) by pulsed laser deposition (PLD) to study the effect of the yttria-stabilized zirconia (YSZ) substrate orientations ((001), (110) and (111)) and film thickness (25, 50 and 100 nm) on electrochemical performance for SOFCs. Sm-doped Ceria (SDC) is deposited between YSZ and perovskite thin films in this study as an interlayer.

C.2.5

The phase structure, surface morphology and roughness of the BSNC thin films are characterized by X-ray diffraction and atomic force microscope. X-ray photoelectron spectroscopy is used to analyze the elemental composition and chemical state of the deposited thin film. Electrochemical impedance spectra measurements obtained from the symmetric cells with the configuration of BSNC /SDC/YSZ/SDC/ BSNC reveal that polarization resistance of BSNC (001) thin films (50 nm) is as low as ~0.1 Ω cm2 at 700 °C and 0.21 atm oxygen pressure. The polarization resistances of BSNC are lower than those of other perovskite electrodes, e.g. La0.6Sr0.4Co0.8Fe0.2O3-δ. It is also found that the oxygen reduction reaction (ORR) is highly dependent on both the substrate orientation and film thickness. The ORR results from thin films prove this BSNC material to be a promising candidate cathode for SOFCs to be operated in the intermediate temperature region.

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16:00 **BREAK**

16:30 **Ion transport in SrTiO3 thin films under bias load**

Authors : J. Fleig, S. Huber, K. Langer-Hansel, H. Hutter, G. Fafilek

Affiliations : Institute of Chemical Technologies and Analytics, TU Vienna, Austria

Resume : Field driven oxygen vacancy motion with (partially) blocking electrodes may lead to substantial conductivity variations in SrTiO3. In single and polycrystalline macroscopic samples, this stoichiometry polarization can be monitored by local conductivity measurements [1] and it is detrimental in dielectric applications (resistance degradation). In SrTiO3 thin films, the field driven oxygen vacancy motion is assumed to be the basis of the resistive switching effect employed in memristors [2]. However, charge transport in thin SrTiO3 films (within and without bias) is still far from being completely understood. In this study, field induced ion transport and conductivity variations in slightly Fe-doped SrTiO3 thin films (100-400 nm) were investigated by impedance spectroscopy, DC methods (I-V-curves), and 18O tracer diffusion at elevated temperatures (300-700°C). Surprising effects were found such as bias-dependent inductive loops in impedance spectra, and the unusual behavior turned out to be a consequence of time dependent current voltage relations. It can be quantitatively understood by equivalent circuit models with resistive and capacitive elements of unusual meanings. Also the role of different types of space charges (at dislocations, electrodes and within the film bulk) is discussed and polarization as well as relaxation kinetics is quantified. [1] S. Rodewald, et.al., J. Am. Ceram. Soc. 83 (2000) 1969 [2] R. Waser, Adv. Mat. 21 (2009) 2632

C.2.6

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17:00 **Oxygen Transport in Epitaxial Thin Film Cathode for Solid Oxide Fuel Cells**

Authors : Kiyong Ahn, Hyungchul Kim, Ho-Il Ji, Jongsup Hong, Kyung Joong Yoon, Ji-Won Son, Byung-Kook Kim and Jong-Ho Lee

Affiliations : High-Temperature Energy Materials Research Center, Korea Institute of Science and Technology Seoul 136-791, Republic of Korea

Resume : Micro-solid oxide fuel cells (μ-SOFCs) have received great attention as novel power sources for mobile applications because of their many intriguing properties. Electrode polarization is usually thought to be a main contributor to the performance losses of μ-SOFC, especially in relation to sluggish kinetics in cathode reactions. There is still a lack of basic understanding of the physicochemical properties of thin film cathodes. Thus far, most studies on the thin film cathodes have dealt with the measurement of their surface exchange coefficients (kchem) rather than the bulk diffusion properties (Dchem), because the surface exchange reaction is thought to be a main rate determining step in thin-film cathode. The very intricate measurement of the bulk diffusion coefficient due to its limited diffusion length is another reason for the lack of bulk diffusion studies on thin film cathodes. In a real μ-SOFC system, however, oxygen diffusion kinetics becomes very important for cathode reactions because of the extremely complex cathode structure. Hence, the transport properties of thin film cathodes should be thoroughly investigated and clarified to provide a substantial contribution on the development of a high performance cathode. Here we present our recent experimental and calculating works to make the proper interpretation of oxygen transport properties in thin film cathodes LaSrCoO3-δ (LSC), and we believe that this study can provide an actual insight into the proper implementation of thin film cathodes for high-performance μ-SOFCs.

C.2.7

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17:20 **Enhanced Oxygen Surface Reaction in $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-\delta}$ by Nanoscaled $(La_{0.6}Sr_{0.4})CoO_{3-\delta}$ Functional Layer**

Authors : L.-S. Unger1, M. Meffert2, C. Niedrig1, H. Störmer2, W. Menesklou1, S. F. Wagner1, D. Gerthsen2, E. Ivers-Tiffée1
Affiliations : 1) Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruher Institut für Technologie (KIT), 76131 Karlsruhe/Germany 2) Laboratorium für Elektronenmikroskopie (LEM), Karlsruher Institut für Technologie (KIT), 76131 Karlsruhe/Germany
lana.unger@kit.edu

Resume : In an oxygen-permeation membrane oxygen transport occurs due to a partial pressure (pO_2) gradient applied across the dense mixed-conducting membrane. $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-\delta}$ (BSCF) is a very promising candidate for such a membrane as its cubic phase, which can be stabilized by suitable doping strategies, exhibits excellent oxygen permeation properties. Electrical conductivity relaxation measurements as a function of pO_2 yield information on the oxygen transport parameters (surface exchange coefficient k_δ, diffusion coefficient D_δ). Using a closed YSZ "oxygen pump" setup facilitates measurements under varying atmospheres ($pO_2 = 10^{-5}…1$ bar). As k_δ values significantly decrease at lower pO_2, the membrane performance can be enhanced by improving the low-pO_2 oxygen surface excorporation reaction. Such an enhancement can be achieved, e.g., by applying a nanostructured oxide functional surface layer. A nanoporous $(La_{0.6}Sr_{0.4})CoO_{3-\delta}$ (LSC) coating is an interesting method as not only the surface enlargement leads to an increased overall k_δ but, moreover, the occurrence of "hetero-interfaces" could considerably contribute to the oxygen surface exchange. With the help of a combined electrochemical and transmission electron microscopy analysis the influence of such a surface activation of BSCF was investigated. Both the aspect of "hetero-interfaces" as well as possible interface reactions between the dense BSCF membrane and the nanoporous LSC functional layer are addressed.

C.2.8

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17:45 **POSTER SESSION 1**

17:45 **First principles modeling of Ag adsorption on the LMO[001] MnO_2- and LaO-terminated surfaces.**

Authors : A.U. Abuova1, T.M. Inerbaev1, A.T. Akilbekov1, Yu. A. Mastrikov2,3, E. A. Kotomin2,4
Affiliations : 1 L.N. Gumilyov Eurasian National University,Mirzoyan str.2, Astana, Kazakhstan 2 Institute of Solid State Physics, University of Latvia, Kengaraga str. 8, Riga, Latvia 3 Materials Science and Engineering Dept., University of Maryland, College Park, USA 4 Max Planck Institute for Solid State Research, Heisenbergstr.1, Stuttgart, Germany

Resume : Metallic silver is a potential component for the SOFC cathode operated at less than 800°C because of its good catalytic activity, high electrical conductivity, and relatively low cost. Different methods have been used to prepare functionalized composite cathodes with improved electrochemical performance and long term stability at reduced operating temperature. [1] In addition, even far below its melting point, silver is relatively mobile. Therefore, these concerns should be addressed prior to a long-term application of silver-based cathodes in SOFCs. To overcome this problem Zhou et. al. presented $(La_{0.8}Sr_{0.2})_{0.95}Ag_{0.05}MnO_{3-\delta}$ as a high performance intermediate temperature cathode material, in which the contained Ag functions as an effective catalyst through an intercalation/deintercalation mechanism. [2] Under cathodic polarization, Ag moves out of cathode to be deposited as small nanoclusters of Ag metal, leaving the remaining $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$ as a catalyst carrier. The Ag nanoclusters which are 5–15 nm are very active and stable in catalyzing the cathode reaction even at a reduced temperature. Under anodic polarization, the Ag moves back into the deficient sites of the LSM. This permits an easy regeneration method to restore Ag nanoclusters which may become degraded over time by fusing together, thereby losing the activity. We present results of ab initio calculations of Ag adsorption on the LMO [001] polar surface. The most energetically favourable adsorption sites on both MnO_2- and LaO-terminations have been determined. Electron charge transfer between the adsorbate and the adsorbent has been analyzed. Optimized interatomic distances have been measured. [1]. S. Uhlenbruck, F. Tietz, V. Haanappel, D. Sebold, H.P. Buchkremer, and D. Stover, Journal of Solid State Electrochemistry 8 (2004) 923-927. [2] W. Zhou, Z. Shao, F. Liang, Z.-G. Chen, Z. Zhu, W. Jin, and N. Xu, Journal of Materials Chemistry 21 15343-15351.

C/P1 1

add to my program **(close full abstract)**

17:45

Half-metallic Ferromagnetism in Cubic PrMnO3 Perovskite

Authors : B.Bouadjemi*1, S.Bentata1, T. Lantri1, W.Benstaali1, A.Zitouni1 and A.Abbad2
Affiliations : 1 Laboratory of Technology and Solid Properties, 2Signals and Systems laboratory, LSS, Faculty of Sciences and Technology, Abdelhamid Ibn Badis Mostaganem University, BO 227, 27000 Algeria E-mail: bbouadjemi@yahoo.fr

Resume : We have investigated the electronic and magnetic properties of the cubic praseodymium oxides perovskites PrMnO3 were calculated using the density functional theory (DFT) with both generalized gradient approximation (GGA) and GGA+U approaches, where U is on-site Coulomb interaction correction. The results show a half-metallic ferromagnetic ground state for PrMnO3 in GGA+U approche, while semi-metallic ferromagnetic character is observed in GGA. The results obtained, make the cubic PrMnO3 a promising condidate for application in spintronics. Keywords : Electronic properties, Transition Metal, Magnetic moment, DFT, half- metallic [1] A.S. Verma, A. Kumar. Journal of Alloys and Compounds,541(2012) 210. [2] P. Blaha, K. Schwars, G.K H.madsen, D. Kvasnicka,and J. Luitz, WIEN2K,an Augmented Plane WaveRLocal Orbitals Program for Calculating Crystal Properties (Technische Universita « tWien,Austria,2001). [3] B.Bouadjemi*, S.Bentata, A.Abbad, W. Benstaali, B. Bouhafs,Solid State Communications168(2013)6-10.

C/P1 2

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17:45

Electronic and magnetic structure of double perovskite Ba2MnMoO6 from first-principales

Authors : B.Bouadjemi*1, S.Bentata1, T. Lantri1, W.Benstaali1and A. Zitouni1
Affiliations : 1 Laboratory of Technology and Solid Properties, Faculty of Sciences and Technology, Abdelhamid Ibn Badis Mostaganem University, BO 227, 27000 Algeria E-mail: bbouadjemi@yahoo.fr

Resume : The structural, electronic and magnetic properties of double perovskite Ba2MnMoO6 are studied by using the first-principales method of the full potential linear augmented plane waves plus the local orbitals (FP-LAPW+l0) within the local spin density (LSDA) and the generalized gradient approximation (GGA) approximations, in order to take into account the strong on-site coulomb interaction that means we included the Hubbard correlation terms : LSDA+U and GGA+U approaches. Our structural calculations are in agreement with the experimental and orders theoretical results which show that compound crystallizes in the cubic space group Fm-3m (a=7.91Å) .The calculated density of state presented in this study identifies the metallic behavior due to dominant Mn spin-up and Mo spin-down contributions. Keywords : Electronic structure, Double perovskite, First-principales, Ba2MnMoO6, coulomb interaction

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17:45

The electronic, structure properties of the TiO2: a first principles investigation within the modified Becke–Johnson exchange potential plus LDA and GGA

Authors : S.Benatmane*1, B.Bouhafs1, B. Bouadjemi 2 and S. Bentata 2
Affiliations : 1Department of physics Faculty of sciences Djillali Liabes University of Sidi Bel-Abbes, 22000, Algeria 2Laboratory of Technology and Solid Properties,Faculty of Sciences and Technology, BP227 Abdelhamid Ibn Badis University, Mostaganem (27000) Algeria Email*1: b.saadia@live.fr

Resume : The TiO2 has been recently used to realize high-temperature ferromagnetic semiconductors. In fact, it has been widely used for a long time as white pigment and sunscreen because of its whiteness, high refractive index, and excellent optical properties. However, its electronic structures and the related properties have not been satisfactorily understood. Here, we use Tran and Blaha's modified Becke-Johnson (TB-mBJ) exchange potential (plus a local density approximation correlation potential) within the density functional theory to investigate electronic structures and optical properties of rutile and anatase TiO2. Our comparative calculations show that the energy gaps obtained from mBJ method agree better with the experimental results than that obtained from local density approximation (LDA) and generalized gradient approximation (GGA), in contrast with substantially overestimated values from many-body perturbation (GW) calculations. As for optical dielectric functions (both real and imaginary parts), refractive index, and extinction coefficients as functions of photon energy, our mBJ calculated results are in excellent agreement with the experimental curves. Our further analysis reveals that these excellent improvements are achieved because mBJ potential describes accurately the energy levels of Ti 3d states. These results should be helpful to understand the high temperature ferromagnetism in doped TiO2. This approach can be used as a standard to understand electronic structures and the related properties of such

C/P1 4

materials as TiO2. Titanium dioxide films have wide applications because of their useful electrical and optical properties, such as high refractive index, high dielectric constant, and excellent transmittance in the visible and near infrared range. Especially, the high refractive index and low absorption coefficient make them suitable for optical coatings. Therefore, many studies on the preparation of TiO2 films by various deposition procedures have been carried out [1-2]. For the preparation of optical coatings, such as TiO2 films, reactive sputtering is very useful technique because of the possibility to produce coatings with high optical quality and a good homogeneity. However, in the case of TiO2 film grown using the sputter method, the film properties, including the stoichiometry, microstructure, and optical characteristics are strongly dependent on growth parameters such as the substrate temperature and the gas composition in the sputtering atmosphere. The rutile and anatase structures are the most important phases for TiO2. Their structural, electric, and optical properties have been experimentally measured with various methods [3-6] and their electronic structures and optical properties have been theoretically investigated in terms of popular density functional- theory (DFT) approaches. [7-10] It is obvious that the electronic structures need to be accurately calculated because they are the starting point for first-principles calculations of other physical and chemical properties. Nevertheless, their energy gaps, like those of other semiconductors and insulators, are underestimated by local density approximation (LDA) and generalized gradient approximation (GGA)[8-9;11;12] in comparison with the experimental values.[4-5] Thus, further approximations, such as scissors approximations, are required to modify the gaps to make the calculated results comparable with the experimental results In this work, we use Tran and Blaha’s modified Becke–Johnson (TB-mBJ) exchange potential (plus LDA correlation potential) [13-14] within the density functional theory to investigate the optical properties of rutile and anatase TiO2. Key words: DFT / FP-LAPW / GGA / LDA / the TiO2 /the mBJ and optical properties References [1] H. K. Jang, S. W. Whangbo, H. B. Kim, Y. S. Lee, I. W. Lyo and C. N. Whang, J. Vac. Sci. Technol. A 18, 917 (2000). [2] J. D. Park and T. S. Oh, J. Korean Phys. Soc. 37, 1072 (2000). [3] Matsumoto Y, Murakami M, Shono T, Hasegawa T, Fukumura T, Kawasaki M, Ahmet P, Chikyow T, Koshihara S Y and Koinuma H 2001 Science 291 854 [4] Cardona M and Harbeke G 1965 Phys. Rev. 137 A1467 [5] Tang H, Levy F, Berger H and Schmid P E 1995 Phys. Rev. B 52 7771 [6] Lin L B, Mot S D and Lin D L 1993 J. Phys. Chem. Solids 54 907 [7] Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864 [8] del Sole R and Girlanda R 1993 Phys. Rev. B 48 11789 [9] Thilagam A, Simpson D J and Gerson A R 2011 J. Phys.: Condens. Matter 23 025901 [10] Kang W and Hybertsen M S 2010 Phys. Rev. B 82 085203 [11] Perdew J P and Wang Y 1992 Phys. Rev. B 45 13244 [12] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865 [13] Tran F and Blaha P 2009 Phys. Rev. Lett. 102 226401 [14] Koller D, Tran F and Blaha P 2011 Phys. Rev. B 83195134

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17:45

REDUCING ERROR & MEASUREMENT TIME IN IMPEDANCE SPEC-TROSCOPY, ELECTRICAL CONDUCTIVITY RELAXATION AND ISO-TOPE DEPTH PROFILING USING MODEL-BASED OPTIMAL EXPERI-MENTAL DESIGN

Authors : Francesco Ciucci
Affiliations : Mechanical & Chemical Engineering. HKUST, Hong Kong SAR, China

Resume : Mathematical models are ubiquitous in science and engineering and are used to interpret and predict the outcome of experiments and the behavior of devices or systems. Models with varying degree of complexity are found in materials research of electroactive materials and they have been used to explain the nature of elec-trochemical reactions both at kinetic and the quantum level, to determine defect chemistry and transport pro-perties, to establish the processes that are rate limiting and to gain insight on reactions occurring at the nanos-cale. In this work, a statistical link between experimental date obtained widely used in solid state electrochemistry, such as Electrochemical impedance spectroscopy (EIS), Electrical Conductivity Relaxation (ECR) and Isotope Exchange Depth Profiling (IEDP), and mathematical model is made in order to increase the quality of the estimated parameters via Optimal Experimental Design (OED).

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17:45

STUDY OF POLARIZABILITY AND HYPERPOLARISABILITY OF POLYACETYLENE CHAINS

Authors : D. Taharchaouche1, F. Mechachti1, A. Djebaili1*
Affiliations : 1 Laboratory of chemistry and environmental chemistry L.C.C.E - University of Batna- Algeria

C/P1 6

Resume : Ab-initio calculations, carried out with different basis sets, for the static longitudinal linear polarizability, αL, and second order hyperpolarizability, γL, of small doubly charged polyacetylene (PA) chains, are presented. The polarizabilities were calculated using the Hartree–Fock (HF) method while the electron correlation effects were included through the second-order Møller–Plesset perturbation theory (MP2). Positively and negatively charged bipolarons were studied. The results obtained for positive and negative chains show that the ionization state effect decreases more rapidly, as the chain length is increased, for αL than for γL. Or both types of charged chains, the incorporation of the electron correlation increase the αL, and γL values, as compared to the HF values. A comparison between the results obtained using the standard 6-31G basis set and augmented versions of this set, obtained by the addition of diffuse and polarization functions, shows that 6-31G basis set does not provide a good description of the negative chains studied here and that the addition of extra diffuse functions on the basis set is needed in order to obtain reliable estimates for polarizabilities, specially for γL. Key words : polarizabilities; hyperpolarisability; polyacetylene; bipolarons; correlation effects.

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17:45 **STUDY OF CONDUCTIVITY AND ISOMERIZATION REACTIONS OF POLYACETYLENE**

Authors : S. Bitam1, F. Mechachti2, A. Djebaili2

Affiliations : 1 Laboratory of Physical chemistry- University of Media- Algeria 2 Laboratory of chemistry and environmental chemistry L.C.C.E - University of Batna-Algeria

Resume : Our work has allowed us to clarify the relations structures / properties and the isomerization reactions of polyacetylene. As regards the relations structures / properties, our results are: 1- The study of the conduction properties of polyacetylene doped with iodine gas at saturation as a function of various parameters regulating morphology and density of the material was optimized. In particular we have shown that the two key parameters governing the electrical conductivity of the polymer are the density and the fibrillar structure of polyacetylene. 2- The comparison of samples prepared horizontally and vertically gave a conductivity of greater than ~ 45 % for those deposited vertically, thereby reflecting the difference in morphology of the two types of film.. 3- The study of the ohmic conductivity of undoped and thermally isomerized samples showed a very different behavior depending on whether the polyacetylene film is deposited horizontally or vertically, thus confirming the different morphologies of the analyzed films. With regard to isomerization reactions of polyacetylene, our results are: i- The study of the thermal isomerization Cis / Trans of undoped polyacetylene by differential thermal analysis allowed us to calculate the activation energy of the reaction Ea=31kcal/M, as well as the pre-exponential factor A = 2.3*1013 /s regardless of the type of polymer considered (deposited vertically or horizontally). ii- The kinetic studies by DSC showed that the isomerization reaction was neither of order 1, nor of a simple order. iii- An additional study of the thermal isomerization was carried out by Raman backscattering . This study allowed us in particular to establish a new original method for the determination of the isomeric composition of samples of polyacetylene. Also a relation for connecting the laser power to the induced temperature at the impact level was proposed. Finally, the kinetics of isomerization approaches the order 2/3. Note that the activation energy and the pre-exponential factor of the isomerization reaction determined by this method are different from those obtained by DSC.

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17:45 **Numerical investigation of a new Junctionless-Multigate design for low- cost pH sensing applications**

Authors : N. Abdelmalek1, F. Djeffal1, T. Bentrcia and M. Meguellati2

Affiliations : LEA, Department of Electronics, University of Batna, Batna 05000, Algeria. E-mail: faycal.djeffal@univ-batna.dz, faycaldzdz@hotmail.com, Tel/Fax: 0021333805494

Resume : The Gate All Around GAA MOSFETs have emerged as excellent devices to provide the electrostatic integrity needed to scale down transistors to minimal channel lengths, and allowing a continuous progress in digital and analog applications. Employing this design for chemical and environment monitoring applications becomes more beneficial if the device is made in vertical cylindrical recrystallized silicon due to highly flexible process integration options. In this paper, a numerical investigation of a new pH-ISFET design, called the Junctionless Gate All Around Ion-sensitive field-effect transistor with oxide kernel (pH-JGAAISFET), is proposed, investigated and expected to improve the fabrication process and the sensitivity behavior for pH-ISFET sensor-based

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applications. The numerical investigation has been used to propose a new sensitivity performance and predict the device behavior. The comparison of device architectures shows that the proposed sensor exhibits a superior performance with respect to the conventional ISFET in term of electrical performances. The obtained results make the proposed sensor a promising candidate for low cost monitoring and high performance pH sensing applications.

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17:45 **THERMODYNAMIC STUDY OF THE TERNARY SYSTEM GALLIUM-ARSENIC-BISMUTH**

Authors : N. Elayech*, H. Fitouri, Y. Soda, A. Rebey, and B. El Jani

Affiliations : Université de Monastir, Faculté des Sciences de Monastir Unité de Recherche sur les Hétéro-Epitaxies et Applications, 5000 Monastir, Tunisia E-mail: * elayech@yahoo.fr

Resume : Phase diagrams for binary system Ga-As and Ga-Bi and have been evaluated using thermodynamic parameters from the literature. In addition, ternary system Ga-As-Bi was calculated. Several vertical and isothermal sections as well as the liquidus surface and selected thermodynamic properties are investigated using the thermodynamic description. The implications of the phase data for solution epitaxy are discussed. The agreement between a few published experimental data and calculated points has been found satisfactory. Keywords: Phase diagram, thermodynamic properties, GaAs, GaBi, GaAsBi. C/P1 9

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17:45 **Water interaction with fluorine-doped Co3O4 (100) and (111) surfaces**

Authors : G. Kaptagai1, T.M. Inerbaev1, A.T.Akilbekov1, Yu.A. Mastrikov2,3, E.A. Kotomin2,4

Affiliations : 1 L.N. Gumilyov Eurasian National University, Mirzoyan str. 2, Astana, Kazakhstan 2 Institute of Solid State Physics, University of Latvia, Kengaraga str. 8, Riga, Latvia 3 Materials Science and Engineering Dept., University of Maryland, College Park, USA 4 Max Plank Institute for Solid State Research, Heisenberg str. 1, Stuttgart, Germany

Resume : Water interaction with fluorine-doped Co3O4 (100) and (111) surfaces Electrochemical water splitting has attracted substantial interest in the recent years as a key process in hydrogen production from sunlight and other sources of electricity. Recent experimental studies have demonstrated that Co3O4 is high-promising anode material for electrochemical water splitting due to its high catalytic activity in the oxygen evolution reaction (OER) [1]. In this context, understanding the interaction of Co3O4 surfaces with water is an essential preliminary step that can help to shed light on the atomic scale reaction mechanisms. Our attention is focused on investigation of Co3O4 (100) and (111) surfaces which are the most abundantly presented in Co3O4 nanoparticles [2]. Density functional method is applied to describe thermodynamics of electrocatalytic water splitting on the Co3O4 (100) and (111) surfaces. We calculated free energy changes along the reaction pathway using the computational standard hydrogen electrode (SHE) allowing us to replace a proton and an electron with half a hydrogen molecule at U = 0 V vs SHE. The analysis performed for the free energies is at standard conditions (pH = 0, T = 298.15 K) and U = 0. Using accurate DFT+U calculations, we shown that water adsorbs dissociatively on Co3O4 on the (100) and intactly on the (111) surfaces. From the computed free-energy changes along the OER, we found that the (100) surface is catalytically inactive while (111) surface demonstrates some electrocatalytic activity on its threefold coordinated surface cobalt ions. In this case free energy changes along the OER is the same to corresponding value for the most stable termination of (110) Co3O4 surface. Fluorine doping of Co3O4 nanoparticles drastically changes their interaction with water. In our investigations solvent effects are generally expected to be small for neutral species, the neglect of the water environment is a rather drastic approximation, for which the main justifications are that it provides a qualitative description of experimentally observed trends, and it is the first step toward more complete treatments that include the solvent. [1] I. C. Man, H.-Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov, and J. Rossmeisl, ChemCatChem (2011) 3, 1159 – 1165. [2] F. Zasada, W. Piskorz, S. Cristol, J.-F. Paul, A. Kotarba, and Z. Sojka, J. Phys. Chem. C (2010), 114, 22245–22253. C/P1 10

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17:45 **First principles calculations of formation and migration of oxygen vacancies in the bulk and at the surface of complex perovskites for solid oxide fuel cell cathodes** C/P1 11

Authors : Yu. A. Mastrikov1,2, E. A. Kotomin1,3, R. Merkle3, M. M. Kuklja2, and J.

Maier3
Affiliations : 1Institute of Solid State Physics, University of Latvia, Kengaraga str. 8, Riga, Latvia; 2 Materials Science and Engineering Dept., University of Maryland, College Park, USA; 3Max Planck Institute for Solid State Research, Heisenbergstr.1, Stuttgart, Germany;

Resume : ABO3-type perovskite solid solutions with a large oxygen deficiency exhibit a perceptible ionic conductivity, leading to their use as electrolytes ((La,Sr)(Ga,Mg)O3-□) or materials for oxygen permeation membranes and solid oxide fuel cell cathodes ((La,Sr,Ba)(Mn,Fe,Co)O3-□) [1]. The oxygen migration occurs by the vacancy mechanism with the migration through a "critical triangle" formed by one B- and two A– site cations, as the bottleneck [2]. Oxygen ionic conductivity is not only important for transport though the cathode material, it also affects the surface chemistry. The formation and migration energies of oxygen vacancies were found to be major factors determining the surface oxygen reduction rate [1]. We analyze these two quantities for a series of complex (La,Sr)(Co,Fe)O3-□ (LSCF) perovskites by means of first principles DFT calculations [2]. The atomic relaxation, electron charge redistribution and energies of the transition states for oxygen ion migration are obtained and differences with Ba1-xSrxCo1-yFeyO3-□ (BSCF) perovskites [3] (which exhibit considerably lower migration barriers) are discussed in detail, with special emphasis on the vacancy formation and migration at the surface. [1]. M. Kuklja et.al. Phys. Chem. Chem. Phys. 15, 5443 (2013). [2] Yu.A. Mastrikov et.al. Phys. Chem. Chem. Phys. 15, 911 (2013) [3] R. Merkle et. al. J Electrochem.Soc. 159, B 219 (2012).

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17:45 **Modelling of impedance spectra of porous SOFC cathodes: effect of grain boundaries**

Authors : Wolfgang Preis
Affiliations : Chair of Physical Chemistry, Montanuniversitaet Leoben, Franz-Josef-Strasse 18, A-8700 Leoben, Austria

Resume : The reduction of oxygen at mixed ionic-electronic conducting SOFC cathodes, e.g. La0.6Sr0.4CoO3-d, is mainly determined by the oxygen exchange reaction at the surface, including pores, as well as the transport of oxygen ions through the thin cathode layer. The kinetics of these processes can be described by means of the surface exchange coefficient and the ionic conductivity. Impedance spectroscopy represents a powerful tool for the investigation of the polarization mechanism. A square grain model has been developed in order to simulate impedance spectra of porous cathodes under OCV conditions by application of a finite element approach. The grains and pores of the thin cathode layer may be squares of equal side length (0.1 - 1 µm), while the grain boundaries as well as the interface between the grains of the cathode and a homogeneous electrolyte may consist of thin slabs with a width of 0.5 nm. The simulated impedance spectra can be interpreted reasonably well in terms of a Gerischer element. An additional semicircular arc is found at high frequencies, which corresponds to the charge transfer resistance (double layer capacitance) of the interface between the cathode and the electrolyte as well as current constriction effects. The surface exchange coefficient and ionic conductivities of bulk and grain boundaries have been varied systematically. The effect of the ionic grain boundary conductivity on impedance spectra of thin porous cathode layers will be presented in detail. C/P1 12

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17:45 **Reaction fronts formation during oxygen chemical diffusion in oxides**

Authors : Misha Sinder, Zeev Burshtein, Joshua Pelleg
Affiliations : Materials Engineering Department, Ben-Gurion University of the Negev

Resume : A theoretical study of the impact of oxygen chemical diffusion transport in oxide materials on metal dopants ionic state and the material conductivity type under thermal equilibrium and dynamic changes is presented. Oxygen vacancy formation acting as shallow double electronic donors is assumed to result from the crystal exposure to a low ambient oxygen pressure. It is shown, that critical transitions from n- to a p-type at an oxygen partial pressure Pi, and in ionization state of the metal dopant at an oxygen partial pressure PM, are usually not simultaneous, and depend on the different reaction constants. Invoking ambipolar diffusion for all participating species, it is shown that oxygen vacancy diffusion exhibits well defined characteristics in specific regions of the vacancy concentration related to the said critical pressures. Particularly, the effective diffusivity is practically constant between Pi and PM, and increases sharply for pressures P << Pi, PM, and P >> Pi, PM. Prominent reaction fronts occur under specific conditions in the two latter regions. C/P1 13

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17:45

Growth and Evaluation of Single-crystalline PrBaCo2O5+δ Thin Films on Oriented Substrates for Solid Oxide Fuel Cells

Authors : Dengjie Chen, Yang Gao, Francesco Ciucci

Affiliations : Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Hong Kong, SAR China

Resume : Single-crystalline PrBaCo2O5+δ (PBC) thin films were prepared on different orientated Y2O3 stabilized ZrO2 substrates (YSZ 001, 110 and 111) via pulsed laser deposition with a Sm-doped Ceria interlayer for the first time. High resolution X-ray diffraction (HRXRD) was employed to examine the crystal's quality as well as the orientations; X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM) were used for the characterization of surface morphology and composition. Sharp peaks in the XRD patterns and small roughness in the AFM map all suggested the high quality of our single crystal. Electrochemical impedance spectroscopy experiments under different temperature and atmosphere were conducted to examine the oxygen reduction reaction (ORR) behavior. All of our thin films have exhibit rather good ORR behavior, while a slight difference also existed among those three different orientated thin films: PBC111 did better than PBC110, while PBC001 was the worst. The difference in ORR activity may be explained by the oxygen vacancy that only exist at the Pr-O layer, and the pathways for oxygen ion only exist in the a-b plane, which makes PBC001 as the worst one for oxygen ion transport. The difference between PBC111 and PBC110, on the other hand, could be attributed to the surface composition difference according to the AFM and XPS results.

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17:45

Experimental and Computational Investigations of Ba0.95La0.05FeO3-δ as Solid Oxide Fuel Cell Cathode Material

Authors : Chi Chen, Dengjie Chen, Yang Gao, Francesco Ciucci

Affiliations : Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Hong Kong, SAR China

Resume : Solid oxide fuel cell (SOFC) is a clean and energy efficient technology that may play a crucial role in solving the future energy crisis. Finding a suitable cathode material for SOFC is key to facilitate its application. Besides developing high performance materials, understanding material intrinsic properties and stability is of equal importance. In this work, Ba0.95La0.05FeO3-δ, a high performance cathode material, was studied combining experimental evaluations on single crystal thin films and molecular simulations. High quality single crystal thin films were grown on yttria-stabilized zirconia substrates using pulsed laser deposition. The polarization resistance of the dense films was evaluated to be 0.07 Ωcm2 at 700 °C and 0.21 atm oxygen pressure, a value lower than the polycrystalline counterpart and most Co-based materials. Lattice dynamics simulations were applied to study the stabilization of barium orthoferrate BaFeO3-δ upon doping La3+. Simulation results reveal that the defect energy for in the cubic phase is lower than that in the monoclinic phase, which contributes to the stabilization. Analogous results were also found by doping the Ba site with Sm3+, Gd3+ and Y3+. In addition, the simulation results suggest that the charge compensation mechanism upon doping is filling oxygen vacancies and La3+ has a tighter binding with oxygen anions. Thus it is concluded that with increasing doping level, the oxygen anion diffusivity should decrease. Molecular dynamics simulations results further support this conclusion.

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The Bias Voltage Dependence of Oxygen Reduction Pathways on Strontium-Doped Lanthanum Manganite (LSM) Model Electrodes

Authors : A. Welzl, T. M. Huber, E. Navickas, A. K. Opitz, H. Hutter, J. Fleig

Affiliations : Vienna University of Technology Institute of Chemical Technologies and Analytics Research Division Electrochemistry

Resume : Sr-doped lanthanum manganite (LSM) is the most used cathode material in solid oxide fuel cells (SOFC). Nevertheless, many aspects of the oxygen reduction at LSM are not completely understood. Even though ionic conductivity of LSM is low, oxygen reduction not only occurs at the three phase boundary via a surface path but also at the LSM surface and thus via a bulk path. By applying a dc-bias to LSM electrodes, their oxygen chemical potential is changing and thus surface kinetics as well as bulk transport kinetics can be modified. In combination with oxygen partial pressure changes, which also affect the defect chemistry of LSM, the contribution and individual relevance of interfacial and transport kinetics can be investigated at elevated temperatures.

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In this contribution, current-voltage and impedance studies are performed on LSM microelectrodes with variation of electrode geometry, dc-bias, oxygen partial pressure and temperature. These experiments provide information on the current voltage characteristics of different kinetic steps, allow separation of reaction pathways and enable identification of rate limiting steps. Moreover 18O incorporation upon cathodic bias is used to visualize the electrochemically active zones of the different reaction pathways and their changing contributions for microelectrodes under different measurement conditions.

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17:45

Atomic Layer Deposition of Ru for Direct Alcohol Solid Oxide Fuel Cells

Authors : Heon Jae Jeong, Jun Woo Kim, Ho Jean Jeong, Kiho Bae, Joon Hyung Shim

Affiliations : School of Mechanical Engineering, Korea University, Seoul, Korea

Resume : For use of solid oxide fuel cells (SOFC) in small and mobile applications, methanol or ethanol has attracted attentions as an alternative fuel source instead of hydrogen. In operation of SOFCs at intermediate temperatures under 500C, bimetallic Pt-Ru catalyst has been known as the most effective for oxidation of alcohol fuels. Various methods have been attempted for the deposition of bimetallic catalysts. Among them, atomic layer deposition (ALD) has been successfully utilized to synthesize high-performance catalysts for fuel cells. ALD can achieve uniform coating of metal layers in thickness of several atomic layers or a few nanometers on meso-porous substrates due to its self-limited chemical reaction per each precursor cycle. This characteristic of the ALD process enables to maximize surface area of the deposited metal layer in minimized volume, which is advantageous especially in manufacturing of core-shell catalysts with precious shell metals including Pt and Ru. In this study, ALD Ru was deposited onto porous Pt and Ni substrates as anodes of Gd0.1Ce0.9O2-δ (GDC)-based SOFCs. Both methanol and eathanol were tested as fuels and performance was examined in terms of maximum voltage, power output, and electrochemical impedance under 500C. To evaluate chemical stability or resistance to carbon coking, surface composition of the ALD Ru-Pt and -Ni catalysts was measured by using x-ray photoelectron spectroscopy (XPS) before and after the fuel cell testing. As a result, the SOFCs with ALD Ru-Pt or ALD Ru-Ni outperform ones with pure Pt demonstrating power output enhanced by at least one order compared to pure Pt-SOFCs with significantly improved long-term stability.

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Influence of magnetron sputtering deposition conditions and thermal treatment on properties of platinum thin films

Authors : Jolita Sakaliuniene, Brigita Abakeviciene, Kestas Slapikas, Sigitas Tamulevicius

Affiliations : Institute of Materials Science of Kaunas University of Technology, Savanorių av. 271, LT-50131 Kaunas, Lithuania

Resume : Platinum is an interesting material due to its unique properties such as high melting point, good chemical resistance and catalytic behavior. Consequently it is used as potential electrode for micro-Solid Oxide Fuel Cells. In the present research the microstructure, porosity as well as conductivity of thin (d~200 nm) platinum electrodes deposited on silicon/silicon oxide substrates and yttria stabilized zirconia films were varied by using different working pressure in the chamber during platinum sputter-deposition process. To obtain good platinum adhesion on silicon/silicon oxide substrate, titanium thin layer (d~20nm) was used as an adhesion and a diffusion barrier layer. Structure of platinum electrodes was analyzed using grazing incidence X-ray diffraction, morphology - by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The ImageJ processing program was used to evaluate the porosity of the Pt thin film from the SEM images. Electrical properties of platinum films were measured using the four-point probe method. Thermal treatment at different annealing temperatures (from 500 to 800C) was applied. It was observed that higher working pressure in the chamber results in denser and smoother platinum films, and correspondingly lower working pressure allows to produce porous platinum thin films without any thermal treatment. Thermal treatment results show that pores start to compose after 15 minutes annealing in 600C in air.

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Strontium delta-doped lanthanum cuprate heterostructures: cation redistribution and high-temperature superconductivity

Authors : F. Baiutti1, G. Logvenov1, G. Gregori1, Y. Wang2, Z. Chen2, W. Sigle2, P.A. van Aken2, J. Maier1

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Stuttgart, Germany; 2 Stuttgart Center for Electron Microscopy, Max Planck Institute for Intelligent Systems, Heisenbergstr. 3, D-70569 Stuttgart, Germany

Resume : Knowledge about charge and ion redistribution is essential to understanding interface effects occurring in many functional oxides. In this contribution, the electrical transport properties of a model system based on hetero-structures of strontium delta-doped lanthanum cuprate (La2CuO4) are considered. Thanks to the unique capabilities of the layer-by-layer oxide molecular beam epitaxy (MBE) technique, that allows the control of the structural composition down to the single atomic layer, we fabricated epitaxial multilayered (La,Sr)2CuO4 structures, in which atomic layers of SrO were precisely inserted in the parent La2CuO4 lattice structure. Remarkably, although both La2CuO4 and SrO single layers do not exhibit superconducting properties, the resulting hetero-structures (obtained by varying the spacing between the La2CuO4 and SrO layers) are high-Tc superconductors with a maximum Tc ≈ 40 K. In order to rationalize this exciting finding and determine the relevance of cation intermixing at the interface, electrical transport data are discussed together with structural information, the latter being obtained from X-ray diffraction (XRD), atomic-column-resolved high-angle annular dark-field (HAADF) imaging in combination with energy-dispersive X-ray spectroscopy (EDXS) and electron energy-loss spectroscopy (EELS) in a spherical aberration-corrected scanning transmission electron microscope.

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17:45 **Characterization of the electrical properties of donor doped barium titanate ceramics by impedance spectroscopy: effect of dc-bias and ac-voltage amplitude**

Authors : Johannes Hofer, Wolfgang Preis, Werner Sitte

Affiliations : Chair of Physical Chemistry, Montanuniversitaet Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria

Resume : The positive temperature coefficient (PTC) of resistivity of donor doped barium titanate, BaTiO3, is the steep increase of the grain boundary resistance by several orders of magnitude around the Curie-Temperature Tc. This effect is caused by Schottky-barriers at the grain boundaries of the microcrystalline material. In comparison to the bulk, the grain boundaries usually show a different local chemical composition. Below Tc these potential barriers are compensated by the spontaneous ferroelectric polarization. Basically, the overall increase and the slope of the resistance curve can be adjusted via processing (sintering program) and composition (dopant concentrations). Donor doped (typically La) and acceptor co-doped (Mn) specimens have been prepared by employing a modified solid state reaction route. Bulk and grain boundary resistivities of densely sintered ceramic samples can be separately observed with impedance spectroscopy (IS). IS-measurements were carried out on disk-shaped n-conducting BaTiO3 samples (thickness 0.5 mm) in the frequency range 10-2 – 106 Hz, at dc-bias of 0 – 140 V or effective ac-voltages ranging from 1 to 90 V, and temperatures of 180, 225 and 300 °C. The dominating grain boundary resistance decreases with increasing voltage load, whereas the bulk resistance is almost independent of the applied voltage. Moreover, the steepness of the resistance vs. temperature curve is diminished owing to the effect of the voltage drop at grain boundaries. C/P1 20

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17:45 **Graphene/gold contact on n-doped GaAs substrate**

Authors : H. Ajlani (1), R. Othmen (1), M. Oueslati (1), A. Cavanna (2), A. Madouri (2)

Affiliations : (1) Unité de Recherche Nanomatériaux et Photonique, Département de physique, Faculté des Sciences de Tunis, Université de Tunis El Manar, 2092, Tunis, Tunisie ; (2) CNRS/LPN, Route de Nozay, F – 91460 Marcoussis, France

Resume : Graphene-based devices, where the extraordinary optical and electronic properties of graphene are combined with the well-known properties of semiconductor substrate such as GaAs may lead to the production of a wide-range of new technological applications. However, although the deposition of graphene layer on semiconductor substrate is now well mastered and the physics of the resulting graphene/semiconductor interface understood, a particular interest must be done on metal contacts in such structures. In this work we study, by means of micro-Raman spectroscopy, the properties of deposed graphene layer on n-doped GaAs substrate as well as on AU/n-doped GaAs substrate. As predicted, a quenching of the background fluorescence of gold on Raman spectra induced by the presence of the graphene layer is observed on the highest n-doped GaAs sample studied. However, an unusual amplification of the background photoluminescence of gold for lower GaAs dopage value is observed. We interpret this enhancement of the photoluminescence to a competition between the quenching of the C/P1 21 photoluminescence by resonance energy transfer from gold to graphene and recombination of photocreated carriers induced by the particular band structure profile of the considered structure.

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17:45 **Transparent p+-TiN:SnO2/n+-ITO tunnel diode**

Authors : Chih-Yi Hsieh, Chin-Han Liao, and Cheng-Yi Liu

Affiliations : Department of Chemical and Materials Engineering National Central University, Jhong-Li, Taiwan

Resume : Many invisible electronic devices have been developed in recent years, such as, transistors and p-n junctions. Yet, so far, no transparent tunnel diode has ever been reported. In this work, we demonstrate an unique approach to fabricate a transparent p+-TiN:SnO2/n+-ITO tunnel diode. The p+-TiN:SnO2 thin film formed by annealing a SnO2/TiN multi-layer structure. The hole carriers in the p+-TiN:SnO2 thin film are mainly generated by the N3--O2- substitution reaction. The p+-TiN:SnO2 thin film has low resistivity (0.2 Ω•cm) and high hole concentration (1.52×1019 cm-3). The I-V characteristics of the p+-TiN:SnO2/n+-ITO junction exhibits distinct tunnel diode characteristics. In addition, the overall transmittance of the p+-TiN:SnO2/n+-ITO tunnel diode is higher than 80% in the visible region. The transparent p+-TiN:SnO2/n+-ITO tunnel diode can be further applied in transparent tunnel field-effect transistor (TFET) and other invisible electronics. C/P1 22

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17:45 **Conductivity and Hall effect relaxation of doped In2O3 thin films**

Authors : Mareike V. Hohmann, Andreas Klein

Affiliations : Technische Universität Darmstadt, Institut für Materialwissenschaft, Fachgebiet Oberflächenforschung, Jovanka-Bontschits-Strasse 2, 64287 Darmstadt, Germany

Resume : The application of transparent conductive oxides in most electronic devices requires a good knowledge of their electrical properties such as conductivity, but also carrier mobility. In addition, oxygen exchange plays a crucial role for post-deposition treatments and the functionality of devices. In order to elucidate the relation between electrical properties and oxygen equilibration a system for in situ Hall effect and electrical conductivity measurements of oxide thin films has been set up, giving the opportunity for temperature dependent measurements in controlled atmosphere. The use of the setup is exemplified with differently doped In2O3 thin films, which are deposited by magnetron sputtering onto quartz glass substrates. The amount of Sn doping, the oxygen pressure during film deposition and during temperature treatment is varied. The results indicate that oxygen equilibration is not the only factor which affects the electrical properties, but also other long term processes. Reversible segregation of Sn to grain boundaries is one possible mechanism contributing to the long term processes. C/P1 23

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17:45 **Nanocomposite structures grown by inserting ionic salt RbNO3 into van der Waals gaps of III-VI layered semiconductors**

Authors : A.P. Bakhtinov (1), V.M. Vodopyanov (1), Z.R. Kudrynskyi (1), Z.D. Kovalyuk (1), V.V. Netyaga (1), O.S. Lytvyn (2)

Affiliations : (1) Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Chernivtsi Department, str. I. Vilde 5, 58001 Chernivtsi, Ukraine, (e-mail: kudrynskyi [at] gmail.com); (2) Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, pr. Nauky 4, 03028 Kyiv, Ukraine.

Resume : The p-GaSe(RbNO3) and n-InSe(RbNO3) nanocomposite materials were prepared by inserting ionic salt RbNO3 from the liquid phase between the layers of the layered crystals. We have obtained self-organized structures that consist of a layered matrix and arrays of nanorings and nanowires formed from solid ionic salt RbNO3 nanocrystals on the atomically smooth van der Waals (0001) surfaces of layered semiconductor crystals. Atomic force microscopy, infrared spectroscopy, X-ray diffraction and impedance spectroscopy are used to characterize morphology, chemical composition, structural and electrical properties of the grown materials. We observed electric field-induced changes in the complex impedance by a factor of 10^5-10^8 in the frequency range 10^-1 -10^6 Hz at T=300K for solid state RbNO3/n-InOx/n-InSe nanostructures with structurally abrupt interfaces when a few volts voltage was applied. Under an applied gate voltage the nanometer-thick electric double layers (nanogap capacitors with a large capacitance) consisting of Rb+ ions and electrons accumulated on the surface of n+-InOx nanoscale layers with a high electron density were formed. In this work, we study the role of structural properties (such as ionic nanocrystals size and density, pyramidal defect density on the C/P1 24

(0001) layered crystals surface) on the electron/ionic carriers transport in the anisotropic structures. Our results suggest that these nanostructures are promising for energy and information applications.

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17:45 **Transparent conductive In-Si-O/Ag/In-Si-O multilayer grown for low-emissivity glass by sputtering at room temperature** C/P1 25

Authors : Young Seon Lee, Jun Young Choi, Sang Yeol Lee

Affiliations : Department of Electronic Engineering, Cheongju University, Cheongju, Chungbuk 360-764, Republic of Korea; Department of Electrical Engineering, Korea University, Seoul, 136-703, Republic of Korea; Department of Semiconductor Engineering, Cheongju University, Cheongju, Chungbuk 360-764, Republic of Korea

Resume : Low-emissivity glasses for high transparency in visible range and low emissivity in IR range were investigated. The multilayers have been fabricated and consisted of two outer oxide layers and a middle layer of Ag as a metal layer. Oxide layers were formed by dc sputtering and metal layers were formed by evaporator at room temperature. In-Si-O (ISO) film was used as oxide layer. The ISO/Ag/ISO coatings were analyzed using transmittance, atomic force microscope (AFM), X-ray diffraction (XRD) and Hall effect measurement. The OMO multilayer structure was designed to investigate the effect of Ag layer thickness on the optical and electrical property. The results revealed that the optical and electrical properties are closely related with Ag layer thickness.

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17:45 **Effect of Thickness of Ag on optical properties of low emissive SIZO/Ag/SIZO multilayer structure** C/P1 26

Authors : Moo Yeol Bae, Jun Young Choi, and Sang Yeol Lee

Affiliations : Department of Semiconductor Engineering, Cheongju University, Cheongju, Chungbuk 360-764, Republic of Korea; Department of Electrical Engineering, Korea University, Seoul 136-701, Republic of Korea; Department of Semiconductor Engineering, Cheongju University, Cheongju, Chungbuk 360-764, Republic of Korea

Resume : In the high oil price age, building is the country's total energy consumption by 22.3% and the glass takes up most of the energy loss of building. Therefore, in order to prevent loss of heat, development of Low-E glass is underway and it is already commercially available. Low-E glass having an oxide-metal-oxide structure has a low emissivity, it transmits visible light area and block makes the IR area, because of reduces heat loss. Oxide-Metal-Oxide on the glass as a SIZO-Ag-SIZO Multilayer was constructed. Silicon indium zinc oxide (SIZO) were deposited by RF-sputter method and Ag by the DC-sputter of change in thickness was deposited. By measuring the transmittance of multilayer depending on the thickness of Ag, optical properties were compared. By changing the thickness of the deposited Ag, optical properties were different. It is possible to optimize the thickness of the Ag indicating the high transmittance of visible light area and low transmittance of IR area for low cost applications.

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17:45 **The study and application of transparent p-type AlN:SnO2 thin films fabricated by cation- anion co-substitution** C/P1 27

Authors : Y. S. Liu, P. M. Lee, and C. Y. Liu

Affiliations : Department of Chemical and Materials Engineering, National Central University, Jhong-Li, Taiwan

Resume : Transparent wide band gap SnO2 oxide is one of the most promising p-type semiconductors, has a stable phase, and has been widely used as a transparent n-electrode in optoelectronic applications. The intrinsic SnO2 phase is a n-type semiconductor because of its oxygen-deficient nature. In addition, p-type SnO2 can be also achieved by doping nitrogen in SnO2 through anionic substitution, but the poor stability of p-type conductivity restricts its application. In this study, the p-type SnO2 thin films fabricated by cation- anion co-substitution AlN doping are discussed, which showed good p-type conductivity stability. Using the produced p-AlN:SnO2 thin film, transparent p-AlN:SnO2/n-SnO2:In2O3 p-n junctions were fabricated with a low leakage current (2.97 × 10^-5 A at -5 V) and a low ideality factor (12.2) compared to the reported p-type SnO2 thin films. In addition, we also successly applied the transparent p-AlN:SnO2 thin films on the n-channel transparent transistor with good on/off current ratio (2.97 × 10^3) and low sub-threshold swing value (3.7 V/dec).

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17:45 **Fabrication and characterization of Ni-Zr Multilayered membrane for Hydrogen separation** C/P1 28

Authors : SungBum Park, Yong-il Park
Affiliations : Kumoh National Institute of Technology
Resume : As a membrane material for gaseous hydrogen separation, the metal must satisfy at least the following four requirements: high hydrogen solubility, high diffusivity, catalytic activity of the surface to dissociate hydrogen molecules into atoms, and mechanical strength in a hydrogen atmosphere. Palladium alloys are the only metals to satisfy all these requirements. However, palladium is prohibitively expensive. Therefore, it is important to develop a new alloy membrane with a minimal addition of Pd or a new non-Pd-based alloy membrane. In this study, NiZr alloy membrane was prepared by a spark plasma sintering(SPS) method, and the characteristics of hydrogen permeation through the alloy membrane were examined. And also a target for sputtering was prepared by applying Ni-Zr amorphous alloy such as Ni64-Zr36 and double layer Ni64-Zr36/Zr36-Zr36. We also suggest that the hydrogen electrode had the composition considering the hydrogen permeability and the oxygen electrode had the graded composition that maximizes the oxidation-resistance. The optimization was done with these electrodes to achieve the desired hydrogen permeability and chemical stability at the same time. The hydrogen permeation properties through those alloy thin films were examined. Moreover, hydrogen solubility and diffusivity were also measured in order to discuss the mechanism for hydrogen permeation. The existing Pd-based metal alloy's permeable membrane and characteristics were comparatively analyzed by measuring microstructure, hydrogen transmittance and mechanical strength, etc. of the manufactured permeable membrane.

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17:45 **Magnetic properties of graphene /nickel composite in different oxidation levels**
Authors : Maryam Salimian, Olena Okhay, Rahul krishna, Joao Ventura, Elby Titus,Jose Gracio
Affiliations : 1.Nanotechnology Research Division, Center for Mechanical Technology and Automation (TEMA), Department of Mechanical Engineering, University of Aveiro, Aveiro 3810-193, Portugal 2. Instituto de Física dos Materiais da Universidade do Porto (IFIMUP) and Faculty of Sciences University of Porto, Porto 4169-007, Portugal
Resume : In this work the magnetic properties of graphene/nickel based composite were studied. We specifically focused on the different levels of oxidation of graphene oxide using series of oxidation treatments. Graphene oxide was successfully synthesized by hummer method and characterized. In each step by reduction of oxygen functionalities with chemical treatment, reduced graphene oxide (RGO) was achieved. In following, different samples which labeled with different level of oxidation, decorated by nickel nanoparticles. Finally magnetic properties of all samples were studied and compared. C/P1 29

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17:45 **Co3O4@Layered Double Hydroxide Core/Shell Hierarchical Nanowire Arrays for Enhanced Supercapacitance Performance**
Authors : Fanyu Ning, Mingfei Shao, Chenglong Zhang, Simin Xu, Min Wei
Affiliations : Beijing University of Chemical Technology
Resume : Co3O4@NiAl-layered double hydroxide (LDH) core/shell nanowire arrays with hierarchical structure have been synthesized by in situ growth of LDH nanosheet shell on the surface of Co3O4 nanowire arrays. The resulting Co3O4@NiAl-LDH material exhibits promising supercatacitance performance with largely enhanced specific capacitance and rate capability, much superior to pristine Co3O4 nanowire arrays. The improvement in electrochemical behavior is attributed to the hierarchically mesoporous morphology and the strong core-shell binding interaction, which facilitates a sufficient exposure of electroactive species as well as the charge transportation process. This work provides a facile and effective strategy for the fabrication of hierarchical materials with core/shell structure, which can be potentially used in the energy storage and conversion devices. C/P1 30

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17:45 **Ultra High Frequency Rectifier Based On Pt-IGZO Schottky Diodes**
Authors : Jiawei Zhang, Aimin Song
Affiliations : University of Manchester
Resume : Amorphous Indium-Gallium-Zinc-Oxide (IGZO) is emerging as a promising semiconductor for low temperature processing, flexible and thin-film devices. Although many research papers have been written on IGZO thin-film transistors, the applications of metal-IGZO Schottky junctions have not drawn much attention. Due to the high carrier concentration and absence of minority carriers, metal-IGZO Schottky diodes have the potential as front end rectifiers in wireless communication devices and radio-frequency energy harvesting C/P1 31

systems. Here we demonstrate ultra-high frequency rectifiers based on IGZO Schottky diodes with the cut-off frequencies extracted from S-parameters higher than 900 MHz without any post-treatment. Diodes fabricated on glass substrates have shown on/off ratios of 10^8 with ideality factors close to unity. By increasing the thickness of IGZO layer, a higher cut-off frequency was obtained. These properties suggest further applications in communication systems such as GSM 900 network and RFID tags. The room temperature fabrication process also provides the potential to be used in flexible devices.

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Solid state ionics: thin films for energy and information applications

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start at	Subject	Num.
	Resistive Switching in Metal Oxides : Prof. R. Dittmann and Prof. X. Guo	
08:30	**Opportunities and Challenges for the Solid State Ionics Community in the Field of Emerging Memory Technologies** **Authors :** R. Meyer **Affiliations :** - **Resume :** With planar NAND Flash memory technologies approaching its physical limits, the semiconductor memory industry is looking into non-silicon alternatives with the potential to compete with and eventually replace the main stream technology. Over the last decade several memory technologies based on a resistance change effect, commonly referred to as resistive RAM, have been developed. Prominent examples are Magnetic RAM (MRAM, STT-MRAM), Phase Change Memory (PCM), Conductive Bridge Memory (CBRAM), and oxide based RRAM. Oxide based RRAM cells comprise of one or more functional oxide layers. The resistance change is based on an electric field driven redistribution of oxygen vacancies within the layers causing a variation of the electrical conductivity. Even though there are similarities in the operation compared to solid oxide fuel cells and batteries, high electric fields, self-heating, interface effects, and the lack of knowledge of the material properties on the nanoscale are key challenges in indentifying underlying mechanisms and improving the performance of oxide RRAM devices. The tunnel RRAM is one example of an oxide based RRAM. The device is formed by a two layer structure comprising of a thin ZrO2 tunnel oxide layer and a conductive perovskite layer, which is typically a manganate. The tunnel RRAM is characterized by a uniform rather than a local change in conductivity, which allows describing the behavior using 1D models. The resistive memory effect is achieved by exchanging oxygen vacancies between the conductive layer and the tunnel barrier. In the presentation, we will review the device functionality and the current state of understanding of the device physics. Opportunities and challenges regarding device modeling and optimization as well as requirements for emerging memory technologies to be able to make the transition from lab to product will be discussed.	C.3.1
add to my program	**(close full abstract)**	
09:00	**Modified point defect chemistry at dislocation networks of TiO2 (Rutile)** **Authors :** Kiran K. Adepalli1*,Rotraut Merkle1,Marion Kelsch2 and Joachim Maier1 **Affiliations :** 1Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany 2Max Planck Institute for Intelligent Systems, Heisenbergstr. 3, 70569 Stuttgart, Germany *present address: Department of Material Science and Engineering, Department of Nuclear Science Engineering, Massachusetts of Institute of Technology, Cambridge, 02139 USA **Resume :** Defects are not only an essential constituent for charge and mass transport in ionic solids but they are also sites with locally increased free energy. This makes them catalytically active centers for heterogeneous reactions and for resistive switching behavior by forming conductive filaments. Change in defect concentration or defect charges would further lead to modification of properties, hence many works related with aliovalent doping, grain boundary engineering, nanosize effects are investigated. Another alternative but important approach is by introducing one dimensional defects (dislocations), whose contribution is not well understood till date. Dislocations are inevitable with device miniaturization and it is critical to understand their	C.3.2

role on point defects. Since dislocations are often charged in ionic solids, they lead to two major synergistic effects; on one hand point defect concentrations are modified by space charge regions adjacent to dislocations and on the other hand defect mobility is affected by the strain around the dislocation core. In this work, dislocations are created in TiO2 single crystals by mechanical deformation and point defect transport is studied along and across dislocations as a function of temperature and oxygen partial pressure. Oxygen isotope and stoichiometric polarization experiments are performed to further characterize charge carriers and their individual contribution in space charge regions. It is observed that dislocations are negatively charged and adjacent space charge regions are accumulated with positive charge defects in TiO2. Further, we discuss some preliminary experiments on SrTiO3. The present understanding may shed light in to memeristor and catalytic behavior in ionic solids.

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09:20 **Current-Voltage Relations and Defect Distribution in Metal1|Mixed Ionic Electronic Conductor|Metal2 Devices**

Authors : Dima Kalaev, Ilan Riess

Affiliations : Physics Department Technion-IIT

Resume : The current-voltage (I-V) relations and charged defect distributions are calculated numerically for a metal1|mixed ionic electronic conductor|metal2 device. The mixed ionic electronic conductor (MIEC) is a thin film that changes its conductivity under a high driving force. The MIEC considered contains one type of mobile donors (or acceptors) and conducting electrons (or holes). Under an applied voltage the mobile donors redistribute and the I-V relations are not linear. Under an applied voltage of periodic waveform the I-V curves show hysteresis and a sharp change in the current derivative, dI/dV. We denote the latter effect as quasi switching. We show that the donor distribution and the I-V relations depend on the following device parameters: the MIEC film thickness, the contact potentials between the MIEC and the metal electrodes, the mobility ratio of donors and electrons and the electrodes impedance for material exchange with the surroundings. The I-V relations also depend on the operation conditions: the waveform and frequency of the applied voltage and the chemical composition of the surroundings. The model assumes a constant temperature, i.e. the stated effects are obtained in the absence of a heating by the current. We shall demonstrate, for the above mentioned MIEC device, the hysteresis and quasi-switching in I-V curves, discuss conditions for I-V curve crossing. We shall also provide a qualitative explanation how the conductive filament grows, whether starting at the cathode or at the anode. While most of calculations must be done numerically, due to the complexity of the differential equations, an approximate analytic solution for the equilibrium state of the device is possible. We present the approximate solution for finite systems with two mobile charge carriers which is a generalization of the Gouy-Chapman solution. C.3.3

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09:40 **Highly disordered thin film oxides**

Authors : M. Martin, L. Nagarajan, J. Brendt, M. Liu

Affiliations : Institute of Physical Chemistry, RWTH Aachen University, Germany

Resume : Ionic and electronic transport in functional oxide materials is of great relevance for applications in the fields of energy and data storage, e.g. solid oxide fuel cells (oxygen ion conductivity), oxygen permeation membranes (ambipolar diffusion of oxygen), or data storage materials (electronic and/or ionic conductivity). In this contribution our recent work on highly non-stoichiometric thin film oxides will be discussed with special emphasis on amorphous, highly non-stoichiometric oxides. In amorphous solids structural disorder can lead to an insulator–metal transition on account of Anderson localization, i.e. the electronic states below the mobility edge are localized. If the Fermi energy passes through the mobility edge the material changes from an electronic insulator to a metal. In addition, large deviations from the ideal stoichiometry of an oxide, that is, high defect concentrations, provide a high concentration of electronic defects (self-doping). We will consider examples of highly disordered oxides that were prepared by pulsed laser deposition and discuss their electronic conductivities and their application in resistive memory devices. C.3.4

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10:10 **BREAK**

10:40

Nanoscale analysis of redox-processes in resistive switching complex oxide thin film devices

Authors : R. Dittmann

Affiliations : Peter Grünberg Institute (PGI 7), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Resume : Although there exists a general consensus that bipolar resistive switching in transition metal oxides is in most cases connected with a redox-process, the details of the underlying physical mechanism are only poorly understood up to now. One of the obstacles for its further elucidation is that the net changes of structure, stoichiometry and valence state during electroforming and switching are very small and occur primarily at the electrode interface ore within nanoscale filaments. In this talk, we will present an overview over the current state of experimental verification of the proposed switching models. For epitaxial SrTiO3 thin film devices, by the combination of scanning force microscopy with photoelectron spectromicroscopy and X-ray absorption spectroscopy, we were able to prove that electroforming goes along with a homogeneous as well a local formation of oxygen vacancies. Moreover, significant changes are detected in the chemical state as well as in the relative stoichiometry of the cation sublattice during electroforming demonstrating the formation of new phases. By performing hard X-ray photoelectron spectroscopy, we could experimentally prove that resistive switching in Pt/Ti/PCMO/SRO/STO devices is based on a redox-process, which mainly happens on the Ti side. The different resistance states are determined by to the amount of fully oxidized Ti-ions in the stack, implying a reversible redox-reaction at the interface, that governs the formation and shortening of an insulating tunnel barrier.

C.3.5

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11:10

Formation and disruption of nano-filaments in HfO2/TiN resistive switching structures

Authors : S. Brivio, G. Tallarida, E. Cianci and S. Spiga

Affiliations : Laboratorio MDM, IMM-CNR, via C. Olivetti 2, 20864 Agrate Brianza (MB), Italy

Resume : In most resistive switching (RS) devices, the commutation of resistance among diverse states is explained in terms of formation and rupture of conductive filaments (CFs) made of ionic species inside a Metal-Oxide-Metal stack. The filamentary-type of operation leads to important implications for downscaling capabilities as well as for operation variability, reasons why a clear understanding of the evolution of the CF shape during formation and rupture processes is a decisive issue. In the present work the tip of a Conductive Atomic Force Microscopy (CAFM) is employed as a mobile electrode on a HfO2/TiN RS structure. First we recognize that in the initial state the conduction is localized in nanometric paths activated by defects sited near the HfO2/TiN interface. The defective paths develop into CFs when a sufficiently high voltage is applied to the structure, reducing the resistance of a RS device. We demonstrate that CFs can be disrupted, closing a RS cycle and restoring a high resistance state. The AFM tip is also used to address single CFs and to study how the operation over one filament influences the neighboring ones. Finally we propose a comprehensive picture of the evolution of CF shape during formation and rupture: rather than a group of nearly parallel and independent CFs, a network of conductive branches ramifies from the defects that activate the conduction in the initial state. This work is partially supported by Fondazione Cariplo (MORE Project n?2009-2711).

C.3.6

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11:30

Resistive switching in SrTixFe1-xO3 Solid Solution Thin Films: Chronoamperommetry as new Tool to Describe Defect Kinetics in Memristive Systems

Authors : F. Messerschmitt, M. Kubicek, S. Schweiger, J.L.M. Rupp

Affiliations : Electrochemical Materials, ETH Zurich

Resume : Redox-based metal oxide resistive switching offers new perspectives towards replacement of classic transistor based memories. Despite the promises of fast non-volatile ns-switching and high package density there is a lack of studies in which carrier contributions (ionic vs. electronic) are systematically varied for an oxide solid solution. Sr(Ti,Fe)O3 is a well-studied model material for which the band gap can be altered by 1.5eV. In this study, cross-bar memory arrays of the model system Pt|Sr(Tix,Fe1-x)O3|Pt were fabricated and discussed towards carrier contributions to kinetics and switching mechanism. First, we classically analyze switching kinetics via cyclovoltametry and pulsed experiments. Independent on doping hysteretic bipolar I-V profiles were recorded; a decrease of the low resistance state (LRS) with reduction of sweep

C.3.7

rate is observed. Unfortunately, pure diffusion kinetics via Randles Sevcik equation cannot be extracted for such redox-based systems in metastable state. Hence, chronoamperometry (CA) measurements to analyze diffusion kinetics and to understand equilibrium vs. non equilibrium transport processes are suggested to the field. Exemplarily, time constants of 200-400s at 1-3V (till stable currents establish) are measured via CA. Through an extension of the classic Cottrell equation we determine bias-dependent diffusion constants of 2x10-19-9x10-20m2/s for 6-2MV/m. Further, humidification effects on the devices` programming voltage and LRS are discussed.

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11:50 **Electrical Characteristics of hybrid Resistive Switching Devices Observed by TEM and Atom probe tomography**

Authors : J. H. Lee, E. J. Cha, B. K. Chae, H. S. Hwang and C. G. Park

Affiliations : Pohang University of Science and Technology

Resume : Resistive switching random access memory has received a great deal of attention as one of the most promising candidates for the next generation non-volatile memory device. In this study, we evaluated hybrid RRAM device consisting of NbO2 and Nb2O5 (Ta2O5) bi-layers. Because the oxidation state of Nb-oxide can be easily modified by a plasma oxidation process, this combination seems to be simple and cost-effective. At first, we demonstrated that NbO2 and Nb2O5 layer act as a threshold switch (TS) and a memory switch (MS), respectively. When we stacked two layers sequentially, however, most of cells showed only simple MS behaviour opposite to our prediction. Cross-sectional TEM images of W(TE)/Nb2O5/NbO2/Pt(BE) device showed that a crystalline Nb-oxide coexists with an amorphous oxide in an operating area. Crystalline Nb-oxide region was identified as the Nb2O5 phase. On the contrary, the amorphous region was identified as the NbO2 and Nb2O5 bilayer by EDS and EELS. An electrical probing has been performed in a TEM chamber to examine the relationship between the phase of oxide layer and I-V properties. As a result, amorphous NbOx layer showed MS TS switching property, while only MS exists at a partially crystalline NbOx layer. We believe that the partially crystalline Nb2O5 region became the leading channel as MS instead of amorphous area. This could be explained with the standard Gibbs free energy of formation of NbO2, Nb2O5, and NbO. According to an Ellingham diagram, it is likely to be happened the compositional fluctuation in a nanometer scale. Atom probe tomography revealed that the cyclic I-V measurement had changed the local concentration of oxygen at NbOx. C.3.8

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12:10 **Investigation of nanoscale ionic transport in oxide materials**

Authors : Nina Balke, Stephen Jesse, Sergei Kalinin

Affiliations : Center for Nanophase Materials Sciences Oak Ridge National Laboratory

Resume : Ionic currents determine the functionality of various devices for energy and information applications, such as Li-ion batteries, fuel cells, or memristor-type applications. To understand device limitations and to draw a roadmap to optimize device properties, the ionic flow has to be studied on relevant length scales of grain sizes, structural defects, and local inhomogeneities, i.e. over tens of nanometers. Knowledge of the interplay between the ionic flow, material properties, and microstructure can be used to optimize the device properties, for example to maximize energy density, increase charging/discharging rates, and improve cycling life for Li-ion batteries for applications in electric vehicles and aerospace. Scanning Probe Microscopy (SPM) is a universal tool to study electromechanical effects in oxide materials. While used extensively to investigate the piezoelectric effect in ferroelectric materials, SPM was used in various ways to study ionic transport in oxides in recent years. Ionic transport in these systems can be studied through the interplay of materials volume changes and ionic concentration and the interaction of near-surface charges and the SPM tip. In this talk, we want to give an overview over what has been achieved in the fields of Li-ion batteries, Li-air batteries, fuel cells, and electrochemical supercapacitors using SPM-based techniques. We will focus on SPM signal generation and data interpretation and provide numerical and analytical models to support various scenarios. The goal is to show the possibilities of SPM-based methods to study ionic transport in various material systems with an unmatched lateral resolution and highlight the interplay between ionic transport and microstructure. Support was provided by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division, Scientific User Facilities Division, and by the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center. C.3.9

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12:40 **LUNCH**

Theory : Prof. M. Martin and Dr. R. DeSouza

14:00 **Elastic Strain and Dislocations in Oxide Thin Films: Hand-in-hand or counter?** C.4.1

Authors : Bilge Yildiz, Lixin Sun, Dario Marrochelli, Yue Fan

Affiliations : Laboratory for Electrochemical Interfaces, Department of Nuclear Science and Engineering, Massachusetts Institute of Technology 24-210, 77 Massachusetts Avenue, Cambridge 02139, USA

Resume : Enhancement of ionic conductivity in thin films or multilayers of oxide materials, i.e. doped zirconia and ceria, has sparked great interest in the search for fast ion conducting structures for fuel cells as well as for red-ox based resistive memories. The enhancement in ionic conductivity in such structures could be attributed to elastic strain arising from the lattice mismatch at the interface. However, this assumes that the interface between two materials is perfectly coherent, while in most cases dislocations are observed, and these dislocations relax the interfacial elastic strain. The strain field and the electrostatic field that arises from the dislocations can also impact the defect stability, distribution and mobility in these materials; and yet, the role of dislocation on the ionic conductivity is not consistently reported in the literature nor is it clearly understood. The aim of our work is to quantitatively assess the dislocation's influence on the ionic conductivity in fluorite and perovskite oxides, exemplified by doped CeO2 and SrTiO3, respectively. Edge dislocations in in these materials are studied by atomistic simulations combining the Monte Carlo, Molecular Dynamics and Nudge Elastic Band calculations. Asymmetric distribution profiles of dopant cations and oxygen vacancies are found as a result of the strain field of the dislocation, and the diffusion kinetics along and across the dislocations is found to depend on the structure and composition.

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14:30 **Migration of cation defects in cerium dioxide** C.4.2

Authors : Stefan Beschnitt, Tobias Zacherle and Roger A. De Souza

Affiliations : Institute of Physical Chemistry, RWTH Aachen University

Resume : CeO2 serves as a model fluorite-type oxide, since it adopts cubic symmetry under ambient conditions without the need for stabilizing substituents, in contrast to other notable fluorite-type oxides, such as ZrO2 and HfO2. In this study we investigated the migration of cerium ions in CeO2 by means of static lattice simulations. Activation energies for migration were obtained from classical simulations based on various sets of empirical pair potentials (EPP) and from quantum mechanical simulations employing density-functional-theory (DFT) calculations. Vacancy, interstitial and interstitialcy mechanisms were considered. In addition, the influence of adjacent oxygen vacancies on cation migration mechanisms was examined, since the defect chemistry of nominally undoped and acceptor-doped systems is dominated by oxygen vacancies. Our results predict that cerium diffusion occurs by a vacancy mechanism in CeO2. Comparisons with experimental and computational data for other fluorite oxides are also made.

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14:50 **MOLECULAR DYNAMICS SIMULATIONS OF PROTONIC AND IONIC CONDUCTORS UNDER STRAIN** C.4.3

Authors : A. Ottochian, D. Frimat, G. Dezanneau

Affiliations : Lab. SPMS, Ecole centrale Paris, Grande voie des vignes 92295 CHATENAY-MALABRY CEDEX, France

Resume : To reach high conduction of ions in materials for Solid Oxide Fuel Cells (SOFC), nowadays the research is pushed to the nanoscale. Often only a multilayered structure can takes synergically advantage of the the single layers. But stacking different materials creates biaxial strains due to the mismatch between the cell parameters of the phases in contact. The cell deformation was shown in experiments [1,2] to seriously affect the ions conduction. Molecular Dynamics (MD), thanks also to recent technique like the "reactive" framework [3], can help the comprehension of these effects. Oxygen conduction in Y-stabilized ZrO2 [5] and proton diffusion in BaZrO3 doped by Yttryum [6] was successfully already studied by the present authors with MD. Here, the know-how to treat isostatic and biaxial strained structure by MD will be applied to the double perovskyte GdBaCo2O5.5 (GBCO): a mixed ion/electron conductor particulary attractive for SOFC due to the low area specific resistance. The bidimensional character of its diffusion can be affected in not trivial forms when the cell is deformed by isostatic pressure or biaxial strain. [1] J. G. Garcia-Barriocanal, et al., Science 321 (2008) 676 [2] C. Korte, et al., Phys. Chem. Chem. Phys. 10 (2008) 4623?4635 [3] A. Warshel, R. Weiss J. Am. Chem. Soc. 102 (1980) 6218 [4] G. Dezanneau, J.Hermet, B. Dup?, Int J Hydrogen Energy 37 (2012) 8081-8086 [5] A. Ottochian, G. Dezanneau, et al., J. Mater. Chem. A, in press.

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15:10 **A comparative study of structural stability of complex perovskites for solid oxide fuel cells: First principles thermodynamic calculations**

Authors : E.A. Kotomin, M.M. Kuklja, D. Fuks, Yu. A. Mastrikov, J. Maier

Affiliations : Max Planck Institute for Solid State Research, Stuttgart, Germany; Institute for Solid State Physics, University of Latvia, Riga, Latvia; Materials Science and Eng. Dept., University of Maryland, College Park, MD, USA; Dept Materials Engineering, Ben Gurion University of the Negev, Israel

Resume : Among advanced materials for clean energy, oxygen-deficient mixed conducting perovskites BSCF and LSCF are considered as promising materials for cathodes in solid oxide fuel cells (SOFC) and oxygen permeation membranes. BSCF exhibits the best oxygen exchange performance amongst similar materials, which can be related to its mixed electronic and ionic conductivity. In particular, its high oxygen vacancy concentration and low diffusion activation barrier contribute to the fast oxygen reduction kinetics. However, it exhibits a tendency to decompose at intermediate temperatures into a mixture of cubic and hexagonal perovskite phases which is detrimental for its use. In order to understand a mechanism of this unwanted process, first principles quantum mechanical calculations of BSCF and LSCF with different oxygen deficiency were performed and possible decomposition scenarios studied. It was shown that formation energies of oxygen vacancies in the cubic and hexagonal phases of BSCF differ considerably not only in absolute values, but also in their variation with the actual oxygen non-stoichiometry. In fact, it is a large oxygen non-stoichiometry that makes the cubic phase more stable than the hexagonal one. LSCF is shown to be much more stable with respect to such a phase transformation. The first principles calculations are accompanied with the thermodynamic analysis of the conditions under which the cubic phase is stable. M. Kuklja, E.Kotomin, R. Merkle, PCCP 15, 5443 (2013). C.4.4

add to my program **(close full abstract)**

15:30 **Band Diagrams for Electrochemical Devices.**

Authors : J.Roqueta, J.Santiso

Affiliations : Institut Catala de Nanociencia i Nanotecnologia (ICN2)

Resume : Around ten years ago Joachim Maier showed the mathematical equivalence between electronic point defects in semiconductors and ionic point defects in electrolytes and mixed conductors. Moreover he introduced the band structure simultaneously for electronic and ionic defects in the same band diagram to explain deviations in carrier concentration in thin films and at grain boundaries [1]. In this work we will show how these double band diagrams can be used to understand a variety of situations in electrochemical systems in equilibrium and out of equilibrium. We introduce a very simple toy model which retains the basic features of MIEC materials and allow us to model currents at heterointerfaces under polarization [2] using the same formalism as in conventional semiconductors. We will show how one can anticipate the electrochemical potentials distribution and charge concentration across a sample under different driving forces like electronic currents, neutral chemical currents or the influence of UV light illumination. Finally, we will try to discuss some device configuration inspired in conventional electronic devices and recent spintronic devices. [1] J. Maier, Nature Materials 4, 805 - 815 (2005) [2] J. Roqueta et al. arXiv:1307.6753 [cond-mat.mtrl-sci] C.4.5

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15:50 **BREAK**

16:20 **Atomistic modelling of symmetric tilt grain boundaries in SrTiO3**

Authors : Amr H. H. Ramadan and Roger A. De Souza

Affiliations : Institute of Physical Chemistry, RWTH Aachen University

Resume : In this study we employ atomistic simulations with empirical pair potentials to model symmetrical [001] tilt grain boundaries in SrTiO3. Various low angle grain boundaries, consisting of periodic arrays of edge dislocations, C.4.6

and high angle grain boundaries are examined. The excess energies and volumes of the grain boundaries are computed. In addition, the interaction of point defects with the grain boundaries is considered. For all boundaries investigated, oxygen vacancies are found to have lower formation energies at the interfaces. On the basis of these formation energies, we use a continuum approach to predict the space-charge potential as a function of the thermodynamics, temperature, dopant concentration and oxygen partial pressure. The results obtained are then compared to the experimental observations found in literature.

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16:40 **Ab initio calculations of SrTiO3, BaTiO3, PbTiO3 and CaTiO3 (001), (011) and (111) surfaces**

Authors : R. I. Eglitis

Affiliations : Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str., Riga LV1063, Latvia

Resume : While the (001) surfaces of SrTiO3, BaTiO3, PbTiO3 and CaTiO3 have been extensively studied, much less is known about the (011) and (111) surfaces [1-3]. As for the (011) surfaces, I consider three types of surfaces, terminating on a TiO layer, a Ba(Pb,Sr or Ca) layer and O layer. The surface relaxation energies for BaTiO3, PbTiO3, CaTiO3 and SrTiO3 (011) surfaces for all terminations are considerably larger than for (001) surfaces. I predict a considerable increase of the Ti-O chemical bond covalency near the ATiO3 (011) surfaces as compared to both the bulk and the (001) surfaces. My calculated SrTiO3, BaTiO3, PbTiO3 and CaTiO3 (111) surface energies are considerably larger than the another ABO3 perovskite (001) and (011) surface energies [4,5]. This work was supported by ESF Grant Nr. 1DP/1.1.1.2.0/13/APIA/VIAA/021. References: 1. R. I. Eglitis and D. Vanderbilt, Phys. Rev. B 76, 155439 (2007). 2. R. I. Eglitis and D. Vanderbilt, Phys. Rev. B 77, 195408 (2008). 3. R. I. Eglitis and D. Vanderbilt, Phys. Rev. B 78, 155420 (2008). 4. R. I. Eglitis, Ferroelectrics 424, 1 (2011). 5. R. I. Eglitis, Phase Transitions 86, 1115 (2013). C.4. 7

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17:00 **Ab initio study of rare-earth compounds for Li-ion battery applications**

Authors : Frank Grosse

Affiliations : Paul-Drude-Institut für Festkörperelektronik Berlin (Germany)

Resume : Discovering new and improving existing materials plays a crucial role especially in energy applications with its increasing demands. For application in Li-ion batteries as cathode, anode, or solid-state electrolyte a central part plays the Li-ion diffusivity. A route to improving Li-diffusion channels by increasing the lattice parameters could be achieved by an appropriate incorporation of dopants with a large atomic radius. Here, rare-earth elements (RE) are considered as dopants in existing cathode materials, like LiMnO2, in order to increase the lattice parameter and improving the Li-conductivity. First, as a prerequisite the thermodynamic stability for the Li-RE-O system is studied. The calculations confirm experimentally observed structures but additional new crystal structures are found. Second, scenarios for doping existing cathode materials with RE are studied. Focus is here on the formation energy of the defects and the introduced lattice variation. Third, the increase lattice parameter is related to the diffusion of the Li inside the material. On this basis scenarios for improving Li diffusivity inside of cathode materials are discussed. C.4. 8

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Solid state ionics: thin films for energy and information applications

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Oxide Interfaces : Prof. Y. Kuru and Dr. G Gregori

08:30

Fast ionic conduction and diffusion in solid electrolytes along interfaces –- Overview on recent studies on oxide ion conductors and an interface strain based model for thin layered systems

Authors : Carsten Korte

Affiliations : Fuel Cell Laboratory, FZ Jülich, Germany

Resume : Ionic conduction and diffusion in micro-/nanoscaled materials differs significantly from bulk materials. This is due to the modified transport properties of solid-solid interfaces and surfaces. In this contribution a literature overview is given on experimental studies treating ionic transport in thin films and multilayers. By reviewing and comparing the data, the magnitudes of the observed interface effects can be classified, considering the total increase of the conductivity/diffusivity together with the layer thickness. The least effect can be found i) in case of transport along boundaries between extrinsic ionic conductors (and insulator). Mediocre effects can be measured for ii) transport along surfaces of extrinsic ionic conductors. The highest effects are reported for iii) transport along boundaries between intrinsic ionic conductors. The effects differ by about two orders of magnitude (1 : 101 : 102). The modified interface transport in category i) is most probably due to strain effects, misfit dislocations or disordered transition regions. Focussing on strain effects, an analytical model, based on a phenomenological description will be presented. A multilayer consisting of crystalline thin films with coherent interfaces and biaxial mechanical strain due to lattice misfit is assumed. The conjoined layers consist of columnar crystallites with constricted cross section, enabling strain relaxation by shear. Expressions for the total ionic transport relative to bulk transport and for the spatial extent of the strained interface regions as a function of the layer thickness are obtained. The model is used to describe experimental data from O2- conductivity and 18O diffusion studies as well as from XRD strain studies, performed on YSZ/rare earth metal oxide multilayers with systematically varied lattice misfit.

C.5. 1

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09:00

The interplay of cationic defects in STO and electrical properties of the LAO/STO -interface

Authors : F.Gunkel, S. Wicklein, S. Hoffmann-Eifert, R. Dittmann, R. Waser

Affiliations : Forschungszentrum Jülich GmbH, Peter Gruenberg Institute 7 & JARA-FIT

Resume : The role of defects is a focus of the ongoing discussion about the electronic properties of the conducting interface between the two insulators LaAlO3 (LAO) and SrTiO3 (STO). In this study, the LAO/STO-interface is discussed from a defect chemical point of view. Utilizing conductance measurements in high temperature equilibrium with the surrounding atmosphere we discuss the conduction mechanism and defect-related charge compensation mechanisms at the LAO/STO interface. In particular, we will show that at high oxygen partial pressures Sr-vacancies are formed as a result of an unavoidable thermodynamic equilibrium process (Schottky-equilibrium). These acceptor-type defects reduce the electron density finally resulting in insulating interfaces. We furthermore investigated the transport properties of LAO/STO-bilayers. The interplay of cationic defects in the STO layer and electronic properties of the bilayer-interface is systematically analyzed by a growth-controlled variation of the cation-stoichiometry in the STO thin films. Resistance

C.5. 2

measurements and Hall measurements on various bilayer-samples reveal a stoichiometry-effect on both electron mobility and carrier density. The results indicate an enhancement of scattering processes in as-grown non-stoichiometric samples which is in line with an increased density of defects.

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09:20 **Step-conformal deposition of TiO2 and MnO2 electrodes on advanced silicon microstructures for 3D Li-ion microbatteries and micro-supercapacitors,**

Authors : E. Eustache1,2,3, C. Douard2, P. Tilmant1,3, L. Morgenroth1,3, P. Rousse4l, T. Brousse2,3 and C. Lethien1,3

Affiliations : 1 Institut d'Electronique, de Microélectronique et de Nanotechnologie, CNRS UMR 85202 2 Institut des Matériaux Jean Rouxel, CNRS UMR 6502 France, 3 Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR 3459 4 Unité de Catalyse et de Chimie du Solide (UCCS), CNRS UMR 8181

Resume : To get autonomous smart microsystem, a miniaturized power source should be integrated. As the device is surface limited, the energy and power performances of commercially available planar microbatteries and micro-supercapacitors are not sufficient to reach this goal. To improve their performances while keeping constant the footprint area of such devices, a 3D topology is proposed. The silicon micropillars and microtubes fabricated by a top down approach allows to reach a high area enlargement factor (AEF). Energy density can be increased by one or two orders of magnitude compared to standard planar micro-devices, thus providing improved autonomy to the powered microsytems. Step conformal deposition of platinum (current collector) and TiO2 (negative electrode of the Li-ion microbattery) are performed on the 3D structures by Atomic Layer Deposition facility. With a 3D scaffold having an AEF close to 25 combined with a 150 nm thick TiO2, a surface capacity of 0.2 mAh/cm2 at C/10 is reported. A micro-supercapacitor electrode based on a thin manganese dioxide film is conformably grown by pulsed electrodeposition on the 3D topologies. A MnO2 film (275 nm thick) reaches 250 mF/cm? at 5 mV/s. The surface capacitance is drastically enhanced compared to a standard 2D electrode with a comparable thickness. This study shows promising AEF leading to high energy density while keeping enough spacing in the microstuctrures array to allow the deposition of the overlying layers. C.5.3

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09:40 **In-situ Hall-effect monitoring of vacuum annealing of In2O3:H2O thin films**

Authors : H. Wardenga, M. V. Hohmann, A. Klein

Affiliations : Technische Universität Darmstadt, Institute of Materials Science, Surface Science Division, Jovanka-Bontschits-Straße 2, 64287 Darmstadt, Germany

Resume : In2O3 is an important transparent electrode material for solar cells. In order to obtain sufficiently high carrier concentrations, Sn-doping is widely used. Such films show electron mobilities of 30-40 cm2/Vs and have a high reflectivity in the infrared region of the light spectrum. While this is desirable for energy efficient (low-E) windows, it can cause noticeable reduction of the photocurrent of solar cells with semiconductor energy gaps around 1 eV. One way to prepare In2O3 films with high carrier mobility (up to 100 cm2/Vs) is vacuum annealing of films deposited at room temperature under the addition of H2O to the process gas. We have deposited such films using magnetron sputtering. The samples are analyzed in-situ using photoelectron spectroscopy, and ex-situ using X-ray diffraction, optical transmission and Hall-effect. Moreover, we present in-situ Hall-effect studies during vacuum annealing, revealing distinct dependence of carrier concentration and mobility with time at different annealing temperatures. For all annealing temperatures, the evolution with annealing time occurs in three steps, which occur faster with higher temperature. The strong changes of carrier concentration and mobility are related to the decomposition of the partially present hydroxide into oxide, crystallization and strain relaxation, as well as to H and O diffusion. It is suggested that H passivation of grain boundaries is the main origin of the high mobilities obtained with In2O3:H2O films. C.5.4

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10:00 **BREAK**

10:30 **Electrical conducting thin films: The importance of charge carrier redistribution at interfaces** C.5.5

Authors : G. Gregori, M.C. Göbel, F. Baiutti, E. Gilardi, G. Logvenov, J. Maier

Affiliations : Max Planck Institute for Solid State Research, Heisenbergstr. 1, D-70569 Stuttgart, Germany

Resume : The ability of fabricating thin films and multilayered heterostructures with different microstructures by simply modifying the growing conditions or choosing different substrates has disclosed an exciting playground to (i) investigate how boundary effects (e.g. charge carriers redistribution and strain) impact the electrical transport properties and (ii) explore new solutions to improve conduction properties of materials. Over the last years, we have quantitatively investigated how (i) boundaries affect the charge carrier concentrations by comparing the conductivities of nanocrystalline and epitaxial thin films; (ii) how a charge carrier enrichment can be safely detected at the film/substrate interfaces and to which extent it can affect the transport properties of the film; (iii) how ion redistribution at interfaces of heterostructures can modifies the overall electrical properties of multilayered systems. In the present contribution, a series of fascinating examples will be illustrated, which emphasize the relevance of interface effects on the ionic and the electronic transport properties of the above mentioned situations.

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11:00 **Tuning the Ionic Conductivity of Er2O3-Gd0.1Ce0.9O2-x Multilayer Dot Micro-Devices by Lattice Strain: Implications for Fabrication and Oxide Near Order-Transport Interaction**

Authors : S. Schweiger, M. Kubicek, C. Murer, J.L.M. Rupp

Affiliations : Electrochemical Materials, Department of Materials Science, ETH Zurich, Switzerland

Resume : The concept of strain at internal interfaces in heterostructures can be used to tune material properties, like conductivity, far beyond the change accessible by doping. In particular, strain engineering at metal oxide heterostructure interfaces is a versatile concept and is currently discussed for potential fuel cell applications but so far no micro-devices have been demonstrated. Also, near order-ionic transport interaction requires attention to relate effective strain to the lattice and ionic hopping. In this work, a new approach to fabricate electrochemical devices composed of a strained multilayer micro-dot with sidewise contacting is reported. The material system Gd0.1Ce0.9O2-x/Er2O3 was investigated by changing the number of interfaces from 1 to 60 while keeping the device at a constant thickness. Electrical measurements showed that the activation energy of the devices could be altered by Δ0.31 eV by changing the compressive strain of a micro-dot ceria-phase by 1.6%. Furthermore, a way to investigate the anion-cation near-order of the strained metal oxide heterostructures by Raman spectroscopy is shown. A strain activated volume tensor model is extended to the experimental near-order-transport findings. Contacting over the top electrodes does not allow measuring strain effects in heterostructures; micro-dot side-wise contacting is required to measure all strained interfaces. Finally, very first memristive current-voltage profiles of micro-dots under strain are reported. C.5.6

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11:20 **The effect of orientation, thickness and lattice strain of the surface segregation in CGO thin films**

Authors : George F. Harrington, Stephen J. Skinner, David W. McComb and John A. Kilner

Affiliations : 1) Department of Materials, Imperial College London, London, UK 2) Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio, USA

Resume : Cation segregation to the surface of materials for SOFC applications is known to impact on overall device performance and hence is of great interest both fundamentally and practically. Experimental studies focused on the transport properties of ion conductors when grown as strained thin films have recently attracted considerable interest, yet cation segregation is rarely considered. However, changes in the chemical composition cannot be neglected especially when the dimensions of the films approach those distances (tens of nanometers) over which cation segregation is expected to occur. In this work we have employed Low Energy Ion Scattering (LEIS) to study the (100) surface of CGO films on STO, YSZ and LAO substrates and the (111) surface grown on sapphire fabricated by pulsed laser deposition (PLD). We show that as-grown films show minimal segregation despite high temperatures used during fabrication (600 - 800?C), yet the surface composition varies drastically from the nominal bulk when heated post growth to temperatures associated with processing or conductivity measurements (800 - 1000?C). Furthermore we find that the strain induced on the films by the substrates, as measured by XRD, affects the extent of the surface segregation. After an 800?C anneal CGO films grown on STO are observed to have a surface Gd/Ce ratio of over 7 times that C.5.7

of the bulk composition whereas those grown on LAO show only a three-fold increase, with the CGO/YSZ system being the intermediate case. The effects of lattice strain on the driving force for dopant segregation will be discussed along with the composition profile as the film thicknesses are decreased to the length scales associated with the segregation effects.

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11:40 **Interface Control of Oxide Films vs Silicon for next Generation Memories at IBM**

Authors : Marchiori, C. Fompeyrine J.

Affiliations : IBM Research

Resume : During the last 10 years, the quest for a replacement gate dielectric in field effect transistors has been a powerful driver to investigate the deposition of ultra thin oxide thin films. Replacing SiO2 with HfO2 in transistors was a major breakthrough for the microelectronic industry and generated a lot of know-how. This knowledge is today cross-fertilizing research areas that are not limited to the search for a new gate dielectric. Controlling the interface between the oxide and silicon has for example always been a key issue. This specific research triggered the development of new deposition processes, enabling researchers to grow high quality, crystalline, complex oxide films onto silicon. Such “functional” oxides have physical properties that make them very attractive to perform functions that will be required in future Information and Communication Systems. Properties such as ferroelectricity, piezoelectricity or electro-optic activity is often tightly depending on the ionic character of these materials, on the structural details in the cationic or anionic sub lattice, etc. This presentation will deal with the opportunities and challenges to combine silicon microfabrication techniques with the capability to grow crystalline directly on silicon. It will in particular focus on the use of ferroelectric perovskites for photonic circuits in future systems, and how defect chemistries might play a crucial role. C.5.8

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12:10 **CMOS-compatible 3-D electrostatic supercapacitors fabricated within high surface area nanostructured templates**

Authors : Micheal Burke, Alan Blake, Aidan Quinn

Affiliations : Tyndall National Institute

Resume : We report a wafer-scale CMOS-compatible fabrication route for a metal-insulator-metal electrostatic supercapacitor using hybrid atomic layer deposition/anodised aluminium oxide schemes. Initial results for templates with modest pore depths (< 1 µm) yielded a very large capacitance density (~ 12 µF/cm2) representing an enhancement factor ~8 over calculated planar equivalent capacitance for modest pore depths. We further show that these electrostatic supercapacitors can provide “on-chip” energy storage capabilities, with an energy density value of 0.28 Wh/kg. We expect significant further increases in capacitance density (> 10) through optimisation of metal ALD processes for templates with pore depths > 10 µm. C.5.9

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12:30 LUNCH

14:00 POSTER SESSION 2

14:00 **Synthesis and electrical properties of (CaxSr1−x)TiO3 as anode material**

Authors : Ali Matri , Messaoud Kahlaouia, Abdewaheb Inoublia , Adel Madania,

Affiliations : Material physics laboratory , faculty of sciences of bizerte Tunisia, University Carthage b Appiled Science college , University Um Al-Qura , Makkah Al Mukarramah .KSA

Resume : In this study we try to develop a doped perovskite oxide as anode material for solid oxide fuel cell (SOFC) operating at high temperature (800 to 1000 ? C). SrTiO3 doped with calcium on the A-site, CST (CaxSr1-xTiO3) perovskite material were synthesized by the solid state reaction method. The X-ray diffraction results indicate that strontium calcium titanates powders show two crystalline structures: perovskite quadratic for x=0.2 and orthorhombic for x=0.4. Electrical measurements properties on sintered pellets of the materials have been investigated within a wide range of temperature from 200?C to 800? C and frequency range from 10 Hz to 13MHz using complex impedance spectroscopy (CIS) technique. The complex impedance analysis has suggested the presence of grain (bulk) as well as grain boundary contributions in the materials. The CIS studies have suggested the presence of non-Debye type of C/P2 1 relaxation in the materials. The ac conductivity increases with temperature increasing following the Arrhenius law, The lowest activation energy value of 0.79 eV was derived for (x = 0.4). Ea value reaches to 1.03 eV for (x = 0.2). The frequency dependence of the electric conductivity follows a power law behavior of Jonsher at low and high temperature.

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14:00 **Electrochemical properties of $La_{0.2}Sr_{0.7}TiO_3$ thin film electrodes under reducing conditions** C/P2 2

Authors : Fritscher G. (1), Kogler S. (1), Huber T. (1), Opitz A. (1), Fleig J. (1), Heel A. (2), Burnat D. (3), Holzer L. (4)

Affiliations : (1) Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9, 1060 Vienna; (2) ZHAW, Zurich University of Applied Sciences, Institute of Materials and Process Engineering, Technikumsstrasse 9, CH-8400 Winterthur, Switzerland; (3) EMPA, Swiss Federal Laboratories for Material Science and Technology, High Performance Ceramics, Ueberlandstasse 129, CH-8600 Duebendorf, Switzerland; (4) ZHAW, Zurich University of Applied Sciences, Institute of Computational Physics, Wildbachstrasse 21, CH-8400 Winterthur, Switzerland

Resume : $La_{0.2}Sr_{0.7}TiO_3$ (LST27), an A-site deficient lanthanum doped strontium titanate, is a potential anode material for solid oxide fuel cells (SOFCs). In contrast to most other SOFC-relevant perovskite-type electrodes it exhibits n-type conductivity [1]. Reaction paths and the role of ion conduction are still under debate and experiments on geometrically well-defined thin film micro-electrodes can yield further information. LST27 microelectrodes were prepared by pulsed laser deposition (PLD) and subsequent micro-patterning by photolithography. A defined initial state of all samples was established by pre-annealing in reducing atmosphere at 1273 K. The electrode characterization was done by impedance spectroscopy (IS) and van der Pauw (vdP) measurements on microelectrodes and thin films, respectively. All measurements were performed at 773 - 1023 K in H_2 2.5%/H_2O 2.5%/Ar-atmosphere. A high electronic conductivity in reducing atmosphere could be measured in the vdP experiments and is in accordance with literature data on bulk samples. The observed transmission-line-like behavior of the electrode impedance indicates that a transport process affects the polarization resistance of the electrode reaction. Long time measurements and temperature cycling can cause significant changes of the polarization resistance (partly an improvement) and those are discussed in terms of defect chemical changes. [1] D. Burnat, et al., Journal of Power Sources 201 (2012) 26-36.

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14:00 **Electrochemical properties of acceptor doped ceria electrodes in reducing atmosphere: The separation of elementary processes** C/P2 3

Authors : Peter Velicsanyi, Andreas Nenning, Edvinas Navickas, Alexander K. Opitz, Herbert Hutter, Juergen Fleig

Affiliations : Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-EC, 1060 Vienna, Austria

Resume : In surface science ceria is a highly interesting material owing to its attractive catalytic surface activity and it was thus intensively investigated within the last decade. This high catalytic activity was recently demonstrated to be also very beneficial for the electrochemical H_2 oxidation on Sm doped CeO_2 electrodes with noble metal current collectors [1]. For further improvement and understanding, analysis of the effect of (co-)doping on transport and surface kinetics is helpful. In the present study, model-type thin films of Gd doped and Gd/Mn co-doped ceria were investigated by means of impedance spectroscopy in humid H_2 atmosphere. A novel measurement technique for microelectrodes with interdigitating Pt current collectors was employed. This method allows a separation of the different elementary processes contributing to the electrode impedance. After annealing at 650 °C in humid H_2 atmosphere, the electronic conductivity of Gd-doped ceria is higher than that of the co-doped material. In terms of surface exchange rate, however, the Gd/Mn co-doped ceria shows the higher activity. In addition ^{18}O tracer incorporation into Gd-doped ceria electrodes from a $H_2/H_2{}^{18}O$ atmosphere was performed with and without cathodic polarization. The tracer distribution within the ceria thin film was subsequently analyzed by secondary ion mass spectrometry (SIMS) and correlated with the electrochemical results. [1] Chueh et al. Nat. Mat. 11 (2012), p.155

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14:00 **New water-based sol-gel synthesis routes for $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$-nanolayers** C/P2 4

Authors : Martin Perz, Edith Bucher, Werner Sitte

Affiliations : Chair of Physical Chemistry, Montanuniversitaet Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria

Resume : In this study two newly developed synthesis routes for approximately 100 nm thick layers of the mixed ionic-electronic conducting perovskite LaNi0.6Fe0.4O3-δ (LNF64) are presented. Potential applications for these thin films include electrodes for micro-solid oxide fuel cells and active layers for gas sensors or catalysts. A major advantage of LNF64 as compared to other SOFC cathode materials (e.g. La0.6Sr0.4Co0.2Fe0.8O3-δ) is an improved long-term stability against Cr-poisoning. Aqueous solutions of acetate- or nitrate-precursors and a polymeric binder were deposited on Ce0.9Gd0.1O2-δ substrates by spin coating. After thermal annealing at 700°C the thin films were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). The electrical conductivity of the LNF64-nanolayers was measured by the van der Pauw method as a function of temperature (20≤T/°C≤700) and oxygen partial pressure (10-3≤pO2/bar≤1). It could be confirmed that the thin films exhibit the perovskite structure and that the chemical composition is close to the nominal one. At the surface and cross section a nanocrystalline microstructure with a grain size of approximately 50 nm was observed. The electrical conductivity increases with increasing temperature and increasing pO2. A maximum electrical conductivity of 650 S/cm, which is as high as that reported in the literature for the bulk material LNF64, was found at 700°C and pO2=1 bar.

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14:00

Microstructure and oxygen mobility of doped ceria- Pr(Ni,Co)Ox nanocomposites

Authors : Vladislav Sadykov1,2, Nikita Eremeev1, Ekaterina Sadovskaya1, Arkady Ishchenko1, Vladimir Pelipenko1, Vitaly Muzykantov1, Tamara Krieger1, Vladimir Belyaev1, Vladimir Rogov1,2, Vyacheslav Ivanov1, Zakhar Vinokurov1, Aleksandr Shmakov1,Uvarov3, Yurii Ohlupin3, Artem Ulikhin3

Affiliations : 1Novosibirsk State University; 2Boreskov Institute of Catalysis; 3Institute of Solid State Chemistry and Mechanical Activation, Novosibirsk, Russia

Resume : Nanocomposites comprised of mixed Pr nickelates –cobaltites and Y/Gd-doped ceria are efficient and stable to carbonation cathodes of IT SOFC. In this work factors controlling their oxygen mobility and reactivity were studied. Nanocrystalline samples of doped ceria and Pr nickelates –cobaltites with perovskite and Ruddlesden-Popper structure were synthesized by Pechini method. Nanocomposites were prepared via ultrasonic dispersion of oxide mixtures in isopropanol. Thin layers of nocomposites were supported by slip casting on YDC/YSZ/NiO+YSZ anode substrates. Bulk samples and thin layers were sintered up to 1300 oC in air. Phase composition, morphology, microstructure and elemental composition of domains in nanocomposites were studied by XRD, HRTEM/SEM with EDX and SIMS. Oxygen mobility and reactivity were characterized by oxygen isotope exchange (including C18O2 SSITKA), weight loss and conductivity relaxation studies. Redistribution of Pr between perovskite-like and doped ceria domains and segregation of (Ni,Co)O domains as dependent upon sintering temperature and nanocomposite composition result in broad variation of these domains composition and disordering. Such microstructure provides fast oxygen self diffusion (DO up to 2*10-10 cm2/s at 600 K) via chains of Pr cations with disordered coordination sphere. Even faster oxygen diffusion (Dchem.~ 10-4 cm2/s at 600 K) occurs along domains interfaces amounting to ~1% of oxygen positions in nanocomposites

C/P2 5

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14:00

Characterization of Oxygen Stoichiometry Changes of Selected Mixed Conducting Perovskites

Authors : C. Niedrig, L.-S. Unger, S. F. Wagner, W. Menesklou, E. Ivers-Tiffée

Affiliations : Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe/Germany

Resume : For high-temperature energy applications, e.g., as solid oxide fuel cell cathodes or as dense ceramic oxygen-permeation membranes, mixed ionic-electronic conducting (MIEC) perovskites, namely of the composition (AxSr1-x)(CoyFe1-y)O3-delta (A = La, Ba, Pr), are promising candidates given their excellent oxygen-ionic and electronic transport properties. A high level of oxygen non-stoichiometry is an important prerequisite for a high performance; however, the structural stability of the oxide is also affected by oxygen deficiency. Changes in oxygen stoichiometry Δdelta were determined by coulometric titration experiments performed on selected state-of-the-art MIEC samples (BSCF, LSCF, PSCF) in a tubular zirconia “oxygen pump” setup. This setup facilitates precise oxygen partial pressure control in the entire range

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between pO2 = 10^-18 ... 1 bar between 700 °C and 900 °C. By monitoring the electric current necessary for pumping oxygen through the solid electrolyte into or out of the measurement chamber, the amount of oxygen transported and, thus, changes in oxygen stoichiometry can be determined with a high resolution. All experiments were performed on fine-grained powders to avoid kinetic influences resulting from non-equilibrium conditions. The Δdelta(pO2) behaviour was investigated for the above-mentioned high-performance MIEC oxides down to their low-pO2 stability limits which were similar for all compositions (< 10^-10 bar at temperatures of 700…900 °C).

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14:00

Evaluation of ECR Measurements on MIEC Oxides Performed in an “Oxygen Pump” Setup

Authors : C. Niedrig, L. Willms, L.-S. Unger, W. Menesklou, S. F. Wagner, E. Ivers-Tiffée

Affiliations : Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe/Germany

Resume : The kinetics of oxygen transport is essential for an application of mixed ionic-electronic conducting (MIEC) oxides as solid oxide fuel cell (SOFC) cathodes, as high-temperature gas sensors or as oxygen-permeation membranes. The performance of the materials is determined by the chemical diffusion coefficient D and the surface exchange coefficient k. Commonly, D and k values are determined by electrical conductivity σ relaxation (ECR) using different gas mixtures. Here, however, a closed tubular zirconia “oxygen pump” [1] was used which facilitates precise control of oxygen partial pressure pO2 continuously within the entire range between 10^-18...1 bar at temperatures above 700 °C to determine D and k values for several MIEC oxides such as BSCF and LSCF [2]. In this study we evaluate D and k values by numerical analysis (using MATLAB) of both pO2(t) and σ(t) with the focus on the influence of sample response behaviour, sample geometry, amplitude of pO2 steps (in the range from 10^-5...10^-1 bar), and setup-dependent flush times on the determinability and accuracy. This analysis tool was developed in order to identify a confidence region for (ideally) a set of both D and k values or (in the case of diffusion control) only a D value or (for surface control) only a k value. References [1] C. Niedrig et al., J. Electrochem. Soc. 160, F135 (2013) [2] C. Niedrig, H. J. M. Bouwmeester et al., manuscript in preparation

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14:00

High-Temperature Setup for Hall Measurements on Mixed Conductors

Authors : C. Niedrig, L. Wolff, L.-S. Unger, W. Menesklou, S. F. Wagner, E. Ivers-Tiffée

Affiliations : Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe/Germany

Resume : A high-temperature measurement setup was developed to deconvolute the electronic conductivity in mixed ionic-electronic conducting (MIEC) oxides at temperatures as high as 600 °C. We focus on (Ba0.5Sr0.5)(Co0.8Fe0.2)O3-δ (BSCF) which is a very promising candidate for an application as oxygen-permeation membranes due to its excellent permeation properties [1]. Its conductivity mechanism as a function of temperature has, however, so far not been fully understood. Determination of the (p-type) electronic carrier concentration and mobility may contribute to this understanding. The very low Hall mobilities require frequency-selective measurements which we realized by lock-in technique. The setup includes an alumina high-temperature sample holder with which a 5-point contacted homogeneous sample can be inserted into an external magnetic field of variable flux density B (up to 700 mT), resulting in a Hall voltage perpendicular to both B and the electrical current I. Additionally, a sealed setup enables measurements in different gas atmospheres [2]. By using BSCF thin-film samples chemically deposited onto NdGaO3 single-crystalline substrates [3] a satisfactory signal-to-noise ratio is ensured for the Hall voltage. References [1] J. Sunarso et al., J. Membrane Sci. 320,13 (2008) [2] R. Moos, W. Menesklou, K.H. Härdtl, Appl. Phys. A 61, 389 (1995) [3] K. Asano et al., Solid State Ionics (2013), submitted

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14:00

Characterizations of physical pin-holes in thin film electrolyte via spark discharge method

Authors : Ikwhang Chang1, Sanghoon Ji1, Taehyun Park2,Suk Won Cha1,2

Affiliations : 1Graduate School of Convergence Science and Technology(GSCST), Seoul National University, Gwanakro 1 Gwanakgu, Seoul, 151744, Republic of Korea. 2Department of Mechanical and Aerospace Engineering, Seoul National University, Gwanakro 1 Gwanakgu, Seoul, 151744, Republic of Korea.

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Resume : Electrolytes of solid oxide fuel cells(SOFCs) are the most important component, which transports only oxygen ions without electrical shortages between the electrolyte and the electrode. We carried out the selective deposition (Ag) onto YSZ electrolyte with physical pin-holes via spark discharge method, and thus the pin-holes were characterized by scanning and transmission electron microscopes. Also, we measured electrical properties of pin-holes area and YSZ surfaces via conductive atomic force microscope(C-AFM). As results, we observed the pin-holes originated from the disordered and the defected substrates.

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14:00 **The temperature dependent conductivity of YSZ revisited: Serial two barrier model vs. association model**

Authors : C. Ahamer, A.K. Opitz, G. Rupp, J. Fleig

Affiliations : Institute of Chemical Technologies and Analytics, TU Vienna, Austria

Resume : Yttria stabilized zirconia (YSZ) is probably the most famous oxide ion conductor and numerous studies have dealt with its ionic conductivity. At first glance one might not expect that basic properties such as the temperature dependence of the conductivity (with its characteristic bend in an Arrhenius plot) can still trigger novel considerations. However, owing to the very high doping levels, the common interpretation of the temperature dependence in terms of free and associated vacancies is questionable. In this contribution, we suggest a simple alternative way of data analysis by means of a serial two barrier model. Temperature-dependent conductivity measurements on single or poly-crystals of different Y dopant content were performed. Surprisingly small high temperature activation energies (ca. 0.6 eV) and a reversible dependence of activation energies on heat pre-treatment are found. All results were quantified by the two barrier model and by an association model and possible meanings (or absence of simple meanings) of the fit parameters, particularly of the activation energies are discussed. Based on a comparison with numerical calculations in literature we speculate that dynamic traps including many defects and strong vacancy-vacancy interaction might play a decisive role.

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14:00 **Enhanced ionic transport at the film/substrate interface of epitaxial Y2Zr2O7 layers grown on MgO**

Authors : E. Gilardi, G. Gregori, J. Maier

Affiliations : Max Planck Institute for Solid State Research, Heisenbergstr. 1, D-70569 Stuttgart, Germany

Resume : Thin films and multilayered hetero-structures of mixed and ionic conductors are particularly relevant because (i) they can be employed in micro-SOFC and (ii) they are excellent model systems to investigate specific aspects such as the role of interfaces between two oxides or strain effects which are instead not easily accessible in ceramics. Here, we investigate rare earth pyrochlore and defective fluorite with the chemical formula A2B2O7, which have been already considered as possible electrolyte in SOFC because of their ionic conductivity and high chemical stability. Specifically, thin films of the model system Y2Zr2O7 grown on different substrates by pulsed laser deposition technique have been characterized by impedance spectroscopy together with XRD (including pole figures analysis) and AFM. Remarkably, film grown on different substrates and under different deposition conditions exhibit very similar electrical properties, suggesting the microstructure to only slightly affect the transport properties. Moreover, the study of epitaxial thin films of different thicknesses grown on MgO (110) reveals strong films/substrate interface effects particularly at moderate temperatures, with a significant enhancement of the ionic transport. The role of the interface microstructure as well as possible space charge effects are discussed.

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14:00 **Bismuth oxide thin films grown by radiofrequency-assisted pulsed laser deposition for solid oxide fuel cells applications**

Authors : Catalin Constantinescu (1), Valentin Ion (1), Simona Condurache-Bota (2), Petre Rotaru (3)

Affiliations : (1) INFLPR – National Institute for Laser, Plasma and Radiation Physics, 409 Atomistilor bd., RO-077125, Bucharest, Romania; (2) "Dunarea de Jos" University, Faculty of Sciences; 111 Strada Domneasca St., RO-800201, Galati, Romania; (3) University of Craiova, Faculty of Physics, 13 A.I. Cuza St., Craiova RO-200585, Dolj, Romania;

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Resume : Bismuth oxide has seen interest as a material for solid oxide fuel cells, since it is an ionic conductor, i.e. oxygen atoms move through it. Herein, we present results on bismuth oxide thin films grown by pulsed laser deposition and radiofrequency-assisted pulsed laser deposition, in oxygen atmosphere. The influence of the deposition parameters, i.e. laser wavelength, fluence, oxygen pressure, the use of an oxygen plasma, and substrate type and temperature, on the thin film structure and morphology, are discussed. A comparative study is presented here, on the advantages of using laser processing and micro-/nano structuring vs. other techniques, for applications in solid oxide fuel cells.

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14:00 **Determination of strain states in multilayers of YSZ and Rare Earth Metal Oxides and their effect on ionic conductivity**

Authors : Johannes Keppner, Carsten Korte, Jürgen Schubert, Willi Zander, Mirko Ziegner, Detlef Stolten

Affiliations : IEK-3: Electrochemical Process Engineering; IEK-3: Electrochemical Process Engineering; PGI-9: Semiconductor Nanoelectronics, JARA: Fundamentals of Future Information Technologies; PGI-9: Semiconductor Nanoelectronics, JARA: Fundamentals of Future Information Technologies; IEK-2: Microstructure and Properties of Materials; IEK-3: Electrochemical Process Engineering, Chair for Fuel Cells RWTH Aachen University Germany. All: Forschungszentrum Jülich GmbH, Leo-Brandt Straße 1, 52425 Jülich, Germany

Resume : Ionic conduction in interfaces has been extensively studied in the last decade. Different approaches explain the alteration of transport properties with space charge layers, dislocation networks, disordered transition zones or lattice mismatch induced strain fields. For extrinsically doped oxygen ion conductors like yttria stabilized zirconia YSZ space charge layers play only a minor role. Using model systems with coherent phase boundaries the ionic transport can only be influenced by lattice mismatch induced strain fields. Due to the epitaxial structure of these model systems the investigation of the strain fields is difficult and the usual methods to determine stresses in thin films fail. We have developed a method to describe strain fields in alternating multilayers of YSZ and Rare Earth Metal Oxides RE2O3. We measure the strain induced shift of distinct reflections, e.g. the (111) YSZ and (222) RE2O3 reflections, parallel and (nearly) perpendicular to the interface plane as a function of the layer thickness by XRD. Using an analytical model to describe interfacial strain fields and their influence on interface transport, we are able to estimate the extent of the strain fields. We present data for systems with a compressive and a dilative lattice mismatch with respect to YSZ (9.5 mol% Y2O3). The determined interface thicknesses are in agreement to values from conductivity and diffusion measurements and are well able to explain the altered conduction properties. C/P2 13

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14:00 **High energy x-ray photoemission of fluoride based ion conductors**

Authors : K. Koshmak(1,2), A. Banshchikov(2), T. Vergentiev(3), M. Montecchi(4), D. Ceolin(5), J.P. Rueff(5), N.S. Sokolov(2), L. Pasquali(1,4)

Affiliations : 1) Dipartimento di Ingegneria E. Ferrari, Università di Modena e Reggio Emilia, Via Vignolese 905, 41125 Modena (Italy) 2) Solid State Physics Division, Ioffe Physical-Technical Institute of Russian Academy of Sciences, 26 Polytechnicheskaya str., 194021, St. Petersburg, Russia 3) St. Petersburg Polytechnical University, 29 Polytechnicheskaya str., 195251, St. Petersburg, Russia / T. Vergentiev 4) IOM-CNR, s.s. 14, Km. 163.5 in AREA Science Park, 34149 Basovizza, Trieste, Italy 5) Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, F-91192 Gif-sur-Yvette Cedex, France

Resume : Ionic transport at interfaces between different materials presents unique properties. Investigation of interfaces by direct element and chemical sensitive approaches is of paramount importance for the comprehension and control of the ionic transport phenomena at the nano-scale. Ionic fluoride interfaces present paradigmatic nano-ionic transport and promise to be model systems for nano-ionics. We focussed on LaF3, LaF3-SrF2 heterostructures and La1-xSrxF3-x solid solutions grown by molecular beam epitaxy on Si. Crystallinity, epitaxial relations and surface morphology were probed by reflection high-energy electron diffraction and atomic force microscopy. High-energy photoemission measurements at GALAXIES beamline, SOLEIL Synchrotron were applied to study the composition and chemical properties of the films, disentangling spectroscopic information from surface region, bulk and buried interfaces between adjacent materials. This was possible owing to the high sampling depth of the technique compared to conventional photoemission. We revealed that i) LaF3 reacts easily with oxygen from the environment due to high fluorine vacancy density; ii) sample treatments like ion sputtering, temperature cycles or prolonged photon irradiation induce fluorine depletion, formation of metallic La precipitates and oxofluorides; iii) SrF2/LaF3 interfaces, either in heterostructures or in solid solutions, are fluorine depleted, which is correlated with the high ionic conductivity of these system. C/P2 14

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14:00 Optical and Electrical Investigation of Oxygen Diffusion in Thin Films of Gd-doped Ceria

Authors : Guy Lazovski, Olga Kraynis, Roman Korobko, Ellen Wachtel and Igor Lubomirsky

Affiliations : Dept. Materials and Interfaces, Weizmann Institute of Science, Israel

Resume : Impedance spectroscopy (IS) is the most commonly used technique for studying conductivity of ionic and mixed ionic/electronic conductors. Though being simple and versatile, it has the disadvantage of inability to distinguish between ionic and electronic charge carriers at a fixed chemical composition. In addition, the interpretation of IS spectra is not unambiguous. We propose a technique based on null-ellipsometry with lock-in detection, which can distinguish between ionic and electronic carriers. It monitors changes in refractive index caused by ion migration due to applied voltage. Using this technique, we determined the activation energy of oxygen ion diffusion (EAion) in thin films of 20mol% Gd-doped ceria with columnar grain structure between 100?C to 160?C. In parallel, we measured the same film with IS, both along and across grain boundaries. The optical technique yields EAion=1.5?0.1eV, whereas IS yields activation energies of 0.4eV along, and 0.8eV across, the grain boundaries. This difference demonstrates the inability of IS to properly account for effects such as anisotropic grain boundaries and presence of more than one conduction mechanism. We conclude that the optical technique is the more reliable probe of grain core ion diffusion in thin films.

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14:00 Impact of Laser Irradiation on Properties of micro-SOFC Electrolytes

Authors : Mindaugas Maciulevičius1, Jolita Sakaliūnienė2, Brigita Abakevičienė2 3, Sigitas Tamulevičius2, Gediminas Račiukaitis1

Affiliations : 1 Center for Physical Sciences and Technology, Savanoriu ave. 231, LT-02300 Vilnius, Lithuania; 2 Institute of Materials Science, Kaunas University of Technology, Savanoriu ave. 271, LT-50131 Kaunas, Lithuania; 3 Department of Physics, Kaunas University of Technology, Studentu str. 50, LT-51368 Kaunas, Lithuania;

Resume : The research work presents results of the experimental investigation of e-beam evaporated yttria stabilized zirconia (with different concentrations 5, 8 and 10 mol% of Y2O3, (YSZ)) and gadolinia doped ceria (with different concentrations 10, 15 and 20 mol% of Gd2O3, (GDC)) thin films deposited on silicon (100) substrate as potential electrolytes for micro-Solid Oxide Fuel Cells (μ-SOFC). The initial YSZ and GDC powders were synthesized by co-precipitation synthesis method. As-deposited, YSZ and GDC films have pores and defects, and annealing at high temperatures usually is used for densification. The results of laser irradiation, as a promising way to improve the density of thin films, are presented. Radiation of a high power diode laser working at the wavelength of 808 nm and a Q-switched diode-pumped nanosecond Nd:YVO4 laser (Baltic HP, Ekspla), working at the wavelength of 532 nm and with a pulse length of approximately 10 ns, were used. X-ray diffraction, scanning electron microscopy, impedance two probe measurements were applied to characterize the structure and electrical properties of evaporated and laser irradiated thin films. XRD analysis data clearly indicates the formation of a single-phase YSZ and GDC evaporated thin films with cubic crystal structure. Impedance spectroscopy was performed in the frequency range 0.1÷3x106 Hz. The activation energy ΔEa was determined from the slope in Arrhenius plot (log(σ) versus 103/T) in the measurement temperature range of 200-800 °C.

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14:00 New ion-conducting glasses in the AgI-HgS-As2S3system

Authors : S.Khaoulani 1,2,3 M. Kassem 2, S.Fourmentin ,1,3 E. Bychkov 1,2

Affiliations : 1 Univ. Lille Nord de France ,F-59000 Lille, France ; 2 LPCA, ULCO EA 4493, Dunkerque F-59140, France ; 3 ULCO, UCEIV EA-4492, F-59140 Dunkerque, France ;

Resume : Chalcogenide glasses are promising materials for various solid-state devices. They allow a number of advanced applications to be realized in different fields: (i) optics and photonics (fibers, infrared biosensors, optical data storage, waveguides, solar cells), and (ii) environmental monitoring and industrial process control (chemical sensors for detection of heavy metal ions as Hg, Pb, Cu, Cd, etc…). Novel chalcogenide glasses in the AgI-HgS-As2S3 system have been synthesized and characterized for the first time. The glass-forming range for the (AgI)x(HgS)0.5−x/2(As2S3)0.5−x/2 compositions varies between 0.0≤x≤0.6. Macroscopic properties such as density and glass transition temperature, Tg, have been measured. The density of the alloys was found to increase monotonically with x. The glass transition temperature shows an

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inverse composition trend ; Tg decreases from 169°C to 80°C. These silver-doped glasses belong to Ag+ ion conductors and their conductivity increases drastically with increasing x. The room temperature conductivity increases by 10 orders of magnitude from 2.2 □10–16 S.cm-1 (x=0.0) to 1.2□10–6 S.cm-1 (x=0.6) with simultaneous decrease of the activation energy from 1.05 eV to 0.41 eV. Raman scattering measurements have also been carried out to provide a structural interpretation of the origin of conductivity changes in AgI-HgS-As2S3 glasses.

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14:00 **`Fabrication and Characteristic of Niobium Phosphate Glass Thin Film**

Authors : Dae Ho Kim, Sung Bung Park, Deok-hwan Yun, Sung gwan Hong and Yong-il Park

Affiliations : Kumoh National Institute of Technology

Resume : The materials based on phosphate have proton conductivity because of hopping mechanism of proton in non-bridging oxygen (NBO) between phosphorous and oxygen bond by thermal vibration with increasing temperature. Recently, defects like volatilization of phosphorous and destruction of bonding structure are remarkably improved by introduction of cation such as Zr4+ and Nb3+ into phosphate. Yunjie Huang et al.1) show that niobium phosphate of bulk was achieved at the highest conductivity of 1.6 x 10-2 S/cm around 250℃. The existence of hydroxyl group in the phosphate is confirmed and found to be preserved after heat treatment at 500℃ or higher. Niobium has proton conductivity on surface because of higher surface acidities. It can also retain phosphorous content during heat treatment and improve chemical stability by bonding with phosphorous. In this study, we fabricated niobium phosphate glass thin film through sol-gel processing and report the chemical stability and electrical properties. The obtained data was compared to those of bulk NbP

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14:00 **Structure and Properties of the Ni1-xLixCo2O4 Spinel Thin Films**

Authors : Jung- Hee Kim; Hae-Kyoung Kim; Hee Young Lee; Jai-Yeoul Lee

Affiliations : Yeungnam University

Resume : Li doped spinel, Ni1-xLixCo2O4, thin films were fabricated by sputtering and pulsed laser deposition. Thin films were grown on glass and c-sapphire single crystal substrates at various substrate temperatures and oxygen partial pressures. The effects of the processing parameters on the crystal structure, electrical and optical properties of Li- doped spinel thin films were analyzed by XRD, AFM, four point probe method, and UV spectrometer. As the doping concentration x increased, the electrical conductivity increased up to x=0.3. The optical transmittances increased with increasing substrate temperature up to 400℃. The thin films growth with strong (111) preferred orientations were observed on the sapphire substrates. Li doped Ni1-xLixCo2O4 spinel thin films with electrical conductivity of 60 S/cm and optical transmittance about 50% were fabricated with optimum processing parameters.

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14:00 **Fabrication and Electrical Properties of Phosphate Glass Thin Films with High Water Concentration**

Authors : Suk Hee Lee1, Sung Bum Park1, Gyu Hyeon Nam1, Yong-il Park1#

Affiliations : School of Advanced Materials and System Engineering, Kumoh National Institute of Technology Gumi,Gyeongbuk, Korea, 730-701

Resume : In most oxide glasses, electric charge carriers are not protons but mobile alkali ions or electrons. However, protons in phosphate glasses have been reported to have much higher mobility than those in silica glasses because the mobility of proton is one of the electrical properties of phosphate glasses. The O-H bonding in phosphate glasses is generally weak owing to the formation of hydrogen bonding and mobile protons. Phosphate glasses are expected to maintain high proton conductivity at the intermediate temperature (200~400℃) and the proton conductivity is known to be affected by content of water molecule, proton concentration, mobility and content of P2O5. The water molecules and content of P2O5 are related to a glass network structure due to formation of P-OH groups and work as a catalyst through lowering the activation energy for conduction and increasing proton mobility. Although large amount of P2O5 improve proton conductivity, it also drastically decrease chemical durability and induce severe volatilization of P2O5 during heat treatment. In this study, phosphate glass thin films of BaO-P2O5 and BaO-La2O3-Al2O3-P2O5 were fabricated using water-based precursor solution. The observed properties were compared with the reported properties of the bulk glasses. Especially, the

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concentration of non-bridging oxygen (NBO) of the fabricated glass films is measured and its effect on the obtained proton conductivity was analyzed.

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14:00

Effect of Simultaneous Doping with Group V and Lanthanide Elements on the Stability of Al-substituted Li7La3Zr2O12 Ceramic Electrolyte

Authors : M. Rawlence1,2, M. Kubicek2, J.L.M Rupp2, S.Buecheler1

Affiliations : 1 Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland 2 Laboratory for Electrochemical Materials, Department of Materials Science, ETH Zurich Schafmattstr. 30, 8093 Switzerland

Resume : The development of solid electrolyte materials in lithium ion batteries has drawn much interest due to the increased stability and safety of all-solid-state lithium ion batteries. In particular, the garnet-type ceramic electrolyte Li7La3Zr2O12 demonstrates a promising bulk ionic conductivity of 5x10-4 S cm-1 at 25°C with good stability against metallic Li.1 In this work high density pellets of Li7La3Zr2O12 were synthesized by sol-gel processing followed by pressing and sintering at high temperature. Stoichiometric quantities of the precursor salts Li2CO3, La2(NO3)3 and ZrOCl2 were used with a slight excess of Li. Al, which is assumed to replace Li in the lattice, was incorporated by adding a molar ratio of AlCl3 between 0.15 and 0.25 to determine the optimum Al content for achieving a stable and phase-pure cubic phase. A doping regime was carried out by adding additional salts during the sol-gel processing. The aim is to improve the ionic conductivity by substituting on both the La and Zr sites using Lanthanide and group 5 elements, respectively. The pellets were characterized by XRD and SEM to determine the stability of the cubic phase and observe the formation of any impurities. 1. R. Murugan, V Thangadurai, W. Weppner, Angew. Chem. 179 (2006) 974.

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14:00

Al2O3/HfO2 Functional Stack Films based Resistive Switching Memories with Controlled SET and RESET Voltages

Authors : Lin Chen, Qing-Qing Sun, Jiao-Jiao Guo,Wen Yang, Peng Zhou, Hong-Liang Lu, Peng-Fei Wang, Shi-Jin Ding, David Wei Zhang

Affiliations : Fudan University

Resume : Two Resistive Random Access Memory (RRAM) devices were designed with the thin low k/thick high k stack as functional layer. The two devices used different thickness of Al2O3 layer as low k film and same thickness of HfO2 layer as high k film. The fluctuation of the SET and the RESET voltages, the main obstacle which blocks the application of RRAMs based on transition metal oxide, leads to the instability of the RRAM. The random circuit breaker network (RCB) model points out that the fluctuation of the voltages is the universal problem of RRAM devices and it is originated from the working principles of devices. With this structure, the randomly formation and rupture of conducting filaments is limited within the low k Al2O3 film near the anode region instead of randomly formation and rupture in the whole functional layer. And our experiments find that for the device with 5 nm Al2O3 film, the distributions of the 80% VSET and VRESET are limited within 0.2 V (from 0.6 V to 0.8 V) and 0.25 V (from -0.5 V to-0.25 V), respectively. For comparison, distributions for the device with 10 nm Al2O3 film are within 1.1 V (from 0.6 V to 1.7 V) and 1 V (from -1.3 V to 0.3 V), respectively.

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add to my program **(close full abstract)**

14:00

Impedance characterization of resistive switching conduction mechanism in TaOx-based memory

Authors : Yu-Lung Chung, Jiun-Jie Fang and Jen-Sue Chen*

Affiliations : Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan

Resume : Resistive switching memory is one of emergent memories for next generation because of its simple fabrication process and good reliability. In this work, we investigate the impedance characteristics of Ta/TaOx/Pt and Ag/TaOx/Pt resistive switching memory devices to understand their conduction and switching mechanisms. Both Ta/TaOx/Pt and Ag/TaOx/Pt memory devices exhibit a pure capacitor characteristic in pristine state. When switching to LRS (low resistance state), both devices are indentified as a pure resistor. The frequency dependent impedance of Ag/TaOx/Pt reverts to a pure capacitor characteristic when the memory device switches from LRS to the HRS (high resistance state). However, a parallel combination of a resistor and a capacitor is observed in Ta/TaOx/Pt memory device at HRS. Based on the impedance analysis, the resistance switching mechanisms of Ag/TaOx/Pt and Ta/TaOx/Pt

C/P2 23

memory devices are respectively attributed to migration of Ag ions and oxygen vacancies, which relates decisively to the nature of the electrode/TaOx interface.

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14:00 **Resistive switching characteristics of La doped HfO2 for nonvolatile memory application**

Authors : Hailing Tu, Hongbin Zhao, Feng Wei, and Jun Du

Affiliations : Advanced Electronic Materials Institute, General Research Institute for Nonferrous Metals, Beijing 100088, China

Resume : In recent years, HfO2 has attracted considerable attentions for its application in resistance random access memory (RRAM) devices which have potential advantages such as simple structure, high integration density, and nondestructive readout. However, several issues still exist on HfO2 based RRAM devices, including high operation voltage, low resistance ratio, and the necessity of a high-voltage electro-forming process, which needs to be investigated in order to render the HfO2-based RRAM performance competitive for practical nonvolatile memory applications. As for the mechanism of HfO2-based RRAM, the localized conductive filaments made of oxygen vacancy or metallic ions play the key roles in the resistive switching behavior. First principles calculation indicates that trivalent La ion doping in HfO2 matrix materials can decrease oxygen vacancy formation energy and consequently induce the performance improvement of HfO2-based RRAM devices. Herein, rare earth element La was doped into HfO2 thin film by co-sputter deposition tech-nology with a series of concentrations, and the corresponding resistive switching properties have been investigated in relation to the oxygen vacancies. Low concentration La doped HfO2-based device shows threshold resistance switching. In contrast, pure and high concentration La doped HfO2-based devices exhibit forming-free memory resistive switching. The physical mechanisms for the memory and threshold resistive switching are fully discussed. It is concluded that the formation of oxygen vacancy conductive filaments and the electrical field induced breakdown without forming a conductive filament can lead to memory and threshold resistive switching, respectively.

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14:00 **Highly Uniform, Electroforming-free, and Self-rectifying Resistive Memory in Pt/Ta2O5/HfO2-x/TiN structure**

Authors : Jung Ho Yoon,* Seul Ji Song, Il-Hyuk Yoo, Jun Yeong Seok, Kyung Jean Yoon, Dae Eun Kwon, Tae Hyung Park, and Cheol Seong Hwang

Affiliations : Department of Materials Science and Engineering and Inter-university Semiconductor Research Center, Seoul National University, Seoul 151-744, (Korea)

Resume : The development of resistance switching (RS) memory cell which contains rectification functionality in itself, highly reproducible RS performance, and electroforming-free characteristics are the impending tasks for development of resistance switching random access memory. In this work, two-layered dielectric structure consisted with HfO2 and Ta2O5 layer which are in contact with the TiN and Pt electrode is presented for achieving these tasks simultaneously in one sample configuration. HfO2 layer works as the resistance switching layer by trapping or detrapping of electronic carriers, while Ta2O5 layer remained intact during the whole switching cycle, which provides the rectification. With the optimized structure and operation conditions for the given materials, excellent RS uniformity, electroforming-free and self-rectifying functionality could be simultaneously achieved from the Pt/Ta2O5/HfO2/TiN structure.

C/P2 25

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14:00 **Development of artificial SEI layers for battery materials**

Authors : Mercedes A. Carrillo S., René Hausbrand, Prof. Wolfram Jaegermann

Affiliations : Technische Universität Darmstadt, Material- und Geowissenschaften, Surface Science

Resume : Li-ion industry has suffered a big expansion in the last decades. For years research on secondary Li-ion batteries has focused on making efforts to improve their stability and rate capability. The main problems that have affected the development of these batteries are the difficulty to find efficient electrode and electrolyte systems, as well as understanding the interfaces present. These interfaces formed have been known to have a key role in the behavior and cyclability of the electrochemical cell. Interfacial side reactions lead to electrode deterioration and electrolyte chemical decomposition. One method used to avoid this problem is to have a surface modification of the cathode material by having a thin protective layer. Several materials have been studied and documented for the improvement of cell stability. Among them, both LiPON and ZrO2 have shown promising good results also in cyclability. In this work Li-ion permeable

C/P2 26

protective layers for LiCoO2 cathode materials were deposited by magnetron sputtering. A variation of the protective layer thickness was performed and characterized electrochemically. X-ray photo electron spectroscopy was employed to determine the composition and characteristics of the initial solid electrolyte interface layer formed for each case and for the later cycled batteries.

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14:00

Coating-Development for Al3+-Conducting Thin Film Batteries by PLD

Authors : W. Förster, S. Braun, A. Leson, T. Nestler, T. Leisegang, D. C. Meyer

Affiliations : Fraunhofer Institute for Material and Beam Technology IWS

Resume : A steadily increasing demand of high-energy density batteries for mobile devices, electronic vehicles, the storage of renewable energy, as well as the shortage of lithium resources, spur the research on suitable elements as active species in battery-systems. Multivalent-ions, such as Mg2+, Ca2+ and Al3+ have become popular candidates as they can transfer more electrons per atom. In fact Al3+-conducting batteries can reach higher energy densities and specific capacities than conventional lithium-ion batteries. Besides high energy densities, a long cycle lifetime is a main aspect for future energy storage materials. One way to satisfy both demands and simultaneously ensure a highest level of safety is to focus on thin film batteries (TFBs). Next to utilizing a non-flammable solid electrolyte, TFBs do not suffer from possible passivation of the electrodes surface during cycling what in turn expands their lifetime. However, only a few reports on rechargeable aluminum batteries have been published. Focus of the Fraunhofer IWS is to develop new all-solid Al3+-conducting coating systems mainly by PLD-processing. Optionally this technology can be supported by other PVD-coating-methods. All-solid cathode/anode systems are not limited by a decomposition voltage, as it is the case for liquid electrolytes. Moreover solid electrodes can be investigated in an unmixed condition what makes them an ideal model system to examine specific intrinsic ionic transfer- and insertion-processes.

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14:00

Electrochemical and structural studies in lithium borophosphorus oxynitride electrolyte for thin film batteries

Authors : Chanhwi Park, Sungbo Hong, Minjeong Kim, Giho Lee, Dongwook Shin *

Affiliations : Division of Materials Science and Engineering, Hanyang university

Resume : In order to realize all-solid-state thin film batteries, many inorganic glass electrolytes with high ionic conductivity, thermal stability and good chemical durability have been required. The lithium phosphorus oxynitride (LiPON) is the most widely used thin film solid electrolyte because of its chemical stability in contact with lithium and superior durability during repeated cycling. To enhance the conductivity of LiPON glass electrolytes, the LiBPON thin film electrolytes were fabricated by radio frequency (RF) magnetron sputtering system from Li3PO4 and Li3BO3 targets in high purity N2 gas. All added boron atoms successfully replaced the phosphorus sites in the fabricated LiBPON thin films, which results in the maximum conductivity of 1.85 μS/cm at room temperature. The combined "mixed former effect" and "nitridation effect" in the lithium ion conducting glass systems are effective way to stabilize the amorphous structure and improve the ionic conductivity.

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14:00

THIN FILMS DEPOSITION OF LITHIUM ORTHOSILICATES AND GARNETS FOR LITHIUM MICRO-BATTERIES

Authors : I. Quinzeni, S. Ferrari, E. Quartarone, D. Capsoni, P. Mustarelli, M. Bini

Affiliations : I. Quinzeni, S. Ferrari, E. Quartarone, D. Capsoni, P. Mustarelli, M. Bini; Dipartimento di Chimica, Sezione di Chimica Fisica, Università di Pavia, viale Taramelli 16, 27100 Pavia, Italy

Resume : A new generation of electrolytes and electrodes for lithium microbatteries is required in order to overtake the limits shown by the conventional systems. For what concern the electrodes, cathode materials of the orthosilicate family with formula Li2MSiO4 (M= Fe, Mn) have very low toxicity, are easily available and low cost. Besides, garnet compounds such as LixLa3M2O12 (x>3) are very attractive as electrolytes. In this work we investigated the role played by the substrate, the deposition temperature and the film thickness on the crystallographic, microstructural and electrochemical features of Li2MSiO4 (M=Fe, Mn) and of Li7La3Zr2O12 thin films. The thin films have been deposited in a high vacuum r.f. magnetron sputtering system. The Li/M/Si/O (M = Fe, Mn) amorphous films, with nominal composition Li2Fe1-xMnxSiO4 (x=0, 0.5) have been prepared for the first time at our knowledge. The structural and microstructural properties of the thin films were investigated

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by means of XRD, SEM, AFM and XPS techniques. The electrochemical performances were found comparable to those currently reported for the corresponding crystalline bulk materials. In particular, capacities of the order of 50 mAhg-1 were obtained at 2.5C with a coulombic efficiency near 90%. For $Li_7La_3Zr_2O_{12}$, the main issue is represented by the deposition of this complex ceramic material with the correct stoichiometry. In this regard, the use of different kind of substrates seems to have a critical role on the formation of the desired product. However, further improvements can be envisaged by optimizing the deposition parameters to obtain crystalline materials with advanced electrochemical performances. Acknowledgements - We gratefully acknowledge Cariplo Foundation for the grant 2011-0325.

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14:00 **Flux Coating Fabrication of $LiNi_{0.5}Mn_{1.5}O_4$ Crystal Layer for Lithium-Ion Rechargeable Battery Cathode with High Energy and Power Densities** C/P2 30

Authors : Katsya Teshima[1,2], Hajime Wagata[1,2], Nobuyuki Zettsu[1,2], Shuji Oishi [1]

Affiliations : [1] Shinshu University, [2] JST-CREST

Resume : For development of lithium-ion rechargeable batteries (LIB), enhancement of energy densities and power densities has been required. To obtain high energy and power density, our group have suggested a model of desired LIBs in which "active material layers are composed of densely-packed single crystalline lithium-ion conductors", "outermost crystal plain is designed for preferential lithium-ion intercalation/deintercalation", and "contact resistance between active materials and current collector is sufficiently decreased". To realize the desired LIBs, we have researched direct fabrication of lithium-ion conductive crystal layers on current collectors and control of the crystalline orientation. Among the cathode materials, $LiNi_{0.5}Mn_{1.5}O_4$ has various merits such as high voltage, high cycle stability, and relatively low cost. Here, we report direct fabrication of densely-packed $LiNi_{0.5}Mn_{1.5}O_4$ crystals on current collectors and control of orientation at the same time by flux coating method, which is a film fabrication technique based on flux concept. The filling rate of the fabricated $LiNi_{0.5}Mn_{1.5}O_4$ crystal layer was over 95 % due to absence of additives. The orientations of the crystal layers were depended on the flux coating conditions. The first charge and discharge capacities of a LIB using the crystal layer as an additive-free cathode are 111 and 105 mAh·g-1. After 30 cycles, the coulombic efficiency was kept at over 95 % at 0.3 C measurement. As a result, the additive-free $LiNi_{0.5}Mn_{1.5}O_4$ crystal layers fabricated by flux coating method could achieve much higher capacity density than that of commercially available electrode with filling rate for active materials of around 45 %.

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14:00 **Hydrogen as effective modificatory tool of thin films of vanadium dioxide or germanium: quasichemical approach to understanding proton state and mobility in them** C/P2 31

Authors : Baikov Yu.M., Klimov V.A.

Affiliations : Ioffe Physical Technical Institute of RAS

Resume : Hydrogen in solid ionic activity is considered in any forms of charged species (proton, hydride ion, hydroxide ion or more complex molecular forms likely hydrosulfate ion). It is possible to separate hydrogen-containing compounds on two groups. One of them consists of hydrogen species as stoichiometric compounds where hydrogen is the "host". Alternative state of hydrogen species, as the "guest", characterized factually nonstoichiometric compounds, relatively frequently only to hydrogen. Namely in this case the opportunity to effect on different properties of materials appears. Different ways to introduce or to remove any part of hydrogen are out of object of this paper . We are considering the phase transition modification in dioxide vanadium, which was used for information techniques of different aims. The phenomenological description was made for hysteresis behavior of temperature runs of optical and conducting properties at different hydrogen content intercalated in thin films. The role of mechanical loading is discussed also. We are considered also the change the mixed proton-electron conductivity of Ge in the course of using them as electrode to the membrane of solid protonic electrolyte. In this case Ge can work in electrochemical devices for energy storage using the penetration of hydrogen through Ge film. The using of isotopic methods was useful.

add to my program **(close full abstract)**

14:00 **Influence of changes in the transport properties of the radiation and on the heat transfer of a silicon particle immersed in a plasma.** C/P2 32

Authors : Zeggai Hichem, Zeggai Oussama , Ould-Abbes Ammaria

Affiliations : Research unit of Materials and Renewable energies (URMER), University Abou Bakr Belkaïd, B.P. 119, Tlemcen, Algeria

Resume : Various research is currently being conducted on the development of thin film photovoltaic cells or the development of photovoltaic silicon purification of metallurgical grade silicon. It is in this context that the work undertaken which has the main objective of producing a thin layer of crystalline silicon solar grade, from powder metallurgical grade silicon, purified and projected onto a ceramic substrate with an inductive thermal plasma. The silicon particles injected into an argon plasma slightly hydrogenated, are melted in a first time by partial evaporation, then purified to finally be deposited in a liquid state on the substrate. The layers obtained are hydrogenated by interaction between the liquid silicon and the atomic hydrogen from the dissociation of hydrogen gas in the plasma. In this article, we seek to highlight the influence of changes in transport properties on heat transfer to a silicon particle immersed in a plasma. The plasma heating of the particles of interest increasingly important in several applications (chemical synthesis, thin film deposition, decomposition, spheronization, melt ...). In these applications, fine powders or liquid droplets are injected into the plasma. The high temperature of the latter leads to a rapid heating of the particles to melt and optionally followed by evaporation.

add to my program **(close full abstract)**

14:00 **Morphology and structural properties of nc-Si:H thin films deposited on monocryslalline Silicon: Effect of the substrate temperature**

Authors : Malek Atyaoui, Ben Amor Sana,Wissem Dimassi, Brahim Bessaïs and Hatem Ezzaouia.

Affiliations : Laboratoire de Photovoltaïque, Centre de Recherche et des Technologies de l'Energie, PB: 95, Hammam Lif 2050, Tunisia

Resume : We report on the effects of substrate temperature (Ts) on the morphology and structural properties of Hydrogenated nanocrystalline silicon (nc-Si:H) thin films, grown by radio frequency Plasma Enhanced Chemical Vapor Deposition (PECVD) on silicon single crystal (1.0 0) using a gas mixture of silane (SiH_4) and hydrogen (H_2). Substrate temperature was varied from room temperature to 450 °C. Characterization of these films X-ray diffraction (XRD), Raman spectroscopy revealed that the crystallite size and at same time the volume fraction of crystallites in the films tends to decrease with increase in Ts. The Fourier transform infrared spectroscopic analysis (FTIR) showed at low temperature the hydrogen is incorporated in the nc-Si:H films in the mono-hydrogen (Si-H) bonding configuration. With increasing Ts the hydrogen bonding in nc-Si:H films shifts from mono-hydrogen (Si-H) to di-hydrogen (Si-H2) and (Si-H2)n. The hydrogen content in the nc-Si:H films decreases with increase in Ts. From The Atomic Force Microscopy (AFM), it was shown that the increase in Ts tends to increase the porosity and decrease the crystalline grain size. In order to more understand the effect of Ts on this structural change, Minority Carrier Lifetime (MCL) measurement show that only the films with a nanocrystalline silicon structure present an enhancement in MCL which could be related to a quantum size effect and to the SiH-related bonds C/P2 33

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14:00 **Liquid transport through nanoporous graphene**

Authors : Jakob Buchheim, Roman Wyss, Kemal Celebi, Ali O Altun, Hyung Gyu Park

Affiliations : Nanoscience for Energy Technology and Sustainability, Department of Mechanical and Process Engineering, ETH Zurich

Resume : A two-dimensional (2D) mesh can provide a unique platform to realize membranes with ultimate permeation. Theorist predicts exceptional high water permeance through graphene pores. However, the quantification of mass transport through such membranes has been hampered due to the absence of suitable experimental devices. We developed a technique to perforate double layers of graphene with narrowly distributed pore sizes down to 5 nm. This device allows the quantification of mass transport through graphene membranes at macroscale. Here, we report experimental investigation of liquid transport through these nanoporous graphene membranes. We study the influence of temperature and viscosity of the liquid media on the transport rate through the graphene pores and compare the results with simulations and classical theoretical results for this atomically thin membrane. C/P2 34

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14:00 **Enhanced sensitivity in the VIS-NIR range under UV light in a-SiC pinpin device**

Authors : V. Silva1,2, P. Louro1,2, M. A Vieira1,2, M. Vieira1,2,3

Affiliations : 1Electronics Telecommunication and Computer Dept. ISEL, R. Conselheiro Emídio Navarro, 1949-014 Lisboa, Portugal Tel: +351 21 8317290, Fax: +351 21 8317114; 2 CTS-UNINOVA, Quinta da Torre, Monte da Caparica, 2829-516, Caparica, C/P2 35

Portugal.; 3 DEE-FCT-UNL, Quinta da Torre, Monte da Caparica, 2829-516, Caparica, Portugal

Resume : The use of UV steady state illumination increases the spectral sensitivity of a double pi’n/pin photodiode beyond the visible spectrum. Increased sensitivity in the range of 400 nm-850 nm is experimentally demonstrated. Results show that the spectral current under UV front light irradiation (350 nm) increases with the background intensity in the 470nm-800nm range and decreases for low power wavelengths in the visible range. Under back irradiation the spectral current decreases for wavelengths higher than 550nm and strongly increases beneath them. Under front irradiation and low power intensity the gain is high and presents a well defined peak at 750 nm and strongly quenches in the visible range. As the power irradiation increases the peak shifts to the visible range and can be deconvoluted into two peaks one in the red range and another in the green range. In the blue range the gain is much lower showing the filtering properties of the device at different UV background intensities. Under back irradiation the gain is high in the violet/blue ranges and strongly quenches for higher wavelengths whatever the intensity of the background. Results show that, front background enhances the light-to-dark sensitivity of the medium, long and infrared wavelength channels and quench strongly the low wavelength, depending optical amplification on the background intensity. Back UV background enhances only the channel magnitude in short wavelength range and reducing it in the long ones.

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16:00 **PLENARY SESSION**

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Solid state ionics: thin films for energy and information applications

26 May 2014	27 May 2014	28 May 2014	**29 May 2014**	30 May 2014

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Mixed Conducting Perovskites I : Prof. W. Preis and Dr. M. Burriel

08:30

Ion beam analysis techniques applied to mixed conducting thin films: from surface reconstruction to combinatorial screening

Authors : M. Burriel1,2, A.M. Saranya1, A. Morata1, H. Téllez2,3, Y. Chen4, N. Tsvetkov4, B. Yildiz4, A. Tarancón1 and John A. Kilner2,3

Affiliations : 1 Catalonia Institute for Energy Research (IREC), Department of Advanced Materials for Energy 2Department of Materials, Imperial College London, London, SW7 2AZ, UK 3International Institute for Carbon-Neutral Energy Research, Kyushu University 4Laboratory for Electrochemical Interfaces, Massachusetts Institute of Technology, US

Resume : In order to design novel optimized compositions with improved MIEC (Mixed Ionic Electronic Conducting) properties for IT-SOFC cathodes it is of high importance to: 1) acquire a better understanding of the oxygen incorporation, oxygen diffusion and surface reconstruction processes and 2) achieve fast screening of new materials and properties by fine tuning compositions. In this sense, low-energy ion scattering (LEIS) has emerged as a unique technique capable of quantifying the chemistry of the outermost surface with single-atomic-layer sensitivity. In addition, by combining LEIS with oxygen isotope exchange coupled with time-of-flight secondary ion mass spectrometry (ToF-SIMS) it has been possible to correlate exchange kinetics with chemical processes at materials atomic surfaces. Examples of the application of these ion beam analysis techniques for the characterization of epitaxial layered MIEC thin films will be presented, emphasizing the valuable and unique insight provided in the oxygen-incorporation and cation segregation processes. Moreover, by applying the Isotope Exchange Depth Profiling technique to a binary perovskite composition system generated by combinatorial PLD, spatially-resolved oxygen exchange and mass transport properties (k* and D*) have been obtained. This combinatorial approach to material synthesis and characterization has recently opened a new avenue on the generation of entire compositional diagrams in a single experiment.

C.6.1

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09:00

Visualization of electrochemical reduction zones by cathodic 18O incorporation at model electrodes: strengths and limitations

Authors : Alexander K. Opitz (1), Markus Kubicek (1,2), Stefanie Huber (1), Tobias Huber (1), Andreas Nenning (1), Edvinas Navickas (1), Gerald Holzlechner (1), Herbert Hutter (1), and Jürgen Fleig (1)

Affiliations : (1) Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-EC, 1060 Vienna, Austria; (2) ETH Zurich, Department of Materials, Electrochemical Materials, Schafmattstraße 30, 8093 Zurich, Switzerland

Resume : Recently, model-type thin film electrodes were demonstrated to be powerful tools for investigation of solid state electrochemical systems. One of their major advantages is that electrochemically active zones are relatively easy accessible by surface analytical methods. Oxygen incorporation zones, for example, can be visualized by polarization-driven 18O tracer incorporation in combination with time-of-flight secondary ion mass spectrometry analysis. In the present contribution, application of this technique to a number of different electrode materials is discussed. By 18O incorporation at Pt electrodes two different reaction pathways could be identified at high cathodic polarization. A successful separation of different oxygen reduction pathways was also possible

C.6.2

for La0.8Sr0.2MnO3-δ (LSM) electrodes. Under lower polarization a surface path with oxygen incorporation at the three-phase boundary is found to dominate, whereas at higher cathodic polarization a bulk path becomes more pronounced. Measurements on La0.6Sr0.4CoO3-δ (LSC) and La0.6Sr0.4FeO3-δ (LSF) in 18O2 illustrate the limitations of the tracer incorporation method in case of very high electrochemical activity (LSC) and due to polarization-induced changes of the electrode’s electronic conductivity (LSF). Finally, reaction zones of cathodic water reduction at SrTi0.7Fe0.3O3-δ (STF) electrodes were investigated in a H2/H218O atmosphere and results are compared with electrochemical impedance measurements on this system.

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09:20 **Preparation of La(Sr)Fe(Mn)O3 Film for dense anode of SOFC using LaGaO3 thin film electrolyte** C.6.3

Authors : Tatsumi Ishihara, Young-Wan Ju, Shintaro Ida

Affiliations : International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka, Japan; Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan

Resume : Solid oxide fuel cells (SOFCs) have been attracting much interest as alternative energy conversion system for next generation. At present, improvement of long term stability is strongly required for SOFC and one reason for decrease in power density could be assigned to the sintering of porous anode, Up to now, three phase boundary is considered as the active site for anode. In this study, we applied La(Sr)Fe(Mn)O3 film as a dense anode for low temperature SOFCs. Dense La(Sr)Fe(Mn)O3-δ (LSFM) nano-film anode is introduced between a Ni–Fe metallic support and LaGaO3 based oxide electrolyte. It was found that the cell using LSFM thin film anode exhibits much improved power density comparing with that of cell with a simple porous Ni-Fe anode. The maximum power density of the cell having LSFM film is approximately 3.0 W/cm2 at 973 K. The improved power density is mainly originated from enhanced anodic properties. Furthermore, the dense LSFM thin film anode is effective for increasing fuel utilization of Ni-Fe metallic anode supported cell. This suggests that two phase boundary (anode and gas phase) is also highly active for anodic reaction. The cell stably shows high power density over reasonably long period. This could be explained by the low dependency of anodic overpotential of LSFM on fuel concentration. Consequently, this study reveals that two phase boundary of LSFM/gas phase is highly effective for high energy conversion efficiency of SOFC.

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09:40 **Cathode materials for H-SOFC: bulk properties and oxygen exchange kinetics** C.6.4

Authors : D. Poetzsch, R. Merkle, J. Maier

Affiliations : Max Planck Institut for Solid State Research Stuttgart Germany

Resume : Little is known about the oxygen reduction mechanism at the cathode of fuel cells based on oxidic proton conductors, e.g. if typical cathode materials exhibit sufficient proton conductivity to allow for oxygen reduction to extend beyond the triple phase boundary and to occur on the whole surface ("bulk path"). In presence of three carriers (H , Vo.., holes) proton uptake can occur by hydration of oxygen vacancies (acid-base reaction) as well as including a valence change of transition metal ions (redox reaction), and complex diffusion kinetics can arise (two-fold relaxation [1]). For Ba0.5Sr0.5Fe0.8Zn0.2O3-d (BSFZ) ceramics lower bounds for proton concentration and mobility are extracted from thermogravimetry transients [2]. Comparing this lower bound for proton conductivity with the ionic conductivity of (La,Sr)MnO3 films on YSZ indicates that the bulk path for oxygen reduction is possible on BSFZ cathodes. Impedance spectroscopy on dense thin-film microelectrodes on Ba(Zr,Y)O3-d electrolytes shows that the resistance related to the oxygen reduction scales inversely proportional to the electrode area, supporting that the reduction proceeds by the "bulk path" on the whole BSFZ/gas surface. For these measurements, one has to properly account for the nonnegligible hole conductivity of Ba(Zr,Ce,Y)O3-d in high pO2 [3]. 1 J.H.Yu, J.S.Lee, J.Maier, Angew.Chem.Int.Ed. 46 (2007) 8992 2 D.Poetzsch, R.Merkle, J.Maier, in revision 3 D.Poetzsch, R.Merkle, J.Maier, J.Pow.Src. 242 (2013)

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10:00 **BREAK**

10:30 **Defect Chemistry of Alkaline Earth Metal (Sr/Ba) Titanates** C.6.5

Authors : Xin Guo

Affiliations : Laboratory of Solid State Ionics, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, P.R. China

Resume : Owing to their wide applications in oxygen sensors, multi-layer ceramic capacitors (MLCC), positive temperature coefficient resistors (PTCR), etc., doped SrTiO3 and BaTiO3 are one of the most important electroceramics. Perovskite structure can tolerate high concentrations of defects, for example, oxygen vacancies, electrons and holes, without changing its structure. Defect reactions and reaction parameters of SrTiO3 and BaTiO3, published in literatures, over the doping range from acceptor to donor, temperature range from room temperature to >1500 K and oxygen partial pressure range of 10^-23 to 1 bar are summarized in this work, and a Windows□based DefectChemCal program is developed. With the program, we can calculate the defect concentrations and the electrical properties of acceptor and donor-doped SrTiO3 and BaTiO3, and the validity of the program is demonstrated by comparing the calculation results and experimental results.

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11:00

Electrochemical properties of La0.6Sr0.4FeO3-δ thin film electrodes under oxidizing and reducing conditions

Authors : Kogler S., Langer-Hansel K., Nenning A., Opitz A., Hutter H., Fleig J.

Affiliations : Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9, 1060 Vienna

Resume : Perovskite-type oxides are common electrode material in solid oxide fuel/electrolysis cells for oxidizing conditions. Some of these oxides, e.g. La0.6Sr0.4FeO3-delta (LSF64), show an acceptable stability also in reducing conditions, making them to a potential alternative to Ni/YSZ as well as offering the advantage of building a symmetrical cell. We investigated the electrical and electrochemical behavior of LSF64 by impedance spectroscopy using a special microelectrode design with interdigitally arranged metal fingers underneath the LSF64 thin film electrodes. This allows time and temperature dependent analysis of both in-plane electronic conductivity as well as electrochemical polarization in one and the same electrode under reducing and oxidizing conditions. Measurements showed that in both atmospheres a variation of the electronic conductivity is not correlated with changes of the polarization resistance. The processes are discussed in terms of phase changes and surface modification. The oxygen exchange in reducing and oxidizing conditions were further analyzed using O18 and H2O18 tracer and subsequent area-resolved detection by secondary ion mass spectrometry. As expected the tracer diffusion coefficient D* is high under reducing conditions, due to the higher concentration in oxygen vacancies, but surprisingly the values of the tracer oxygen exchange factor k* under wet reducing and oxidizing conditions are similar, despite very different electronic properties.

C.6.6

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11:20

Chemical Expansion in La0.5Ca0.5MnO3

Authors : M. H. Seren(1), H. –U. Habermeier(2), Y. Kuru(1)

Affiliations : (1)- Department of Metallurgical & Materials Engineering, Middle East Technical University, Dumlupinar Bulvari No:1, 06800, Ankara, Turkey (2)- Max Planck Institute for Solid State Research, Heisenberg str. 1, D-70569, Stuttgart, Germany

Resume : Rare earth doped manganites have been thoroughly investigated in recent years due to their possible use in electronic devices. The electrical and magnetic properties of manganites are governed by a delicate balance between numerous mechanisms such as orbital, charge, spin ordering, Jahn-Teller distortion and double exchange. As a result, these properties are highly sensitive to external effects. Some examples to these perturbations are electrical field, magnetic field, X-ray flux and strain. Since creation or annihilation of O vacancies creates a volume change (i.e. chemical strain) in the lattice and, in turn, acts as a new contribution to the strain parameter, it is imperative to know the extent of this volume change and the relationship between O vacancy concentration and chemical strain in the material. In the present study, perovskite type La0.5Ca0.5MnO3 was selected as a model material for manganites and the volume change in the structure during O loss was determined by a combination of dilatometry and thermogravimetric analysis. Microstructural and chemical analyses were performed by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray spectroscopy, respectively. The results indicate that the chemical expansion coefficient of La0.5Ca0.5MnO3 is 0.014. Interestingly, chemical expansion coefficient was observed to depend on the O vacancy concentration in the structure.

C.6.7

add to my program **(close full abstract)**

11:40 **Anion and Cation Diffusion in Thin-Film SrRuO3**

Authors : Henning Schraknepper, Regina Dittmann, Roger A. De Souza

Affiliations : Institute of Physical Chemistry RWTH Aachen University and JARA-FIT, Landoltweg 2, 52056 Aachen, Germany; Peter-Grünberg-Institute 7, Forschungszentrum Jülich, 52425 Jülich, Germany; Institute of Physical Chemistry RWTH Aachen University and JARA-FIT, Landoltweg 2, 52056 Aachen, Germany

Resume : The high electronic conductivity and small lattice mismatch with other perovskite oxides makes SrRuO3 ideal for integration as the bottom- and/ or the top- electrode in a variety of all oxide devices. In order to understand and control the performance and durability of devices incorporating SrRuO3, knowledge of anion and cation mobilities in thin-film samples is crucial. In this study we deposited, by means of pulsed laser deposition (PLD), thin-films of SrRuO3 on (100) oriented single crystal SrTiO3 substrates. We performed 16O/18O exchange anneals in a temperature range of 850 < T/K < 1100 at an oxygen activity of aO2 = 500 mbar, and subsequently analyzed the samples with Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). In this manner we obtained oxygen tracer diffusion coefficients D*O, oxygen surface exchange coefficients k*O thin-film SrRuO3. Analysis yielded an activation enthalpies of ΔHD*= 2.1 eV and of ΔHk*= 2.3 eV. Diffusion of Ti into SrRuO3 was also observed in ToF-SIMS profiles, and it was characterized by an activation enthalpy of ca. 3 eV. Comparisons of the transport data with those for other perovskite types oxides are made, in order to gain insights into the behaviour of point defects in thin-film SrRuO3. C.6.8

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12:00 **LUNCH**

Batteries : Prof. E. Kelder and Prof. P. Simon

14:00 **Lithium-ion batteries: the role of passivation films in ageing processes of high energy systems**

Authors : Rémi DEDRYVERE, a Lucille BODENES, a Dominique FOIX, a Hervé MARTINEZ, a Danielle GONBEAU, a Florent FISCHER, b Cécile TESSIER, b Jean-Frédéric MARTIN, c Sébastien PATOUX c

Affiliations : a IPREM, University of Pau, Hélioparc, 2 av. Pierre Angot, 64000 Pau, France b SAFT, 111/113 bd Alfred Daney, 33074 Bordeaux cedex, France c CEA/DRT/LITEN, 17 rue des Martyrs, 38054 Grenoble cedex 9, France

Resume : Lithium-ion batteries are the well-established energy source of portable electronic devices. Current research efforts are motivated by the quest for improved systems able to store more energy for renewable energies and urban transportation. Future Li-ion battery applications, such as electric vehicles, require higher energy or power densities. Other applications require a good electrochemical behavior at high temperatures (>60°C). The reactivity at electrode/electrolyte interfaces is a very important issue. Li-ion batteries are able to work thanks to the formation of a passivation film at the surface of the electrodes (especially the negative) that is called "solid electrolyte interphase" (SEI). The use of higher energy, nanosized electrode materials, or operating at unusual temperatures, for new applications increases the importance of these interphase issues that directly impact the safety and the life span of batteries. In this presentation I will show some of the latest results obtained by X-ray Photoelectron Spectroscopy (XPS) on the role of passivation films in ageing processes in Li-ion batteries. C.7.1

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14:30 **Surface science investigations on the interface formation between thin film lithium ion conductors and electrode materials**

Authors : André Schwöbel, René Hausbrand, Wolfram Jaegermann

Affiliations : Technische Universität Darmstadt, Materials Science Department, Surface Science Division, Jovanka-Bontschits-Straße 2, 64287 Darmstadt, Germany

Resume : All solid state thin film lithium ion batteries offer high energy densities at small footprints. The interfaces between the ion conducting solid electrolyte and the cathode or anode material play an important role. For example interface reactions can have strong effects on the performance of batteries because reaction layers can be formed which increase the transfer resistance at the interface. Our research focuses on interface reactions and double layer formation of the solid electrolyte LiPON (lithium phosphorus oxynitride) which is of interest due to its use in commercial cells. Because C.7.2

interfaces in real batteries are buried we use a model approach by preparation of the interface of interest by stepwise deposition of one material on top of another. At each step in-situ photoemission (PES) spectra are taken without breaking the ultra-high vacuum. Because of its high surface sensitivity PES is ideally suited for the identification of new chemical species at the interface. We present results on the interface formation between sputtered LiPON thin films with electrode materials, e.g. lithium vapor or LiCoO2. In our spectra evidence for the formation of new phases at the interface can be found. Additionally we find that the reactivity of the LiPON depends on its composition.

add to my program **(close full abstract)**

14:50 **Systematic design of thiophosphate-based all-solid-state batteries**

Authors : S. Adams, R. Prasada Rao, M.H. Chen, H.M. Chen

Affiliations : National University of Singapore, Department of Materials Science and Engineering, Singapore

Resume : Rechargeable all-solid-state lithium batteries are attractive power sources for small scale applications and electrochemically stable Li+ fast ion conductors (FIC) can help to widen their application field. Identifying stable fast ion conductors is thus the key to building practical solid-state batteries. Among the most promising compounds with high ionic conductivities are the thiophosphate-based solid electrolytes. Our studies shed light on the role of disorder in the immobile sublattice as a crucial factor for maximizing their conductivity. This is exemplified both for argyrodite-type halide-doped thiophosphates Li6PS5X (where the S2-/X- disorder for X = Cl, Br opens up local paths for Li+ motion), Li7P3S11, Li9+xGexP2-xS12 (LGPS, where local P/Ge disorder limits the packing density) and isostructural compounds in comparison to a series of known and newly designed thiophosphates. Ab initio structure optimisations and bond-valence based atomistic simulations highlight the role of free volume for fast ion transport and the effect of the chemical sulfur-bonding on the structural and electrochemical stability of the compounds. To reduce the synthesis costs of the thiophosphate solid electrolytes, we designed low temperature or no heating routes for their preparation. Electrochemical impedance studies and the performance of these solid electrolytes in all solid state Li-ion and Li-sulfur batteries (reaching theoretical capacity) will be presented. C.7.3

add to my program **(close full abstract)**

15:10 **Electrical characterization of LiAlO2 thin films prepared by Atomic Layer Deposition (ALD)**

Authors : Yang Hu, Amund Ruud, Ville Miikkulainen, Truls Norby, Ola Nilsen, Helmer Fjellvåg

Affiliations : Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo P.O. Box 1033, Blindern, N-0315 Oslo, Norway

Resume : A promising step towards safer and more durable Li–ion batteries is by application of solid–state thin film electrolytes. Atomic Layer Deposition (ALD) is a suitable and promising tool to achieve these designs, even on geometrically complex electrodes. Such solid electrolytes are a prerequisite for realization of all-solid-state batteries, and have been recently deposited by ALD. However, there are currently very few reports on measurement of the conductivity in such thin films, especially at room temperature. Our work aims at investigating the transport properties of LiAlO2 thin films prepared by ALD on various substrates, and to evaluate their potential as electrolyte in Li–ion batteries. Various methods for formation of electrodes have been investigated, resulting in the preferred choice of E–beam physical vapor deposition. Electrical characterization has been carried out using impedance spectroscopy from ambient to elevated temperature in controlled atmosphere. Special focus has been drawn to extract the bulk conductivity of thin films, both cross-plane and in-plane, and to elucidate the influence of geometry, electrodes, interfaces, atmospheres, and parasitics on the apparent results. The conductivity of LiAlO2 thin films increases with increasing temperature, exhibiting comparatively low room temperature conductivity but reasonable low activation energy. Moreover, DC measurement was also used to help identify the predominant charge carrier in the LiAlO2 thin films. C.7.4

add to my program **(close full abstract)**

15:30 **Organic electrode material for all-solid-state Li-ion batteries: Investigations using UHV-based model approach**

Authors : R. Precht, R. Hausbrand, W. Jaegermann

Affiliations : Darmstadt University of Technology Department of Material Sciences Surface Science Division Jovanka-Bonschits-Straße 2 64287 Darmstadt Germany C.7.5

Resume : Electronic organic materials are usually promoted as low cost, easy to process, environmentally friendly and flexible materials. Research on organic materials as electrodes for Li-ion batteries showed promising properties in electrochemical experiments and in cells containing liquid, gel or polymer electrolyte. In cells with liquid electrolyte the organic electrode material is prone to dissolution, therefore an all-solid-state approach is appropriate. However electrode/solid-electrolyte ionic interfaces often suffer from kinetic inhibitions. In order to investigate the electrode material and the electrode/solid-electrolyte interface we performed UHV-based model experiments using surface science techniques. Interfaces were prepared stepwise by evaporation on a substrate material and were intermitting analyzed with photoelectron spectroscopy (XPS and UPS). Tetracyano¬quino¬di¬methane (TCNQ) was used as organic cathode material and lithium phosphorous oxynitride as solid electrolyte. First results show an interface reaction between TCNQ and the solid-electrolyte. Functional all-solid-state batteries were assembled showing so far low capacities. Additionally, TCNQ was exposed stepwise to Li vapor and Li-insertion or rather the charge compensation as well as the evolution of the electronic structure were monitored.

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15:50 **Pore filling ion conducting membranes for vanadium redox flow batteries** C.7.6

Authors : Young-Woo Choi, Mi-Soon Lee, Kyoung-Hee Shin

Affiliations : Korea Institute of Energy Research, South Korea

Resume : Novel ion exchange pore-filling membranes with low vanadium crossover were developed for the application to a vanadium redox flow battery. The polymer electrolytes consisting of the whole hydrocarbon materials were introduced into porous hydrocarbon substrates and crosslink-polymerized by radical polymerization in this work. The thickness of the prepared membranes was controlled between 20 and 25 micrometers to extremely lower membrane resistances. Finally, film-like polymer electrolyte membranes were prepared. The prepared pore-filling membranes are able to drastically decrease vanadium co-ion crossover through the membrane because the porous substrate suppresses a swelling factor of highly functionalized electrolytes in water media such as liquid phase operation conditions. The physico-chemical properties of the prepared membranes such as swelling behavior, membrane area resistance, vanadium co-ion crossover were investigated in correlation with the electrolyte composition. Also the thermal and the structural property of the prepared pore-filling membranes were evaluated.

add to my program **(close full abstract)**

16:10 **BREAK**

Mixed Conducting Perovskites II : Prof. J.L.M. Rupp and Dr. N.H. Perry

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16:40 **Investigating the Role of Electronic Structure in Oxygen Exchange Kinetics Using Model Thin Film (Sr,Ba,La)(Ti,Fe)O3-α Fuel Cell Cathodes** C.8.1

Authors : Nicola H. Perry, Jaejin Kim, Melanie Kuhn, John W. Druce, Takeshi Daio, Sean R. Bishop, and Harry L. Tuller

Affiliations : Department of Materials Science and Engineering, MIT, Cambridge MA USA & I2CNER, University of Kyushu, Fukuoka, Japan, Department of Materials Science and Engineering, MIT, Cambridge MA USA, Department of Materials Science and Engineering, MIT, Cambridge MA USA, I2CNER, University of Kyushu, Fukuoka, Japan, I2CNER, University of Kyushu, Fukuoka, Japan,Department of Materials Science and Engineering, MIT, Cambridge MA USA & I2CNER, University of Kyushu, Fukuoka, Japan, Department of Materials Science and Engineering, MIT, Cambridge MA USA & I2CNER, University of Kyushu, Fukuoka, Japan,

Resume : To raise solid oxide fuel cell efficiency at intermediate temperatures, the rate-limiting step for surface oxygen exchange at the cathode must be identified and improved. Thin films serve as an ideal platform for such studies, owing to their surface exchange limited behavior and ability to precisely control active area and diffusion lengths. Previous work by our group (Jung et al., Adv. Energy Mater. 1, 2011) on p-type Sr(Ti,Fe)O3-α films demonstrated the key role that the minority electron concentration and the corresponding position of the Fermi level relative to the conduction band can have on charge transfer kinetics. To improve electron transfer, two strategies to modify the electronic structure were tested: 1) reducing the band gap by substitution of Sr with Ba and 2) raising the Fermi level by donor doping with La. Model thin film (Sr,Ba,La)(Ti,Fe)

$O_{3-\alpha}$ cathodes with varied A-site chemistries, fabricated by pulsed laser deposition, were analyzed with in situ optical absorption relaxation and impedance spectroscopy to determine oxygen exchange rates. Their corresponding electronic structures (band gap, Fermi level) were studied by optical absorption and defect chemical modeling. Parallel studies of surface chemistry evolution during operation shed light on the key role of surface (vs. bulk) chemistry in performance degradation. Progress, limitations, and future prospects for modifying surface oxygen exchange by chemically tailoring electronic structure will be discussed.

add to my program **(close full abstract)**

17:10 **Long-term stability of the IT-SOFC cathode materials $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and $La_2NiO_{4+\delta}$ against chromium poisoning**

Authors : Nina Schrödl, Edith Bucher, Andreas Egger, Patrice Kreiml, Christian Teichert, Werner Sitte

Affiliations : Chair of Physical Chemistry, Montanuniversitaet Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria

Resume : Chromium poisoning caused by volatile Cr species released from stainless steel interconnectors has been identified as one of the main degradation mechanisms limiting the life-time of IT-SOFC cathode materials. In this study, the effect of chromium contamination on the long-term stability of two promising IT-SOFC cathode materials $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) and $La_2NiO_{4+\delta}$ (LNO) is investigated using dc-conductivity relaxation experiments. To assess the performance of the cathode material and monitor the degradation process the chemical surface exchange coefficient of oxygen (kchem) is determined as a function of time at 700°C in O_2/Ar-atmospheres during subsequent time periods of 1000 hours. Cr poisoning is simulated by positioning a Cr source close to the samples in dry and humidified gas streams. In addition, the electronic conductivity is measured using the van der Pauw method. Changes in surface topography and composition are determined by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM/EDX). In contrast to LSC, LNO shows a slight decrease of kchem in dry atmosphere in the presence of a Cr source. After humidification of the gas streams, both samples exhibit a strong degradation of kchem due to enhanced gas phase transport of volatile Cr species in humid atmospheres.

C.8.2

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17:30 **Identifying, Quantifying and Modifying Reaction Pathways of Oxygen Reduction on Lanthanum Manganite (LSM) Model Electrodes**

Authors : T. M. Huber (1), A. K. Opitz (1), M. Kubicek (1), A. Welzl (1), G. Holzlechner (1), E. Navickas (1), Y. Chen (2), H. Hutter (1), B. Yildiz (2), J. Fleig (1)

Affiliations : (1) Vienna University of Technology Institute of Chemical Technologies and Analytics Research Division Electrochemistry, (2) MIT Department of Nuclear Science and Engineering Laboratory for Electrochemical Interfaces

Resume : Sr-doped lanthanum manganite (LSM) is a widely used cathode material in commercially produced solid oxide fuel cells (SOFC). Despite being a poor ion conductor, LSM electrodes may reduce oxygen via different pathways: a path which includes surface diffusion of oxygen species (surface path) and a path based on oxygen bulk diffusion (bulk path). Separation of effective reaction rates on LSM cathodes into contributions of each path is experimentally highly non-trivial. Accordingly, a detailed knowledge of the rate limiting steps and their dependence on experimental parameters is still missing. In this contribution several methods are employed to identify, quantifying and modify the oxygen reduction paths of $(La_{0.8}Sr_{0.2})MnO_3$ and $(La_{0.8}Sr_{0.2})_{0.95}MnO_3$ thin film model electrodes: (i) LSM films on strontium titanium oxide (STO) and yttria-stabilized zirconia (YSZ) with different microstructures, from epitaxially growth to columnar textured, were investigated by ^{18}O tracer diffusion. Numerical analysis allowed separating surface exchange and bulk diffusion properties of both, grains and grain boundaries. (ii) Impedance spectroscopy was used to measure polarization resistances and capacitive effects of micro-patterned and macroscopic thin film, dense LSM microelectrodes. Three phase boundary length and exposed surface areas were varied. (iii) Field driven ^{18}O incorporation and subsequent SIMS analysis revealed quantitative information on the contributions of both reaction paths.

C.8.3

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Solid state ionics: thin films for energy and information applications

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start at	Subject	Num.
	Cation Conductors : Dr. H. Tellez and Dr. A. Opitz	
09:00	**hydrogen membrane fuel cell based on glassy electrolyte thin film** **Authors :** Yoshitaka Aoki, Etsushi Tsuji, Hiroki Habazaki **Affiliations :** YA; ET; HH; Faculty of Engineering, Hokkaido University YA; JST, PRESTO **Resume :** Novel thin film fuel cell based on the 100 nm-thick electrolyte of amorphous ZrP2.5Ox, working at 400□C, was demonstrated. The hydrogen permeable membrane fuel cell (HMFC) using a Pd foil as a nonporous solid anode was fabricated. Ni interlayer of several hundreds nm thickness was introduced between the Pd anode and the ZrP2.5Ox electrolyte in order to suppress the deterioration of the electrolyte nanofilm by the deformation of the Pd anode during hydrogen absorption. In the ZrP2.5Ox electrolyte the transport number of proton was unity at 400□C as determined by an EMF measurement. The modification of the Ni anode surface by an ultrathin Pt or Pd layer effectively decreased the anode/electrolyte interfacial polarization. Consequently, the HMFC revealed the OCV of 1.0 V and the maximum power density of 20 mW cm-2 at 400 degree C.	C.9. 1
add to my program	**(close full abstract)**	
09:20	**Tuning and In-Situ Monitoring of Stress in Proton Conducting Y-doped Barium Zirconate Thin Films** **Authors :** Aline Fluri, Daniele Pergolesi, Thomas Lippert, Alexander Wokaun **Affiliations :** Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland **Resume :** Y-doped barium zirconate (BZY) is a proton conductor with good chemical stability and high protonic conductivity. It is a promising candidate as an electrolyte for solid oxide fuel cells in the intermediate temperature range (400-700 °C), and therefore a possible alternative to oxygen ion conductors. It has been shown that BZY with compressive stress results in larger bulk activation energies for proton migration. By extrapolation, it is expected that tensile lattice distortions may lower the activation energy leading to larger proton conductivities at lower temperatures. However, up to date no experimental evidence has been reported on this effect of tensile stress. For this work, pulsed laser deposition is used for the fabrication of higly textured BZY thin films. Epitaxial thin films free of high angle grain boundaries have been grown with the fully relaxed crystalline structure, in compressive and in tensile stress. In our deposition chamber two in situ diagnostics, i.e. Reflective High Energy Electron Diffraction (RHEED) and a Multi-beam Optical Stress Sensor (MOSS) are combined for the first time. This combination allows an understanding of the connection between the growth mechanism and the stress generation/evolution during film growth. X-ray diffraction (XRD) is employed to characterize the crystalline structure, while electrical characterisations will be performed and correlated to the stress state and the growth mechanism, as revealed by MOSS, XRD, and RHEED.	C.9. 2
add to my program	**(close full abstract)**	
09:40	**Lowering the operating temperature of SOFCs: Protonic conductors and the role of local structure on understanding ionic conductivity** **Authors :** Luke Sperrin, Frederic Blanc, Riza Dervisoglu, Gunwoo Kim, John M. Griffin, Lucienne Buannic, Yoshihiro Yamazaki, Sossina M. Haile, Clare P. Grey **Affiliations :** Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK (Sperrin, Blanc, Dervisoglu, Kim, Griffin, Grey); Department of Chemistry, Stephenson Institute for Renewable Energy, University of Liverpool, Crown	C.9. 3

Street, Liverpool, L69 7ZD, UK (Blanc); Japan Science and Technology Agency, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan (Yamazaki); Materials Science Department, California Institute of Technology, 1200 East California Boulevard, Pasadena, California, 91125, USA (Yamazaki, Haile); Department of Chemistry, State University of New York, Stony Brook, New York, 11790-3400, USA (Dervisoglu, Buannic, Grey)

Resume : Inorganic materials containing mobile protons in the 300-600 °C temperature regime have found applications as protonic conductors in fuel cell devices. Structural analysis of the protonic defects is not straightforward by conventional diffraction techniques, whilst 1H solid-state NMR spectroscopy (often in combination with double resonance NMR techniques) provides a method with which to directly probe local structure. Some of the key questions that are important in these protonic materials are related to trapping defects where protons become less mobile and thus hinder the overall protonic conductivity. Typical examples of such materials include cation doped perovskites such as yttrium doped BaZrO3 (BZY). Identification of these trapping defects, and reducing the trapping energies, are key for designing new materials having better protonic conductivity. In this study, a joint multinuclear NMR spectroscopy, and density functional theory (total energy and GIPAW NMR calculations) investigation of yttrium doped BaZrO3 was performed. The results are consistent with a vacancy-dopant and proton-dopant trapping model in dehydrated and hydrated BZY, respectively. The agreement between spectroscopy and first principle calculations provides a path for material design of next generation protonic conductors.

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10:00 **BREAK**

Carbon Conductors : Dr. C. Marchiori and Prof. HG Park

10:30 **Microcroporous carbons for micro-supercapacitors: materials and systems** C.10.1

Authors : P. Huang, P.L. Taberna, and P. Simon

Affiliations : Université Paul Sabatier, CIRIMAT UMR CNRS 5085, 118 route de Narbonne, 31062 Toulouse, France

Resume : Electrical Double Layer Capacitors (EDLCs), also known as supercapacitors, are electrochemical energy storage devices for high power delivery or energy harvesting applications [1]. EDLCs store charge through the reversible adsorption of ions from an electrolyte onto high surface area carbons, thus charging the double layer capacitance. Large-size ECs are already used today for power supply and energy harvesting in various applications such as aeronautics, tramways, HEVs (…) [1]. The recent boom in multifunction portable electronic equipment and the increasing need for wireless sensor networks for the development of smart environments has raised the problem of developing sufficiently compact or flexible energy storage. Designing efficient, miniaturized energy-storage devices that can achieve high energy delivery or harvesting at high discharge rates with a lifetime that matches or exceeds that of the machine being powered remains a challenge. Integrating the storage element as close as possible to the electronic circuit (directly on a chip) is another challenge. This talk will present an overview of the results obtained using carbons in micro-supercapacitors. We will show results obtained using exohedral and microporous carbons, as well as bulk carbon films in micro-devices prepared from different methods. The performance achieved to date addresses the need for microscale energy storage in numerous areas where electrolytic capacitors cannot provide sufficient volumetric energy density, such as nomad electronics, wireless sensor networks, biomedical implants, active radiofrequency identification (RFID) tags and embedded microsensors. References [1] P. Simon and Y. Gogotsi, Nature Materials, 7 (2008) 845-854.

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11:00 **The First Membrane comprising Vertically Aligned Single Walled Carbon Nanotubes** C.10.2

Authors : Seul Ki Youn, Jakob Buchheim, Hyung Gyu Park

Affiliations : Nanoscience for Energy Technology and Sustainability, Department of Mechanical and Process Engineering, ETH Zurich

Resume : Membranes based on carbon nanotubes (CNTs), particularly single-walled CNTs (SWCNTs) with small diameters comparable to molecular sizes have drawn a great attention due to their potential in studying the fundamental nanofluidic phenomena as well as developing new separation and energy conversion technologies. The atomically smooth surface and hydrophobic nature of CNT channels with high curvatures are known to be responsible for a remarkable slip at the CNT wall, thereby enhancing both gas and liquid diffusivities far beyond conventional theoretical predictions. Despite a large number of molecular simulations about various aspects of the fluid transport through CNTs, only a handful amount of experimental data have been reported so far due primarily to the difficulties in reliable manufacturing options. As the result, vast discrepancies are found for flow enhancements between these experiments and theoretical calculations, as well as between experimental data to a great extent. Here, we present a new approach for membrane fabrication that is shown applicable even to gaunt SWCNTs, via reinforcement of each nanotube bundle and subsequent encapsulation by low-viscosity polymer. This new method allows us for the first time to manufacture a membrane consisting solely of vertically aligned SWCNTs with small diameters in the sub-5-nm regime. The behaviors of gas and water flow enhancements can be clarified from these membranes.

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11:20 **Development of the novel structure for intermediate temperature fuel cell using thin films of proton conductive electrolyte deposited on Pd-plated porous stainless steel substrate**

Authors : Tetsuro Kariya 1,2), Hiroki Tanaka 1), Tomoki Hirono 2), Tetsuji Kuse 2), Kiyoshi Uchiyama 3), Mitsunori Henmi 4), Mitsutaka Hirose 4), Isao Kimura 4), Koukou Suu 4), and Hiroshi Funakubo 1)

Affiliations : 1) Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, Japan; 2) Sanyo Special Steel Co., Ltd, Himeji, Japan; 3) Tsuruoka National College of Technology, Tsuruoka, Japan; 4) ULVAC Inc., Chigasaki, Japan

Resume : Solid oxide fuel cell (SOFC) is a promising future energy source. Heat resisting ceramics are currently used for anode electrodes in anode-supported type SOFCs because of high operating temperatures of 700 to 1000 °C. However, toughness and electric conductivity, significant for those applications, of ceramics are generally inferior to alloy materials. In order to apply alloy, SOFC's operating temperature needs to be lowered and thinner electrolytes with superior conductivity are required. Ito et al. proposed to use a thin film of the proton conductor of $BaCe_{0.8}Y_{0.2}O_3$, however, they used an extremely expensive thick Pd foil (40μm) for its anode electrode [1]. In order to succeed those challenges, we proposed a novel structure of SOFC, using Pd-plated porous stainless steel consists of sintered alloy powders as an anode electrode and the thin film (1μm) of proton conductor, $Sr(Zr_{0.8}Y_{0.2})O_3$, as an electrolyte. Dense and thin Pd-layer can selectively permeate proton effectively, and low internal resistance is obtained due to electric conductive stainless steel. In addition, high proton conductivity is obtained due to thin films of electrolyte deposited by PLD or sputtering. Furthermore, ferritic stainless steel with similar thermal expansion coefficient to Pd and $Sr(Zr_{0.8}Y_{0.2})O_3$ was selected as alloy powders and it demonstrated OCV of 0.8V and power output properties at low temperatures of 400 to 600 °C. [1] N. Ito, et al., J. Power Sources 152 (2005) 200-203. C.10.3

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11:40 **Mixed cation effect in Tl_2S-Ag_2S-GeS-GeS_2 glasses: conductivity and tracer diffusion studies**

Authors : M. Bokova, I. Alekseev, E. Bychkov

Affiliations : Univ Lille Nord de France, F-59000 Lille, France ULCO, LPCA, EAC CNRS 4493, F-59140 Dunkerque, France ; St. Petersburg University, 199034 St. Petersburg, Russia V.G. Khlopin Radium Institute, 194021 St. Petersburg, Russia; Univ Lille Nord de France, F-59000 Lille, France ULCO, LPCA, EAC CNRS 4493, F-59140 Dunkerque, France

Resume : Chalcogenide glasses containing Ag+, Li+, Na+ or Cu+ exhibit high ionic conductivity which makes them suitable for many applications, i.e., all-solid-state batteries, chemical sensors, etc. While large effort has been directed toward investigations of ion transport properties of single cation chalcogenide glasses, there are only few studies on the mixed cation effect in chalcogenide systems. In this work we will present mixed thallium-silver thiogermanate glasses in the $(Tl_2S)_x(Ag_2S)_{50-x}(GeS)_{50}(GeS_2)_{50}$ system, where thallium concentration changes from 0 to 36 at.%. Glass transition temperature, 204Tl tracer diffusion and ac impedance measurements have been used to study the mixed cation effect in the Tl-Ag-Ge-S glassy system. The glass transition temperature decreases from 231 °C (0 at. % Tl) to 160 °C (36 at. % Tl) passing by a slight minimum at 157°C (≈ 10 at% Tl). The room temperature C.10.4

conductivity decreases by 4 orders of magnitude with increasing thallium concentration, ranging between 10-4 S cm-1 for the Ag-Ge-S glasses and 10-8 S cm-1 for the Tl-Ge-S system with a minimum at 10-9 S cm-1 (≈ 10 at% Tl). The activation energy increases from 0.34 to 0.63 eV, respectively, with the maximum at 0.73 eV. The 204Tl tracer diffusion coefficient at 170°C increases with thallium concentration from 10-12 cm2 s-1 (0 at. % Tl) to 10-10 cm2 s-1 (extrapolated from lower temperature measurements for 36 at. % Tl). The obtained results indicate a classical mixed cation effect.

add to my program **(close full abstract)**

12:00 **Printable thermosetting composite solid-state electrolyte for flexible electrochemical devices** C.10.5

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Resume : Solid state ion conductive thin films are expected to play a key role in the development of printed electrochemical devices such as: electrochromic (EC) display, electrolyte-gated thin film transistor (EG-TFT), lithium battery or photovoltaic cell. A large range of materials have been already identified as possible candidates and have been described in the State-of-the-Art. Unfortunately, their common problems are poor processability, inferior conductivity, limited stability and high price which make them unattractive for commercial use. We are demonstrating an effective strategy for creating highly conductive, optically and mechanically stable ion conductive materials, easily scalable to mass production via printing techniques. Novel electrolytes were prepared based on plastic crystal (i.e. Succinonitrile), lithium salt, thermosetting resin and metal oxide nanoparticles. This soft matter electrolyte meets requirements for electrochemical applications, exhibiting ionic conductivities of 10^-6 to 10^-4 S cm-1 at RT, Young's Modulus in the range of 0.1 - 1.4 MPa and operational T up to 115 C. Systematic studies using Design of Experiment (DOE) show an effective increase in performance of these materials along with concentrations and process parameters. Developed composites, with their beneficial combination of properties, are expected to have significant potential for printed electronics. Prototypes of EC display and EG-TFT together with their performances are also discussed.

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