



Strasbourg (France)

E-MRS 2005 Spring Meeting
May 31 – June 3, 2005

SYMPOSIUM L

Hydrogen and Fuel Cells

Symposium Organizers :

Louis Schlapbach, CEO EMPA, Duebendorf, Switzerland

Armin Reller, University of Augsburg, Germany

Guenther Scherer, PSI, Villigen, Switzerland

Andreas Züttel, University of Fribourg, Switzerland

E-MRS 2005 Spring Meeting

SYMPOSIUM L

Tuesday, May 31, 2005
Mardi 31 mai 2005

Morning
Matin

Session I : Hydrogen production and Materials Interaction Session chair : L. Schlapbach

- L-I.01** 9:00 STABILITY IN WATER OF PHOTOELECTRODE MATERIALS OF TUNGSTEN OXIDE (WO₃)
A. Duta, A. Enesca, Centre for Sustainable Energy, Transilvania University of Basov, Romania and R. van der Kroel, J. Schoonman, Delft University of Technology, The Netherlands
Sustainable hydrogen technology imposes production processes based on renewable energy sources. The aim of this work is to obtain a photoelectrochemical cell, for obtaining hydrogen via water photolysis.
The photoelectrode materials must exhibit - among other properties - a very good water stability. The paper presents the results obtained in testing the stability of dense and nanoporous WO₃ thin films in water solutions at three pH values (2, 6.5, 11), up to 48 hours of immersion. Porous layers of WO₃ were obtained using (NH₄)₂WO₄ precursor while dense layers were obtained using tungsten ethoxide (W(OC₂H₅)₆) in ethanol solutions, complexed by small amounts of acetylacetonate (AcAc). Precursors' thermal behaviour was investigated via DSC. Spray Pyrolysis Deposition (SPD) allow obtaining thin, nanostructured films with controlled morphology (SEM analysis) by varying the technological parameters involved in the process (temperature, pressure, etc). The XRD and Raman tests reveal that the predominant monoclinic phase; the orthorhombic phase is also expected in lower extent. The structural stability at different pH values was tested. A series of impedance analysis were made on porous, thick films and the defect density was estimated in a magnitude order of 10¹⁷. The stability of electrical properties of the films was tested via current - voltage (I -V) curves and photocurrent analysis, for different immersion times, at pH = 2; 6.5; 11 in the aqueous electrolyte.
- L-I.02** 9:20 PREPARATION AND CHARACTERIZATION OF PALLADIUM BASED MEMBRANES INVOLVING CHEMICAL AND ELECTROCHEMICAL DEPOSITION
A. Petica, L. Anicai, Laboratory of Non-Conventional Engineering, ICPE-Advanced Research, Splaiul Unirii 313, sector 3, 030138 Bucharest, Romania
Pd based membrane are suitable to be applied to separate/purify hydrogen, also representing a key part in a membrane reactor deposition. In the case of chemical formation of Pd based membranes on porous alumina support, a novel procedure has been investigated, involving a laboratory synthesized complex compound after a relatively classical activation step, that allows further a low decomposition temperature around 200°C. The fabrication parameters of the membranes in the plating process have been also investigated. The applied procedure drastically diminishes the Pd wastes, exhibiting a reaction efficiency of min.93%. In the case of electrochemical procedures, Pd and Pd alloys films of about 2-10 μm thick have been deposited on flexible electroformed Cu and Ni foils, involving Pd complex compounds based electrolytes, exhibiting a very good adherence and uniformity, when a cathodic efficiency of min.67% was evaluated. The influence of electrolyte composition, current density and operating temperature on the final Pd based film has been taken into account. The thickness, surface morphology of the specimens have been investigated involving SEM, AFM and laser confocal microscopy. Some results on hydrogen permeation rate applying Devanathan-Stachurski permeation technique are also discussed.
- L-I.03** 9:40 ONE-STEP ETCH-THROUGH POROUS SILICON MEMBRANE WITH AN OPEN CAVITY AND TUNING THE PORE SIZE
P.Y.Y. Kan and T.G. Finstad, Dept of Physics, University of Oslo, PO Box 1048, Blindern, Oslo 0316, Norway
A new method has been successfully applied to fabricate a thin porous silicon (PS) membrane. It was done by electrochemical etching in hydrofluoric acid (HF) electrolyte. A Si wafer was first coated with a negative resist, SU8, having a circular pattern with a diameter of 600 μm and it was defined by photolithography. A single step etching was then carried out with two different conditions : etching at higher current density follow by a lower one. This resulted in a thin PS membrane with an open cavity and it was characterized by scanning electron microscopy (SEM JEOL 6400F). The whole process takes under 2h which is fast and simple. The critical step in this process is that the SU8 must be thick enough to withstand the long time etching in HF. An isotropic property from HF etching gives about two times the open circular diameter. The geometry of the membrane cannot be controlled precisely. However, it is easy to obtain a thickness of 50-100 μm, with pores in the membrane. The size of the pores can also be tuned easily by choosing different doping density of the Si wafer. The higher the doping, the smaller the pore size and vice versa. This thin PS membrane can be used for microfluidic separation or filtration, and it could be well suitable for bio-medical/chemical applications.

10:00

BREAK

Session II : Complex hybrid

Session chair : **A. Züttel**

- L-II.01** 10:30 -Invited- RECENT ADVANCES ON Li- AND Mg-BASED COMPLEX HYDRIDES FOR SOLID-STATE HYDROGEN STORAGE
Yuko Nakamori and Shin-ichi Orimo, Institute for Materials Research (IMR), Tohoku University, Japan
M-N-H and M-B-H systems (M = alkaline and alkaline rare-earth elements) are regarded as potential candidates for high-performance hydrogen storage. In the presentation, the recent research progresses on the systems will be systematically summarized, viewpoints both from elemental substitutions and from designing of composite materials. Also, the electronic and atomistic characterizations using neutron and synchrotron radiation X-ray diffractions will be introduced for the fundamental understanding of the newly prepared complex hydrides.
- L-II.02** 11:00 INSIGHT OF THE TRUE CATALYST IN TITANIUM-DOPED ALANATE AS A HYDROGEN STORAGE MATERIAL
Shu Zhang, Nobuhiro Kuriyama, Tetsu Kiyobayashi, National Institute of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan
Ti dopant plays a very important role in the development of sodium alanate as a hydrogen storage material. In this sense, it is necessary to investigate the real catalyst species and the reaction mechanism. In this study, we have designed an experiment to determine the stoichiometric relation between NaAlH₄ and Ti catalyst precursors. The result gives further information of the formation of the real titanium catalyst.
- L-II.03** 11:20 DEHYDROGENATION KINETICS OF Ti DOPED NaAlH₄: DEPENDENCY ON THE PREPARATION METHOD
M. Onkawa, H.T. Takeshita, Materials Science and Engineering, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-0073, Japan, T. Kiyobayashi and N. Kuriyama, AIST, Kansai-Center, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan
Inorganic hydrides, such as alanates, borates, metal amide-imide systems, etc, have been considered as promising candidates for hydrogen storage. Recent upsurge in the research activity was fueled by the pioneering discovery in 1996 by Bogdanovic et al. that a few mole fraction of a certain Ti species significantly enhances kinetics of the thermal dehydrogenation of NaAlH₄ and renders the rehydrogenation possible. Yet the mechanism whereby the reaction is enhanced is unclear.
In the present study, we will compare the kinetics of dehydrogenation of Ti doped NaAlH₄ prepared via different procedures, such as the doping method (by ball milling or by co-precipitation from solution) and the dopant (titanium chlorides or alkoxides), so that we can obtain some insight into understanding the reaction mechanism of doped alanates. Isothermal dehydrogenation was carried out under near vacuum condition so as to keep the influence on the kinetics from the gaseous hydrogen constant. The amount of hydrogen evolution was determined by means of mass spectrometer.
- L-II.04** 11:40 STRUCTURE, STABILITY AND REVERSABILITY OF COMPLEX HYDRIDES
A. Züttel(a,b), T. Matsunaga(a), F. Buchter(a), P. Wenger(a), R. Gremaud(b), A. Borgschulte(b), Ph. Mauron(b), B. Dam(b), R. Griessen(b), (a)University of Fribourg, Physics Department, Institute for Renewable Energy Switzerland (IFRES), Pérolles, 1700 Fribourg, Switzerland, (b)Vrije Universiteit, Faculty of Sciences, Division of Physics and Astronomy, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands
- L-II.05** 12:00 -Invited- NEW OPTICAL METHOD FOR THE SEARCH OF NOVEL METAL HYDRIDE MATERIALS
A. Borgschulte, R. Gremaud, R.J. Westerwaal, J.H. Rector, H. Schreuders, B. Dam, A. Züttel, R. Griessen, VU Amsterdam, FEW, Condensed Matter Physics, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands
- 12:30 **LUNCH**

Session III : Hydrogen adsorption
Session chair : A. Züttel

L-III.01 14:00 -Invited-

PHYSISORPTION OF HYDROGEN IN MICROPOROUS MATERIALS

Barbara Panella and Michael Hirscher, Max-Planck-Institut für Metallforschung, Heisenbergstr.3, 70569 Stuttgart, Germany

One promising way for storing hydrogen is physical adsorption of H₂ molecules on nanostructured lightweight solids. The process, which is due to van der Waals forces between hydrogen gas and the solid, is completely reversible, fast and a very small energy loss is involved in desorption. The hydrogen adsorption may be enhanced by lowering the temperature and by using materials with a high surface area and porosity.

Carbon nanomaterials are very attractive candidates for hydrogen storage, because of interesting properties like high specific surface area, microporosity, and low mass. Apart from these characteristics, materials like activated carbons are cheap and easy to produce. Zeolites are aluminosilicates with a very open microporous structure with channels that are large enough to contain gas molecules. Moreover the presence of electrostatic forces within the channels is a unique characteristic of the zeolites. In recent years a new class of materials with high specific surface area, the Metal-Organic Frameworks (MOFs), have been developed and studied for gas adsorption. These materials are crystalline structures consisting of metal oxide clusters connected by rigid aromatic linkers giving a three dimensional porous structure. The presentation will give an overview of the experimental situation of hydrogen storage media based on physisorption comparing carbon materials, Zeolites, and MOFs. In addition we will present our newest results on hydrogen storage in different carbon nanomaterials, which show that the storage capacity depends linearly on the BET surface area and is independent of the nanostructure. Furthermore, our measurements on hydrogen storage in MOFs at RT and 77K will be discussed.

L-III.02 14:30

HYDROGEN STORAGE IN PRISTINE AND MODIFIED CARBON NANOTUBES FROM DIFFERENT ORIGINS

M. Pérez-Mendoza(a), **C. Vallés(a)**, **A.M. Benito(a)**, **W.K. Maser(a)**, **M.T. Martínez(a)**, **T. Belin(b)**, **F. Epron(b)**, (a)Instituto de Carboquímica (CSIC), C/ Miguel Luesma Castán 4, 50018 Zaragoza, Spain, (b)Laboratoire de Catalyse en Chimie Organique, 40 Avenue du Recteur Pineau, 86022 Poitiers cedex, France

Trying to satisfy the automotive industry demands for hydrogen storage is a major challenge for the near future. In this sense, hydrogen adsorption in carbon nanotubes is being studied, but their storage capacity is still far from being optimum for such application. Moreover, a lot of controversy about if these materials are really the solution has arisen after the great expectations suscitied at the beginning.

We present here the hydrogen adsorption measurements shown by carbon nanotubes obtained by different synthesis methods, such as arc-discharge method, floating catalyst chemical vapor deposition (FC-CVD) and supported catalyst chemical vapor deposition (SC-CVD). We have measured not only the hydrogen adsorption values (wt %) presented by the as-produced materials, but also the values presented by the samples after various post-treatments, such as acid purifications, air oxidations, high temperature treatments under an inert atmosphere, chemical and physical activations, trying to improve the adsorption capacity of the samples. All the samples were characterized by various techniques, such as electron microscopy (SEM, TEM), Raman spectroscopy, XRD, EDX, ICPS, TGA and adsorption isotherms, trying to find out a clear relationship between the textural characteristics and the H₂ storage capacity. Some of them present promising hydrogen adsorption values (up to 1.8 wt %) but still far from what the automotive industry requires.

L-III.03 14:50

RELATION BETWEEN THE REVERSIBLE HYDROGEN CAPACITY OF ACTIVATED CARBONS AND THEIR POROUS NANOTEXTURE

E. Frackowiak(a), **K. Jurewicz(a)**, **M. Friebe(a,b)**, **K. Kierzek(c)**, **J. Machnikowski(c)**, **C. Vix-Guterl(d)**, **F. Béguin(b)**, (a)Poznan University of Technology, ul. Piotrowo 3, 60-965 Poznan, Poland, (b)CRMD, CNRS-University, 1b rue de la Férollerie, 45071 Orléans, France, (c)Wroclaw University of Technology, Gdanska 7/9, 50-344 Wroclaw, Poland, (d)ICSI, CNRS, 15 rue Jean Starcky, 68057 Mulhouse, France

Although the optimal pore size for an efficient hydrogen adsorption in nanoporous carbons has been predicted by some theoretical reports, there are only few experimental studies to verify this assumption. In this work, the reversible hydrogen sorption capacity of a wide range of nanoporous materials is measured and correlated with their nanotextural parameters. The electrodecomposition of a KOH aqueous solution has been selected for its high accuracy. A first set of samples were highly ordered porous carbon materials prepared by a replica technique from MCM-48, SBA-15 and MSU-1 molecular sieves, which were impregnated with carbon using different precursors (sucrose solution, propylene and pitch). For this series of carbons, of comparable nanotexture, a linear dependence has been found between the amount of electrochemically stored hydrogen and the ultramicropores (pores smaller than 0.7 nm) volume determined by CO₂ adsorption. The second set of samples were activated carbons (ACs) prepared from different precursors by KOH, CO₂ and steam activation. For these ACs, the hydrogen sorption capacity is not perfectly proportional to the Dubinin-Radushkevitch micropore volume determined by CO₂ adsorption. A better correlation is found considering the nanopore size distribution obtained from CO₂ adsorption by the DFT method. The amount of hydrogen reversibly adsorbed demonstrates a proportional trend with the volume of micropores smaller than 0.6 - 0.7 nm. However, in all cases, a part of the micropore volume estimated by CO₂ adsorption is ineffective.

15:10

BREAK

L-III.04 15:30

EXPERIMENTAL AND THEORETICAL STUDY OF H₂ STORAGE IN NANOSTRUCTURED CARBON MATERIALS

R. Gadiou, A. Didion , C. Vix-Guterl, ICSI, 15 Rue Jean Starcky BP 2488, 68057 Mulhouse cedex, France, R.J.-M. Pellenq, T. Roussel, C. Bichara, CRMCN, Campus de Luminy, 13288 Marseille cedex 09, France

The storage capacity of hydrogen in porous carbon materials by physisorption is mainly controlled by microporosity. Compared to classical activation of carbon materials, the negative templating technique allow the synthesis of highly microporous carbons with a narrow pore size distribution. In this study, carbon materials were synthesized by this process with NaY zeolite as template. Carbon precursors used for the insertion in the template were furfuryl alcohol and propylene. The texture of the carbon materials was characterized and the adsorption isotherms of hydrogen were then obtained at 77 K and at room temperature with a manometric experimental setup up to 7 MPa. A theoretical carbon structure of the carbon replica was computed and the adsorption isotherm was calculated using the Monte-Carlo technique and Lennard-Jones inter-molecular potentials for H₂-H₂ and H₂-carbon interactions. We found that the carbon replica of NaY zeolite can store 1.5 w% of hydrogen at room temperature under pressure of 30 Mpa. These computed isotherms were compared with the measured ones.

L-III.05 15:50

MECHANISM OF ELECTROCHEMICAL HYDROGEN STORAGE IN NANOPOROUS CARBONS

F. Béguin(a), K. Jurewicz(b), M. Friebe(a,b), J. Dentzer(c), C. Vix-Guterl(c), E. Frackowiak(b), (a)CRMD, CNRS-University, 1b rue de la Férollerie, 45071 Orléans, France, (b)Poznan University of Technology, ul. Piotrowo 3, 60-965 Poznan, Poland, (c)ICSI, CNRS, 15 rue Jean Starcky, 68057 Mulhouse, France

This paper presents an overview of the electrochemical hydrogen storage mechanism in various nanoporous carbons, expecting from this study guidelines for further optimisation of storage capacity. Electrodecomposition of aqueous solutions by galvanostatic and voltammetry techniques has been selected for its higher accuracy than the gas adsorption techniques. Applying a negative polarization to a carbon electrode, the electrical double layer is first charged, and once the potential becomes lower than the equilibrium potential, hydrogen in the zero oxidation state is formed by water reduction and adsorbed physically (Had) in the nanopores of carbon. Reversing the polarisation, hydrogen is oxidised at potentials which depend on the energy of the sites where it is trapped. Upon reaching the maximum possible value of oxidation potential, a part of hydrogen remains trapped in the carbon substrate. Thermo-programmed desorption (TPD) on the carbon material after a reduction/oxidation cycle allows to analyse the hydrogen irreversibly stored. About 50% of the total hydrogen stored is desorbed at ca. 200°C, that suggests an intermediate state between chemisorption and physisorption. The amount of hydrogen reversibly stored is precisely determined, by subtracting the contribution of charging the electrical double layer from the measured discharge capacity, and compared to nanotextural data as the micropore volume measured by CO₂ adsorption. We have found that pores in the range of 0.6 - 0.7 nm seem to be optimal for storing hydrogen. However, we have clearly proved that some of them participate to the irreversible trapping mentioned before. The contributions of pore shape and surface functionality to this irreversible phenomenon are discussed.

L-III.06 16:10

POROUS Si NANOSTRUCTURES AS HYDROGEN RESERVOIRS

V. Lysenko and D. Barbier, Materials Physics Laboratory (LPM), CNRS UMR-5511, INSA de Lyon, 7 av. Jean Capelle, Bat. Blaise Pascal, 69621 Villeurbanne, France, F. Geobaldo, P. Rivolo and E. Garrone, Department of Material Science and Chemical Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy, C. Turpin, Electrical Engineering and Industrial Electronics Laboratory, LEEI, CNRS UMR-5828, INP de Toulouse, 2 rue Camichel, BP 7122, 31071 Toulouse, France

The enormous internal specific surface (up to 1000 m²/cm³) of porous silicon (PS) nanostructures is well-known to be covered by SiH_x species influencing significantly all physical properties of the Si nanoparticles constituting the PS nanostructures. Upon heating, such species release molecular hydrogen (H₂), as revealed by thermal desorption spectroscopy. This allows imagining of PS nanostructures for applications as hydrogen reservoirs. In our work, hydrogen content of the PS nanostructures is quantitatively analyzed by infra-red and thermal desorption spectroscopies. The amount of hydrogen covering specific surface of the PS nanostructures is studied as a function of the nanoscale porous morphology. In particular, the influence of porosity, nanoparticle dimension and shape on the hydrogen concentration will be quantitatively described. Data concerning reproducibility of PS nanostructures as hydrogen reservoirs, as well as thermally and chemically induced desorption of hydrogen will be also reported. Through the amount of hydrogen desorbed from the PS nanostructures, the electrical energy obtainable through fuel cells is estimated and compared with known materials applied for hydrogen storage.

16:30

POSTER SESSION

Poster L/P01 – LP06

Session IV : Metal Hydrides
Session chair : L. Schlapbach

L-IV.01 14:00 -Invited-

MODELLING OF HYDRIDE-FORMING MATERIALS CHARACTERISTICS

P.H.L. Notten(a,b), A.V. Ledovskikh(b), D. Danilov(c), E. Verbitski(a) and W. Rey(c), (a)Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands, (b)Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands, (c)Eurandom, Den Dolech 2, 5612 AZ Eindhoven, The Netherlands

Hydride-forming compounds are nowadays of great importance for both electrochemical (rechargeable Nickel-MetalHydride batteries) and gas phase (e.g. purification and fuel cells) applications. In particular, it is anticipated that hydrogen storage is one of the most crucial aspects in the future hydrogen economy.

A thermodynamic approach will be presented allowing an accurate description of the hydrogen formation/decomposition process in various hydride-forming materials. This generic approach is based on the principles of statistical thermodynamics using a lattice gas model. To describe second order phase transitions and two-phase coexistence regions a binary alloy approach has additionally been taken into account. Both Pressure-Composition Isotherms and corresponding electrochemical Open-Circuit-Voltage characteristics are mathematically described. The derived model has been adopted to simulate Pressure-Composition Isotherms of (i) model-type of non-stoichiometric, hydride-forming, materials (LaNi₅Cu_{1.0}-type), extensively described in the literature, (ii) "standard" MischMetal-based hydride-forming materials, nowadays widely applied in commercial Nickel-MetalHydride (NiMH) batteries and (iii) a new class of high energy density, fluorite-structured, hydrogen storage materials. This latter class of materials were recently reported to be very attractive as these occlude more than 6 wt.% at a significant rate in both thin film and powder form. Excellent agreement between experimental and theoretical results has been found in all cases over a wide compositional and temperature range. The contribution of both the entropy and H-interaction energies to the Pressure-Composition Isotherms will be discussed.

L-IV.02 14:30

LOW TEMPERATURE HYDROGEN DESORPTION FROM AGED MAGNESIUM HYDRIDE

J.F. Fernández, F. Leardini, J. Bodega and C. Sánchez. Dpto. Física de Materiales, Facultad de Ciencias, Universidad Autonoma de Madrid, 28049 Madrid, Spain

It is well known that magnesium hydride (MgH₂) degrades very fastly when exposed to ambient conditions. This degradation takes place mainly by interaction of MgH₂ with atmospheric water vapour resulting in the formation of a magnesium hydroxide layer covering the magnesium hydride core. The conditions of formation of the magnesium hydroxide layer, room temperature and low vapour water pressure, are such that the layer grows with a nanometric morphology and with a high number of co-ordination defects. MgH₂ aged samples have been studied by means of Thermal Desorption Mass Spectrometry combined with Differential Scanning Calorimetry. Thermal desorption spectra consist of several desorption peaks (H₂O, H₂ and CO₂ gases) at different temperatures from 300K to 900K. In particular, the hydrogen desorption spectrum is composed of three groups of peaks. The first one shows two small peaks around 500K and 550K. A second larger one is observed at 673K, partially overlapped to the main H₂O desorption. Finally, the last one takes place around 825K. In this work, the origin of the several peaks in the TD spectrum of aged MgH₂ will be discussed. Special attention will be paid to the low temperature ones which appear at much lower temperatures than the corresponding one for fresh MgH₂ (~600K).

L-IV.03 14:50

BENEFITS OF CARBON ADDITION ON HYDROGEN SORPTION PROPERTIES OF Mg-Ni THIN FILMS GROWN BY PULSED LASER DEPOSITION

Xavier Darok, Aline Rougier, Luc Aymard and Jean-Marie Tarascon, Laboratoire de Réactivité et de Chimie des Solides, CNRS UMR-6007, Université de Picardie Jules Verne, 80039 Amiens Cedex, France

Thanks to their high hydrogen capacity, Mg-based alloys have received a great interest. For the past 10 years, their range of applications has suddenly widened with the discovery of spectacular optical and electrical changes observed in thin films [1-3]. The main difficulty with these systems remains their high reactivity towards oxygen. In our group, enhanced hydrogen absorption/desorption performances were achieved via the preparation of ball-milled Mg-Ni/C composites due to the reducing character of carbon. Herein, such carbon addition was implemented to Mg-based thin films grown by Pulsed Laser Deposition. The influence of the amount and nature of carbon on the morphology, structure, optical and sorption properties of the as-deposited Mg-Ni/C thin film grown under various deposition conditions will be discussed.

L-IV.04 15:10

HYDROGEN STORAGE IN NANOSIZED Mg-Ni(Fe) ALLOYS

P. Palade, G. Principi, A. Maddalena, S. Sartori, INFM and Setore Materiali, DIM, Università di Padova, via Marzolo 9, 35131 Padova, Italy; S. Lo Russo, INFM and Dipartimento di Fisica, Università di Padova, via Marzolo 8, 35131 Padova, Italy; G. Shinteie, V. Kuncser, G. Filoti, Solid State Magnetism Department, National Institute for Materials Physics, Atomistilor st.105 bis, Ro- 77125 Bucharest Magurele, Romania

Recent results obtained on Mg-based hydrides by the "Hydrogen Group" of Padova University are presented.

Two kinds of samples were prepared: - magnesium-rich Mg-Ni(Fe) compounds obtained by ball milling mixtures of elemental powders; - melt spun pellets of Mg-Ni(Fe) alloys ball milled for short times. Hydrogen absorption and desorption tests, as well as pressure-composition-isotherms (PCI), were obtained on the treated materials by means of a Sievert volumetric device operating in automatic cycling mode. The structure of the materials was investigated by x-ray diffraction before and after hydrogenation. Mössbauer spectroscopy was used to get information on the Fe atoms co-ordination inside the Mg-Ni matrix before and after hydrogenation. It is shown that the small amounts of Fe added to samples have a catalytic effect on hydrogen absorption/desorption kinetics and that samples prepared by melt spinning and subsequent milling behave better than those prepared by ball milling elemental mixtures.

15:30

BREAK

L-IV.05 15:50

INSTABILITIES IN MAGNESIUM HYDRIDES INDUCED BY LATTICE STRAINS

R. Checchetto, N. Bazzanella, A. Miotello, Dipartimento di Fisica, Università di Trento, 38050 Povo (TN), Italy, C. Maurizio, OGG, c/o ESRF, GILDA CRG, 38043 Grenoble, France, P. Mengucci, Dipartimento di Fisica, Università Politecnica delle Marche, 60131 Ancona, Italy

The interface between nanocatalyst particles and hydride forming materials plays a major role in the hydrogen absorption and desorption process representing a fast migration paths for the H atoms to the hydride forming material. In Pd coated MgH₂ films with thickness in the 100 nm range, the catalytic action of the Mg-Pd interface on the H₂ desorption process seems to be connected with the clamping action of the Pd coating on the MgH₂ layers. The crystalline stresses produced in this way give rise to important effects as the dissociation of the MgH₂ phase at temperatures lower than 450 K [1,2].

We present an experimental study showing that the elastic effects control the dissociation of MgH₂ in samples with thickness in the 10 micrometer range. Mg samples containing 5 at. % Nb were prepared by sputtering and their H₂ desorption kinetics was studied by Sievert techniques. The activation energy and the reaction order controlling desorption are 141 ± 5 kJ mol⁻¹H and $n \approx 0.776$; 4 in the pure Mg, 51 ± 5 kJ mol⁻¹H and $n \approx 0.776$; in Nb-doped Mg [3,4]. The local geometric structure surrounding the Nb atoms was studied by Extended X-rays Absorption Fine Structure. EXAFS measurements indicates that Nb atoms are atomically dispersed into the as-deposited Mg matrix, while H-containing Nb nanoclusters are formed upon H₂ absorption in the MgH₂ samples. We suggest that the lattice strains in the MgH₂ layers related to H-containing Nb clusters stimulate the hydride decomposition.

L-IV.06 16:10

LOCAL STRUCTURE OF Nb in Nb-DOPED MG FILMS UPON HYDROGEN ABSORPTION AND DESORPTION PROCESSES

C. Maurizio(a), R. Checchetto(b), N. Bazzanella(b), A. Miotello(b) and F. D'Acapito(a), (a)INFM-GILDA beamline, European Synchrotron Radiation Facility-ESRF, 6 rue J. Horowitz, 38043 Grenoble, France, (b)Dipartimento di Fisica dell'Università di Trento, via Sommarive 14, 38050 Povo (TN), Italy

Among the light metals forming hydride phase, magnesium is one of the most interesting for application in hydrogen storage technology because of the very high capacity, close to 7.6 wt. % : unfortunately, the very slow kinetics in hydrogenation and dehydrogenation reactions requires the addition of a proper catalyst even at temperatures as large as 673 K. The catalyst, typically in form of metallic nanoparticles (Nb, PdFe₃, Pd) dispersed at the Mg surface, favours the H₂ dissociation and the jump of H atoms towards the subsurface layers of the Mg matrix by the formation of the metastable Nb-H phases [1] or by the transfer of H atoms to Mg after the H migration through the Mg-Nb interface [2].

Recent analyses on Mg films prepared by rf-magnetron sputtering containing 5 wt.% Nb have evidenced that the catalytic effect of Nb is effective even if the metallic additive is atomically dispersed in the Mg lattice (X-ray diffraction and Transmission Electron Microscopy analysis did not detect Nb-containing clusters in the as-deposited film) [3,4]. To this respect, the use of the x-ray absorption spectroscopy (EXAFS, Extended X-ray Absorption Fine Structure) is attractive, since quantitative information on the local structure around Nb can be achieved independently of the aggregation state of Nb atoms (either Nb dispersed into the matrix, or Nb or Nb-H aggregates). In this work, the results obtained by the EXAFS spectroscopy (performed at the Nb K-edge) are presented: they show a quite complete picture of the structural changes around the Nb atoms at different steps of the H₂ absorption/desorption cycle. In particular, while the Nb atoms are dispersed into the Mg matrix upon sputtering deposition, H-containing Nb nanoclusters are present in the film upon H₂ absorption, while Nb single metal clusters remain upon the H₂ desorption process. The effect of these structural modifications of the Nb site on the dynamics of the whole absorption/desorption process will be discussed.

[1] J. F. Pelletier, J. Huot, M. Sutton, R. Schultz, A. R. Sandy, L. B. Lurio and S. G. J. Mochrie, Phys. Rev. B63 (2001) 052103

[2] A. R. Yavari, J. F. R. de Castro, G. Vaughan, G. Heunen, J. Alloys Comp. 353 (2003) 246

[3] N. Bazzanella, R. Checchetto and A. Miotello, Appl. Phys. Lett. 85 (2004) 5212

[4] R. Checchetto, N. Bazzanella, A. Miotello and P. Mengucci, J. Alloys Comp. (in print)

[5] R. Checchetto, G. Trettel and A. Miotello, Meas. Sci. Technol. 15 (2004) 127

- L-IV.07** 16:30 INFLUENCE OF PRESSURE ON THE CONVERSION OF MG INTO MG₂H₂ PERFORMED BY BALL MILLING UNDER HYDROGEN ATMOSPHERE
S. Doppiu, M. Heinrich, B. Gebel, O. Gutfleisch, IFW Dresden, Institut für Metallische Werkstoffe, Helmholtzstr. 20, 01069 Dresden, Germany
Reactive ball milling is a suitable method for the synthesis of metal hydrides for hydrogen storage applications. Mechanical activation induces severe plastic deformation resulting in the formation of highly defective, nanoscale structures with increased atomic mobility. In this study, synthesis of MgH₂, starting from Mg, was performed by reactive ball milling under hydrogen atmosphere. The effect of different H₂ pressure on the conversion of Mg into the hydride was investigated for the well-known alloy Mg₉₉Ni₁. Milling was performed in an especially designed high-pressure vial, allowing in-situ monitoring of pressure, able to work in a pressure range of 1-150 bars. The characterization of the samples was done by X-ray diffraction analysis (XRD), high-pressure differential scanning calorimetry (DSC) and intelligent gravimetric analysis (IGA). The samples were milled under a H₂ pressure of 10, 40 and 90 bars respectively. For both the samples milled at higher pressure very fast transformation of Mg into the hydride was observed. After only 12 hours of milling the peaks of Mg are no longer visible in the XRD patterns. The sample milled at 10 bars shows an incomplete conversion after 18 hours of milling. As expected, thermal analysis shows that the hydride's thermostability remains unaffected, whereas the degree of nano-crystallization is influenced by the applied pressure.
- L-IV.08** 16:50 KINETICS OF HYDROGEN LOADING AND RELEASE IN YTTRIUM METAL DURING ITS ELECTROCHEMICAL POLARIZATION
V. Parkhutik, E. Matveyeva, E. Rayon, R&D Centre MTM, Technical University of Valencia, Spain, N. Bordel, R. Pereiro, University of Oviedo, Spain, J.M. Albella, Institute of Materials Science of Madrid, Spain and H. Fujii, University of Hiroshima, Japan
Electrochemical loading/unloading of hydrogen into yttrium metal is a process which can be important for fabrication of Smart Optical Windows, if only all physical and chemical effects involved are optimized to yield high optical contrast and longevity of devices. In our previous studies we have shown that optical changes assisting the hydrogen loading/unloading into the Y metal are not fully reversible. First run of loading/unloading cycle would result in 250% change of the optical reflectivity of the sample, while subsequent cycles yield only 150% reflectivity changes. This effect is customary to ascribe to incomplete reversibility of hydrogenation reaction. We have studied optical and electrical properties of 100nm thick Y films covered by 20nm of Pd or Ni to protect material from oxidation and corrosion. Besides, we have conducted atomic analysis of the Ni/Y samples corresponding to different stages of hydrogenation reaction using Optical Emission Spectroscopy. We have also performed a.c. impedance measurements on Ni-Y samples during their loading/unloading with hydrogen. Very unusual effect of sharp growth of impedance (four-five orders of magnitude) is observed below some critical frequency (about 0.5-1.0 Hz). We discuss possible reasons for incomplete restoration of reflecting state of the samples and their unusual impedance characteristics. One of them could be partial oxidation of the Y metal during electrochemical treatment.
- L-IV.09** 17:10 -Invited- HIGH DESORPTION PRESSURE METAL HYDRIDE FOR HIGH PRESSURE MH TANK
T. Matsunaga, T. Shinozawa, H. Suzuki, D. Mori, Higashifuji Technical Center, Toyota Motor Corporation, 1200 Mishuku, Susono, Shizoka 410-1193, Japan
- 17:40 **POSTER SESSION**
Poster L/P07 – LP10
- 19:00 **AWARD CEREMONY**
The symposium organizers and the candidates to the graduate student award are requested to attend.
- CONFERENCE RECEPTION**

Session V : PEFC

Session chairs : A. Reller

- L-V.01** 9:00 -Invited- TRENDS IN MEMBRANE ELECTRODE DEVELOPMENT FOR PEFC
L. Gubler et al., PSI, Villigen, Switzerland
- L-V.02** 9:30 THE ORIGIN OF THE OVERPOTENTIAL FOR OXYGEN REDUCTION AT A FUEL CELL CATHODE
J. Rossmeisl, A. Logadottir, T. Bligaard, L. Lindqvist, J.K. Nørskov, Center for Atomic-scale Materials Physics, Department of Physics, Technical University of Denmark, 2800 Kgs.-Lyngby, Denmark, J.R. Kitchin, Department of Chemical Engineering, University of Delaware, Newark DE 19716, USA, H. Jónsson, Faculty of Science, VR-II, University of Iceland, 107 Reykjavik, Iceland
We present a method for calculating the stability of reaction intermediates of electrochemical processes on the basis of electronic structure calculations. We use the method in combination with detail density functional calculation to obtain a detailed description of the free energy landscape of the electrochemical oxygen reduction over Pt(111) as a function of applied bias. This allows us to identify the origin of the overpotential found for this reaction, which is the cathode reaction in PEM fuel cells. The key descriptor for the reaction is found to be the adsorption energies of oxygen and hydroxyl. On the basis of a data base of calculated oxygen and hydroxyl adsorption energies the trend in the oxygen reduction rate for a large number of different transition and noble metals can be accounted for.
- L-V.03** 9:45 OBTAINMENT OF FREE NOBLE METAL CATALYZERS USING COLDS PLASMA TECHNIQUES
N. Tricás, J. Herranz and S. Borrós, Institut Químic de Sarrià, Av. Sarrià 390, 08017 Barcelona, Spain
In this work a free noble metal catalyst for fuel cells cathode has been developed. This kind of catalyst present many advantages from the economical and environmental point of view in comparison with the common noble metal supported catalysts used nowadays. Other research groups have already reported the possibility to create active sites on the surface of the carbonaceous support such as carbon black. The nitrogenation of this support may lead to a coordination complex which is able to catalyze the oxygen reduction. In the present work our goal was to obtain this type of sites by using cold plasma techniques. These techniques present many advantages compared to the wet chemistry treatments. The absence of solvents as well as a very rich and powerful chemistry are two of the most important characteristics to be emphasized.
The CB plasma treatment was optimized to obtain the maximum amount of nitrogen on the surface. A downstream reactor coupled to a Radio Frequency generator was designed and adapted to modify powders. Ammonia was used as main nitrogenation agent although other gases were also mixed in a smaller content. Pressure levels were 10⁻³ mbar before the gas introduction and 0,4mbar final tests chemical composition was studied using XPS, other tests such as pH and solubility in water were also carried out showing the surface modification during the treatment. To confirm the oxygen reduction activity a rotary disk electrode was used. Although some improvements should be studied, this method is presented as a very interesting possibility to obtain self-containing active sites supports for fuel cells cathodes.
- L-V.04** 10:00 CARBON NANOTUBES SUPPORTED CATALYSTS FOR DMFC
B. Rohland(a), Mihaela-C. Bunescu(b), B. Ruffmann(a), Marlies Pietrzak(a), Marion Wienecke(b), S. Möller(a), (a)HIAT gGmbH, Hagenower Straße 73, 19061 Schwerin, Germany, (b)Hochschule Wismar, Institut für Oberflächen- und Dünnschichttechnik, Philipp-Müller-Str., 23952 Wismar, Germany
Aiming to improving the power density of the Direct Methanol Fuel Cells (DMFC), we report about preparation and properties of catalysts nano-particles supported on multi-wall carbon nano-tubes (MWCNTs). Prior to catalyst deposition, the surface activation of commercially available carbon nanotubes was performed in two steps, in a mixture of HNO₃ and H₂SO₄. Pt and Pt/Ru catalysts were then electrodeless deposited using a procedure with a liquid phase exchange substance. The microstructure and micro-composition analysis of the MWCNTs was performed by electron microscopy (TEM, SEM and EDS). Uniform distributed catalyst nano-particles with diameters in the 2-4 nm range were observed for a certain combination of the process parameters. The membrane-electrode-assembly (MEA) using the new catalysts, was tested at 70°C and 3.5% CH₃OH in air under normal pressure. Impedance spectroscopy measurements were performed and information about polarisation of cathode and anode were obtained. The performances were improved as compared with the standard DMFC electrodes by a factor of five at the same Pt loading of 1 mg/cm².
- L-V.05** 10:15 PLATINUM NANOPARTICLES DISPERSED IN A CARBON MATRIX FOR FUEL CELL CATALYSTS
A. Reiner, F. Hajbolouri, A. Wokaun, G.G. Scherer, Paul Scherrer Institut, Electrochemistry Laboratory, 5232 Villigen, Switzerland
- 10:30 **BREAK**

- L-V.06** 11:00 NEW HYBRID NANOPOROUS SOL-GEL MATERIALS FOR HIGH TEMPERATURE PEMFC
K. Vallé(a), F. Pereira(a), Ph. Belleville(a) and C. Sanchez(b), (a)CEA/Le Ripault, BP16, 37260 Monts, France, (b)LCMC, UPMC Paris VI, 75000 Paris, France
 Fuel cell technology has merged in recent years as a keystone for future energy supply. The proton exchange membrane fuel cell (PEMFC) is one of the most promising project of this energy technology program ; the PEMFC is made of a conducting polymer that usually operates at temperatures in the range 20-80°C. In order to reach high energy consumption application like transportation, the using temperatures need to be increased above 100°C. Sol-gel organic/inorganic hybrids have been evaluated as materials for membranes to fulfill the high temperature using requirement. Since the sol-gel process allows the molecular scale construction of tailor-made materials, specifically designed hybrids for high temperature membranes are proposed. These new materials for membrane need to retain water content and therefore proton conductivity property with using temperature and time. The membranes also need to be chemical-resistant to strong acidic conditions and to keep their mechanical properties regarding stacking requirements. In order to answer all these specifications, the proposed hybrid membrane is based on nanoporous inorganic phase embedded in an organic polymer in which chemical grafting and conductivity network microstructure are optimized to preserve water content and proton conductivity in the temperature range of 100-120°C. As a matter of fact, the as-designed grafted hybrid microstructure lead to higher conductivity performances compared to pure polymeric membrane. Such very promising results on these new hybrids are presented and discussed regarding properties/microstructure features.
- L-V.07** 11:15 MODELING AND SIMULATION FOR STUDYING ION-CONDUCTIVITY OF CHITOSAN MEMBRANES FOR BUILDING ELECTROLYTES OF FUEL CELL
Ernesto López-Chávez, José Manuel Martínez-Magadán, Raúl Oviedo-Roa, Javier Guzmán-Pantoja, Joel Ramírez-Salgado, Jesús Marín-Cruz, Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, México D.F. 07730, México
 The objective of this work is to provide with some elements for developing a theoretical methodology aimed to describe the mechanism of chitosan-membrane ion conductivity and to obtain its magnitude. Atomistic molecular modelling has been utilized to construct an ionic conducting polymer electrolyte system consisting of poly(chitosan), H₂O molecules, and H₃O⁺, OH⁻, ions, inside of the simulation cell. The COMPASS force field was used. The simulation allows describing the mechanism of ionic conductivity along the polymer matrix. The theoretical results obtained are compared with previously-reported experimental data for chitosan membranes. The present methodology can be considered as a first step towards understanding these complex problems of technological interest.
- L-V.08** 11:30 BIPOLAR MINIATURISED PROTON EXCHANGE FUEL CELL FULL INTEGRATED IN A MICROMACHINED SILICON SURFACE
G. D'arrigo, C. Spinella, CNR-IMM, Stradale Primosole 50, 95121 Catania, Italy, G. Arena, S. Lorenti, ST-Microelectronics, Stradle Primosole 50, 95121 Catania, Italy
 In most engineered systems, a trend toward miniaturisation is pursued to diminish size, weight and complexity while reducing cost and improving performance. In the recent history of fuel cell design, particularly in PEM fuel cells we have witnessed a similar sort of rapid design evolution leading to improved performance. It is reasonable to expect the drive toward size reduction to continue, particularly since the ultimate cost of fuel cell devices will be related primarily to the volume and weight of raw materials. Recent advances in the understanding of micro-scale micromachining fabrication and thermo and electrical transport suggest tremendous enhancements in heat and mass transport and electrochemistry could be obtained by engineering fuel cells at this scale. Therefore we anticipate potential order of magnitude improvements in fuel cell performance can be achieved through concerted design efforts focussed on the exploitation of micro-scale phenomena for fuel cell systems design. Ours contribution, coming from the achieved experience of prototyping and fabricating of a traditional PEM fuel cell using a microfluidic system and porous electrode fabricated on silicon substrate as shown in fig. 1, consist in the creating a breakthrough in the traditional fuel cell stack (that use the glowing the two stack by using the proton exchange membrane) fabrication, projecting a new Single Bipolar Multi-function Plate in which are created the delivery system for gases (hydrogen and oxygen) or for liquid (Methanol), the two porous semielement (anode and cathode) and the PEM with a cooling system and conductive electronic paths full integrated in a silicon structures.

Session VI : SOFC

Session chair : **A. Reller**

- L-VI.01** 11:45 -Invited- MATERIALS DEVELOPMENT FOR SOLID OXIDE FUEL CELLS: PROGRESS AND CHALLENGES
E. Ivers-Tiffée, University Karlsruhe, Institute of Materials for Electrical Engineering, 76131 Karlsruhe, Germany

L-VI.02 12:15

THE SILID STATE OXIDES IS ADVANCED MATERIALS FOR FUEL CELL TECHNOLOGIES

I.Kh. Abdukadirova, Institute of Nuclear Physics Academy of Science Uzbekistan, Ulugbek, 702132 Tashkent, Usbekistan

Solid state oxides Al_2O_3 has been advanced materials for MOS structures in semiconductor technologies and for fuel cell technologies. The influence of some doses neutron radiation at the high temperature on structure stability and defect formation in solid state oxides (for example of crystal Al_2O_3) with application of spectroscopic and X-ray methods was investigated. The fracture our maximum on the dose curves $Y(F)$ of intensity photoluminescence, colour centers 230, 257 nm (F^- -center) and 358 nm (F_2^- -center) in the range of identical doses was determined at the analysis of the obtained results. The conclusion was made about the connection of the fracture point with the intensification of radiation damages of crystalline oxides. Monotonous changes of this functions $Y(F)$ were observed with a stable measurement result at high level exposures of the samples. During the stage of damage structure on the optical spectra acceleration of anion vacancies, F^- and F_2^- -aggregate defects formation was found. In diffraction patters of the Al_2O_3 were found changes of some reflexes intensity and position depending upon fluency. The intensity and reflection angle decreases with an increase in dose. This means that damaging radiation acts at the ordering of initial structure and its lattice parameters. It may be assumed that these changes are due to particular damage of oxides. The striking mechanism of atom displacement out of lattice knots plays the main role in it.

12:30

LUNCH

Session VI : SOFC (continue)
Session chair : A. Reller

L-VI.03 14:00

FABRICATION AND CHARACTERISATION OF MIXED CONDUCTING PEROVSKITES FOR SOFC APPLICATIONS

Ulrich F. Vogt, Joseph Sfeir and Peter Holtappels, Swiss Federal Laboratories for Materials Testing and Research (EMPA), Ueberlandstr. 129, 8600 Dübendorf, Switzerland

Several types of nanosized ceramic powders are required for the development of electrochemical systems like Solid Oxide Fuel Cells (SOFC). Especially the lanthanide transition-metal oxides are of technological importance for their use in SOFCs, catalysis, oxygen membrane reactors and sensors.

Today's state of the art SOFCs is based on the so-called anode supported cell technology which allows to minimize the overall ohmic losses and to decrease the working temperature to below 800°C. In the current development, there is an increasing demand for cathode materials performing suitably at these intermediate temperatures and possessing a lasting stability for their use in a commercial end-product. For a SOFC cathode application, high electronic and ionic conductivity, good oxygen reduction activity, long term stability and compatibility towards yttria stabilized zirconia (YSZ) or doped ceria electrolytes are needed. Strontium substituted lanthanum manganite (LSM) is commonly used as a high temperature cathode material. For intermediate temperatures, substituted lanthanum ferrites (LF) among others are investigated as alternative cathode materials for SOFC. The results of the actual work with respect to improving SOFC performance and reliability will be discussed.

L-VI.04 14:15

LSMF PEROVSKITE POWDERS SYNTHESIS BY A DERIVED SOL-GEL PROCESS. INFLUENCE OF THE ORGANIC/INORGANIC RATIO ON STRUCTURAL AND MICROSTRUCTURAL PROPERTIES

P. Lenormand, M. Nouasse, S. Castillo, F. Ansart, Centre Interuniversitaire de Recherche et d'Ingénierie des MATériaux, Laboratoire de Chimie des Matériaux Inorganiques et Energétiques, UMR N°5085, Université Paul Sabatier, Bât. 2R1, 118 route de Narbonne, 31062 Toulouse Cedex 4, France

Mixed oxides, particularly those with perovskite structure, have received much attention as cathode materials for solid oxide fuel cells. To improve the cathode material conductivity, it is necessary to optimise both composition and microstructure of the electrode. Strontium-substituted lanthanum manganites are the usual cathode materials, owing to their chemical stability versus yttria stabilized zirconia, which is the conventional electrolyte for SOFC systems. In this work, the manganese is partially or totally substituted by iron in LSM, in order to obtain both electronic and ionic conductivity. Strontium-substituted lanthanum ferromanganites, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3+d}$, ($y = 0; 0.2; 0.5; 0.8; 1$) LSMF2Y ($Y = 10y$) have been synthesized by a polymeric sol-gel route derived from the Pecchini process and dip-coated on YSZ substrates.

In this work, the influence of the sol synthesis parameters (oxide composition, organic compounds and/or metal salt concentration) on the structure and the microstructure of the obtained nanopowders has been investigated by X-ray diffraction experiments. LSMF2Y mixed conducting oxides crystallize in the perovskite structure, rhomboedral (R-3c) system, at about 650°C. Whatever the calcination temperature, both the cell parameters and the crystallite size increase with the iron content. The obtained nanoparticles are monocrystalline and this is maintained during thermal treatments from 700°C to 900°C; i.e. at the time of the first steps of the granular growth. Unlike what is observed on LSMF2Y layers, where the organic/inorganic ratio appears as a key parameter to control the microstructural properties of final coatings, no influence has been really observed for this parameter on the structural and microstructural properties of the powders.

L-VI.05 14:30

TOWARDS NOVEL MIXED-CONDUCTING PEROVSKITES WITH IMPROVED IONIC AND ELECTRONIC TRANSPORT

B. Dabrowski, Department of Physics, Northern Illinois University, DeKalb IL, USA

Mixed-conducting oxide ceramic membranes and cathodes of solid oxide fuel cells (SOFC), used for oxygen separation and transport, are of prominent importance in present and emerging technologies for hydrogen production and use. Materials with greatest prospects as cathodes of SOFC are transition metal perovskites because of a wide range of unique physical and thermal properties, stability against CO poisoning, and possibility of use with variety of fuels. Most developers of SOFC use $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ cathodes with compositions $x = 0.1 - 0.4$ which are compatible with the state-of-the-art electrolyte based on yttrium stabilized ZrO_2 . Compositions with $x > 0.5$ have not been considered to date for application because they could not be synthesized. Using novel description of structural and physical properties of manganites in terms of the tolerance factor $t(x,T,d)$, which is dependent on composition (x), temperature (T), and oxygen-content (d), we have recently established synthetic methods for these compositions and completed composition-structure-properties phase diagram for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. Thermogravimetric and conductivity measurements show that compositions with $x > 0.5$ exhibit increasing range of oxygen deficiency which permits 10 - 100 times higher ionic conductivity than compositions currently used. We will present results of the structural measurements by high temperature neutron diffraction and chemical substitution study that show how to enhance thermodynamic stability of these compounds. Development of these materials would alleviate significant challenges hindering implementation of fuel cell technology through lowering the operational temperature of present SOFC by 200°C to 600 - 700°C.

- L-VI.06** 14:45
- ENHANCED IONIC CONDUCTIVITY IN CRYSTALLINE $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$; FILMS GROWN BY PULSED LASER DEPOSITION**
- Chun-Nam Wong, Boscope Mo-Kun Sze and Kin-Hung Wong, Department of Applied Physics and Materials Research Centre, Hong Kong Polytechnic University, Hung Hom, Hong Kong Special Administrative Region, People's Republic of China
- $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$ (LSGMO) perovskite oxide ion conductor thin films of about 300 nm thick were deposited on a LaAlO_3 (LAO) at various substrate temperatures by pulsed laser deposition. Their structural characteristics were studied by x-ray diffractometry and transmission electron microscopy. Polycrystalline and epitaxially grown films were revealed for samples grown at different temperatures. Their ionic conductivities were investigated with a two-probe DC technique as a function of temperature over 300 C - 800 C range in air. The polycrystalline LSGMO films show a conductivity of 0.17 S/cm while the epitaxial LSGMO films exhibit values of about 0.56 S/cm at 600 C. This represents a substantial enhancement from the 0.018 S/cm of the bulk LSGMO measured at the same temperature.
- L-VI.07** 15:00
- CORRELATION BETWEEN MICROSTRUCTURE AND DEGRADATION OF IONIC CONDUCTIVITY IN Y_2O_3 DOPED ZIRCONIA**
- B. Butz, P. Kruse, H. Störmer, D. Gerthsen, Laboratory for Electron Microscopy, University of Karlsruhe (TH), 76128 Karlsruhe, Germany, A. Müller, A. Weber, E. Ivers-Tiffée, Institute of Materials for Electrical Engineering, University of Karlsruhe (TH), 76128 Karlsruhe, Germany
- Ytria-stabilized Zirconia (YSZ) is well established as electrolyte in solid oxide fuel cells. YSZ doped with 8.5 mole% shows die highest ionic conductivity which decreases significantly at high temperature. To contribute to the understanding of the degradation of ionic conductivity, transmission electron microscopy (TEM) was applied to study the microstructure of as-sintered and aged 8.5YSZ as well as 10YSZ. The samples were produced from high-purity YSZ powder, sintered at 1550 °C and heat treated at 950 °C for 1000-2500 h. The TEM studies were combined with dc-conductivity measurements and impedance spectroscopy.
- Electron holography and high-resolution TEM did not yield any indication for the formation of amorphous grain boundary films or grain boundary charging after aging. Short range ordering of vacancies and cluster formation between vacancies and cations can be studied qualitatively from the background intensity of selected area electron diffraction (SAED) patterns. However, there was no significant change after aging. SAED and conventional TEM images show that the tetragonal phase is still present up to 10 mole% of Y_2O_3 . The tetragonal phase occurs as nanometer-scaled particles in the cubic phase. The precipitates strongly grow in 8.5YSZ (highest degradation), while they remain almost unchanged in 10YSZ (negligible degradation rate). This suggests, that the presence and change of the distribution of the tetragonal phase is connected with the degradation of the ionic conductivity in YSZ materials.
- L-VI.08** 15:15
- ANALYSIS OF STRUCTURAL STABILITY IN TRANSPORT PROPERTIES OF YTTRIA-ZIRCONIA-ALUMINA NANOPARTICLES**
- J. Santoyo-Salazar(a), J. Tartaj-Salvador(b), M.E. Villafuerte-Castrejón(a), G. González-Reyes(a), J.A. Chávez-Carvayar(a), (a)Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito exterior s/n. C.U.A. Postal 70-360. C.P. 04510. México, D.F. México, (b)Instituto de Cerámica y Vidrio, CSIC, Madrid, Spain
- Recently zirconia (ZrO_2) solid electrolytes have had special attention to develop solid oxide fuel cells (SOFCs). Stable structure ZrO_2 allows the replacement of zirconia cations by less charge cations producing oxygen vacancies through the lattice, so that charge transport can be present, and ion conductivity can be maintained with the structural condition it will keep on stable structure. Cubic and tetragonal structures zirconia (ZrO_2) are applied like electrolytes in SOFCs by their ion conductivity properties; however, instability of these structures at 600-1000°C can modify the functionality of these devices. In this work, yttria stabilised zirconia (YSZ) used in SOFCs has been selected searching to increase its stability at high temperature. Cubic (8mol.% YSZ) and tetragonal (3mol.% YSZ) zirconia phases had been added with different proportions of alumina (Al_2O_3) in ratio of 40-10wt.%, both series were obtained by co-precipitation route. YSZAl_2O_3 nanoparticles were sintered at 800-1100°C during different time intervals. Structural analysis by X-ray diffraction indicate tetragonal zirconia phase presence as concentration of Al_2O_3 is decreased to 20-10wt.% and Cubic phase (8mol.% YSZ) is present with alumina addition of 4010wt.%. Results of stability in the structures, losing weight, conductivity, hardness, morphology, size and distribution particle of these materials which were obtained by XRay Diffraction, Thermogravimetry Analysis (TGA), Differential Thermal Analysis (DTA), Impedance Spectroscopy (IS), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Microindentation are shown.
- 15:30 **BREAK**
- 16:00 **POSTER SESSION**
Poster L/P11 – LP22

POSTER

L/P01

HYDROGEN DEGRADATION OF STEELS USED IN CHEMICAL AND POWER INDUSTRY

H.M. Nykyforchyn(a), O.Z. Student(a), H. Matysiak(b), A. Zagórski(b), K.J. Kurzydowski(b), (a)Karpenko Physico-Mechanical Institute of the NAS of Ukraine, 5 Naukova St., 79601 Lviv, Ukraine, (b)Warsaw University of Technology, Faculty of Materials Science and Engineering, 141 Woloska St., 02-507 Warsaw, Poland
Materials used in the chemical and power installations are frequently subjected to elevated temperatures, high stresses and aggressive agents. Long operating periods of the installations (often over 200 000h) result, under such conditions, in degradation of microstructure and mechanical properties. This degradation is especially severe in the presence of hydrogen, which currently emerges as the energy carrier of the future.

Hydrogen induced degradation of the properties and microstructure of the low carbon low alloy and Cr-Ni cast steels due to the exposure to the hydrogenated environment at elevated temperatures have been considered in the paper. The materials of boiler steam pipes, shells of the hydrocracking reactors (subjected to high temperature hydrogen charging) and reactor pipe from reforming furnace have been studied. The characteristic parameters describing the materials deterioration, including fracture mechanics parameters, microstructure features, hydrogen content and hydrogen transport parameters have been evaluated. A fast-method for high temperature hydrogen degradation by thermocyclings between the working and ambient temperature in the hydrogen environment has been proposed. In this method the change of the equilibrium hydrogen solubility at low and high temperature causes the metal super saturation at cooling and in turn accelerated deterioration. The effective fatigue threshold ΔK_{th} , describing the crack closure phenomenon, has been proposed to be used as the mechanical parameter sensitive to high temperature hydrogen degradation of materials under the service and the laboratory conditions.

L/P02

ELECTRICAL AND OPTICAL PROPERTIES OF SMART OPTICAL WINDOWS BASED ON Mg-Ni ALLOYS

V. Parkhutik, Yu. Makushok, E. Matveyeva, R&D Centre MTM, Technical University of Valencia, Spain, P. Notten, Philips Research Laboratories and Eindhoven University of Technology, The Netherlands and T. Richardson, Lawrence Berkeley National Laboratory, USA

Mg-Ni alloys can reversibly be loaded with hydrogen and converted into hydrides, which are optically transparent in the visible range of the electromagnetic spectrum. This effect can be employed in Smart Optical Windows, which make use of the fact that the transparency can be fine-tuned by the hydrogen content, either via the gas phase or by cathodic polarization in electrolytes.

We have studied optical and electrical properties of Mg(80%)-Ni(20%) alloys covered with a thin (20 nm) layer of Pd during their electrochemical loading with hydrogen in an alkaline solution. The electrochemical kinetics shows several stages of hydrogenation/dehydrogenation reaction similarly to other electrochromic metals, revealing optical activity in hydrogen-containing media. Optical data acquired during loading/unloading of the samples with hydrogen reveal very high contrast between the reflecting and transparent states (about 500%), good reversibility of the reaction (reflecting state is completely restored after removal of protons from the sample) and, finally, fair longevity (hundreds of hours) of switching. We have also performed ac-impedance measurements during their loading/unloading with hydrogen. When the hydrogenation reaction is completed, i.e. when the electrodes are fully hydrogenated, spectacular growth of the impedance (four-five orders of magnitude) is observed below some critical frequency (about 0.5-1.0 Hz depending on the degree of hydrogenation). Modeling of the impedance data, using equivalent circuit formalism, gives a good fit of the experimental data if distributed electrical resistance of the thin hydride layer is taken into account.

L/P03

METALLIC, OXIDE AND HYDRIDE PALLADIUM THIN FILMS GROWN BY PULSED LASER DEPOSITION: SYNTHESIS AND STRUCTURE

Xavier Darok, Aline Rougier, Luc Aymard and Jean-Marie Tarascon, Laboratoire de Réactivité et de Chimie des Solides, CNRS UMR-6007, Université de Picardie Jules Verne, 80039 Amiens Cedex, France

Palladium thin films have received a special interest in hydrogen storage systems for their role as a protective layer against oxidation and as a catalyst for the hydrogen dissociation. However, after hydrogen absorption, the low optical transmittance of the Pd hydride layer generally limits the transparency of the (metal-Pd/hydride) multilayer. Recent studies from our group on Palladium thin film grown by pulsed laser deposition in optimized deposition conditions, namely a 10⁻¹ mbar pure Ar/H₂ (90/10%) gas mixture and a room temperature substrate have shown the in situ growth of highly transparent PdH_x thin films. Herein, we will especially discuss the structure, morphology, and optical properties of the Pd thin films grown under various atmospheres such as vacuum, pure Ar/H₂ (90/10%) gas mixture and oxygen.

L/P04

EFFECT OF CATALYSTS ON PRODUCTION OF HYDROGEN FROM HYDROLYSIS OF SODIUM BOROHYDRIDE AT ROOM TEMPERATURE

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We analyzed the effect of different catalysts on hydrolysis of sodium borohydride (NaBH₄) at room temperature. Catalysts in the form of films and powders were used. Catalysts film, about 0.2 micron thick, of nickel and palladium were deposited on glass substrate using Pulsed Laser Deposition technique. For the powder catalyst, 5% palladium in carbon and nickel (< 1 micron) were used.

The hydrolysis experiments were carried out by using a gas-volumetric method. During the experiments, the catalysts were placed in a glass reactor containing 0.02M NaBH₄ in water and the temperature was maintained at (25±0.1)°C. The displacement of water column was measured using a level sensor connected to a data acquisition system. The hydrogen production rate was evaluated using time vs volume plot. To compare the effective production volume we performed experiments without catalyst to establish a baseline. Pd & Ni films showed no improvement in the rate of production when compared with the baseline. The nickel powder catalyst showed an improvement over the baseline. After 20 hours of experiment the production volume was 30% more than baseline. It is argued that the difference in production rate between the film & powder catalysts could be due to the difference in the geometry of catalysts. The film catalyst has a smooth surface (two dimensional) structure while the powder catalyst has a rough surface (three dimensional) structure. The palladium in carbon catalyst showed the highest rate of production. This catalyst produced more than 80% volume of hydrogen in about 10 minute. Rate reduction was observed after this time which was attributed to the absorption of hydrogen by carbon in the catalyst.

L/P05

RELATION BETWEEN MELTING OF LiAlH_4 AND ITS HYDROGEN DESORPTION

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The relation between melting and hydrogen desorption accompanied by disproportionation was investigated for LiAlH_4 . A starting material was LiAlH_4 of 95% in purity, purchased from Aldrich Co Ltd., and it was purified before supplied to the experiments. The phase transitions and chemical reactions were examined by the combination of thermal analysis with X-ray diffraction. In thermal analysis, the experiments were performed in hydrogen atmosphere of 3MPa and at 10K per minute in heating and cooling rate from room temperature to 423K, 439K, 453K and 473K. The samples heated to 439K, 453K and 473K exhibited a sharp endothermic peak corresponding to melting of LiAlH_4 and then an exothermic peak indicating the decomposition of LiAlH_4 into Li_3AlH_6 and Al, whereas the sample heated to 423K showed no peak. The melting of LiAlH_4 started at a constant temperature (about 435K), independent of heating temperature, however, the hydrogen desorption accompanied by disproportionation occurred at 465K for the sample heated to 473K, 450K for the sample heated to 453K and 431K for the sample heated to 439K, dependent on the heating temperature. The more detailed analyses indicated that the decomposition of LiAlH_4 occurred within about 90s after melting, independent of sample temperature. This fact implies that the mobility of constituent metal atoms which were obtained by melting plays an important role of the decomposition kinetics for LiAlH_4 . Therefore, the improvement of diffusion of lithium and aluminum atoms is necessary to accelerate the decomposition of LiAlH_4 .

L/P06

PREPARATION AND CHARACTERIZATION OF CARBON NANOFIBER BY SOLVOTHERMAL METHOD

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Especially, CNF can be expected to play an important role in catalyst supports for fuel cell electrode and chemical reaction.

In this research, we will introduce the unique synthesis method of CNF from liquid phase carbon source by a solvothermal treatment. The Co metal (ex. Co, Ni, Fe) nanoparticles as the seeds of CNF were prepared from cobalt (Ⅱ) acetate tetrahydrate and Na metal. Some reaction aids were also added for formation and dispersion of the Co nanoparticles. On the other hand, diphenyl ether as a source of CNF growth was applied for the solvothermal reaction. The reaction conditions, such as temperature, time, and concentration of reactants were investigated. Actually, the CNF was prepared at as low temperature as 450℃ for 1h. The CNF with diameter of about 10 ㎚ was confirmed by HRTEM. It was found that the platelet - structured CNF was synthesized.

L/P07

FORMATION ABILITY AND HYDRIDING PROPERTIES OF THE PEROVSKITE-TYPE HYDRIDES

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Formation ability of the perovskite-type structure in $\text{Li}_x\text{Na}_{1-x}\text{MgH}_3$ with $x = 0, 0.5$ and 1.0 was experimentally studied in the present work. NaMgH_3 ($x = 0$) with the perovskite-type structure was successfully synthesized for the first time just by mechanical milling. The diffraction peaks corresponding to the structure shift to higher angles due to the partial substitution of Na by Li in the intermediate composition ($x = 0.5$), while there is no evidence of the perovskite structure in LiMgH_3 ($x = 1.0$). The experimental results are reasonably explained from the viewpoint of the geometric restrictions of ions, that are described by so-called Goldschmidt's tolerance factor. In NaMgH_3 ($x = 0$), two plateau pressures of about 0.04 and 0.15 MPa were clearly detected by p-c isotherm measurement at 673 K. NaMgH_3 ($x = 0$) can be reversibly formed in 1.0 MPa hydrogen at 673 K, from the decomposed phase of elemental Na and Mg.

L/P08

HYDROGEN DESORPTION IN NANOSTRUCTURED MgH_2 -Co

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Mg based alloys are potentially the best materials for hydrogen storage due to their high weight and volume capacity. Their practical use is limited, among other factors, by poor hydrogen absorption and desorption kinetics. The mechanical processing of MgH_2 , instead of pure Mg, reduces oxygen contamination and powder size of ball milled Mg based hydrogen storage materials. It has been shown that ball milling of MgH_2 powders with small amounts of 3d-transition metals leads to marked improvements of the hydrogen absorption/desorption kinetics. The addition of Co improves the sorption properties of Mg, while the effect on the decomposition of MgH_2 has not been already reported. The aim of this paper was to investigate the influence of Co addition and of the synthesis route on the desorption properties of MgH_2 . Ball milling of MgH_2 -Co blends with different weight ratios was performed under Ar in a Spex 8000 mixer/mill. The powders were characterized by XRD to assess the details of the phase structure by Rietveld analysis, while microstructural studies were performed by SEM. Thermal stability and hydrogen desorption properties were investigated by DSC which suggests a complex desorption behaviour, characterized by more than one single peak. In addition, in this case the fine dispersion of the catalytic particles appears to play the main role on the desorption performances.

L/P09

ISOTOPIC EFFECTS IN THE THERMAL DESORPTION SPECTRA OF PALLADIUM HYDRIDE

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Thermal desorption spectroscopy (TDS) has been extensively used to investigate the kinetics of hydrogen desorption from metal hydrides and the energetics of metal-hydride systems. When studying metal hydrides with a mixture of hydrogen isotopes, this technique can also be used to quantify the relative amount of the different hydrogen isotopes in the metal matrix. This is of importance because the relative content of isotopes in metal hydrides give information about their mechanisms of formation.

Polycrystalline samples of palladium hydride-deuteride has been formed by electrolysis of H_2O - D_2O mixtures. After doing that, TDS of the samples were recorded by using a calorimeter connected to a mass spectrometer. The obtained results allows to obtain information about the activation energies on the reaction orders for the H_2 , HD and D_2 desorption processes. On the other hand, the total amount of desorbed H and D has been measured and the separation factor of the electrochemical palladium hydride formation has been calculated. Comparison with previous values of the separation factor obtained by other authors for the palladium hydride formation by gas phase reaction has been accomplished.

L/P10**NEW FUNCTIONAL INTERMETALLIC MATERIAL FOR HYDROGEN STORAGE APPLICATIONS**

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Hydrogen storage alloys of intermetallic hydride compounds are new functional materials for various applications. They began with the negative electrode of Ni-MH (metal hydride) batteries in 1990 and with fuel cells (FC) that were developed especially for the emission-free vehicles. Hydrides tank on FC-cars is realized because of their compactness and safety for hydrogen energy storage. But the hydrogen storage capacity of the alloys is insufficient for hydrogen tanks, heat pumps, hydride air-conditioners and so on. According to the data so far, the hydride alloys are mostly in the AB₂-type Ti- or Zr- based alloys.

In this work, the (Zr-Ti)(Fe-Cr)₂ based compounds have been synthesized while charging-discharging hydrogen ability has been examined. Relatively low hydrogen pressure has been used for the hydrogenation of the samples. After following the discharging procedure, a high desorbed amount of hydrogen ~180 (ml of H₂)/(gr of the alloy) has been measured on the first 15 min by using a volumetric devise. The crystal structure has been analyzed by means of x-ray diffraction (XRD) while a Rietveld analysis has been performed on the x-ray diffraction patterns in order to determine the crystal structure characteristics. The scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) have been used for microstructural studies and quantitative analysis, respectively. Magnetic measurements have been performed on the samples and a paramagnetic behavior has found to be at room temperature. A differential thermal analysis (DTA) has been performed in order to investigate the phase transformations on the as cast samples.

L/P11**MICROBIAL FUEL CELL BASED ON ESCHERICHIA COLI WITH NEW CARBON ELECTRODE DESIGN**

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The need to have the highest conductivity and active surface area, combined with biocompatibility for working bacteria in microbial fuel cells (MFCs) is one of biggest challenges for biological fuel cells. Even though MFCs have not reached the performances of other fuel cells, they remain important in the biotechnology field. Their study will enlarge our knowledge of the electrochemistry of the human body - where micro and nano MFCs can work in a cooperative way. Enlarging as much as possible the specific area for electrodes with improved biocompatibility with microorganisms our studies have shown two possibilities: electrodes with foam structure and electrodes with a coral design, where the fractal structure is dominant. The paper deal with the first type of electrode in the form of a foam of carbonized polymers with ferrocene catalysts. Highly cross-linked novolac with hexamethylenetetramine-HMTA containing ferrocene (NH-Fc) and polyvinyl alcohol containing ferrocene (PVA-Fc) have been investigated. The electrode structures have been characterized by XRD, TEM, and SEM and showed a large amount of nanotubes, with large defects, in a randomly interconnected network. Activation of the electrode has been carried out in an Ar plasma. The electrodes were tested in a regular MFC with Escherichia coli, glucose and methylene blue as mediator. The power density of the MFC increased with specific surface area of the electrodes up to 1.0 W/g electrode.

L/P12**DEVELOPMENT FROM POLYMERS PYROLYSIS OF THE NEW ELECTRODES FOR FUEL CELLS**

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The need to design new materials for electrodes with improved microfluidic remains a challenge in the fuel cells performances. The paper deals with the study of new carbon materials and new techniques. For carbon materials, we selected highly cross-linked novolac with hexamethylenetetramine-HMTA and polyacrylonitrile (PAN) carbonized over 10000C. The techniques are combinatorial top-down/bottom-up. Submicron and micron-sized powders are assembled in electrodes with porosity gradient. Finally, the PtPd bimetallic catalyst systems are deposited in small clusters using electrospray plasma deposition with subsequent reduction in hydrogen atmosphere rise to self-assemble on electrode surface. It is common knowledge that the CO coverage decrease with increasing Pd content and nanostructured Pd could increase the proton transfer through PEM by hydrogen accumulation at interface associated with higher hydrogen diffusivity. The structural properties investigated by XRD, HRTEM, SEM, shown a good gradient porosity from micron to nanosize scale along with electrode axis. The deposited catalyst size is less than 10nm and coverage area reached 90%. The clusters are well individualized and no agglomeration has been observed. The electrical conductivity is twice better than carbon paper. The overall results clearly indicate that new materials were expected as high performance electrodes, particularly for direct methanol fuel cell.

L/P13**RADIATION GRAFED MEMBRANES FOR POLYMER ELECTROLYTE FUEL CELLS**

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- L/P14** COMPOSITES MEMBRANES BASED ON SULPHONATED POLYPYRIDINES DERIVATIVES WITH NANOMETRIC OXIDES PARTICLES FOR DMFC APPLICATIONS
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 Well recognized the limits of Nafion series (112-117) as PEM are around of 100 OC. In same time, need to increase the efficiency and CO-tolerance of the PEMFC system need high temperature. For DMFC the working temperature over 100 OC has many advantages: the kinetics for both electrode reactions will be enhanced with importance for the direct oxidation of methanol, water management simplifies system design and come to higher driving force for heat transfer. Few sulphonated /carboxylated polymers are know to be competitors for this aim but the interest is more accentuate for hybrid membranes containing various hygroscopic inorganic nanoparticles to strongly reduce the permeability of methanol and water as well with simultaneous ionic conductivity increasing at high temperatures.
 The paper aim is to develop a new class of composite membrane based on sulphonated polypyridyne derivatives containing nanometric oxides particles such SiO₂ and TiO₂. Polypyridine derivatives films were obtained by a proprietary method of thermoxidation of the polyacrylonitrile (PAN) in thermo-centrifugal field. A series of characterization at multistage-level from micro to nanoscopic were employed: FT-IR, XRD and TEM to establish the structure, morphology, orientation, and micro/nanoporosity. Ionic conductivity and methanol permeability have been measured in a special design cell. The results show a very close behaviour with Nafion membranes but in a larger range of temperature up to 300°C.
- L/P15** PREPARATION AND CHARACTERISATION OF PLATINUM ON CARBON SUBSTRATES ELECTROCATALYSTS AS ELECTRODES IN POLYMER ELECTROLYTE FUEL CELLS
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 Gas Diffusion Electrodes (GDE) used in Polymer Electrolyte Fuel Cells (PEFCs) are prepared by catalyst nanoparticles deposition on porous and high surface carbon substrates. These electrocatalysts are traditionally obtained by carbon support impregnation with Pt precursors followed by chemical reduction and heat treatment in hydrogen. By this method, however, it is necessary to deposit high amount of Pt to achieve good performances and Pt nanoparticles localisation in reaction sites is critical. In this work we describe a new electrodeposition method: in fact, applying an electric field to deposit Pt nanoparticles on glassy carbon (GC), on carbon powder (CP) and on carbon nanotubes (CNTs), previous problems are nearly resolved¹. A solution containing H₂PtCl₆ (ECPA) 5mM in 1M H₂SO₄ at 30°C is used for galvanostatic electrodeposition at constant (GED) and pulsed current (PED)². Chemical analysis, cyclic voltammetry (CV) and FEG-SEM technique are used to determine electrochemical characteristics of Pt deposit and the influence of electrodeposition method on the nano-morphology. Electrocatalytic performances were carried out by oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) in H₂SO₄, re-calculating data in the form of mass specific activity (MSA) and surface specific activity (SSA) to take in account the real electrochemical surface of Pt loading³. A comparison with commercial Pt/C catalysts shows an higher activity, at lower Pt loading, for our materials.
- L/P16** MICROFABRICATION OF CHANNELS IN GLASY CARBON BY A COMBINED LASER AND REACTIVE ION ETCHING PROCESS
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- L/P17** PROPERTIES OF SOFC UNIT CELL USING SYNTHESIZED LSCF CATHODE BY OXALATE METHOD
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 Solid oxide fuel cells are clean, pollution-free technology for the electrochemical generation of electricity at high efficiency. Required properties for new cathode materials be devoted to SOFC unit cell is synthesis of nano powders, development of composite, higher conductivity and lower polarization. Specially, the polarization resistance between electrolyte and electrode of SOFC unit cell is of importance, because it is desirable to develop SOFC operating at intermediate temperature below 800°C. Therefore in this study, it was attempted to investigate synthesis of LSCF cathode using oxalate method and polarization resistance of unit cell.
 The LSCF cathode prepared using oxalate method was investigated with different electrolyte. A precursor was prepared with oxalic acid, ethanol and NH₄OH solution. The LSCF precursor was prepared at 800°C, and pH control was 2, 6, 8, 9 and 10. The precursor powder was calcined at 800°C, 1000°C, and 1200°C; for 4hrs. The crystal of LSCF powders show single phase at pH 2, 6, 8 and 9, and the average particle size was about 300nm. The LSCF cathode with heat treatment at 1200°C; showed a plot of electric conductivity versus temperature. Unit cell prepared from the LSCF cathode, buffer layer between cathode and electrolyte and the LSGM, YSZ, ScSZ and CeSZ electrolyte. Also interface reaction between LSCF, buffer layer and electrolyte were measured by EPMA and the polarization resistance for unit cell with cycle measure using a Solatron 1260 analyzer.
- L/P18** ELECTRODE PROPERTIES OF SYNTHESIS (La_{0.75}Sr_{0.25})_{0.9}Cr_{1-x}AxO₃-(A=Mn, Ti, Fe) ANODE FOR SOFC
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 The common used materials Ni/YSZ cermets for solid oxide fuel cell has problems such as low tolerance sulphur and carbon deposition. To overcome these problems, perovskites containing lanthanides substituted with strontium and transition metal like Cr, Mn, Ti or Fe (La_{0.75}Sr_{0.25})_{0.9}Cr_{1-x}AxO₃-(A=Mn, Ti, Fe) were synthesized with regard to application as anode in solid oxide fuel cells using glycine nitrate process. The perovskites powders were carried out using thermogravimetric and differential thermal analysis. The calcined powders were characterized using X-ray diffraction to identify crystalline phase. The electrochemical properties of electrode were studied about unit cell with cycle time using impedance spectroscopy.
 The X-ray diffraction pattern showed that they had single phase. In case of the (La_{0.75}Sr_{0.25})_{0.9}Cr_{1-x}AxO₃-(A=Mn, Ti, Fe) showed orthorhombic structure, the other (La_{0.75}Sr_{0.25})_{0.9}Cr_{1-x}AxO₃-(A=Mn) showed rhombohedral structure. The electrical stability of synthesis (La_{0.75}Sr_{0.25})_{0.9}Cr_{1-x}AxO₃-(A=Mn, Ti, Fe) anode with cycle time showed stabilization. Also, polarization resistances between electrolyte and anode showed stabilization.

L/P19**EFFECT OF CATION NON-STOICHIOMETRY AND ALIOVALENT DOPING ON THE TRANSPORT PROPERTIES OF LANTHANUM CUPRATES**

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It has been estimated that in order for Solid Oxide Fuel Cells (SOFC) to be competitive in the energy generation market, the price per kW should be decreased to 500 £/kW. One way to achieve this goal is to substitute precious metal interconnects with high performance ceramics. Alkaline earth doped lanthanum cuprates with the perovskite structure has been evaluated as possible interconnect materials. In this paper we studied the effect of aliovalent doping on A and B sites as well as A-site deficiency on transport and thermal properties of cuprates.

Cuprates with the general formula $\text{La}_{1-x}\text{A}_x\text{Cu}_{1-y}\text{Li}_y\text{O}_{2.5}$ (A=Ca, Ba, Sr, B=Li, $x=0.1, 0.2, 0.3$, $y=0, 0.1$) were prepared by the citric route. Highest values of electrical conductivity (500 S/cm at 900°C) were observed on 30% Sr doped cuprate which showed thermal expansion coefficient (around $14 \times 10^{-6} \text{ K}^{-1}$) close to the one for YSZ. Reactions between cuprates and other SOFC components (LSM cathode and Pt interconnects) were observed at 1000 °C thus limiting the operating temperature of cuprates. Li doping did not result in the enhancement of conductivity presumably due to the disruption to the copper conductive network. Cation non-stoichiometry was not observed in lanthanum cuprates.

L/P20**SYNTHESIS AND CATALYTIC BEHAVIOR OF NANOCRYSTALLINE Ce-Zr-La-O SYSTEM**

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Processing of oxide catalysts by the sol-gel and related soft chemistry methods, using solutions at the initial step of synthesis, leads to numerous advantages including great surface area and highly defective structure. This work is centered on the synthesis of nanocrystalline Ce-Zr-La-O powders via organic-free modification of the sol-gel technique, and their characterization by TEM, XRD, DTA, TG, FTIR, ESR, XPS and BET methods. The incorporation of La(III) into Ce-Zr-O structure leads to stabilization of highly dispersed (4-5 nm) c-Zr_xCe_{1-x}O₂ solid solution up to 1100°. Lanthanum doping of the Zr_{0.5}Ce_{0.5}O₂ lattice increases also the concentration of Ce³⁺ states detected by ESR. Both these features contribute to the high catalytic activity towards partial oxidation of dry CH₄, promoted by the surface instability of the lattice characteristic of morphotropic phase transformations. The methane oxidation on composite Ce_{0.45}Zr_{0.45}La_{0.10}O_{2-x}/Pt anodes in a model fuel cell-type reactor provided 73% CO selectivity with 54% conversion efficiency at 900°C and CH₄:O₂ ratio equal to 2.

L/P21**YTTRIA STABILIZED ZIRCONIA –TITANIA OBTAINED BY SOL-GEL AND PHYSICAL METHODS**

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This work presents results on ternary materials based on ZrO₂ - TiO₂-Y₂O₃ obtained by sol-gel and physical methods. Zirconium propoxide, titanium isopropoxide and yttrium nitrate have been used for sol-gel technique: ZrO₂ -TiO₂ sol was prepared by partial hydrolysis of alcoxides in the presence of water resulting from the esterification reaction between propylic alcohol (in excess) and acetic acid. Y(NO₃)₃ and the surfactant (tetrabutylammonium bromide) have been subsequently added in a drop wise manner. The porous structure of the composite materials was modified by Zr/Ti molar ratio and surfactant concentration variation. Thin films with similar compositions were obtained by magnetron sputtering and laser ablation. In the case of deposition by magnetron sputtering a disk like target, consisting of single oxides (TiO₂, ZrO₂, Y₂O₃) sectors was used, the ternary oxide being obtained by exposing periodically, for short duration, the substrate to every sector. In the case of the pulsed laser deposition sequential laser ablation was done, where a disk target consist in three sectors of Zr, Y and Ti respectively was exposed to laser beam in oxygen reactive atmosphere. Samples obtained by the three methods were investigated by Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), N₂ adsorption-desorption measurements. The properties are comparatively discussed. The permeation of O₂, CH₄, C₃H₈ through ternary oxide layers was measured with a Wicke Kallenbach cell.

L/P22**SOLID OXIDE FUEL CELLS COMPONENTS BY SELF-COMBUSTION AND TAPE CASTING TECHNIQUES**

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Self Self-combustion techniques have been applied for the synthesis of ceramic oxide materials for SOFC components. These techniques present the advantage of fast production of high quality oxide materials in the nanometer size range. Anode and electrolyte materials such as Ce_{0.1}Gd_{0.9}O₂ have been synthesized by a glycine-nitrate self-combustion process and pure oxides have been obtained. Transmission Electron Microscopy images show the nanoscale particle size of the materials.

For the fabrication of Solid Oxide Fuel Cells, the prepared materials have been processed by tape casting, a simple and scalable technique of industrial interest for the production of SOFC. The obtained ceramics have been studied and their electrochemical properties have been analyzed by impedance spectroscopy and Van der Pauw. A complete fuel cell based on these materials and processed by dual tape casting and thermal spraying techniques is under current development.