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E-MRS Spring Meeting 2003
June 10 - 13, 2003

SYMPOSIUM C

Nanoscale Materials for Energy Storage

Symposium Organizers:

Michael Hirscher, MPI für Metallforschung, Stuttgart, Germany

Peter C. Eklund, The Pennsylvania State University, University Park, USA

Fermin Cuevas, ISCSA-CNRS, Thiais, France

Shin-ichi Orimo, Tohoku University, Sendai, Japan

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E-MRS 2003 SPRING MEETING

SYMPOSIUM C

Tuesday, June 10, 2003 — Morning
Mardi 10 juin 2003 — Matin

09:00 **OPENING**
M. Hirscher (MPI für Metallforschung, Germany)

Session I: Energy strorage in nanomaterials
Session chair: P.C. Eklund

C-I.1 09:20 -Invited-

OVERVIEW OF ENERGY/HYDROGEN STORAGE: STATE-OF-THE-ART OF THE TECHNOLOGIES AND PROSPECTS FOR NANOMATERIALS

Mario Conte, Pier Paolo Prosini, Stefano Passerini, Italian National Agency for New Technology, Energy and the Environment (ENEA), Roma, Italy

The future energy economy will be demanding primary energy sources, preferably renewable and mainly domestically available, using "energy carriers", such hydrogen and electricity, able to solve environmental problems and to assure adequate energy security. The use of electricity or hydrogen in advanced vehicles has driven in the last decades the research and development of new storage systems, based on new materials. The rapid growth of the electronic consumer market has accelerated the development of specialised systems. The lithium- or nickel-based are replacing lead-acid batteries in many sectors. These batteries have features more suitable for new applications: higher gravimetric and volumetric energy; higher specific power for hybrid electric vehicles and other applications in conventional vehicles; and longer cycle life. A few technologies now permit to store hydrogen by modifying its physical state in gaseous or liquid form. The variety of hydrogen needs in the telecommunications sector, in the energy systems and in the vehicular sector, is justifying the effort on solid state (metal hydrides and carbon nanostructures) or chemical systems (chemical hydrides). In this paper, the energy and hydrogen storage methods will be overviewed: selection criteria and technical requirements of major applications (mainly in vehicles) and state-of-art storage technology; major public research programs, with emphasis on the potential role of nanoscale materials will be emphasised.

C-I.2 10:00 -Invited-

HYDROGEN DENSITY IN NANOSTRUCTURED CARBON, METALS AND COMPLEX MATERIALS

A. Züttel, P. Wenger, P. Sudan, Ph. Mauron University of Fribourg, Physics Department, Pérolles, 1700 Fribourg, Switzerland and Shin-ichi Orimo, Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

The challenge in the research on hydrogen storage materials is to pack hydrogen atoms or molecules as close as possible. The density of molecular liquid and solid hydrogen is 42.6 atoms·nm-3 and 42.5 atoms·nm-3 (70.8 and 70.6 kg m-3), respectively. Hydrogen absorbed in metals can reach a density of more than 90.3 atoms·nm-3 (e.g. Mg2FeH6 or Al(BH4)3) at atmospheric pressure. However, due to the large atomic mass of the transition metals the gravimetric hydrogen density is limited to less than 5 mass%. Nanostructured carbon materials, eg. carbon nanotubes or high surface area graphite absorb hydrogen at liquid nitrogen proportional to the specific surface area 1.5 mass% / 1000 m2·g-1. Light weight group 3 metals, e.g. Al, B, are able to bind 4 hydrogen atoms and form together with an alkali metal an ionic or at least partially covalent compound. These compounds are rather stable and often desorb the hydrogen only above their melting temperature. Complex hydrides like NaAlH4, when catalyzed, decompose already at room temperature. We have investigated LiBH4, a complex hydride which consists of 18 mass% of hydrogen. The catalyzed hydride decomposes already at 200°C and liberates up to 13.5 mass% of hydrogen. First attempts to synthesize LiBH4 directly from the elements were partially successful.

10:40 **BREAK**

Session II: H in metal clusters
Session chair: K.A. Friedrich

C-II.1 11:10 -Invited-

HYDROGEN AND METAL CLUSTERS

Astrid Pundt, Insitut für Materialphysik, Universität Göttingen, Hospitalstraße 3-7, 37073 Göttingen, Germany

Clusters possess a large fraction of surface volume relative to the total volume. Therefore, they are used as catalysts, for example in fuel cells. Studies of hydrogen interacting with surfaces have shown that hydrogen sorption sites are present at the surface as well as below the surface. Furthermore, hydrogen can be sorbed on internal sites.

Gasvolumetric hydrogen sorption experiments and structural studies on Palladium clusters (2-8 nm) will be presented focussing on the cluster size effect [1]. Because of the large number of hydrogen sorption sites at clusters, the hydrogen solubility is strongly enhanced compared to bulk Palladium. For all clusters a miscibility gap is found. It is narrowed compared to the bulk Pd-H system but appears in a similar pressure range. However, the cluster structure is icosahedral for the small clusters and of cubic symmetry for the larger ones. For intermediate cluster sizes, a reversible structural change can be seen during loading and unloading.

This work is supported by the Deutsche Forschungsgemeinschaft via PU131/3 and SFB 602.

[1] A. Pundt et al. JALCOM 293-295, 480 (1999); C. Sachs et al, PRB 64, 075408 (2001); M. Suleiman et al., to be published in JALCOM 2003.

C-II.2 11:50

MORPHOLOGICAL EFFECTS ON HYDROGEN STORAGE IN PALLADIUM NANOPARTICULATES

S. Kishore(a), J.A. Nelson(b), J.H. Adair(b), P.C. Eklund(a), (a)Department of Physics; (b)Department of Materials Science, The Pennsylvania State University, University Park PA 16802, USA

Recently, several research groups have shown the benefits of hydrogen storage in metals such as palladium by reducing the particle size to tens of nanometers. Benefits include faster kinetics implying reduced temperatures for efficient storage of hydrogen. This is a intriguing finding considering the effort being expended to produce safe and practical fuel cell-powered vehicles. In this paper, the morphological aspects of improved hydrogen storage are addressed at the nanoscale. Both spherical and nanotabular Pd particles were synthesized in self-assembly systems using reverse micelle and bilayer structures, respectively. Particle dimensions and shape were verified using TEM, AFM, and light scattering techniques. Hydrogen storage properties of spherical particles with diameters from 2nm to 100nm were measured in the pressure range from zero to 20 atmospheres over a range of temperatures from 40°C to 200°C. These results were compared to those from nanotabular Pd particles with thickness in the range 2nm to 200nm and also as function of aspect ratio. Results will be compared to bulk palladium and other recent findings in nano-metal hydrides.

12:10 **LUNCH**

Session III: Nanostructured Mg-based hydrides
Session chair: S. Orimo

C-III.1 14:30 -Invited-

SUPERIOR HYDROGEN SORPTION KINETICS USING NANOCRYSTALLINE Mg WITH CATALYSTS

Thomas Klassen, Gagik Barkhordarian, Wolfgang Oelerich, Zahir Dehouche, Ruediger Bormann, Institute for Materials Research, GKSS Research Centre Geesthacht GmbH, Max-Planck-Str 1, 21502 Geesthacht, Germany, Institut de Recherche sur l'Hydrogène, Université du Québec à Trois-Rivières, C.P. 500, Trois-Rivières, Québec, G9A 5H7, Canada

Hydrogen is the ideal means of storage, transport and conversion of energy for a comprehensive clean-energy concept. Light metal hydrides offer a safe alternative for hydrogen storage in mobile applications. A breakthrough in reaction kinetics was achieved by preparing nanocrystalline light metal hydrides using high-energy ball milling. Furthermore, metallic catalysts, e.g. Pd, Ni, Nb or V, have been added to improve kinetics also at lower temperatures. In this presentation, investigations on the catalytic influence of cheap metal oxides, nitrides, and carbides on the sorption behavior of nanocrystalline MgH2 will be presented. Some of the selected catalysts lead to an enormous acceleration of hydrogen sorption compared to pure nanocrystalline Mg and also with respect to metallic catalysts. Even 0.05 mole% of oxide catalyst show a significant effect, and fastest kinetics are achieved with 0.5 mole%. At 300°C, complete absorption or desorption of more than 7 wt.% are possible in less than 2 min. Significant sorption rates can also be achieved at lower temperatures. Although at a lower pressure, desorption is observed at 200°C, and absorption is possible at room temperature. Long-term cycling tests show no change in absorption kinetics and only a slight slow-down of desorption kinetics after 1000 cycles at 300°C. Kinetics are superior to previous investigations and fulfill the requirements for technical application.

C-III.2 15:10

Withdrawn

C-III.3 15:30

MAGNESIUM HYDRIDE-GRAPHITE COMPOSITES FOR HYDROGEN STORAGE PRODUCED VIA BALL MILLING

S. Dal Toè, S. Lo Russo, INFM and Physics Department 'G. Galilei', Padova University, via Marzolo 8, 35131 Padova, Italy, A. Maddalena, G. Principi, T. Spataru, INFM and Mechanical Engineering Department, Materials Section, Padova University, via Marzolo 9, 35131 Padova, Italy and R. Checchetto, N. Bazzanella, G. Trettel, INFM and Physics Department, Trento University, via Sommarive, 38050 Trento, Italy

MgH2 – graphite composites produced via ball milling exhibit fast H2 absorption/desorption kinetics; moreover, their activation behaviour is particularly attractive if compared with MgH2-based materials obtained so far. In this work we investigate the morphology, the crystal structure and the hydriding/dehydriding behaviour of some MgH2-graphite composites using a home-made Sievert apparatus and thermal desorption spectroscopy. The results are compared with previous work on MgH2-based nanomaterials produced via ball milling.

C-III.4 15:50

INVESTIGATIONS ON THE SYNTHESIS AND DECOMPOSITION OF Mg-Fe-H HYDRIDE PREPARED BY REACTIVE MILLING

N. Ismail(a), M. Herrich(a), A. Pratt(b), O. Gutfleisch(a), (a)IFW Dresden, Institute of Metallic Materials, P.O. Box 270016, 01171 Dresden, Germany, (b)Johnson Matthey Technology Centre, Sonning Common, Reading RG4 9NH, UK

The direct synthesis of Mg2FeH6 by mechanical alloying in hydrogen atmosphere (´reactive milling´) is investigated using different high energy ball milling conditions. Using both planetary and vibration mills, the influence of milling temperatures on the hydride formation is studied. XRD and HRSEM are utilised to follow the evolution of the structure during hydride formation with the time of ball milling. The stability and decompostion of the hydride is studied under different desorption conditions. The effect of the Fe concentration on the structural evolution during synthesis as well as on the hydride decomposition behaviour is investigated. Finally, the role of minor additions of platinum group metals (PGMs) on the kinetics of desorption of Mg2FeH6 alloy is discussed.

This work is part of the EU project FUCHSIA 5th Framework Energy Program.

16:10 **BREAK**

Session IV: Complex hydrides
Session chair: A. Züttel

C-IV.1 16:40 -Invited-

NANOCRYSTALLINE ALUMINUM HYDRIDES FOR HYDROGEN STORAGE

Maximilian Fichtner, Forschungszentrum Karlsruhe, Institute of Nanotechnology, Germany

The group of alkali metal aluminum hydrides has become a matter of topical interest for hydrogen storage, after it was shown that one of the compounds, sodium alanate, is capable of storing reversibly 4.5 wt.% of hydrogen.

Up to now, the kinetics of hydrogen ab- and desorption have been regarded as a particular problem and attempts have been made worldwide in order to lower the kinetic barriers for the hydrogen exchange by catalysts. It will be shown that the state of the precursor is important and a considerable improvement is possible when a nanoscale Ti - cluster is used as catalyst. As higher storage capacities are desired for mobile applications, other compounds have to be investigated, which have the theoretical potential to store 6 wt.% H or more. In the contribution, the state of the art in this field is reviewed and recent results on the thermal properties of magnesium alanate are presented.

C-IV.2 17:20

DOPED SODIUM ALUMINUM HYDRIDE: FUNDAMENTAL STUDIES AND DEVELOPMENT OF A PROMISING NEW HYDROGEN STORAGE MATERIAL

Craig M. Jensen, Dalin Sun, Sesha S. R. Srinivasan, Keeley Murphy, Department of Chemistry, University of Hawaii, Honolulu HI 96822, USA, Sandra Eaton, Department of Chemistry and Biochemistry, 2190 E. Iliff Ave., Denver University, Denver CO 80208, USA, Tetsu Kiyobayashi, Hiroyuki T. Takeshita, Nobuhiro Kuriyama, National Institute of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Osaka 563-8577, Japan, B.C. Hauback, H.W. Brinks, and A.J. Maeland, Department of physics, Institute for Energy Technology, P. O. Box 40, 2027 Kjeller, Norway

In 1997, Bogdanovic and Schwickardi reported that the elimination of hydrogen from solid NaAlH4 is markedly accelerated and rendered reversible under moderate conditions upon mixing the hydride with a few mole percent of selected transition metal complexes. A variation of the doped hydride could possibly be developed as a viable means for the onboard storage of hydrogen. However, no dopant precursors have been found that give a greater kinetic enhancement than those cataloged in Bogdanovic's original 1995 patent. Similarly, only the sodium and mixed sodium, lithium salts of the alanates have been found undergo largely reversible dehydrogenation under moderate conditions upon doping. This lack of progress is surprising in view of the recent "gold rush" flurry of activity that has been direct towards the development of alanates as practical onboard hydrogen carriers. Clearly, these efforts have been handicapped by the dearth in the understanding of the nature and mechanism of action the dopants. We have therefore initiated efforts to elucidate the fundamental basis of the remarkable hydrogen storage properties of this material. X-ray and neutron diffraction as well as ESR spectroscopic studies have led to the development of a model of the doped hydride in which sodium cations are substituted by variable valence titanium cations in conjunction with the generation of the requisite number of Na+ vacancies to maintain charge neutrality. The details of this model and its relationship with the enhanced hydrogen cycling kinetics of the doped hydride will be presented in this seminar.

C-IV.3 17:40

STRUCTURAL STUDIES OF ALANATES

H.W. Brinks, Institute for Energy Technology, B.C. Hauback, Institute for Energy Technology, D. Blanchard, Institute for Energy Technology, C.M. Jensen,University of Hawaii

Alanates, metal hydrides based on the AlH4- unit, is one of the most promising groups of metal hydrides for reversible hydrogen storage at moderate temperatures. Their storage capacity is very large, e.g. NaAlH4 and LiAlH4 can release 5.6 and 7.9 wt%, respectively, below 200ºC. The pioneering work of Bogdanovic et al. in 1997 [1] revealed that Ti doping increased the desorption kinetics of NaAlH4 and furthermore made re-hydrogenation possible. A reversible storage capacity at acceptable rates of 3.1 wt% has been achieved at 125ºC [2]. In order to get a better understanding of the reactions, detailed studies of the structure is essential.

We have studied several alanates with alkali metals and alkaline earth metals by neutron and X-ray diffraction. Crystal structures of LiAlD4, NaAlD4 and Li3AlD6 among others will be presented, as well as in-situ diffraction results of the decomposition. LiAlD4 has been shown to decompose completely to LiD, Al and D2 at 127ºC during slow heating, releasing 7.9 wt% H2. Addition of VCl3 by ball milling increases the reaction rate. Our results from structural studies of doped NaAlD4 samples will also be presented.

[1] B. Bogdanovic and M. Schwickardi, J. Alloys Comp. 253 (1997) 1.
[2] G. Sandrock, K. Gross, G. Thomas, J. Alloys Comp. 339 (2002) 299.

C-IV.4 18:00

Li-N BASED HYDROGEN STORAGE MATERIALS

Yuko Nakamori and Shin-ichi Orimo, Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Just recently, Li3N has been reported to exhibit reversible hydrogen storage properties (more than 6 wt% below 473 K), by Chen et al. [Nature 420 (2002) 302]. We will thus report structural and hydriding properties of Li3N under hydrogen pressures up to 35 MPa in details, using X-ray diffraction, thermal analysis, and in-situ Raman spectroscopy. Elemental substitution/doping effects on Li3N and its imides/amides will be also discussed.

C-IV.5 18:20

NANOSTRUCTURED SPUTTERED AL-LI ALLOYS FOR HYDROGEN STORAGE

A. Rivera, A. van Veen, H. Schut, F. Labohm, Interfaculty Reactor Institute, Delft University of Technology, The Netherlands

Alloys of Al and Li with varying composition were sputter deposited in an argon hydrogen plasma on Si substrates. The substrate temperature during deposition of the deposited layers was kept low (-100ºC — 0 ºC) to reduce the mobility of the arriving metal atoms, thereby enhancing the formation probability of nano-crystalline Al-Li phases. These crystalline phases were studied by X-ray diffraction (XRD) measurements. The deposition method leads to the appearance of high porosity in the layer as revealed by positron beam analysis (PBA). These two structural properties make the material attractive for hydrogen storage. It was observed that more than 1 hydrogen atom can be stored per Li atom in the deposited layers. Thermal desorption measurements (TDS) showed a promising major hydrogen release peak at ~80ºC.

The fresh layers strongly interact with oxygen when exposed to air. This causes serious degradation of the hydrogen uptake properties. The interaction with oxygen even modifies the Li profile in the deposited layers as revealed by neutron depth profiling (NDP). To prevent this undesired effect, a thin (10 nm-thick) Pd layer is sputter deposited on the Al-Li layers directly after their deposition. NDP showed that the Li profile stays uniform upon exposure to air when Pd is employed as a capping material. Elastic recoil detection (ERD) indicated that the hydrogen profile in the sample also remained uniform. The hydrogen uptake and release properties of this class of materials, showing nanocrystallinity and nanoporosity, is discussed in terms of hydride formation, surface adsorption and diffusion along the grains.

Wednesday, June 11, 2003 — Afternoon
Mercredi 11 juin 2003 — Après-midi

Session V: H in intermetallic compounds
Session chair: F. Cuevas

C-V.1 14:30 -Invited-

NANO SCALE STRUCTURE SUCH AS NANO-SIZE CRYSTALLITES AND DEFECTS CAN BE FOUND IN CONVENTIONAL HYDROGEN ABSORBING ALLOYS

E. Akiba, H. Enoki and Y. Nakamura, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Centarl 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Nano scale structure and phenomena of hydrogen absorbing alloys are closely related to their hydrogenation properties. One of the nano scale phenomena observed in hydrogen absorbing alloys is the defect. Hydrogen absorbing alloys expand and contract 20~30% in a volume basis with hydrogenation and dehydrogenation. Expansion/contraction introduce various defects into the lattice at ambient temperature. We analyzed the introduction of dislocation in LaNi5 that consists of crystallites of 100-200nm by means of the Rietveld method using in-situ X-ray diffraction data. We found that dislocation in [110] direction was introduced at the first hydrogenation of LaNi5 and it remains in the lattice. The possibility to observe vacancies introduced by hydrogenation by diffraction technique will be discussed.

Another nano scale phenomenon is morphology of the alloys. We observed morphology of Ti-V based alloys with BCC structure by means of TEM and found that they consist of two BCC phases originated from spinodal decomposition. We assume that strain through the coherent grain boundary gives a positive effect to hydrogenation properties.

C-V.2 15:10 -Invited-

NANOCRYSTALLINE MATERIALS FOR MH BATTERIES

M. Jurczyk(a), L. Smardz(b), A. Szajek(b), (a)Poznan University of Technology, Institute of Materials Science and Engineering, Sklodowska-Curie 5 Sq, 60-695b Poznan, Poland, (b)Institute of Molecular Physics, Polish Academy od Sciences, Smoluchowskiego 17, 60-179 Poznan, Poland

Nanocrystalline metal hydrides are a new class of materials in which outstanding performance may be obtained by proper engineering of the microstructure. In this work, we study experimentally the structure, electrochemical and electronic properties of nanocrystalline and polycrystalline TiFe, ZrV2, LaNi5 and Mg2Ni phases. These materials were prepared by mechanical alloying (MA) followed by annealing and arc melting method, respectively. The amorphous phase of MA samples forms directly from the starting mixture of the elements, without other phase formation. Heating the MA powders resulted in the creation of ordered nanocrystalline compounds with mean crystallite size of about 20-30 nm. The electrochemical properties of nanocrystalline hydrogen storage compounds in conditions of their performance in rechargeable nickel hydride (Ni-MH) batteries will be given. The activation behaviour of nanocrystalline hydrogen storage alloys greatly improved in comparison to polycrystalline materials. The properties of hydrogen host materials can be modified substantially by alloying to obtain the desired storage characteristics. For example, it was found that the respective replacement of Fe in TiFe by Ni and/or Mg, Cr, Mn, Co, Mo or formation composite Ti(Fe,Ni)/C-type materials improved not only the discharge capacity but also the cycle life of these electrodes. Finally, the electronic properties of nanocrystalline alloys will be compared to that of polycrystalline samples. The studies show, that electrochemical properties of Ni-MH batteries are the function of the microstructure and the chemical composition and of used electrode materials.

C-V.3 15:50

INFLUENCE OF THERMAL ANNEALING ON THE HYDROGENATION PROPERTIES OF MECHANICALLY MILLED AB5-TYPE ALLOYS

J.R. Ares, F. Cuevas and A. Percheron-Guégan, Laboratoire de Chimie Métallurgique des Terres Rares, ISCSA-CNRS, 2-8 Rue Henri Dunant, 94320 Thiais Cedex, Paris, France

Among hydrogen storage materials, microcrystalline MmNi5-based alloys are widely used in multiple applications such as Nickel/Metal hydride batteries. However, nanocrystalline alloys may have much better performances as they exhibit modified thermodynamic properties and improvement of hydrogenation kinetics. In this work, nanocrystalline MmNi5-based alloys are prepared by Mechanical Milling (MM) and posterior annealing. Structural characterization of the alloys was done by X-ray diffraction using Rietveld fitting analysis. Results concerning hydrogenation kinetics and thermodynamics of MM and annealed alloys will be presented.

16:10 **BREAK**

Session VI: New H absorbers
Session chair: M. Hirscher

C-VI.1 16:40 -Invited- NANOCUBES BASED ON METAL ORGANIC FRAMEWORK MATERIALS AS HYDROGEN STORAGE UNITS

Ulrich Müller, BASF Aktiengesellschaft, Catalysis Research - Zeolite Catalysts, 67056 Ludwigshafen, Germany

Recently, press informations have been given on novel metal organic framework materials as storage media for hydrogen [1, 2]. Thus the use of mobile electronic equipment, viz. cellphones, computers, camcorders and cordless tools (so called ´C4 market´) powered by hydrogen fuel cells seems feasible if storage media working at ambient conditions are available. Highly porous and thermally stable zinc terephthalate MOF-materials have been detected [3] and are amongst the most porous solids known to date. MOF-5 e.g. exhibits an extremely low framework density of 0,59 g/cm³ combined with a world record in equivalent surface area of more than 3000 m²/g. The larger scale synthesis of MOF-materials will be outlined and experimental results of adsorbing gases using argon, nitrogen, hydrogen, methane and butane will be presented. Finally, energy densities of different storage media (e.g. NiCd, metal hydrides, Li-ion) will be compared to the novel system of hydrogen/MOF.

[1] Journalists and Scientists in Dialogue Nanotechnology in Chemistry - Experience meets Vision, 28/29 October 2002 in Mannheim, Germany
[2] Chemical Week, December 4 (2002) p. 45
[3] Li, Eddaoudi, O´ Keefe, Yaghi, Nature, 402 (1999) 276 - 279.

Session VII: Structural determination of H in nanomaterials
Session chair: M. Fichtner

C-VII.1 17:20 -Invited- STRUCTURAL OBSERVATION OF NANO-STRUCTURED AND AMORPHOUS HYDROGEN STORAGE MATERIALS BY NEUTRON DIFFRACTION

T. Fukunaga and K. Itoh, Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka, 590-0494, Japan

The neutron diffraction technique is a powerful tool to elucidate the structure of hydrogen storage materials. H/D isotopic substitution was employed to observe the location of deuterium atoms because the coherent scattering length of deuterium is enough large to observe in comparison with that of the atoms forming hydrogen absorbing materials. In this work, two kinds of hydrogen storage materials were focused to investigate the location of deuterium atoms. One is the deuterated nano-graphite prepared by mechanical milling under deuterium gas atmosphere and the other is a hydrogen induced amorphized material. The conformation in the graphite was changed by a creation of dangling bonds and deuterium was absorbed by the solid-gas reaction when the milling proceeds. The RDF(r) observed by neutron diffraction indicates two kinds of locations of deuterium atoms, that is, some deuterium atoms bond with the carbon atoms and others exist between layers of the graphite. The structure around a deuterium atom in the crystalline TbFe2D3.8 and amorphous TbFe2Dx (x=3.0, 2.0) informs us not only the location of the deuterium atoms but also rearrangement of metal atoms with transformation from a crystalline to an amorphous phase. Deuterium atoms occupy in the tetrahedral unit consisting 2Tb+2Fe in crystalline TbFe2D3.8. On the other hand, the tetrahedral unit consisting mainly of Tb atoms becomes a stable site of D atoms in the amorphous TbFe2Dx.

Thursday, June 12, 2003 — Morning
Jeudi 12 juin 2003 — Matin

Session VIII: H strorage in carbon nanostructures (I)
Session chair: F. Béguin

C-VIII.1 09:00 -Invited-

HYDROGEN STORAGE IN CARBON NANOSTRUCTURES

Channing Ahn, Division of Engineering and Applied Science, California Institute of Technology, Passadena, USA

Carbons in nano-fiber and nano-tube form generated initial excitement in 1997-98 with claims of high gravimetric, hydrogen-adsorption storage capacities. While numerous reports have since appeared in the literature with similar claims, there has been little subsequent evidence to indicate that these forms of carbon behave much differently than any other sp2 carbon. The driving force for physisorption in carbon must increase substantially, from the 40-50 meV, adsorption enthalpy (typical of graphitic carbon) to several hundred meV, if complete graphitic surface saturation by hydrogen at ambient temperature is to be attained. The upper limit of gravimetric storage in this case would be 8 wt%, provided that two layers of hydrogen molecules could be adsorbed per graphene layer. The rationale for studying nanotubes as opposed to typical graphites is that this geometric configuration can be realized as nanotubes have both inner and outer surfaces onto which hydrogen molecules can adsorb. We will review the area of hydrogen adsorption in nanophase forms of carbon and also address some of our own work in attempting to alter the adsorption enthalpy through the use of additions like Potassium. Potassium intercalated graphites have long been known to absorb hydrogen. We will present our results from neutron diffraction experiments on deuterided KC24 and KC48, intercalation compounds which show lattice expansion when deuterided.

C-VIII.2 09:40

HYDROGEN STORAGE IN SOLAR PRODUCED SINGLE-WALLED CARBON NANOTUBES

David Luxembourg, Gilles Flamant, Daniel Laplaze, IMP-CNRS, Font Romeu, France

We present the results of hydrogen storage in carbon nanotubes synthesized by the solar method. The solar energy is a versatile method to obtain SWNT at small scale (0,1-0,2 g/h of pristine sample) and large scale (10-20 g/h of pristine sample). The pristine and purified products are characterized by scanning and transmission electron microscopy and Raman spectroscopy.

Hydrogen adsorption of SWNT is carefully investigated using a volumetric apparatus developped in our laboratory. The applied pressure is up to 7 MPa and the temperature between -20°C and +20°C.

C-VIII.3 10:00 Oral

ENHANCED HYDROGEN STORAGE ON SINGLE WALL CARBON NANOTUBES BY METAL REDUCTION

M.T. Martinez, A. Ansón, M.A. Callejas, W. Maser, A.M. Benito, Instituto de Carboquímica, C/ Miguel Luesma Castán 4, 50018 Zaragoza, Spain and J.L.G. Fierro, Instituto de Catálisis y Petroleoquímica, Cantoblanco, 28048 Madrid, Spain

Single wall carbon nanotubes, SWCNTs, produced by arc-discharge using Ni/Y as catalysts have been studied for hydrogen storage. As grown and modified SWCNTs have been tested for hydrogen storage at 77 K and moderate pressure. Improved hydrogen storage has been observed when the samples have been reduced before the adsorption. The results suggest hydrogen dissociation promoted by activated catalyst sites.

10:20 **BREAK**

Session IX: H strorage in carbon nanostructures (II)
Session chair: T. Fukunaga

C-IX.1 10:50 -Invited-

HYDROGEN ADSORPTION IN CARBON NANOSTRUCTURES COMPARED

H.G. Schimmel(a), M.G. Nijkamp(b), G.J. Kearley(a), A. Rivera(a), K.P. de Jong(b) and **F.M. Mulder**(a), (a)Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, 2629JB Delft, The Netherlands, (b)Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University, P.O. Box 80083, 3508TB Utrecht, The Netherlands

Recent reports continue to suggest high hydrogen storage capacities for some carbon nanostructures due to a stronger interaction between hydrogen and carbon. Here the interaction of hydrogen with activated charcoal, carbon nanofibers, single walled carbon nanotubes (SWNT), and electron beam 'opened' SWNT are compared and shown to be similar. The storage capacity below 77K of these materials correlates with the surface area of the material with the activated charcoal having the largest. SWNT and 'opened' SWNT have a relatively low accessible surface area due to bundling of the tubes. Pressure-temperature curves give the interaction potential, which was found to be ~580K or 50 meV in all samples, leading to significant adsorption below ~50K. Using the inelastic neutron scattering signal associated with rotation of the hydrogen molecule as a sensitive probe for the surroundings of the molecule, no difference was found between the hydrogen molecules adsorbed in the investigated materials. These combined spectroscopic and macroscopic results show that SWNT, nanofibers and activated carbons store molecular hydrogen due to their graphitic nature and not because they possess special morphologies. Results from a density functional theory computer calculation suggest molecular hydrogen bonding to an aromatic C-C bond of graphite, irrespective of the surface morphology farther away.

C-IX.2 11:30

INTERACTION OF HYDROGEN ISOTOPES WITH CARBON NANOSTRUCTURES

M. Haluska, M. Hirscher, M. Becher, D. Lozano-Castello, U. Dettlaff-Weglikowska, X. Chen, S. Roth Max-Planck-Institut für Metallforschung and Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany

The storage capacity and the interaction mechanism of hydrogen with different carbon nanostructures were investigated utilizing thermal desorption spectroscopy (TDS) and volumetric method. Single walled carbon nanotubes, graphitic nanofibers and activated carbons with different microstructure and specific surface area were loaded with hydrogen between room temperature and 77 K.

The mechanisms of the ad/absorption process were studied by analysing the TDS spectra of specimens exposed to a mixture of deuterium and hydrogen. Dissociative ad/absorption processes followed by the storage of atomic hydrogen/deuterium were observed for specimens containing metal particles which have been loaded at room temperature. A non-dissotiative process of adsorption and storage of molecular hydrogen/deuterium was observed for specimens with large surface area loaded at temperatures around 100 K. The results are discussed with respect to metal content, specific surface area and pore size.

C-IX.3 11:50

ELECTROCHEMICAL STORAGE OF HYDROGEN IN CARBON NANOTUBES AND OTHER CARBONS

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The amount of hydrogen reversibly stored in different nanostructured carbon electrodes using the electrodecomposition of alkaline and acidic aqueous solutions has been investigated. The concentrated KOH solution was a preferable electrolyte in comparison to acidic medium. The association of the hydrogen evolution and its simultaneous storage in a carbon substrate is quite attractice even if the energy efficiency is ca. 40%. Up to 2wt% of hydrogen was released from a microporous carbon during the oxidation process. It is higher than the amount adsorbed under ambient temperature even using a high pressure. This enhancement is due to the formation of nascent hydrogen during water reduction which penetrates easily in the carbon nanostructure. Our results show that pure carbon nanotubes supply negligible values of hydrogen capacity (below 0.5wt%). Generally the greater amount of catalyst impurities and amorphous carbon in nanotubes the higher hydrogen uptake. This confirms that the dimension of nanopores in nanotubes is not optimal for this process. Correlation was done between the hydrogen capacity and the type of pores for all the studied carbon materials to find the optimal sites the most suitable for reversible sorption.

C-IX.4 12:10

HYDROGENATION OF NANOSTRUCTURED GRAPHITE BY MECHANICAL GRINDING UNDER HYDROGEN ATMOSPHERE

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Recently, it has reported that the graphite mechanically ground under hydrogen atmosphere contained several weight percentages of hydrogen. Although it has a relatively high desorption temperature and shows poor rehydrogenation properties, many researchers are trying to see the possibility of applying this material as a hydrogen storage material since then. We have been also intrigued by this material and finally confirmed that under certain circumstances the graphite was hydrogenated up to 5 wt%. Incidentally this is in a marked contrast to the situation of carbon nanotubes and nanofibers which we have so far failed to see the reproducibility at all. We found, however, that the reproducibility of the grinding experiment was significantly influenced by the conditions, e.g. what material the grinding crucible is made of, the ratio of the volume of the crucible to the weight of the graphite powder in it, small amount of inpurities and so on. So far we are yet far from clarifying the causes and effects of this observation, but in this presentaion we provide some clues which will lead to the understanding of the hydrogenation reaction mechanism of this materials.

12:30 **LUNCH**

14:30-16:30 POSTER SESSION

C/P.01 COMPUTER SIMULATION OF SUPPORTED C60 FULLERENES FRAGMENTATION BY ELECTRON BEAM

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Now the particle beam technology is intensively investigated with the purpose of creation and modification of the different electronic nanoscale systems. In particular, the ensembles of supported carbon clusters with extremely low size dispersion and with properties which can be transformed by the variation of the band gap and the density of states near Fermi-level can be used for the development of the new generation of electronic devices. In the present report the computer simulation of the electron beam induced fragmentation of C60 fullerenes supported by surface and in fullerite film was carried out. In particular, we have developed the Monte-Carlo simulation of the radiation-induced defect generation and its dynamics using the TRIM-package for random targets and MARLOW-code for crystal targets, the simulation of the atomic excitation and ionization processes in the target using the Firsov and Lindhard-Schaff models and semi-empirical approximations. The time dependence and spatial distribution of both the radiation defects in the target, specifically vacancies, interstitial atoms and more complicated defects of crystal structure and the electron excitation and ionization of target atoms along the projectile traces were calculated. This work was supported by INTAS grant (N 2136).

C/P.02 CYCLIC DURABILITY OF Ca-Mg-Ni ALLOYS AND FACTORS WHICH CAUSE DEGRADATION OF HYDROGEN STORAGE CAPACITY

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The durability on cyclic hydrogen absorption and desorption for Ca-Mg-Ni hydrogen storage alloys, which are investigated in the Japanese national project WE-NET, were examined by using pure H2 (99.99999%). Tested alloys were induction-heated and annealed Ca0.25Mg0.67Y0.09Ni1.86 (cubic MgCu2-type structure), and sintered Ca0.55Mg0.45Ni3 (hexagonal PuNi3-type) and Ca0.5Mg0.5Ni2 (MgCu2-type). Testing conditions were as follows: hydrogen absorbing and desorbing periods were 30 min., absorbing pressure was 3 MPa and desorbed in vacuo using a rotary pump, temperature was 313 K. Initially the hydrogen storage capacities were H/M ~ 0.7, however, they decreased steeply within a few cycles, and then they declined gradually. At about 400th cycle, they decreased to nearly half of the maximum capacities regardless of crystal structures and compositions of the tested alloys. As for the surface, the results from XPS suggested that the alloys disproportionated during the cyclic process and that the oxidized Ca and Mg as well as the metallic Ni covered the matrix. On the other hand, as for the bulk, XRD did not suggest serious disproportionation but pulverization and lattice expansion. The expansion indicated that some amounts of hydrogen remained in the lattice cells. We will discuss the factors leading the degradation of storage capacity based on the series of results.

C/P.03 HYDROGEN STORAGE PROPERTIES OF NANOSTRUCTURED GRAPHITE MECHANICALLY MILLED UNDER VARIOUS HYDROGEN PRESSURES UP TO 6 Mpa

Takayuki Ichikawa, Demin Chen*, Hironobu Fujii, Faculty of Integrated Arts and Sciences, Hiroshima University, Hiroshima, Japan, *Institute of Metal Research, Chinese Academy of Sciences

We investigated hydrogen absorption-desorption behaviors and nano-structural properties in graphite mechanically milled under various hydrogen pressures ranging from 0.3 to 6.0 MPa. The sample was prepared by a rocking mill equipment with a pressure gauge, by which the absorbed hydrogen concentration during milling could be evaluated. The total absorbed hydrogen concentration in graphite after milling for 80hrs decreased with increasing the milling pressure, in which stable chemisorbed and unstable physisorbed-like hydrogen coexist as well. Although the chemisorbed hydrogen concentration, which was determined by oxygen combustion method, decreased from 6.1 to 4.1 wt.% with increasing the milling hydrogen pressure, the physisorbed-like hydrogen concentration, which was determined by volumetric method at 6 MPa, increased with increasing the milling hydrogen pressure and reached more than 0.5 wt.%. Moreover, from the various structure analyses, we confirmed that the higher pressure hydrogen suppressed the fracture rate of the milled graphite more effectively. Their results also suggested that under higher presseure, hydrogen atoms densely trapped at the edges of the graphene sheets and between the graphene layers near the surface do not come into interlayer and are responsible for preserving the lamellar nanocrystalline structure, which may play role of the host for physisorbed-like hydrogen absorption.

C/P.04 ADSORPTIVE HYDROGEN STORAGE IN CARBON AND POROUS MATERIALS

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Recently, hydrogen storage on carbon materials has attracted attention because of the importance of hydrogen as an ideal energy medium. However, the discrepancy among resent reports with regard to storage capacity of carbon materials still remains. To clarify the capacity and mechanism of the hydrogen storage, it is now required to analyze the storage property accurately by using the samples characterized clearly. In this study, we made the high-pressure adsorption apparatus with sufficient accuracy, and measured the hydrogen adsorption and desorption isotherms of several kinds of activated carbon fibers (ACFs), single-walled carbon nanotubes (SWCNTs) with high purity, and zeolites at 77 - 303 K in a hydrogen pressure of 0 - 3.5 MPa. The relationship between the storage capacity and pore structure estimated from N2 and CO2 adsorption was discussed. The amount of adsorbed hydrogen by weight depended on the micropore volume, except for SWCNT. The storage capacity of SWCNT treated with nitric acid (O-SWCNT) against the micropore volume was higher than that of ACF and zeolite. Although the hydrogen storage capacity at 303K and 3 MPa in this study did not reach to the DOE target, O-SWCNT indicated the maximal amount of adsorbed hydrogen by volume. The surface area of micropore of O-SWCNT is 710 m2/g, whereas the theoretical surface area is 2630 m2/g. This suggests that the hydrogen storage capacity can be enhanced by SWCNT with ideal structure, which has higher surface area.

C/P.05 ZR-SUBSTITUTION IN LANI5-TYPE HYDRIDE COMPOUND BY ROOM TEMPERATURE BALL MILLING

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Intermetallic compounds store reversibly a large amount of hydrogen near room temperature and ambient pressure. This has made them very attractive as energy storage materials. However, further improvement in terms of weight capacity, cycle life or kinetic is still needed for practical applications. Thermodynamic modifications can be easily achieved by substitutions on the metallic sublattices. An interesting aspect is the possible replacement of La by lighter element keeping the CaCu5-type structure in the LaNi5-type family. However some elements remain difficult to use as they do not react with the parent compound by classical metallurgic routes. A typical case is observed with Zirconium. Attempt to substitute La by Zr is hindered by the fact that these two elements are not miscible even in the liquid state [1]. Indeed, solubility domains in the system LaNi5-ZrNi5 are very limited [2]. In this work we will show how this problem can be overcome by high energy ball milling at room temperature to prepare such materials in amorphous state. After appropriate annealing treatment, nanocrystalline La0.5Zr0.5Ni5 alloy is obtained. Its hydrogen properties have been measured and will be presented.

[1] F. H. Spedding and A. H. Daane, The rare Earths, (1961) 296.
[2] V.G. Ivanchenko & G.F. Kobzenko, Inorganic materials, 19, 7 (1983) 995.

C/P.06 DEUTERIUM ADSORPTION/DESORPTION IN Mg-Nb FILMS PRODUCED BY PULSED LASER DEPOSITION

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The aim of this work was to obtain alloy films (Mg-Nb) with a desired content of alloying element (2-10 wt% of Nb) and to study deuterium absorbtion/desorption kinetics. The Pulsed Laser Deposition (PLD) was used as a good technique to produce high quality and high purity thick films with a high deposition rate. To produce alloy films a structured target was used: it was containing separate zones made of matrix element (Mg) and alloying element (Nb) in the appropriate ratio. In this case there was a central circle of Nb and a surrounding zone of Mg. The target moving system of the used apparatus has permitted to realize a co-deposition in a rapid sequence of Mg shots and Nb shots. The deuteration was achieved exposing the samples to deuterium gas at a fixed pressure at high temperature. The structure of the obtained samples were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The kinetics of deuterium release was studied with Thermal Desorption Spectroscopy (TDS) analysis. The results of XRD and TDS analysis revealed that the release of deuterium from the hydride phase is strongly affected by the microstructure of the film. In particular, the results show an improvement of the desorption kinetics by reducing the structure to the nano-scale.

C/P.07 MATERIAL PROPERTIES OF LiBH4 AND LiBD4

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Volumetric and gravimetric densities of hydrogen in LiBH4 are 18.5 mass% and 121 kgH2m-3, respectively, and thus, the material properties of LiBH4 are of great interest for the application of hydrogen energy storage. We will report atomistic vibrations on hydrogen (deuterium) cluster in [BH(D)4]-, using in-situ visual Raman Spectroscopy on LiBH4 and its deuteride LiBD4 from R.T. up to 593 K, just after their melting reaction. Also, a combined analysis both in-situ Raman spectroscopy and thermal analysis will be presented.

C/P.08 ADSORPTION BEHAVIOR OF WATER AND METHANE ON SURFACE-MODIFIED CARBONS WITH METAL NANOPARTICLES

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Polymer electrolyte fuel cell consists of large active area with optimized utilization of the platinum catalyst. The void spaces of agglomerates formed by grains of Pt/carbon catalyst, gas accessible channels, should be hydrophobized desirably in order to avoid flooding of them with product water in the electrode/electrolyte interface. However, it is presumed that the product water can be adsorbed, despite of the hydrophobicity of carbon surface, on the catalyst by the promotion of platinum or polymers mixed with carbon. This promoted adsorption is attractive in the case of methane storage; namely, the adsorbent such as metal/carbon composites should enhance the energy density of natural gas. In this study, the promoted-adsorption effect on carbon surface modified with metal or metal oxide nanoparticles was investigated for water and methane that are representatives of polar and non-polar molecules, respectively. As a result, micropore filling of water on carbon black was promoted by Pt-nanoparticles that behave as an active site of water adsorption as surface functional groups. On the other hand, the less promoted effect of micropore filling was observed for activated carbon fibers (ACF) as a support. However, the loading of metal oxide such as MgO promoted significantly the micropore filling even on ACF. In the case of methane, such promotion effect was poor because of its non-polar nature, and chemisorbed water into micropore prevented penetrating of methane molecules.

C/P.09 ABOUT A POSSIBILITY TO APPLY POWDERED $InSeF_X$ AND $Bi_2Se_3F_X$ AS CATHODE MATERIALS IN LITHIUM POWER SOURCES

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The exposition of powdered samples of InSe and Bi_2Se_3 in a flow of molecular fluorine was carried out in the temperature range between 25 and 400^0 C during 60 min. From the fluorinated powders lithium power sources were prepared. An 1 M solution of LiBF_4 in \gamma-butyrolactone was used as electrolyte and a Celgard – 3401 film was used as separator between electrodes. The energy capacities of such batteries are the highest for InSe fluorinated at T=300^0 C (W=715 A h/kg) and for Bi_2Se_3 fluorinated at T=220^0 C (W=1285 A h/kg). During the discharge of these Li – batteries we have obtained their discharge curves and in situ X-ray diffraction patterns of the cathode materials.

Starting from the X-ray studies the mechanism of current forming chemical reactions under the discharge is proposed.

C/P.10 Withdrawn

C/P.11 RADIATION INDUCED ENHANCEMENT OF PROTON CONDUCTIVITY IN POROUS GLASS

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For development of hydrogen energy it is necessary to increase the efficiency of dissociation of water molecules and hydrogen accumulation, which depends on electrode material. We studied effect of ionizing gamma-radiation of Co60 on the bulk thermal stimulated electric conductivity (TSEC) of porous alumina-silica glass in presence of water vapor. Measurements were carried out in the course of irradiation at a dose power from 0.12 to 29.6 Gy/s within the temperature interval of 230-630 K. The value of the 1-st peak of TSEC at 300 K increases by 6 orders of magnitude, then after decrease at 400 K the 2-nd stage of growth occurs, obeying to the reciprocal Arrenius law. The 1-st peak related with proton conductivity occurs only in highly porous materials, with the magnitude depending on the porosity degree and amount of absorbed water. The irradiation does not effect on the 1-st peak at 300 K, however increases TSEC significantly (by 4 orders of magnitude proportionally to a dose power) in the temperature interval because of radiation induced conductivity and activation of total grain surface in the glass.

C/P.12 STRUCTURAL CHARACTERIZATION AND ELECTRIC DOUBLE LAYER CAPASITANCE OF TEMPLATE CARBONS

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A fluorine expandable mica, having two-dimensional spread in its crystal form, was used as a template for carbonization of organic liquids such as quinoline and pyridine. Despite intrinsic volatile under the ambient pressure, these organic liquids inserted into the interlayer space of mica yielded carbonaceous compound after heat treatment over 500°C in inert atmosphere. The particle size of the compound separated from the mica layer depends on that of mica as a template. Detailed TEM observation revealed unique structure, namely each particle comprised two structural parts: film and surrounding rim part. The film part was very thin, thus being transparent for SEM observation and rim part has constant width of about 20nm. This structure is particularly interesting, because it can be carbon thin film supported by carbon micro-ring. The template carbons indicated a high electric double layer capacitance amounting to more than 100F/g in H2SO4 electrolyte. Because of low surface area of the samples, specific capacitance per unit surface area could reach 1.2-2.3F/m2, which is over ten times as high as the capacitance of ordinary activated carbons. The presence of residual nitrogen may account for such a high capacitance.

C/P.13 SYSTEMATIC INVESTIGATION ON HYDROGEN STORAGE PROPERTIES OF RNi5 (R: RARE EARTH) INTERMETALLIC COMPOUNDS WITH MULTI-PLATEAU

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Some hydrogen storage materials with hexagonal CaCu5-type crystal structure have multi-plateau pressures during hydrogen absorption and desorption processes, but a systematic study on multi-plateau, especially the plateau at higher hydrogen pressure, has yet to be done. We investigated the hydrogen storage properties of several RNi5 (R = La, Ce, Pr, Nd, Sm and Gd) intermetallic compounds at pressures up to 35 MPa by using a conventional Sieverts' method from 195 K to 323 K. Pressure-composition isotherms of hydrogen absorption and desorption show that the maximum hydrogen content exceeds 6 atomic hydrogen per formula unit in all cases. NdNi5, SmNi5 and GdNi5 as well as PrNi5 have two well-separated plateaux, indicating that two hydrides with compositions of RNi5H4 and RNi5H6 are formed. Two plateau pressures in desorption increase with decreasing the lattice volume of compounds due to the decrease in the size of interstitial site which can accommodate hydrogen atom. This is attributed to the decrease in absolute value of two enthalpies of hydride formation. Further high pressure leads to slight additional hydrogen absorption in the RNi5H6 without new plateau.

C/P.14 STRUCTURE AND HYDROGENATION PROPERTIES OF Zr7Ni10 PREPARED BY QUENCHING

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Intermetallic compound Zr7Ni10 has following unusual hydrogenation properties: Its intermediate hydride phase appears only in hydrogen desorption and, for its continuous hydrogen solid solution phase, the hydrogen solubility in hydrogen absorption is quite larger than that in hydrogen desorption [1]. The mechanisms to explain the above-mentioned phenomena have not been clarified and various kinds of information are required for the elucidation of the mechanisms. In this study, rapid cooling technique was applied in order to evaluate the effect of the metallographic structure on the hydrogenation properties of Zr7Ni10. Pure Zr and Ni metals were firstly alloyed by arc melting and then the samples remelted in a high-frequency induction-heating furnace were quenched with a Cu wheel rotating at high speeds under Ar atmosphere. The samples thus prepared had the tetragonal structure, different from the orthorhombic structure of the ingot prepared by arc melting. The metallographic structure and hydrogenation properties of the quenched sample were evaluated from the standpoint of the difference from those of the sample prepared by the conventional method.

[1] H. T. Takeshita, T. Kiyobayashi, H. Tanaka, N. Kuriyama, M. Haruta, J. Alloys Comp., 311 (2000), L1.

C/P.15 HYDROGENATION PROPERTIES AND STRUCTURE OF Ti-Cr ALLOY PREPARED BY MECHANICAL GRINDING

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Certain alloys with a bcc structure can absorb a large amount of hydrogen. It is difficult to obtain the single phase bcc-solid solution in Ti-Cr binary system without addition of other elements. It is reported Intermetallic compounds with Cr3Si type crystal structure can be transformed into solid solution with bcc and CsCl type crystal structure by mechanical grinding (MG)[1]. C14 type intermetallic compound TiCr1.9 was subjected to grinding in a ball mill. The XRD profiles showed that the crystal structure was transformed from C14 to bcc after 18 hours of MG. As far as we know, this is the first example of a phase transition from C14 phase to bcc phase by MG. The hydrogenation properties of the bcc-TiCr1.9 were examined by DSC and pressure-composition isotherm measurements. The sample started to react with hydrogen under 1MPa at 573K with maintaining the bcc structure. The pressure-composition isotherm was significantly sloped, and the maximum hydrogen capacity was determined to be 0.5 H/M at 298K and 35MPa. The hydrogen capacity and equilibrium hydrogen dissociation pressure of the sample prepared by MG was less and higher than those of bcc type Ti-Cr-V alloys prepared by melting, respectively. We will discuss the relation among the hydrogenation properties, lattice defects and local atomic structure.

[1] V.P.Balema, A.O.Pecharsky and V.K.Pecharsky, J.Alloys Comp., 307(2000)184

C/P.16 DOPING AND DECOMPOSITION OF LiAlD4

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The alkali-metal aluminohydrides (alanates) have high potential as solid hydrogen storage (e.g. LaAlH4 10.6 wt % H2, NaAlH4 7.5% H2). Until recently, they were regarded to be irreversible at moderate pressure and furthermore suffered from slow desorption kinetics. Bogdanovic [1] showed in 1997 that Ti-doping improved the kinetics of NaAlH4 and made re-hydrogenation possible. Since then, numerous studies have been carried out in order to identify some new possible doping agents. Nevertheless, the mechanisms involved in the doping effects are still not understood, and improvements are necessary to meet the IEA goal of 5 wt% reversible H2 storage capacity.

On the basis of previous works, showing the improved kinetics of both Ti and V compounds on the desorption kinetics of LiAlH4 [2,3], we have performed an extended study on the behaviour of these additives. LiAlD4 doped with VCl3 or 3TiCl3×AlCl3, prepared by ball-milling, exhibit lower desorption temperatures: 20 - 50oK and 20 - 40oK for the two decomposition steps (formation of Li3AlD6 and LiH), respectively. By means of in-situ neutron and synchrotron X-ray diffraction, a closer examination of the doped LiAlD4 decomposition is carried out and possible mechanisms related to the action of the doping agent investigated.

[1] B. Bogdanovic , M.Schwickardi, J. Alloys Comp. 253-254 (1997) 1.
[2] J.Chen J. and al.. J. Phys. B Chem. 105 (2001) 11214-11220.
[3] B. Bogdanovic and al.. J. Alloys Comp. 302 (1-2) (2000) 36-58.

C/P.17 THE VIBRATIONAL SPECTRUM OF MAGNESIUM HYDRIDE FROM INELASTIC NEUTRON SCATTERING AND DENSITY FUNCTIONAL THEORY

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Light-weight magnesium metal can reversibly store up to 7 wt.% hydrogen and is therefore interesting for application as hydrogen storage material. Neutron vibrational spectroscopy has been used to study the interactions of hydrogen atoms with its surroundings. The neutron spectra are compared directly with Density Functional Theory calculations providing detailed insight in structure and dynamics. Strongly dispersive interactions have to be taken into account (motions changing the unit cell dimensions) in order to reproduce the data. This study on bulk magnesium hydride will provide a bench mark for similar studies on nanostructured magnesium alloys: these are more promising as hydrogen storage materials because of their significantly faster hydrogen sorption processes. Because of its sensitivity and the compatibility to calculations, the vibrational spectra of these nanostructured compounds can be used as a probe for the local structure and the influence of the nanostructure on the potential landscape experienced by the hydrogen. Parameters can be extracted for MD and Monte Carlo calculations of slower diffusion processes.

C/P.18 INVESTIGATION OF HYDROGEN ABSORPTION PROPERTIES OF NANOSTRUCTURED CARBON THIN FILMS BY NEXAFS SPECTROSCOPY

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Carbon based materials are interesting system for hydrogen storage which is a technological challenge of primary interest for mobile power units in many different applications. We used NEXAFS spectroscopy [1,2] to study the capability of hydrogen absorption by porous nanostructured carbon (ns-C) grown in the form of thin films by supersonic cluster beam deposition (SCBD). The effectiveness of different hydrogen loading methods has been investigated. All ns-C samples show similar carbon K-edge spectra with three main features in the pre-edge part of the spectrum: sp2 C=C resonance at 285.4 eV, a peak at 286.8 eV, and the C-H* resonance at 289 eV. The relative intensities of the three features show a remarkable correlation with the extent of their exposure to hydrogen.

The NEXAFS measurements on nanostructured carbon films indicate the presence of chemisorbed hydrogen sites. Previous thermal programmed desorption (TPD) analysis completes the picture showing the population of physisorption sites [2]. The relevance of the C-H* peak in the investigated samples induce to retain that nanostructured carbon could have a bigger adsorbing capacity. The obtained results are encouraging with regard the possible hydrogen uptake capacity of ns-C films and their use for hydrogen storage devices. 1. C.Lenardi, P.Piseri, V.Briois, C.E.Bottani, A.Li Bassi, and P.Milani "NEXAFS and Raman Characterization of Amorphous and Nanostructured Carbon Films", J. Appl. Phys. 85, 7159 (1999). 2. C.Lenardi, E.Barborini, V.Briois, L.Lucarelli, P.Piseri, and P.Milani "NEXAFS characterization of nanostructured carbon thin films exposed to hydrogen", Diamond Relat. Mater. 10, 863 (2001).

C/P.19 DIRECT SYNTHESIS OF A CARBON-PLATINUM NANOCOMPOSITE LAYER ON A NAFION PROTON EXCHANGE MEMBRANE

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We report on the synthesis of a nanocomposite porous carbon layer with embedded Pt nanoparticles. The material is deposited at room temperature under vacuum in the form of thin films by Supersonic Cluster Beam Deposition using a PMCS (Pulsed Microplasma Cluster Source). The cluster source is operated with a compound cathode which is eroded by an electric discharge providing simultaneously the two elements. The Pt content can be easily varied between 1 and 20 atomic percent modifying the position of the interface between the two materials in the compound cathode relative to the ablation point. A TEM investigation reveals that the material is formed by a ns-C matrix (with mainly sp2 hybridized carbon and many observable graphene sheets and sparse hollow particles) with 1-4nm Pt particles dispersed in. A Nafion membrane has been coated on both sides by such material and a working prototype fuel cell built on this technology has been tested. The functional properties of this membranes relevant for fuel cell applications are currently under study.

C/P.20 AN ELECTROCATALYST LAYER FOR POLYMER ELECTROLYTE FUEL CELLS FABRICATED BY SOL-GEL SYNTHESIS

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Polymer electrolyte membrane fuel cells (PEMFC) have received great attention as an energy source. Although there are many advantages of PEMFC technology, there are also some disadvantages. The main one is the high cost of Pt loading of the membrane-electrode assembly (MEA). Owing to intensive investigations carried out for last decade Pt content in the MEA catalyst layers was succeeded to decrease up to 0.05-0.1 mg/cm2 under keeping of the main operative characteristics of PEMFC, such as voltage and current density, at the same level. However, the further decrease of Pt content in the electrocatalyst layer is the necessary condition of the commercial use of PEMFC. The new methods of sol-gel technology were used by us for fabrication of the thin film low-Pt loading electrocatalyst layers in PEMFC. To this end some tetraethoxysilane-derived sols doped by platinum were used to form the catalyst layer for anodic hydrogen oxidation in the NAFION-based semi-fuel cell. The catalyst layers of about 300 nm in thickness were deposited onto the surface of NAFION membrane. It was shown the Pt nano-particles about 0.5 – 2 nm in size were uniformly distributed in the silicate matrix. The estimation of current density based on the stationary polarization curves of anodic hydrogen oxidation show that the same current density can be obtained, using the catalyst layers designed, at more less Pt loading than in the case of the catalyst layers prepared in accordance the conventional technology..

C/P.21 INTERCALATION AS A WAY OF NANOSTRUCTURE FORMATION

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It is well known, nano-structures are the objects with nearly 10nm sizes at least in one direction. Layer crystals are the objects with a unique property, caused by existence of weak van de Waals interaction between layers, which allows to fulfill such technological process as intercalation, namely the insertion of guest atoms into the van der Waals gaps. At certain conditions guest atoms can create order structure both in the plane of the gap and along its normal. The formed guest structure can be as incommensurate with host structure as well as commensurate one. Thus, intercalated layer crystal might be considered as structure with the elemental cell with basis. However special type of guest-host binding, allows to consider guest atoms as consequence of monoatomic layers inside the host, namely as quasi-two-dimensional structure. The change of free energy of layered crystal electron subsystem caused by intercalation is analyzed. It is shown, that the intercalation at certain correlation between the energy characteristics of host, guest and host-guest interaction may lead to the thermodynamic equilibrium structure. Thermodynamic restrictions on the guest concentration are established.

C/P.22 ELECTRON MICROSCOPY OF MECHANICALLY GROUND Mg-Ni ALLOYS CONTAINING HIGH AMOUNT OF HYDROGEN ATOMS

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Investigation of nanostructured materials has become more important to search a new functional materials. Mechanical alloy method is one of the most popular ways to produce nanostructured materials. It has become well known that the nanostructured Mg2Ni or Mg-Ni alloys have an excerllent property of hydrogen absorption, that is, a large capacity of the hydrogen atoms and a performance of absorption and disorption at rather lower temperatures.

In this paper, microstructures are investigated by the electron microscopy for the Mg2Ni as well as several Mg-Ni alloys synthesized by the treatment of the mechanical grinding and mechanical alloying. Especially the changes in the microstructures not only due to the time of the mechanical treatments but also the addition of the Ni metal into the materials. In an earlier stage of the mechanical treatments, a fragment of the Mg2Ni crystal consists of two areas: one contains dislocations which show an array of the dislocations forming a small angle grain boundary, and the other shows heavily faulted or crashed areas which show already an ensanble of nanocrystals. Along the boundaries between two areas mentioned above, a characteristic structures are found to be an array of the pinning centers for dislocations as well as for grain boundaries. After the mechanical treatment of 100 hours, materials are made of nanocrystals of several ten nm in diameter. By an addition of Ni metal, a heavy kneeding began in the earlier stage of the mechanical treatments. The materials easily changed into a state of the amouphous.

C/P.23 CARBON NANOTUBES AS SUPPORT FOR CATALYSTS OF METHANOL OXIDATION

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Carbon nanotubes have attracted great interest for many applications due to their unique morphological, mechanical and electrical properties. Electrochemical storage of energy with a possible application for the fuel cell is also considered.

Multiwalled carbon nanotubes (MWNTs) have been used as a support for catalytic particles (Pt, Ru or Pt/Ru alloys) for methanol oxidation in 1M sulfuric acid. Efficiency of this process was definitively enhanced in comparison to other carbon supports. Careful investigation was performed to select the optimal dispersion of catalytic particles on nanotubular material. Different types of MWNTs, i.e. catalytically grown as well as obtained by chemical vapor deposition technique (CVD) in the alumina membrane, were used as a support of catalysts used for anodic oxidation of methanol.

C/P.24 DETECTION OF THE Co2+ ION TETRAHEDRAL COORDINATION IN THE Co(OH)2 NANODISPERSED HYDROXIDE BY UV-VIZ

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It is known that for ß-Co(OH)2, the coordination of ions Co2+ (d6-electron configuration) is octahedral and characterized by transition 4T1g(F)(r)4T1g(P) in the 19000 cm-1 region.

In this report we have described the Co2+ hydroxide with a predominantly tetrahedral coordination of ions Co2+. For this coordination, the absorption bands of ions Co2+ are in the 15000 cm-1 range and exhibit the multiple spectrum structure, which is typical of the tetrahedral coordination. The particles of the prepared hydroxide are (1.0-2.0 nm) in size. This hydroxide is also characterized by a weak tetrahedral distortion of the octahedron detected at 19000¸21000 cm-1. In the mother solutions, the Co2+ ions preserve their tetrahedral coordination in the Co(OH)2 hydroxide during three months. The obtained result may be of utility in preparing of catalysts and synthesis of high tech materials and Li-Co rechargeable batteries.

C/P.25 HYDROGEN AND METHANE STORAGE IN CATALYTIC FILAMENTOUSE CARBON NANOSTRUCTURES

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Catalytic filamentous carbon (CFC) produced by hydrocarbon decomposition over 3d-metal catalysts represents a novel mesoporous carbon material. CFC possesses a specific framework of fibers, which consist of graphitic planes stacked at some angle ( ) to the fiber axis. The present work is devoted to investigation of the properties of CFC prepared by methane decomposition over Ni-Al2O3, Co-Al2O3, Ni-Cu-Al2O3, Fe-Co-Al2O3 catalysts by methods of TEM, SEM, XRD. The comparative studies of H_2 and CH_4 adsorption have been conducted at the pressure up to 100 atm on the samples of catalytic filamentous carbon (CFC) and supermicroporous active carbon (SAC) with surface area higher than 2000 m^2/g.

It is shown, that more H_2 is sorbed on CFC (up to 25-35 mg H_2/g carbon) than on SAC, while the opposite is observed for CH_4 adsorption (200mg CH_4/g carbon). The observed data of H_2 sorption on CFC with the surface area of 100-300 m^2/g is explained by the hydrogen intercalation between the graphite-like CFC layers.

This paper is supported by grants of INTAS 1044 and NWO.

C/P.26 THERMALLY ACTIVATED IONIC CONDUCTION IN LiNbO3 ELECTROLYTE THIN FILMS

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$LiNbO_3$ thin films have been introduced as electrochromic materials. Its conductivity could make the material useful as electrolyte in solid state microbatteries. When preparing the films though, some Li is lost. By forming a thin layer of Li on top of the evaporated $LiNbO_3$ film the ionic conductivity increases.

Such an electrolyte (with the Li layer on top of the Li_xNbO_3) could create extra resistance and blocking areas in a microbattery. In order to avoid such an influence in a microbattery the electrolyte was prepared by forming an interlayer of metallic Li between two layers of Li_xNbO_3. By annealing a structure like this Li is diffused in the two layers of Li_xNbO_3. Samples have been prepared by e-gun evaporation having the structure Al_2O_3/Co/Pt/Li_xNbO_3/Li/Li_xNbO_3/Au or Stainless_steel/TiN/Li_xNbO_3/Li/Li_xNbO_3/Au. Various thicknesses of the metallic Li interlayer were tried. AC impedance spectroscopy measurements on the as deposited structures showed mainly electronic conduction. The measurements were repeated after annealing the samples either at 150°C or at 300°C (lower temperature than the melting point of Li or higher one respectively). Ionic conduction was obvious after the annealing, depending on the time and the temperature of annealing. Crucial parameter in manipulating the specific conductivity of the $LiNbO_3$ thin film materials was the thickness of the metallic Li interlayer.

16:30 **BREAK**

Session X: H strorage in carbon nanostructures and supercapacitors
Session chair: C.C. Ahn

C-X.1 17:00

HYDROGEN STORAGE USING FULLERENE MATERIALS: CHEMICAL AND PHYSICAL ADSORPTION

A.V.Talyzin, IMRA-EUROPE S.A. (private research company), Sophia Antipolis, France

Hydrofullerides with hydrogen content up to 5 at.% were obtained by following methods:
- direct reaction with hydrogen gas -
- catalytic reaction with hydrogen gas -
- transfer hydrogenation reaction using 9,10-Dihydroanthracene (DHA).

Characterisation of obtained samples was performed using XRD, Raman and IR spectroscopies. Hydrogen content (for reaction with hydrogen gas) was monitored in situ using gravimetric system and verified by chemical analysis ex situ. It was found that pure C60 reacts rapidly when exposed to H2 gas at 673K and 50-100Bar. Gravimetric study of this reaction showed that hydrogenation is saturated at about 5 at.% of hydrogen. Hydrofullerenes with higher hydrogen content are not stable and strong hydrogenation results in collapse of C60 molecules. XRD study showed that these samples retain an original FCC structure with increase of cell parameter. Catalytic hydrogenation of C60 with hydrogen gas results in decrease of the reaction temperature and formation of hydrofullerides with structures other then fcc. Formation of C-H bonds in hydrogenated samples was also confirmed by IR spectroscopy. Physical sorption near the room temperature was studied for different fullerene based materials: C60 polymers, oxides, some organic derivatives. Long time ball milling treatment was used to produce ultra dispersed samples of C60 and C60/metal mixtures. For all these samples adsorption of hydrogen was found below 1 Wt%.

C-X.2 17:20

MEASURING REVERSIBLE H STORAGE IN C AND Si-DOPED C NANO-FIBERS FROM ISOVOLUMETRIC DESORPTION TESTS

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Isovolumetric Desorption Experiments (IDE) offer the way to characterise macroscopically new materials as reversible H loader/de-loaders. In such as tests, the material is charged with H in a close reservoir at given temperature and pressure. A very fast pumping of the reservoir breaks equilibrium conditions and makes the H stored to release from the material. During the three phases (loading/pumping/releasing) the H pressure signal is registered. Results derived from IDE have been largely validated in the past for diverse series of metallic, ceramic and composite materials. In parallel, specific models to derive hydrogen solubility from IDE were developed.

H storage in bundles of long C and Si-doped (1:10 ratio) C fibres separated at nanometric distances of about ~ 20 nm have been investigated at low pressures up to high temperatures. Fibre arrays stand within a pyrolised-carbon matrix structure. Thus a specific analysis of the H sorption and desorption signal is done in order to discriminate the net and reproducible bundles' H pressure signal contribution. Reversibility of the sorption/desorption processes itself, meaning an important issue for the final qualification of the material, is directly assessed by IDE. Even if obtained values are below the expectable of litres per gram of storing material that have being reported in the field's literature for tubular, herringbone or platelet GNF nano-structures the results reported show a promising hydrogen reversible storage capability for such as system when compared with other materials and alloys (Pd, LaxNiy, MnxNiyAlz) activated carbon or graphite. Values of 0.77 l/g at RT and h.p. are derived.

C-X.3 17:40

CARBON NANOTUBES FOR SUPERCAPACITOR APPLICATION

E. Frackowiak, K. Jurewicz, K. Lota ICTE, Poznan University of Technology, ul. Piotrowo 3, 60-965 Poznan, Poland and S. Delpeux, F. Béguin CRMD, CNRS-Universite, 1B rue de la Ferrolerie, 45071 Orleans, France

Carbon nanotubes were carefully investigated for supercapacitor applications. The values of capacitance widely range from 5 to 80 F/g depending on their surface area, micropores, catalyst impurities and presence of amorphous carbon. An increase of capacitance was reached by functionalization with hot nitric acid but aggravation was observed during cycling. A chemical KOH activation was an attractive method for development of microporosity and a few-fold increase of capacitance values was reached. Another way to enhance the specific capacitance is the preparation of carbon nanotubes/conducting polymers composites. Such a modification supplies apart from electrostatic attraction also stable pseudocapacitance effects. In the case of nanotubes/polypyrrole composites the capacitance values reached ca. 200 F/g with a good cycleability over 2000 cycles. Conducting polymer deposited on nanotubular network supplies a perfect three-dimensional volumetric charge distribution.

C-X.4 18:00

SUPERCAPACITOR ELECTRODES FROM NEW ORDERED POROUS CARBON MATERIALS OBTAINED BY A TEMPLATING PROCEDURE

C. Vix-Guterl(a), S. Saadhallah(a), E. Frackowiak(b), K. Jurewicz(b), J. Parmentier(c), J. Patarin(c), F. Beguin(d), (a)Institut de Chimie des Surfaces et Interfaces, UPR CNRS 9069, 15 rue Jean Starcky, B.P. 2488, 68057 Mulhouse Cedex, France, (b)Poznan University of Technology, ul. Piotrowo 3, 60-965 Poznan, Poland, (c)Laboratoire de Matériaux Minéraux, Ecole Nationale Supérieure de Chimie de Mulhouse, UMR CNRS 7016, Université de Haute Alsace, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France, (d)Centre de Recherche sur la Matière Divisée, UMR 6619 CNRS-Université d'Orléans, 1B rue de la Férollerie, 45071 Orléans Cedex2, France

An interesting porous carbon material with a highly ordered pore structure and a well balanced micro-mesoporosity was successfully prepared by a templating procedure using organised mesoporous silica (MCM-48, SBA-15) as template. Carbon was introduced into the silica matrix via two routes (gas phase and liquid impregnation). After dissolution of the silica matrix by hydrofluoric acid, a carbon material with a controlled porosity is obtained corresponding to the negative replica of the silica matrix. Its properties will be discussed in relation to the type of silica matrix used as template, the preparation route and the nature of the carbon precursor. In all cases, this synthesis strategy leads to a carbon materials with an interconnected porosity and optimal characteristics for using it as active material for supercapacitor electrodes. The performance of supercapacitors was investigated in acidic, alkaline and organic electrolytic solutions. High values of capacitance (130-200F/g) were obtained with a rectangular shape of cyclic voltammograms over a wide range of scan rates indicating a quick charge propagation. Detailed characteristics of supercapacitors such as frequency response, leakage current and self-discharge were carefully studied.

Session XI: Fuel Cells and nanomaterials
Session chair: A. Pundt

C-XI.1 09:00 -Invited- NANOSCALE MATERIALS FOR ELECTROCHEMICAL ENERGY CONVERSION IN POLYMER ELECTROLYTE FUEL CELLS

K.A. Friedrich, J. Garche, Center for Solar Energy and Hydrogen Research Baden-Wuerttemberg, Division 3: Energy Storage and Conversion, Helmholtzstraße 8, 89081 Ulm, Germany

Nanoscale materials play an important role in low temperature fuel cell technology and are discussed in this contribution. For example, in fuel cells with a proton conducting membrane, e.g. polymer electrolyte fuel cells (PEMFC) and direct methanol fuel cells (DMFC), the catalysts consist of particles of Pt or Pt alloys, which are of nanometer size and often supported on carbon in order to optimize the surface area as well as minimize the costs of the noble metals. The fuel cells are often operated with reformer gas which leads to a high content of carbon monoxide in the fuel gas. Therefore, the development of catalysts particles in gas-diffusion electrodes is aimed at improving the structural stability optimizing the chemical composition and achieving a high CO tolerance.

Also for the reactions in the peripheral reactors used in fuel cell technology, e.g. the PROX reactor, the use of nanoscale materials is crucial. The reactor accomplishes the selective (preferential) CO oxidation in H2-rich gases (PROX) which is employed for the purification of feed gas streams for PEM fuel cells. In particular, oxide supported Au catalysts (Au/MeOx) have been shown to exhibit an outstanding activity already at low temperatures of 90 °C for several hydrogenation and oxidation reactions, in particular for CO oxidation. The mechanism of this high activity is associated with the nanometer size of the gold particles and with the facile supply of oxigen via the support.

C-XI.2 09:40 NANOSIZED POROUS Si FOR FUEL CELL APPLICATIONS

H. Presting(a), J. Konle(a), V. Starkov(b), A. Vyatkin(b) and U. König (a), (a)DaimlerChrysler Research, Wilhelm-Runge-Str-11, 89081 Ulm, Germany, (b)Institute of Microelectronics Technology, Russian Academy of Sciences, 142432 Moscow District, Chernogolovka, Russia

Randomly, self-organized and ordered anodically etched porous silicon with pore sizes down to hundred nanometers have been fabricated for a variety of automotive applications which range from carrier structures in fuel cells up to shower heads for fuel injection in combustion engines. The porous wafers are produced by deep anodic etching which is a very effective and cheap fabrication method compatible to standard Si CMOS fabrication technology. The density of nano- (and micro-) pores can be varied in a wide range by choice of substrate doping level and appropriate electrolyte solution. Surface enlargement up to a factor of 1000 can be achieved [1]. After deposition of a catalyst on the inner surface of the pores these structures can be used as an effective catalytic reaction area for the injected hydrocarbons in a micro-steam reformer unit with a small reaction volume. The accompanying fuel cell is used as auxiliary power unit (APU) for the energy supply of the on-board electronics in vehicles [2]. In addition deep anodic etching (DAE) of a pinhole array with very high aspect ratios is demonstrated using a pre-patterned inverted pyramidal array which is produced by lithography and subsequent wet chemical potassium hydroxide (KOH) etch. The structures are also used as carrier structures for hydrogen separation of the reforming gas in a fuel cell reformer unit when a thin layer of palladium is evaporated prior to the anodic etching of the pores. The noble metal foil serves as anode contact during the etch as well as hydrogen separating membrane of the device.

[1]A. Vyatkin, V. Starkov, V. Tzeitlin, H. Presting, J. Konle, and U. König. Random and Ordered Macropore formation in p-Type Silicon. Journal of the Electrochemical Society,149(1) G70-G76 (2002)-

[2]J.Konle, H.Presting, U.König, V.Starkov, and A.Vyatkin. Nano-sized pore formation in p-type silicon for automotive applications. Proc. 2ed IEEE –NANO2002, pp.457-460

C-XI.3 10:00 SURFACE HYDROGEN COVERAGE OF AS-PREPARED NANOCRYSTALLINE POROUS SILICON

P. Martín, J.F. Fernández and C. Sánchez, Dpto. Física de Materiales, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco 28049 Madrid, Spain

Nanocrystalline porous silicon (PS) has been extensively studied after the discovering of its room temperature visible photo-luminiscence. PS is formed by electrochemical etching of crystalline silicon in an electrolyte containing HF. During this process, silicon atoms are dissolved by the HF acid leaving a porous skeleton of nanocrystalline silicon. After preparation the PS surface is covered by hydrogen atoms which passivate the silicon dangling bonds. A study of the PS surface coverage by hydrogen has been done by Thermal Desorption Spectroscopy (TDS). The desorption rate of H2 and SiHx molecules was monitored with a mass spectrometer during linear heating of the samples in vacuum. The almost simultaneous desorption of several species containing hydrogen gives rise to a complicated TD spectra. The full spectra can be understood as due to the desorption from different bonding states of the hydrogen atom on the PS surface, namely a Si-H surface monohydride, a Si-H2 dihydride and an Si-H3 trihydride. In order to obtain clean spectra for a kinetic analysis, as prepared samples were annealed at selected temperatures to isolate the contributions from the different bonding states. From these experiments a detailed knowledge of kinetic parameters for the desorption process has been obtained. In this communication, the order of the reaction, activation energy and preexponential factor for the desorption of each hydrogen bonding state will be presented.

10:20 **BREAK**

Session XII: Li-batteries
Session chair: M. Jurczyk

C-XII.1 10:50 -Invited- NEW INTERPRETATIONS ON THE INSERTION PROPERTIES OF NANOSTRUCTURED CARBONS USED IN RECHARGEABLE Li-Ion Batteries

François Béguin, Centre de Recherche sur la Matière Divisée, CNRS-Université d'Orléans,

Negative electrodes of Lithium-Ion batteries are generally based on graphite. Higher storage capacities can be obtained with nanostructured carbons, however they demonstrate a noticeable hysteresis and irreversibility, which can preclude a practical application. In this paper, the main parameters which affect the reversible and irreversible capacities are analyzed, and new interpretations for the electrochemical behavior of nanostructured carbons in lithium batteries are proposed.

The irreversible lithium consumption which occurs at the negative carbon electrode during the first charge (Cirr) is related to the active surface area (ASA). The ASA of a hard carbon has been reduced to a value smaller than graphite after coating with a thin film of pyrolytic carbon, keeping the profit of more than 50% higher reversible capacity. For the first time, in-situ solid-state 7Li-Nuclear Magnetic Resonance (7Li-NMR) spectra have been successfully recorded during the galvanostatic cycling of a supple ultra-thin plastic lithium/carbon cell, allowing the electronic state of the reversibly stored lithium to be determined. Crossing these data with TEM observations on the host carbon, we propose a model which shows that lithium first occupies the small intervals between nanometer size graphitic type layers and then penetrates in nanopores where growing quasi-metallic clusters are formed.

C-XII.2 11:30 -Invited- BENEFICIAL ROLE NANO PARTICLES WITHIN THE FIELD OF RECHARGEABLE LI BATTERIES

J.-M.Tarascon, S. Grugeon, S. Laruelle, D. Larcher and L. Dupont, Laboratoire de Réactivité et Chimie des Solides, Université de Picardie Jules Verne and CNRS (UMR-6007), 33 rue Saint Leu, 80039 Amiens, France

Nano-materials, characterized by a fine grain size, have attracted a lot of interest in recent years due to their unusual mechanical, electrical and optical properties, and are now at the origin of today’s staggering microelectronic progresses. They are presently capturing the field of energy storage. To stress this point, a few novel nano particle-driven findings such as 1) the sustained reversibility of conversion reactions involving up to 2 or 3 electrons per 3d-metal, 2) the feasibility of conducting insertion reactions in numerous disregarded poorly conducting inorganic materials, and 3) the unexpected achievement of Li-driven room temperature chemical/alloying reactions will be detailed. However, although a very attractive and rich domain of investigation lies behind the issue of using nano-materials within the field of energy storage, there are practical considerations that need to be strongly observed in order not to stray from the original idea.

12:10 **CLOSING**

12:30 **LUNCH**