# MM 14: Functional Materials - Hydrogen

Time: Monday 15:45–18:15 Location: H26

MM 14.1 Mon 15:45 H26

**Design and synthesis of core/shell $SnO_2/MnO_2$ nanotube arrays for high performance supercapacitor application** — •Fabian Grote, Huaping Zhao, Ranjith Vellacheri, and Yong Lei — Fachgebiet 3D-Nanostrukturierung, Institut für Physik & IMN MacroNano (ZIK), Technische Universität Ilmenau, Prof. Schmidt Str. 26, 98693 Ilmenau, Germany.

Recently, we focused on the development of nanostructured three-dimensional electrode materials for applications in supercapacitor devices. Therefore, we developed a synthesis process to fabricate nanostructured free-standing core/shell $SnO_2/MnO_2$ nanotube arrays. The core/shell nanotube arrays were prepared by atomic layer deposition (ALD) of $SnO_2$ into porous alumina membranes and a subsequent coating by $MnO_2$. The essential features of this structure are its high surface area, hollow nature of the structure, good conformal coating of the $SnO_2$ nanotubes with $MnO_2$, and the desired core/shell structure. The electrochemical performance of the prepared electrodes was studied in CV, charge/discharge, and long-term cycle stability experiments and exhibited excellent performance. These results so far address key challenges of supercapacitors and shall pave the way to realize a high performance supercapacitor with not only high power density, but also high energy density. For further investigation the morphology of the core/shell $SnO_2/MnO_2$ nanotube arrays was analyzed by SEM and TEM. The chemical composition was determined by XPS, EELS, and XRD measurements.

MM 14.2 Mon 16:00 H26

**High-performance supercapacitors based on orderd nanoarrays** — •Ranjith Vellacheri, Huaping Zhao, Ahmed Al-Haddad, Fabian Grote, and Yong Lei — Fachgebiet 3D-Nanostrukturierung , Institute fur Physik & IMN MacroNano (ZIK), Technische Universitaet Ilmenau, Prof. Schmidt Str. 26, 98693 Ilmenau, Germany

Supercapacitors are electrochemical energy storage devices potentially useful for high power demanding applications. Three-dimensional nanostructures of metal oxides and conducting polymers are considered as promising candidates for the development of high-performance supercpacitor electrodes. Here, we will discuss about the preparation of different kinds of nanoarrays such as nanotube arrays and core-shell nanowire arrays, by using anodic alumina nano-templates. Alumina templates can be employed to make well ordered three-dimensional nanostructures with superior surface properties. Our strategies mainly include the preparation of MnO2 and PEDOT nanotube arrays, Ni-NiCo2O4 core-shell nanowire arrays and NiCo2O4-TiO2-NiCo2O4 sandwich-structured nanotube arrays, and the fabrication of supercapacitors by utilizing these nanoarrays shall be useful for wide range of applications.

MM 14.3 Mon 16:15 H26

**Nano-engineered three-dimensional Pt/MnO2 thin films for flexible, high performance supercapacitors** — •liaoyong wen, yan mi, fabian grote, ahmed al haddad, zhibing zhan, huaping zhao, and yong lei — Institut für Physik & IMN MacroNano* (ZIK), Institute for Physics and IMN MacroNano* (ZIK), Technische Universität Ilmenau, Ilmenau, Germany

Supercapacitors, also called ultracapacitors or electrochemical capacitors (ECs), have become some of the most promising candidates for next-generation power devices because of their high power density, fast charging-discharging rate, and excellent cycle stability. Manganese Oxide (MnO2), owing to its high theoretical specific capacitance, has been considered to be one of the most attractive electrode materials for supercapacitors. Here we construct mechanically flexible three-dimensional thin film supercapacitors by assembling nano-engineered Pt/MnO2 electrodes, prepared in anodic alumina nano-porous templates with Atomic Layer Deposition (ALD) technology and electrodeposition process. The well-defined three-dimensional Pt nanostructures, acting as electrodes and also current collectors, address the inherit disadvantage of the poor electrical conductivity (10-5*10-6 S/cm) of MnO2. Meanwhile, the nanostructured morphology of the Pt electrode can provide very large surface, which largely enhance the energy and power density of the supercapacitors. The much improved performance (energy and power density) and excellent mechanical flexibility of the supecapacitor make it a unique design in various power delivery applications.

MM 14.4 Mon 16:30 H26

**Synthesis and characterization of nanoparticulate $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ cathodes for thin film solid oxide fuel cells** — •Cahit Benel[1,2,3], Azad J. Darbandi[1,2], Anna Evans[4], René Tölke[4], Michel Prestat[4], and Horst Hahn[1,2] — [1]Institute for Nanotechnology, Karlsruhe Institute of Technology, Germany — [2]Joint Research Laboratory Nanomaterials, Technische Universität Darmstadt and Karlsruhe Institute of Technology, Germany — [3]Center for Functional Nanostructures, Karlsruhe Institute of Technology, Germany — [4]Nonmetallic Inorganic Materials, ETH Zurich, Switzerland

Solid oxide fuel cell cathode materials with mixed ionic and electronic conductivity (MIEC) such as strontium doped lanthanum cobalt oxide ($La_{0.6}Sr_{0.4}CoO_{3-\delta}$) show enhanced oxygen reduction kinetics compared to the conventional cathode materials. In this work, nanocrystalline $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) powder with ultrafine microstructure and high specific surface area (60 $m^2/g$) was synthesized via salt-assisted spray pyrolysis method. Nanoparticulate cathode thin films of LSC and LSC-GDC (Gadolinium doped ceria) with thicknesses between 150 and 500 nm were prepared via single step spin coating of water-based nanodispersions on yttria stabilized zirconia (YSZ) substrates. LSC cathode thin films (250 nm) with 30 wt% GDC content exhibit the lowest area specific resistance (ASR) values of 0.32, 0.78 and 2.04 $\Omega.cm^2$ in ambient air at 650, 600 and 550 °C, respectively. The future work will focus on detailed chemical and microstructural analysis of the nanoparticulate thin film cathodes to gain more understanding on the electrochemical processes.

MM 14.5 Mon 16:45 H26

**Diffusion of hydrogen in strained Fe and Ni lattices** — •Davide Di Stefano, Matous Mrovec, and Christian Elsaesser — Fraunhofer Institute For Mechanics Of Materials IWM, Freiburg, Germany

A correct description for the diffusion of hydrogen in metals is prerequisite for understanding the phenomenon of hydrogen embrittlement. The H diffusion in bulk materials has been studied extensively in the past both experimentally and theoretically. Nevertheless, the knowledge of diffusion processes in distorted environments, e.g. in the vicinity of crystal defects, is still limited.

In this comparative study, we perform atomistic calculations of diffusion barriers in strained structures of Fe and Ni using accurate first-principles methods based on the density functional theory and semi-empirical tight binding. Our results show that the diffusion barriers are indeed strongly influenced by the lattice distortions and depend sensitively on the type of deformation. In addition, our analysis confirms that a proper treatment of quantum effects is crucial for a reliable theoretical determination of the diffusion barriers.

MM 14.6 Mon 17:00 H26

**Influence of hydrogen on Gd(0001) thin films** — •Sara Wanjelik, Volkmar Hess, and Mathias Getzlaff — Institute of Applied Physics, University of Düsseldorf

Hydrogen in metals as an area of research has been of great interest for the past few decades. But only few investigations are carried out by imaging techniques with resolution on the nm-scale. Even less works deal with the inital stage of hydride formation.

Here we present STM measurements on thin Gadolinium films grown on a W(110) surface concentrating on the inital steps of hydrogen absorption. Due to the existence of a surface state only on the clean Gd(0001) surface, hydrogen covered areas appear lower in the topography image. Consequently, we can estimate the coverage and the time being necessary for absorption due to the reappearance of the surface state. Our measurements show that there is a lower limit for the amount of hydrogen to initiate the absorption process.

With increasing absorption hydride formation occurs. The larger volume of the hydride results in plastic deformations. On the one hand, there are disk-like islands with a diameter of approximately 3 nm and a height of 0.3 nm, while on the other hand there are coherent areas formed by ramps. The islands were found to arrange in chains. Therefore, we concentrate particularly on the direction of the chains being indicative for crystallographic properties inside the film.

MM 14.7 Mon 17:15 H26

**In-situ EELS studies on the dehydrogenation of nanocrystalline $MgH_2$** — •Alexander Surrey[1,2], Inge Lindemann[1,2], Christian Bonatto Minella[1], Ludwig Schultz[1,2], and Bernd Rellinghaus[1] — [1]IFW Dresden, Institute for Metallic Materials, P.O. Box 270116, D-01171 Dresden, Germany — [2]TU Dresden, Institut fur Festkörperphysik, D-01062 Dresden, Germany

In the field of hydrogen storage there is a still ongoing search for a material that provides both high $H_2$ storage density and good $H_2$ sorption properties. Here, nanosized or nanoconfined hydrides promise improved thermodynamics and kinetics. As for the structural characterization utilizing TEM, however, most materials degrade fast upon the irradiation with the imaging electron beam due to radiolysis. $MgH_2$ is one of the best studied binary hydrides due to its relatively high storage capacity of 7.6 wt.% $H_2$. Therefore, ball milled $MgH_2$ was used as a reference material for in-situ TEM experiments on submicron particles. Hereto, EELS measurements were conducted in an aberration-corrected FEI Titan$^3$ 80-300 microscope. From an observation of the plasmonic absorptions it is found that $MgH_2$ successively converts into Mg upon electron irradiation. The temporal evolution of the spectra is analyzed quantitatively to determine the fractions of pure and hydrogenated Mg at different stages of the reaction and to determine the critical electron doses for both incident electron energies of 80 keV and 300 keV. By comparing these critical doses the dehydrogenation kinetics of individual particles can be investigated. This understanding is also crucial for TEM studies on other hydrides such as $AlH_3$.

MM 14.8 Mon 17:30 H26

**Hydrogen Retention in Metals** — •Katrin Peeper[1], Marcus Moser[1], Patrick Reichart[1], Elena Markina[2], Matej Mayer[2], Zhijie Jiao[3], and Gary Was[3] — [1]Universität der Bundeswehr, Angewandte Physik und Messtechnik, München, Germany — [2]Max-Planck-Institute for Plasma Physics, EURATOM Association, Garching, Germany — [3]Department of Engineering and Radiological Sciences, College of Engineering, University of Michigan, Ann Arbor, MI, USA

Degradation of wall materials used in fission and fusion reactors due to extreme conditions and radiation is investigated in order to develop improved materials. Hydrogen plays a key role in metal embrittlement and is trapped at various natural and ion induced defects. We present detailed study of the hydrogen retention in tungsten in 3 dimensions and its correlation with structural features e.g. grain boundaries and blisters performed by proton-proton-scattering.

We show that we obtain a sensitivity better than 10^15 at/cm^2 (2 at-ppm) in metals. We utilised 22 MeV protons to study hydrogen distributions in 50 um Stainless Steel and 25 um Tungsten samples. The steel samples have been irradiated with 2 MeV protons. The depth profiles show that less than 0.3% of the implanted hydrogen is retained and is localized mostly in the end of range peak. The Tungsten samples have been implanted using a Hydrogen ion beam with the energy of 200 eV/H. At these conditions, which mimic the conditions in future fusion reactors, blisters and cracks are created in the near-surface layer due to hydrogen-induced stress in the material.

MM 14.9 Mon 17:45 H26

**Quantitative 3D Microscopy of Hydrogen by Proton-Proton Scattering** — •Marcus Moser[1], Stefan Wagner[2], Katrin Peeper[1], Patrick Reichart[1], Astrid Pundt[2] und Günther Dollinger[1] — [1]Universität der Bundeswehr München, 85579 Neubiberg, Germany — [2]Institut für Materialphysik, Universität Göttingen, Göttingen 37077, Germany

Proton-proton scattering at the Munich microprobe SNAKE gives the unique possibility for sensitive 3D hydrogen microscopy [1]. Quantification of the hydrogen content without the need of any reference sample, a sensitivity of few or even less than one atomic part per million, a lateral resolution of about 1 *m and a depth resolution of a few micrometers are the main characteristics. We use proton energies between 10 MeV and 25 MeV for analyzing any kind of unsupported samples with thickness between 10 um and 250 um depending on the atomic density of the investigated material. With this method, we measured hydrogen in thin Nb-films. The Nb- films with a thickness of 700nm are electrochemically doped with hydrogen. We have been able to detect and quantify lateral hydrogen distributions and variations induced by hydrogen charging. Hydrogen within the crystallites was measured to be below 0.08 at-ppm.

References [1] P. Reichart, et al., Science 306 (2004) 1537.

MM 14.10 Mon 18:00 H26

**Changes in the Electronic Structure of Deuterium Implanted Molybdenum and Rhodium** — •Baran Eren, Laurent Marot, Marco Wisse, Roland Steiner, and Ernst Meyer — Klingelbergstrasse 82 4056 Basel Schweiz

In this presentation, two recent works of our group are going to be presented. In the first work molybdenum coatings and in the second work rhodium coatings were treated with low temperature deuterium plasma. Both are considered as candidates as light reflection components in the next generation fusion reactors, therefore changes in their electronic properties may be important for the optical diagnostic systems.

It is shown that hydrogen acts as an electron acceptor in molybdenum, but an electron donor in rhodium. Both cases are investigated with various experimental techniques including photoelectron spectroscopy, spectroscopic ellipsometry, spectroscopic reflectometry, spectrophotometry, specific resisvity and direct surface morphology imaging techniques. Rhodium/hydrogen system is not stable in air due to a catalytic reaction between hydrogen and oxygen, whereas molybdenum/hydrogen system is stable because hydrogen is strongly bound to defect sites.