

Applied Surface Science

Room 210A - Session AS-ThA

Fuel Cell, Catalytic, and Nanomaterials Characterization

Moderator: B. Beard, Akzo Nobel Chemicals

2:20pm **AS-ThA2 Nanoscale Effects on Ion Conductance of Layer by Layer Structures of Gadolinia-doped Ceria and Zirconia**, *S.A. Azad, A.A. El-Azab, L.S. Saraf, O.M. Marina, C.W. Wang, D.E. McCready, S.V. Shutthanandan, S.T. Thevuthasan*, Pacific Northwest National Laboratory

Development of electrolyte materials that possess high oxygen ion conductance at relatively low temperatures is essential to improve the performance of electrochemical devices. Ceria, doped with a divalent or trivalent cation, exhibits higher ion conductance compared with yttria-stabilized zirconia, the major component currently used in solid oxide fuel cells (SOFC). In this research, we have synthesized layer by layer structures of gadolinia doped ceria and zirconia in order to determine the nanoscale effects on the ion conductance of these films. Highly oriented multilayered nanostructures of gadolinia-doped ceria and zirconia were grown on sapphire substrates using molecular beam epitaxy and were characterized by in situ reflection high energy electron diffraction (RHEED) and ex situ x-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and Rutherford backscattering spectrometry (RBS). The oxygen ion conductance, measured by surface impedance spectroscopy at relatively low temperatures, was found to increase with increasing number of layers in these films. Theoretical calculations were also performed to understand the effects of space charge regions induced by the thermodynamic equilibrium and impurity segregation as well as the influence of the grain microstructures on the electric transport processes in solid oxide materials. The defect electrochemistry model developed in our study allows the extrinsic element (Gd) to transfer across the interfaces and space charge regions are created as a result, counterbalancing the purely blocking effect observed in polycrystalline structures of ceria or zirconia. The elastic interactions in ceria and zirconia lattice as well as the individual layer thickness largely influence the transfer of Gd across the interfaces.

2:40pm **AS-ThA3 Physical and Chemical Properties of Ce@sub1-x@Zr@subx@O@sub2@ Nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) Surfaces: Synchrotron-based Studies**, *X. Wang, J.A. Rodriguez, G. Liu, J.C. Hanson, J. Hrbek*, Brookhaven National Laboratory; *C.H.F. Peden*, Pacific Northwest National Laboratory; *A. Iglesias-Juez, M. Fernández-García*, Instituto de Catálisis y Petroleoquímica, CSIC, Spain

The physical and chemical properties of Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces ($x \leq 0.5$) were investigated with synchrotron-based techniques (high-resolution photoemission, time-resolved X-ray diffraction and X-ray absorption near-edge spectroscopy). CeO@sub2@ and Ce@sub1-x@Zr@subx@O@sub2@ particles in sizes between 3 and 7 nm were synthesized using a novel microemulsion method. The results of XANES (O K-edge, Ce and Zr LIII-edges) indicate that the Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces have very similar electronic properties. The lattice constant decreased with increasing Zr content, varying from 5.40Å in CeO@sub2@ to 5.27Å in Ce@sub0.5@Zr@sub0.5@O@sub2@. Within the fluorite structure, the Zr atoms exhibited structural perturbations that led to different types of Zr-O distances and non-equivalent O atoms in the Ce@sub1-x@Zr@subx@O@sub2@ compounds. The nanoparticles were more reactive towards H@sub2@ and SO@sub2@ than the (111) surfaces. The Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces did not reduce in hydrogen at 300°C. At temperatures above 250°C, the Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles reacted with H@sub2@ and water evolved into gas phase. XANES showed the generation of Ce@super3+@ cations without reduction of Zr@super4+@. There was an expansion in the unit cell of the reduced nanoparticles probably as a consequence of a partial Ce@super4+@->Ce@super3+@ transformation and the sorption of hydrogen into the material. S K-edge XANES spectra pointed to SO@sub4@ as the main product of the adsorption of SO@sub2@ on the Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces. Full dissociation of SO@sub2@ was seen on the nanoparticles but not on the (111) surfaces. The metal cations at corner and edge sites of the nanoparticles probably play a very important role in interactions with the H@sub2@ and SO@sub2@ molecules.

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3:00pm **AS-ThA4 Physical and Chemical Properties of Iron and Iron-Oxide Nanoparticles @footnote 1@**, *D.R. Baer, J.E. Amonette*, Pacific Northwest National Laboratory; *J. Antony*, University of Idaho; *J.C. Linehan, D.W. Matson*, Pacific Northwest National Laboratory; *J.T. Nurmii*, Oregon Health and Sciences University; *K.H. Pecher*, Pacific Northwest National Laboratory; *R.L. Penn*, University of Minnesota; *Y. Qiang*, University of Idaho; *P.G. Tratnyek*, Oregon Health and Sciences University

Iron particles in solution have interesting and potentially useful chemical properties, including an ability to reduce chlorinated hydrocarbons in geochemical environments. Reaction studies indicate that the dechlorination reaction pathway can be altered by the structure and chemistry of the nanoparticles. To understand some of these effects we are synthesizing, characterizing, and examining the properties of Fe nanoparticles using a variety of methods. We have synthesized particles in solution and by vapor deposition methods and obtained commercially available materials for detailed study. Methods of particle characterization include TEM, XAS, Mossbauer, XRD, and XPS. A variety of properties are being examined including stability, physical, chemical and electronic structure, magnetic properties and reactivity. Similarities and differences of particles formed in different ways will be discussed along with results relating to particle stability and the impact of particle preparation and processing on reactivity in solution. @FootnoteText@ @footnote 1@ This work is supported by the US Department of Energy Office of Science and parts of the work were performed in the Environmental Molecular Sciences Laboratory a national scientific user facility sponsored by the DoE's Office of Biological and Environmental Research.

3:20pm **AS-ThA5 High-Pressure X-Ray Photoelectron Spectroscopy for Catalysis Research and Environmental Science**, *H. Bluhm, D.F. Ogletree*, Lawrence Berkeley National Lab; *G. Ketteler*, Lawrence Berkeley National Lab, Univ. of California; *M. Haevecker, A. Knop-Gericke, E. Kleimenov, D. Teschner*, Fritz Haber Inst. of the Max Planck Society, Germany; *E.L.D. Hebenstreit*, Lawrence Berkeley National Lab; *V.I. Bukhtiyarov*, Borekov Inst. of Catalysis, Russia; *M.K. Gilles, T. Tyliszczak*, Lawrence Berkeley National Lab; *R. Schloegl*, Fritz Haber Inst. of the Max Planck Society, Germany; *M. Salmeron, D.K. Shuh*, Lawrence Berkeley National Lab

High-pressure X-ray photoelectron spectroscopy is a versatile method for the study of gas/solid and gas/liquid interfaces. Recently two synchrotron-based high-pressure XPS spectrometers have been developed, one located at the Molecular Environmental Science beamline at the Advanced Light Source in Berkeley, the other operating at BESSY in Berlin. We have used these high pressure XPS instruments to investigate problems in environmental science and heterogeneous catalysis. In this talk we will discuss the influence of the gas phase on the XPS spectra. Since the incident X-ray beam does not only irradiate the sample surface but also the gas phase in front of the sample, gas phase XPS peaks appear alongside the surface peaks at sufficiently high pressures. The gas phase signal can be used to probe the composition of the gas in the volume in front of the sample and get information about, e.g. the conversion and yield in heterogeneous catalytic reactions. An important group of materials in environmental science are minerals, which are often insulators and therefore charge when irradiated by X-rays. However, the sample surface is discharged due to the ionization of the gas phase by the incident X-rays. The amount of this effect depending on gas pressure and composition will be discussed. We will also consider the proper referencing of the binding energy, and the FWHM of the gas phase peaks depending on gas pressure and work function of the surfaces in the vicinity of the probed gas phase volume. @FootnoteText@ The Advanced Light Source and this work are supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and the Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy at Lawrence Berkeley National Laboratory under Contract No. DE-AC03-76SF00098.

3:40pm **AS-ThA6 The Structure and Growth of Single- and Double-Walled Carbon Nanotubes**, *J.-M. Zuo*, University of Illinois at Urbana-Champaign
INVITED

Single- and double-walled carbon nanotubes have potential applications for future electronics and nanomachines. However, as-grown carbon nanotubes have a dispersion of structures, which differ in both diameter and chirality, and electric and mechanical properties. Characterization of these nanotubes has been a challenge. Recently, we developed a coherent electron diffraction/imaging technique by forming a nanometer-sized parallel beam of electrons that can be used to record diffraction patterns from individual nanotubes. Furthermore, the combination of coherence

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and high angular resolution allows the over-sampling of diffraction pattern and solution of phase problem by ab initio phase retrieval, thus, imaging of carbon nanotubes. Using this technique, we have investigated a large number of single- and double-walled carbon nanotubes. We found that neither zig-zag nor arm-chair tubes is preferred for growth. Double-walled carbon nanotubes are generally incommensurate and there is a peaked distribution of spacings between two tubes. The implication of these findings will be discussed based on the growth mechanism of carbon nanotubes. The technique of coherent electron nanodiffraction and diffractive imaging by the solution of the phase problem is general and applicable to other nanostructures. @FootnoteText@ *In collaboration with J. Tao, J. Bording, Boquan Li, M. Gao, L. Nagahara, R. Zhang, R. Twesten and I. Petrov.

4:20pm AS-ThA8 Carbon Nanotubes and Mo@sub 2@C Reduced Pt Usage for Fuel Cells, T. Matsumoto, T. Komatsu, University of Tsukuba, Japan; Y. Chiku, Sekisui Chemical Co., LTD., Japan; Y. Nagashima, T. Yamazaki, E. Yoo, University of Tsukuba, Japan; H. Shimizu, Y. Sato, Y. Takasawa, Sekisui Chemical Co., LTD., Japan; J. Nakamura, University of Tsukuba, Japan

Pt has been considered to be an essential catalyst for the polymer electrolyte fuel cell (PEFC), and one of the difficulties in spreading fuel cells due to the high price, limited resource and no substitute of Pt. We successfully reduce Pt loads by using carbon nanotubes and Mo@sub 2@C. The PEFC with the 0.2 mg/cm@super 2@-Pt/CNT catalyst is found to show higher cell voltage at 0-600 mA/cm@super 2@ than that of the PEFC with the 0.5 mg/cm@super 2@-Pt/CB catalyst. The PEFC with the only 0.06 mg/cm@super 2@-Pt/CNT gives more than 60% of the cell voltage of the PEFC of the 0.5 mg/cm@super 2@-Pt/CB catalyst at 0-600 mA/cm@super 2@. Carbon nanotubes (CNTs) are better electrodes of Pt than carbon blacks (CBs) presumably due to the more triple-phase formation, better conductivity and more space for gas diffusion [J. Nakamura et al., Chem. Comm., 2004, 840 and Catal. Today, in press]. TEM images showed that 2-4 nm Pt nanoparticles are deposited on the CNT surfaces. The Pt nanoparticles from H@sub 2@PtCl@sub 6@ are well-dispersed, while those from K@sub 2@PtCl@sub 4@ are agglomerated due to an auto catalytic reaction. XPS spectra show Pt was fully reduced to be deposited as metallic Pt nanoparticles. The pretreatment of CNTs to remove amorphous carbon is also important, and a careful treatment is necessary for dissolution by HNO@sub 3@ not to form bundles. We also find that Mo@sub 2@C can be a substitute of Pt for PEFC. It is surprising that a PEFC with the Mo@sub 2@C/CNT catalyst in the anode exhibits 60% cell voltages of the current PEFC with the Pt/CB catalyst (0.5 mg/cm@super 2@). XPS and XRD showed that Mo was fully carburized to form Mo@sub 2@C nanoparticles.

4:40pm AS-ThA9 Surface Characterization and Surface Science Needs in Support of Automotive Fuel Cells, F.T. Wagner, General Motors Fuel Cell Activities

INVITED

Polymer electrolyte membrane fuel cells (PEMFC's) show promise as power sources for high-efficiency light-duty vehicles giving very low emissions. This talk reviews some of the critical interfacial phenomena that must be understood if this promise is to be fully realized. Examples will be given of cases where surface analytical techniques have provided useful insights. Additional cases will be discussed in which extension beyond the capabilities of current surface analytical techniques will be required if critical information is to be obtained. Fuel cells predate the internal combustion engine, but two developments since the 1980's led to the ten-fold increase in power density that generated the current enthusiasm for automotive PEMFC's. First, catalyst makers learned to pack $\sim 3 \times 10^3$ active platinum sites into a cubic cm of porous catalyst layer through the synthesis of $\sim 50\%$ Pt (by weight) catalysts with $>25\%$ dispersion on carbon supports with high electronic conductivity. Second, incorporation into the catalyst layer of ionomer similar to that used in the membrane allowed adequate ionic conductivity to be maintained between these active sites and the electrolyte membrane. While the resulting complex nanostructures must maintain some water content to allow ionic conductivity, excessive retention of product water can prevent access of the gaseous reactants to the catalyst particles. The system contains many interfaces: gas/liquid, gas/ionomer, liquid/ionomer, ionomer/metal, metal/carbon, ionomer/carbon (and perhaps gas/metal), all of which must be carefully controlled. Vacuum surface analytical techniques have yielded major clues as to why Pt-alloy catalysts, the enhanced activity of which is necessary if automotive cost targets are to be met, can be stable in the strongly acidic PEMFC environment. Similar analytical successes on water/ionomer/Pt/carbon interfaces are needed to speed progress toward fuel cells that fully meet automotive requirements.

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