

# Wednesday Afternoon, November 5, 2003

## Applied Surface Science

Room 324/325 - Session AS-WeA

### Fuel Cell & Battery Materials/Corrosion

Moderator: B. Beard, Akzo Nobel Chemicals Inc

2:00pm **AS-WeA1 Development of Multi Layered Oxide Nanofilms for Fast Oxygen Ionic Conduction**, *S. Thevuthasan, S. Azad, O.A. Marina, C.M. Wang, V. Shutthanandan, L.V. Saraf, D.E. McCready, I. Lyubinetzky, A. El-Azab, C.H.F. Peden*, Pacific Northwest National Laboratory

There has been considerable interest in solid oxide fuel cell (SOFC) devices since they provide relatively clean alternative energy to the conventional fossil fuels. Several research groups are working on developing electrolyte materials with higher oxygen ionic conductivity at low temperatures to improve the efficiency of SOFC device at low temperatures. It is well known that nanoscale materials often display properties very different from the base coarse-grained bulk materials. In particular, it has been recently demonstrated that a nanoscale lamellar structure of two different fluorides (calcium fluoride and barium fluoride) can exhibit significantly higher ionic conductivity along the interfacial directions at moderate temperatures. If such a remarkable finding could be transferred into practice, it would provide the ability to design similar structures from oxygen ion conductors to enhance the performance of SOFC devices at temperatures substantially lower than the current operating temperatures. In this study, we investigated the effect of multiple interfaces on oxygen ionic conductivity in Gd-doped single crystal ceria/zirconia multi layers as a function of Gd concentration. Pure and Gd-doped ceria and zirconia films were grown by oxygen plasma assisted molecular beam epitaxy (OPA-MBE) and characterized by reflection high-energy electron diffraction (RHEED), x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS) and high-resolution transmission electron microscopy (HRTEM). The preliminary results are encouraging and four layered Gd-doped ceria/zirconia multi layered structure shows higher oxygen ionic conductivity compared to two layered structures. @FootnoteText@ @footnote 1@N. Sata, K. Eberman, K. Eberl and J. Maier, Nature 408 (2000) 946.

2:20pm **AS-WeA2 Surface Science Studies of Model Fuel Cell Electrocatalysts**, *P.N. Ross*, Lawrence Berkeley National Laboratory **INVITED**

Progress in the understanding of the electrocatalytic reactions in fuel cells will be reviewed. The emphasis is on the study of model electrocatalysts with in-situ surface spectroscopies. It is shown that Pt single crystals and well-characterized Pt bimetallic bulk alloys have been used with some success as models for real (commercial) catalysts. The electrode reactions discussed include hydrogen oxidation evolution, oxygen reduction, and the electrooxidation of C1 compounds (carbon monoxide, formic acid, and methanol). Surface spectroscopies discussed are infrared reflection absorption spectroscopy (IRRAS), scanning tunneling/atomic force microscopy (STM/AFM), and surface x-ray scattering (SXS). The discussion will focus on the relation between the energetics of adsorption of intermediates and the reaction pathway and kinetics, and how the energetics and kinetics are effected by extrinsic properties of the model system, e.g. surface structure and composition. Finally, we conclude by discussing some limitations of these model systems and suggest some directions for studying more realistic systems with the same rigor.

3:00pm **AS-WeA4 Identifying Factors Responsible for Capacity and Power Loss in Lithium-ion Cells**, *D. Abraham*, Argonne National Laboratory **INVITED**

High-power battery technology is crucial to the commercial success of hybrid electric vehicles. In the United States, high-power lithium-ion batteries are being studied as part of the Advanced Technology Development (ATD) program. Lithium ion-cells, ranging in capacity from 1 mAh to 1Ah, are built and tested to determine suitable electrode-electrolyte combinations that will meet the calendar life, safety and cost goals of the ATD program. The cells are aged, cycled, and/or abused according to established test procedures. After test completion, the cell components are examined by various diagnostic tools to determine the nature and extent of physical, chemical, and structural changes that resulted from the testing conditions. These diagnostic results are used to improve cell chemistries and cell designs of the next generation of lithium-ion batteries. The capacity and power loss of lithium-ion cells are governed by the chemical and electrochemical side reactions that occur at the electrode-electrolyte interface. The formation of a Solid Electrolyte Interface (SEI) layer on negative electrodes that are polarized below electrolyte reduction potential (~0.8 V vs. Li/Li+) is a well-known

phenomenon. The SEI layer, which contains various organic and inorganic electrolyte decomposition products, protects the negative electrode from further reduction and allows stable lithium-intercalation processes at low potential. Capacity loss appears to result from changes and growth of the SEI layer during cell aging. The cell power loss results from impedance increases at the positive electrode, which may be the consequence of changes in the electrode surface films. Data from X-ray photoelectron spectroscopy, secondary ion mass spectroscopy, transmission electron microscopy, electron energy loss spectroscopy, and nuclear magnetic resonance analysis will be presented to support the conclusions of our study.

3:40pm **AS-WeA6 The Chemical Nature of LiCoO<sub>2</sub>, LiNiO<sub>2</sub> and LiCo<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> Surfaces by X-ray Photoelectron Spectroscopy**, *M.A. Langell*, University of Nebraska; *A.W. Moses*, University of California; *J.G. Kim*, University of Nebraska

Many lithium metal oxides find use in lithium batteries as a result of their Li<sup>+</sup>/Li redox properties coupled to their high lithium conductivity and their ability to be multiply cycled between the near-stoichiometric and severely de-lithiated electrode material. In its stoichiometric form, LiCoO<sub>2</sub> presents a straightforward picture in charge balance. Lithium is formally Li<sup>+</sup>, cobalt is Co<sup>3+</sup> and, with the exception of the occasional defect, the lattice oxygen is comparable to that found in 3d transition metal monoxides, O<sup>2-</sup>. By simple analogy, LiNiO<sub>2</sub> should contain nickel formally in its Ni<sup>3+</sup> oxidation state. Ni<sup>3+</sup> is not as thermodynamically favored as the low-spin, octahedrally-coordinated Co<sup>3+</sup>, however, and this tends to destabilize the LiNiO<sub>2</sub> surface composition. We present results from XPS and Auger electron spectroscopy that show LiCoO<sub>2</sub> forms stable, stoichiometric surface compositions once surface hydroxylation and carboxylation are properly taken into account. These latter surface adsorbates are variable, depending upon the history of the material and the surface pretreatment prior to UHV analysis. LiNiO<sub>2</sub>, however, is not as well behaved, even when XRD indicates that the bulk is well-ordered. The surface is severely depleted in lithium and phase separation to NiO and cubic LiNiO<sub>2</sub> is common. Adding cobalt to the lattice does not completely stabilize the structure and LiCo<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> substrates behave much like LiNiO<sub>2</sub> from the viewpoint of the nickel with nickel found predominantly in the Ni<sup>2+</sup> state. In contrast to literature reports that nickel is Ni<sup>2+</sup> in LiNiO<sub>2</sub>, with charge compensation resulting from a localized Ni<sup>2+</sup> - O<sup>-</sup> adjacent lattice ion pairs, we see no evidence that the oxygen is significantly different in the three materials, at least within the near-surface area.

4:00pm **AS-WeA7 Formation of Protective Coatings on Depleted Uranium - 0.75 wt% Titanium Alloy**, *D.F. Roeper, C.R. Clayton, D. Chidambaram, G.P. Halada*, SUNY at Stonybrook

The process of enriching uranium for nuclear power plants results in the formation of a toxic and mildly radioactive waste. Exposure to this byproduct called depleted uranium (DU) may have deleterious health effects. The leaching of uranium into the environment and its prevention have become issues of concern. Protective coatings could prevent leaching of DU as well as prevent localized corrosion. In this study, we explore the formation of silicate-based coatings on DU-0.75 wt% Ti alloy (0.75 wt% Ti, less than 0.2 wt% <sup>235</sup>U and ~0.0008 wt% <sup>234</sup>U, rest being <sup>238</sup>U with some trace impurities); a common DU alloy. These coatings are compared with a molybdate-based coating that has been demonstrated earlier. The optimal concentrations of the inhibitors and activators have been used, as determined from the earlier study. The morphological information has been obtained using optical microscopy and scanning electron microscopy. While open circuit potential measurements and potentiodynamic polarization have been utilized for characterization of the electrochemical behavior, the use of X-ray photoelectron spectroscopy has provided the chemical information regarding the coatings. Our results indicate the primary constituent of the coating to be an oxide complex. We discuss the approach currently undertaken to develop protective complex coatings on the alloy surface. The characteristics of these coatings have been compared with other coatings similarly formed using different inhibitors and accelerators. Acknowledgement: The U.S. Army Research Laboratory under contract DAAD190110799 supported this work. Dr. Derek J. Demaree, PhD., has served as contract officer. S. Jones, I. lowles and A. Smith, Lancet, 357 1532 (2001). C.R. Clayton, D.F. Roeper, D. Chidambaram and G.P. Halada, 203<sup>rd</sup> Meeting of the Electro Chemical Society, Abstract No. 318, April 30, 2003 Paris, France.

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4:20pm **AS-WeA8 The Mechanism of Protection of Mechanical Damages to Chromate Conversion Coatings Formed on Aluminum Alloys**, *D. Chidambaram, C.R. Clayton, G.P. Halada*, State University of New York at Stony Brook

Inhibitive action of dichromate based solutions have been known for nearly a century. Hexavalent chromium present in these coatings is toxic and a well-known mutagenic agent. Aluminum alloys used widely in the aerospace industry are given a treatment to form chromate conversion coatings (CCCs). The development of alternative coatings requires the precise knowledge of the underlying mechanisms of protection offered by hexavalent chromium, which are unclear. Defects or mechanical damages in CCCs are protected without further treatment by "self-healing" properties. "Self-healing" has been associated with migration of chromates to actively corroding sites. The formation of a protective Al(III)-Cr(VI) complex at damaged sites was first suggested by Abd Rabbo et al. Electrochemical techniques have been used in this study to provide a direct observation of the repassivation of a scratch. XPS analysis of pure aluminum exposed to chromate solution indicates the presence of high amount of hexavalent chromium at higher depth of analysis. This result is in agreement with theories proposing the formation of stable Al(III)-Cr(VI) compounds. Atomic force microscopy (AFM) confirmed the physical presence of these compounds. Synchrotron infrared micro spectroscopy (SIRMS) clearly showed the formation of Al(III)-Cr(VI) complex in these regions. Al(III)-Cr(VI) complex was found to form at active regions and protect the surface irrespective of the nature of the chromate source (adsorbed chromate film or CCCs). A novel study involving scratching of AA2024-T3 prior to the formation of CCC was performed. The surface morphology studied using scanning laser confocal microscopy showed the physical presence of some compounds in the scratches. The increase in the hexavalent chromium content with the number of scratches as observed using XANES explained the mechanism of protection of mechanical damages to the CCCs formed on aluminum alloys.

4:40pm **AS-WeA9 The Role of Hexafluorozirconate in the Formation of Chromate Conversion Coatings on Aluminum Alloys**, *D. Chidambaram, C.R. Clayton, G.P. Halada*, State University of New York at Stony Brook

Alodine 1200S<sup>®</sup> process is widely used to form chromate conversion coatings (CCCs) on aluminum alloys. Potassium hexafluorozirconate (K<sub>2</sub>ZrF<sub>6</sub>) forms a major component of Alodine. Although the roles played by most of the other components of the treatment bath are known, there is no knowledge about the interaction of hexafluorozirconate with aluminum alloys. Electrochemical and surface analytical techniques have been employed to study the nature of interactions between hexafluorozirconate and constituents of aluminum alloy AA2024-T3. AA2024-T3 is widely used in the aerospace industry. Studies on the interactions between major components found in Alodine<sup>®</sup> with aluminum alloys showed maximum activation to occur in the case of hexafluorozirconate pretreatment. This is contrary to the belief that sodium fluoride, another major component of Alodine<sup>®</sup>, acted as an activator. Contact angle measurements have also been performed. Hexafluorozirconate was found to decrease the interfacial tension besides leading to increased surface wetting. The results obtained from electrochemical techniques have also been compared with similar studies conducted using other fluoride components found in Alodine such as sodium fluoride and potassium fluoborate. X-ray photoelectron spectroscopy (XPS) has been used to study the surface chemistry of the alloys after exposure to hexafluorozirconate, thereby giving an insight into the mechanism of activation and surface wetting. The results indicate hexafluorozirconate to play an important role in the formation of chromate conversion coatings on aluminum alloys. This will be useful to the development of coatings based on benign components. Acknowledgements The U. S. Air Force Office of Scientific Research under contract F49620-96-1-0479 supported this work. Lt. Col. Paul Trulove, Ph.D. served as the contract officer.

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