

Tuesday Afternoon, October 29, 2013

Actinides and Rare Earths Focus Topic
Room: 102 C - Session AC+AS+EN-TuA

Actinides and Rare Earths: The Nuclear Fuel Cycle and Critical Materials

Moderator: L. Petit, Daresbury Laboratory, UK

2:00pm **AC+AS+EN-TuA1 Prospects for Accident Tolerant Fuels in Light Water Reactors**, S.J. Zinkle, K.A. Terrani, L.L. Snead, Oak Ridge National Laboratory **INVITED**

Further enhancement of safety margins in current and next generation commercial fission reactors in general requires an integrated engineering systems design approach. However, tangible gains in safety margin (and performance) may be achievable by utilizing one or more materials science modifications to the fuel system. In this paper the specific attributes of what would constitute *accident tolerant* (or *enhanced safety margin*) fuels will be presented. There are four key metrics to be considered for such a fuel under transient accident conditions: reduced enthalpy production, reduced hydrogen production, improved resistance to clad ballooning and rupture (maintaining coolability of the core), and suppressed fission product release. There are a variety of materials science approaches that can be considered to address one or more of these four metrics for accident tolerant fuels, ranging from relatively incremental modifications to the cladding material to dramatic alternatives to the historical monolithic UO₂ ceramic fuel pellets surrounded by seamless Zr alloy tubing. For example, solute modifications and/or highly adherent coatings that improve the high temperature steam oxidation resistance of Zr alloy cladding would directly lead to reduced enthalpy and hydrogen production. For extended high temperature transient conditions, deployment of high thermal-creep strength, oxidation-resistant cladding (e.g. advanced steels, coated molybdenum, or SiC/SiC) would maintain the coolant channel geometry and significantly suppress the rate of enthalpy and hydrogen production in the core compared to current Zr alloy cladding. This will effectively delay the threshold for fission product release from the fuel while providing longer time periods for emergency core cooling systems to become activated to halt core degradation processes. In addition, the critical heat removal limit in the core to prevent severe degradation would be lowered. Utilization of microencapsulated fuel forms (i.e., triple-encapsulated fuel kernels) within a high thermal conductivity matrix (i.e. SiC) would reduce the stored energy under normal operating conditions compared to standard fuels, resulting in suppressed fuel temperature increase under loss of coolant accident conditions that could limit fuel cladding ballooning and burst. Improved fission product retention within the fuel during high temperature accidents would also be anticipated. This presentation will review several potential fuel system options and outline key feasibility challenges that need to be resolved, along with briefly discussing potential impact on reactor neutronics and overall electricity production costs.

2:40pm **AC+AS+EN-TuA3 Photoelectron Spectroscopy Study of Uranium Materials**, S. Fujimori, Japan Atomic Energy Agency, Japan **INVITED**

Electronic structure of uranium materials have been studied by means of photoelectron spectroscopy (PES) as well as angle-resolved PES (ARPES) using synchrotron radiations. The results on the nuclear fuel material UN as well as uranium heavy Fermion superconductors UPd₂Al₃ will be presented.

Uranium monoxide (UN) is a promising fuel material for the generation-IV advanced nuclear reactors since it has high melting point, a very good thermal conductivity at high temperatures as well as a high fuel density. We have revealed its electronic structure by ARPES, and found that they are well explained by the band structure calculation based on local density approximation (LDA) [1].

UPd₂Al₃ is a heavy Fermion superconductor. It shows transitions into the antiferromagnetic phase at T_N=14 K and into the superconducting phase at T_{SC}=2 K. Since U 5f electrons in these compounds show both pronounced localized and delocalized characters, the nature of U 5f electrons have been not well understood. Their detailed electronic structure was derived by ARPES by synchrotron radiation as well as very high resolution PES by laser. It was found that quasi-particle bands with strong U 5f character form Fermi surface at low temperatures, suggesting that U 5f electrons have itinerant nature in this compound. Furthermore, we have succeeded to observe the superconducting gap of this compound by PES [2]. This is the first observation of the superconducting states of actinide materials by PES.

[1] Shin-ichi Fujimori *et al.*, Phys. Rev. B **86**, 235108 (2012).

[2] Y. Ohta *et al.*, in preparation.

4:00pm **AC+AS+EN-TuA7 Interaction of γ -U alloys with Hydrogen**, L. Havela, I. Tkach, S. Maskova, Z. Matej, Charles University, Czech Republic, N.-T.H. Kim-Ngan, Pedagogical University Cracow, Poland, A.V. Andreev, Academy of Science of the Czech Republic

Uranium metal absorbs H readily at low pressures, forming a fine highly pyrophoric powder of β -UH₃, which is ferromagnetic with T_C ≈ 175 K. More technologically important than the orthorhombic α -U is the bcc γ -U, known as existing at high temperatures or stabilized by doping to low temperatures.

In the course of the study of fundamental properties of Mo-stabilized bcc U alloys [1] we have been testing their resistance to H. There was no interaction with H₂ at ambient pressure and room temperature. However, increasing pressure over approx. 4 bar a slow hydrogenation was observed after several days if incubation. Increasing the H₂ pressure makes the hydrogenation faster. The product, in which the H concentration corresponds to the 1U-3H ratio, does not turn into powder, but consist of large brittle fragments with metallic luster. X-ray diffraction indicates that the hydride is amorphous, with a basic structure pattern corresponding to β -UH₃, while the grain size is ≈ 1 nm only.

The hydrides obtained were subjected to studies of magnetic properties, electrical resistivity, and specific heat. The most striking fact is that the Curie temperature can be higher than in β -UH₃. It reaches T_C = 200 K for UH₃Mo_{0.18}, for both lower and higher Mo concentrations it weakly decreases. Also the magnetization values increase from 0.93 μ_B /f.u. to 1.2 μ_B /f.u. (both in $\mu_0 H = 14$ T). At low temperatures a striking high coercivity, reaching 4 T, is seen from magnetization loops. It can be understood as due to a high anisotropy randomly distributed over spatial directions.

The Sommerfeld coefficient of electronic specific heat $\gamma = 29.2$ mJ/mol K² is similar to β -UH₃ values (29-33.2 mJ/mol K² by various authors) and higher than pure UMo_{0.18} (18.8 mJ/mol K²). Electrical resistivity exhibits the weakly negative slope known from the bcc U-Mo alloys [2] and other strongly disordered systems with a cusp-like anomaly at 200 K superimposed. The absolute values about 1 m Ω cm are about an order of magnitude higher than for UMo_{0.18}, and even higher than that of UH₃, which exceeds 600 $\mu\Omega$ cm at room T [3]. The most surprising fact is that the 5f magnetism, which is normally suppressed by disorder, is supported in the case of UH₃Mo_x, probably due to enhanced U-U spacing due to Mo included in the lattice.

This work was supported the Czech Science Foundation under the grant No. P204/12/0285.

[1] I. Tkach, N.-T.H. Kim-Ngan, S. Mašková, M. Dzevenko, L. Havela, J. Alloys Comp. 534 (2012) 101.

[2] B.S. Chandrasekhar, J.K. Hulm, J. Phys. Chem. Solids 7 (1958) 259.

[3] J.W. Ward, L.E. Cox, J.L. Smith, G.R. Stewart, J.H. Hood, J. Phys. 40 (1979) C4-15.

4:20pm **AC+AS+EN-TuA8 The Effect of U and Fe Cations on the Reduction of CeO₂ for Thermal Water Splitting to Hydrogen**, Y. Al Salik, SABIC, Saudi Arabia, I. Al Shankiti, SABIC and University of Colorado, H. Idriss, SABIC, Saudi Arabia **INVITED**

Thermal water splitting to hydrogen on reducible materials is one of the promising methods to secure renewable energy vectors for the future. The process relies on a redox cycle whereby steam is introduced to a prior reduced CeO₂ to generate hydrogen which is consequently oxidized. However to achieve this cycle CeO₂ needs be reduced at elevated temperatures (> 1500°C) [1, 2]. Mixing CeO₂ with metal cations can lower the energy needed for the reduction process. Among the methods of changing CeO₂ are the incorporation of metal cations smaller in size than Ce⁴⁺ cations such as Zr⁴⁺ [3] or the addition of a metal cation that can transfer electrons to Ce⁴⁺ [4, 5]. In this work we present a core and valence level study of the extent of reduction of Ce⁴⁺ cations by the addition of Fe and U cations. We compare XPS Ce3d, Ce4d of stoichiometric CeO₂ to those of Ce_xFe_{1-x}O₂ and Ce_xU_{1-x}O₂ (x<1). We also investigate the reduction of these materials upon Ar ions sputtering. We find that the addition of Fe or U cations in any proportions increases the reduction of Ce⁴⁺ cations. In particular considerable enhancement of the reduction of CeO₂ with Ar ions was noticed (compared to CeO₂ alone) when x>0.5 in both Ce_xFe_{1-x}O₂ and Ce_xU_{1-x}O₂ series of the oxide materials. The reasons for the enhancement of CeO₂ reduction by Fe cations can be linked to both size and electron transfer effect while in the case of U cations it is mainly due to electron transfer from the U5f to Ce4f levels. Tests for hydrogen production by thermal water splitting for both series were conducted and indicated the enhancement of the activity of the mixed oxide when compared to CeO₂ alone.

- [1] W.C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S. M. Haile, A. Steinfeld, *Science* (2010) **330**: 1797-1801.
- [2] K-S Kang, C-H Kim, C-S Park, J-W Kim, *J. Ind. Eng. Chem.* (2007) **13**: 657-663.
- [3] S. Abanades, A. Legal, A. Cordier, G. Peraudeau, G. Flamant, A. Julbe, *J Mater Sci* (2010) **45**:4163–4173.
- [4] I. Al-Shankiti, F. Al-Otaibi, Y. Al-Salik, H. Idriss, *Topics in Catalysis* (2013) *in press*.
- [5] B.E. Hanken, C.R. Stanek, N. Grønbech-Jensen, M. Asta, *Phys. Rev. B* (2011) **84**: 085131-1 to 085131-9.

5:00pm **AC+AS+EN-TuA10 Soft X-ray Investigations of Covalent Orbital Mixing in Metal Oxides**, S. *Minasian*, Lawrence Berkeley National Lab (LBNL), J. *Keih*, E. *Batista*, K. *Boland*, Los Alamos National Lab (LANL), J. *Bradley*, Lawrence Livermore National Laboratory (LLNL), S. *Daly*, George Washington Univ., S. *Kozimor*, LANL, W. *Lukens*, LBNL, R.L. *Martin*, LANL, D. *Nordlund*, SLAC National Accelerator Lab, G. *Seidler*, Univ. of Washington, D. *Shuh*, LBNL, D. *Sokaras*, SLAC National Accelerator Lab, T. *Tyliszczak*, LBNL, G. *Wagner*, LANL, T.-C. *Weng*, SLAC National Accelerator Lab, P. *Yang*, Pacific Northwest National Lab

Developing a clear understanding of how metal oxide electronic structure changes for a range of compounds and materials will greatly benefit a variety of existing and emerging energy technologies. Many of the technologically desirable chemical, magnetic, electronic, and thermal properties of metal oxides are derived from strongly covalent metal–oxygen multiple bonds (metal oxos). Among approaches explored previously, ligand K-edge X-ray absorption spectroscopy (XAS) has emerged as an effective method for quantitatively probing electronic structure and orbital mixing. The presence of covalent mixing is observed as a pre-edge feature in the ligand K-edge XAS, which only has transition intensity if the final state metal orbital contains a component of ligand p orbital character. Recent advances have shown that insights regarding the nature of orbital mixing in metal oxides can be obtained at the K-edge for oxygen through a combination of XAS with a scanning transmission X-ray microscope (STXM), non-resonant inelastic X-ray scattering (NIXS), and hybrid density functional theory calculations (DFT). The spectroscopic work in this study was performed at the ALS Molecular Environmental Sciences beamline 11.0.2 (STXM), beamline 6.2 at SSRL (NIXS), and the LERIX facility at the APS (NIXS).

Herein, a new effort is discussed that employs these techniques to understand bonding interactions in d- and f-block oxides. Oxygen K-edge XAS measurements and DFT studies began with a series of six tetrahedral oxyanions, MO_4^{2-} and MO_4^{1-} ($M = \text{Cr, Mo, W}$ and Mn, Tc, Re). Despite the similarities of the isoelectronic d^0 MO_4^{2-} and MO_4^{1-} anions, unexpected differences in metal oxo orbital mixing were observed for adjacent metals in the periodic table. The lanthanide dioxides and sesquioxides, LnO_2 and Ln_2O_3 ($\text{Ln} = \text{Ce, Pr, Tb}$), were chosen for subsequent work because their electronic structures are well-established from hard X-ray spectroscopies. Features in the O K-edge XAS follow anticipated trends based on 4f and 5d orbital energies and occupancies. Taken together with L_3 -edge intensities determined previously, a detailed picture of the electronic structure in lanthanide oxides emerges. Overall, the research shows that orbital composition is influenced by a complex interplay between periodic changes in both orbital energy and radial extension.

This work was funded by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under contracts DE-AC02-05CH11231 at LBNL and DE-AC52-06NA25396 at LANL. Operation of the ALS, SSRL, and the APS is supported by the U.S. Department of Energy, Office of Science.

5:20pm **AC+AS+EN-TuA11 The Microstructure of Cerium Hydride Growth Centres**, M. *Brierley*, J. *Knowles*, N. *Montgomery*, AWE, UK, M. *Preuss*, A. *Sherry*, University of Manchester, UK

Considerable work has been undertaken into the hydriding of rare earth metals and actinides [1]; specifically into the reaction rate of various hydrides on the surface of these materials [2]. Cerium is a reactive rare-earth metal and quickly forms a semi-protective oxide layer in air. Upon exposure of an oxide-covered sample to hydrogen, hydride is formed as discrete sites on the surface, often termed ‘Growth Centres’, which then grow radially across the surface [3]. In the present study, the emphasis was to investigate the microstructure of the cerium growth centres with the intention of understanding any hydriding nucleation and growth mechanisms which may occur. The samples were prepared to 1 μm finish before being exposed to ultra-pure hydrogen at pressures between 10 mbar and 300 mbar, for sufficient time to have nucleated a number of hydride Growth Centres. Post-test analysis was performed using Secondary Ionisation Mass Spectrometry (SIMS), Scanning Electron Microscopy (SEM) and Optical Microscopy (OM) to determine the microstructure of the

hydride growth centres. SIMS confirmed that the Growth Centres were comprised of cerium hydride, and that the hydrogen exists specifically within the features. The morphology of individual hydride Growth Centres was examined using OM and SEM and the data reported demonstrates that the hydride-metal interface has a discrete boundary between two distinct phases; a region of deformed metal surrounds the Growth Centres; the microstructure within the Growth Centres indicates that the microstructure of the parent metal was retained by the hydride product.

References

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- [2] K. H. Gayer, W. G. Bos, *J. Phys. Chem.* Vol. 68, No. 9, (1964) 2569-2574.
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Authors Index

Bold page numbers indicate the presenter

— A —

Al Salik, Y.: AC+AS+EN-TuA8, 1
Al Shankiti, I.: AC+AS+EN-TuA8, 1
Andreev, A.V.: AC+AS+EN-TuA7, 1

— B —

Batista, E.: AC+AS+EN-TuA10, 2
Boland, K.: AC+AS+EN-TuA10, 2
Bradley, J.: AC+AS+EN-TuA10, 2
Brierley, M.: AC+AS+EN-TuA11, 2

— D —

Daly, S.: AC+AS+EN-TuA10, 2

— F —

Fujimori, S.: AC+AS+EN-TuA3, 1

— H —

Havela, L.: AC+AS+EN-TuA7, 1

— I —

Idriss, H.: AC+AS+EN-TuA8, 1

— K —

Keith, J.: AC+AS+EN-TuA10, 2
Kim-Ngan, N.-T.H.: AC+AS+EN-TuA7, 1
Knowles, J.: AC+AS+EN-TuA11, 2
Kozimor, S.: AC+AS+EN-TuA10, 2

— L —

Lukens, W.: AC+AS+EN-TuA10, 2

— M —

Martin, R.L.: AC+AS+EN-TuA10, 2
Maskova, S.: AC+AS+EN-TuA7, 1
Matej, Z.: AC+AS+EN-TuA7, 1
Minasian, S.: AC+AS+EN-TuA10, 2
Montgomery, N.: AC+AS+EN-TuA11, 2

— N —

Nordlund, D.: AC+AS+EN-TuA10, 2

— P —

Preuss, M.: AC+AS+EN-TuA11, 2

— S —

Seidler, G.: AC+AS+EN-TuA10, 2
Sherry, A.: AC+AS+EN-TuA11, 2
Shuh, D.: AC+AS+EN-TuA10, 2
Snead, L.L.: AC+AS+EN-TuA1, 1
Sokaras, D.: AC+AS+EN-TuA10, 2

— T —

Terrani, K.A.: AC+AS+EN-TuA1, 1
Tkach, I.: AC+AS+EN-TuA7, 1
Tyliszczak, T.: AC+AS+EN-TuA10, 2

— W —

Wagner, G.: AC+AS+EN-TuA10, 2
Weng, T.-C.: AC+AS+EN-TuA10, 2

— Y —

Yang, P.: AC+AS+EN-TuA10, 2

— Z —

Zinkle, S.J.: AC+AS+EN-TuA1, 1