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LLNL-CONF-499222

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September 14, 2011

29th Compatibility, Aging, and Stockpile Stewardship Conference
Livermore, CA, United States
October 18, 2011 through October 20, 2011

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Computational Modeling of Uranium and Plutonium Hydriding- the role of Surface Oxide Layers, Oxycarbides, Carbides & Impurities

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Uranium hydriding is identified to be the single most important process in uranium corrosion. The academic interest stems from the fact that the role of actinide 6d versus 5f orbitals in chemical reactivity and bonding is not well understood at present. This can be quite puzzling, as under certain circumstances the 6d orbitals of the actinides play a more significant role in reactivity and bonding, while at other circumstances their role is less important. Likewise, the relative importance of the 5f orbitals of actinides seems to vary as a function of the actinide and the ligands that complex with the actinide. Furthermore, relativity plays a key role in determining the reactivity and bonding of actinide species, because inner electrons approach speeds of light due to the large nuclear charge. For all of these reasons, the reaction of uranium with hydrogen gas has received considerable attention of the experimental and theoretical communities. We have elucidated the atomistic level mechanisms and trends with particular emphasis on the role of impurities in the uranium and plutonium hydriding reactions, important processes that cause corrosion of these materials. Recent experimental and computational studies have shown that certain elemental impurity sites in the material could act as the sites that initiate hydriding and initiate the process. In recent times, ion-implantation studies have also been carried out, and these studies have provided substantial insight into which elemental impurities are critical to initiating the hydriding reactions. We have reviewed the recent results

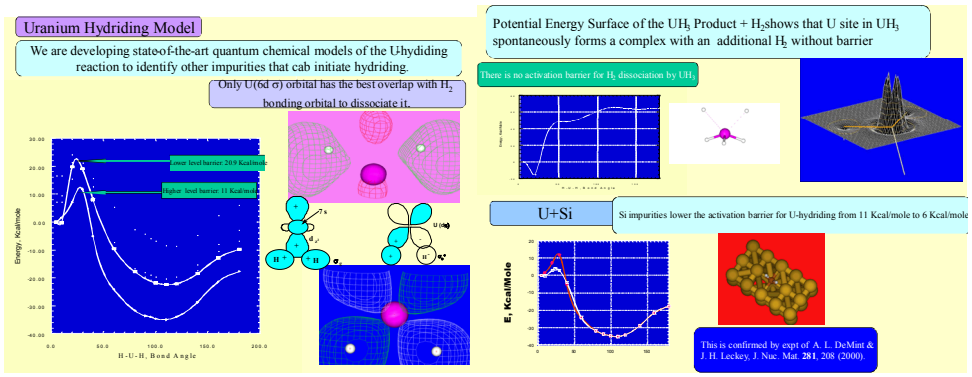
of relativistic quantum chemical modeling studies that have provided considerable insight into uranium hydriding. The potential energy surfaces have yielded the activation energy barriers for the uranium hydriding reactions, thus providing a platform for comparison of the activation barriers with and without impurities. Moreover, Laplacian topographies of charge densities are shown to provide significant new insights into the hydriding sites and the role of impurities in causing the hydriding reaction. In conformity with experimental findings, recent computational studies indicate that the UH_3 product can catalyze further hydriding. This is inferred computationally through the depleted charge peak at the uranium hydride site. We have developed a comprehensive relative assessment of various impurities in either promoting hydriding or slowing down the hydriding reaction. It is shown that such trends can be derived through 3D charge topographic characteristics from relativistic quantum modeling. We have also outlines the results of atomistic level computational modeling at the PuO_2-Pu_2O_3 interfaces which clearly revel that hydriding is initiated at the interface where dangling 5d orbital son Pu are available. It was also shown that PuO_2 was passivating in contrast to Pu_2O_3 where the latter surface seems to exhibit greater propensity to catalyze the hydriding reaction.

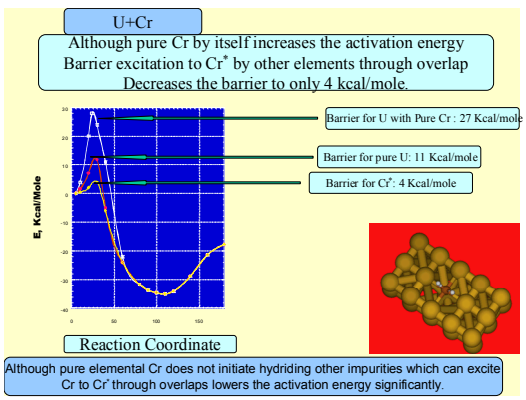
Although significant number of experimental and modeling studies have been carried out concerning thermo chemistry, diffusion kinetics and mechanisms of U-hydriding, very little is known about the electronic structure and electronic features that govern the U-hydriding process. Our modeling efforts focus the electronic feature that controls the activation barrier and thus the rate of hydriding. We have studied the role of a number of impurities in uranium corrosion. We have also compared our computed results with experimental results when available,. For example, . Condon's diffusion model was found to be in excellent agreement with the experimental reaction rates. From the slopes of the Arrhenius plot the activation energy was calculated as 6.35 kcal/mole. Bloch and Mintz have discussed two models, one, which considers hydrogen diffusion through a protective UH_3 product layer, and the second where hydride growth occurs at the hydride-metal interface. These authors obtained two-dimensional fits of experimental data to the pressure-temperature

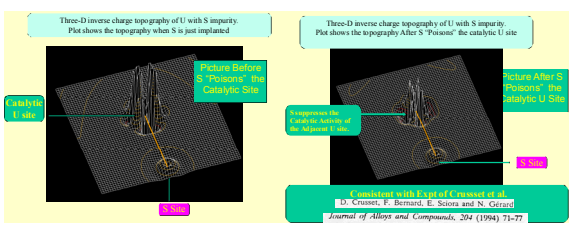
reactions. Powell et al. have studied U-hydriding in ultrahigh vacuum and obtained the linear rate data over a wide range of temperatures and pressures. They found reversible hydrogen sorption on the UH_3 reaction product from kinetic effects at 21 °C. This demonstrates restarting of the hydriding process in the presence of UH_3 reaction product. DeMint and Leckey have shown that Si impurities dramatically accelerate the U-hydriding rates. Our computational models supported all of these experiments and clearly provided atomistic level quantum chemical interpretations for these findings.

Our computations were carried out using relativistic computations that vary from complete active space multi-configuration interaction (CAS-MCSCF) followed by multi-reference configuration interaction (MRSDCI) computations that included up to 60 million configurations for modeling of uranium-hydriding with cluster models will be presented. Our computed potential energy surface for the insertion of a U site into H_2 reveals that pure U site has to surpass a barrier of 20.9 kcal/mole for the U-hydriding. Once the barrier is surpassed a stable product is formed which is 22.4 kcal/mole more stable than the reactants. We have also developed a computational model to study the role of the UH_3 product and other impurities such as Fe, Cr, Si, C, Al, etc., on the uranium hydriding reaction. Our model reveals that the product UH_3 is highly ionic and thus U transfers electron density to the three hydrogens resulting in a U^{+3} state. U^{+3} is shown to insert into H_2 spontaneously thus demonstrating the U-site in the product UH_3 binds to H_2 spontaneously forming a complex in which H_2 is separated far enough so as to cause liberation of H atoms in the presence of U. Our computed potential energy surfaces reveal a 21 kcal/mole activation energy barrier for pure U reaction with H_2. However, the presence of the product UH_3 catalyzes the U-hydriding. We have also modeled the presence of Si impurities for the U-hydriding reaction to show that the activation barrier is lowered by the presence of Si. However carbon impurity does not influence the hydriding process. Our computations reveal an electron donor-acceptor model for the U-hydriding, where H_2 exchanges electronic density from its occupied $1\sigma_g$ orbital to the U(6d σ) orbital and back donation from the U(6d π) orbital back to H_2 $1\sigma_u$ antibonding orbital. As seen from the figures shown below our recent works show that elemental impurities such as Si and W promote hydriding while S when present as an impurity

poisons a catalytic site adjacent to it. The table shown below enumerates the list of impurities that we have considered thus far and their roles in uranium corrosion.





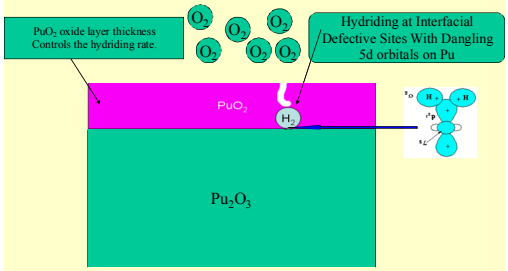


We have shown below the plutonium hydriding propensity as a function of the oxide layer. We find that whereas PuO_2 acts as a protective layer for Pu-hydriding Pu_2O_3 does not. The hydriding is initiated at a defective Pu site at the interface of PuO_2 and Pu_2O_3 where a dangling 6d orbital dissociates the H-H bond causing the hydriding. At the interface there are sites, where such dissociation can happen readily, as can be seen from the figures below. Elemental tungsten impurity promotes hydriding.

Priority Table of Relative Importance of Various Impurities

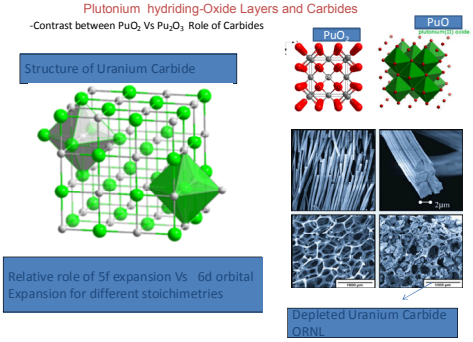
Element	Corrosion Propensity
W	+
Rh	+
Si	+
(Cr, Mn, Fe,Ni)	- but + with excitations/alloy(?)
Cu	- or + with other factors
Al	-
C	-
N	+(element) –(Nitride)
UH_3	+
Pd	+
S	- (Poisons Adjacent U catalytic Site)
P	0
(Fe,Cr)	+

Plutonium Hydriding-Role of Oxide Layers, Their Thickness and needed electronic features

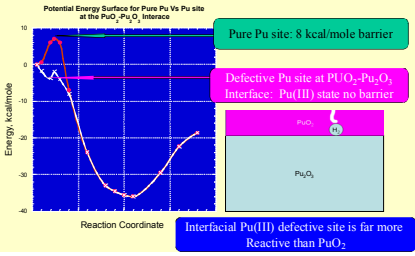


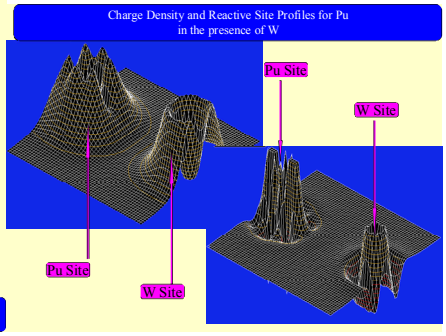
computational investigations of Plutonium hydriding-Oxide Layers and Carbides

-Contrast between PuO_2 Vs Pu_2O_3 Role of Carbides



Reactivity of Pure Pu Vs Defective Pu Site at the PuO_2-Pu_2O_3 Interface





Prepared by LLNL under Contract DE-AC52-07NA27344.