

**Potential Superionic Conductivity in the Actinide Dioxides.** C. E. Whiting, J. M. Douglas, B. M. Cremeans, E. A. Kauffman, C. D. Barklay, and D. P. Kramer, University of Dayton – Research Institute, 300 College Park, Dayton OH, 45469, chris.whiting@udri.udayton.edu

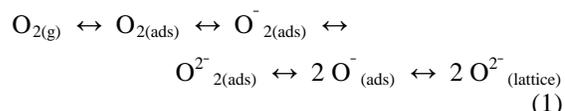
**Introduction:** Neutron emission rates (NER) are a significant concern for worker safety and potential radiation damage to the spacecraft employing  $^{238}\text{PuO}_2$  based Radioisotope Power Systems. The primary cause of NER in  $^{238}\text{PuO}_2$  is a secondary ( $\alpha, n$ ) reaction caused by the interaction of the naturally occurring  $^{17}\text{O}$  and  $^{18}\text{O}$  isotopes with the  $^{238}\text{Pu}$   $\alpha$ -decay. NER is minimized through the use of an  $^{16}\text{O}$  isotopic exchange reaction, which eliminates nearly all of the detrimental  $^{17}\text{O}$  and  $^{18}\text{O}$  from the system. Currently, our understanding of the kinetics and thermodynamics of the oxygen exchange process is very limited. Improving our understanding of the oxygen exchange process will help improve our ability to respond to changes in  $^{238}\text{PuO}_2$  processing and safely produce an RPS. Since experiments with Pu are costly and difficult to perform, initial studies on  $\text{CeO}_2$ , a  $\text{PuO}_2$  surrogate material, have been performed to help us better understand the chemistry of the oxygen exchange process.

Oxygen exchange reactions on  $\text{CeO}_2$  date back to almost 50 years ago [1,2], but very high temperature ( $> 700\text{ }^\circ\text{C}$ ) oxygen exchange reactions have not been discussed previously. This is most likely due to previous researchers having difficulty obtaining consistent and reproducible results [1,2]. Our work here will not only show that very high temperature oxygen exchange reactions are possible, but provide an explanation for why previous studies had difficulty obtaining reportable results.

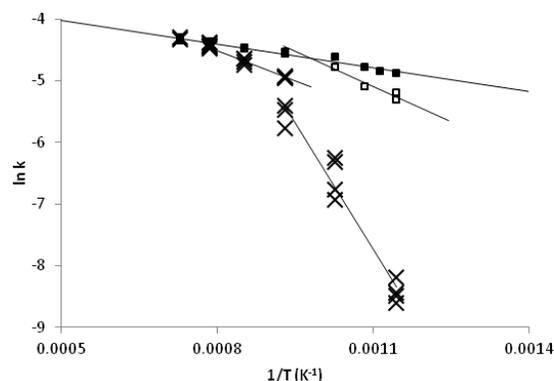
Previous reports from our group discuss the instrumentation used and some of the basic kinetic results obtained from preliminary oxygen exchange experiments on  $\text{CeO}_2$  [3,4]. Here we will discuss some of the mechanistic information obtained during our oxygen exchange experiments. Since  $\text{CeO}_2$  shares the same atomic space grouping as all of the known actinide dioxides (fluorite structure; #225), it is very likely that these results are representative of the behavior on all of the actinide dioxides.

**Results:** Figure 1 presents an Arrhenius plot of the oxygen exchange reactions performed on three different sets of materials. Above  $1000\text{ }^\circ\text{C}$ , it is possible to see that the exchange reaction is dominated by a mechanism with a very low activation energy ( $E_a = 0.114\text{ eV}$ ). This mechanism is independent of all particle characteristics and atmospheric compositions studied, which include: particle size, specific surface area (SSA), oxygen isotope, sample size, oxygen partial pressure, and total atmospheric pressure [4].

Since this mechanism appears to be independent of nearly all particle characteristics, it is possible to conclude that this reaction is dominated by a reaction that is not occurring at the surface of the solid material, suggesting that the reaction is occurring within the bulk of the material. Equation 1 presents the commonly accepted process by which oxygen exchange occurs, and it is easy to see that the entire process essentially occurs at the material surface [4].



This suggests that the reaction being observed in the very high temperature case of Figure 1 is not a part of the exchange reaction proper, but is instead a part of the redistribution of oxygen isotopes in the bulk of the material. Conductivity is a process that describes the motion of charged species through a solid material, so the reaction observed here is most likely related to the conductivity of  $\text{CeO}_2$ .



**Figure 1.** Arrhenius plots of the oxygen isotope exchange reactions with  $\text{CeO}_2$  showing three distinct rate limiting mechanisms. (■) 70–100 nm material. (□) 70–100 nm material after thermal treatment. (X) -325 mesh material.

At  $\geq 1000\text{ }^\circ\text{C}$ , the conductivity of  $\text{CeO}_2$  is known to operate under a p-type mechanism [5], which is the motion of oxygen ions and vacancies through the lattice of the material (aka ionic conductivity). Traditional conductivity operates under an n-type mechanism, which is observed as the motion of electrons, or small polarons, through the material. Since we did not perform conductivity experiments on this material, we

cannot completely rule out the possibility of n-type conduction. However, as previously stated, the results from previous reports suggest p-type conductivity. Additionally, *ab initio* calculations of  $E_a$  for small polaron motion in  $\text{CeO}_2$  produce 0.32 eV [6], which is significantly larger than the 0.114 eV measured here. Thus, we conclude that the apparent rate limiting mechanism observed here is the ionic conductivity of  $\text{CeO}_2$ .

Superionic conductivity is a special case where the motion of ions through a solid is extremely rapid and typical  $E_a$  values are  $\sim 0.1$  eV, and both criteria are observed in these experiments. This suggests that at high temperatures the actinide dioxides will also experience superionic conductivity as the high temperature rate limiting mechanism driving the oxygen exchange reaction.

As the temperature decreases below 1000 °C, the exchange behavior becomes significantly more complex. For the -325 mesh  $\text{CeO}_2$  material (Materion, Milwaukee, WI), the mechanism changed twice as the temperature decreased, while the 70-100 nm material (Alfa Aesar, Ward Hill, MA) was dominated by superionic conductivity over the entire temperature range studied (1100–600 °C). Previously, Winter studied the oxygen exchange behavior on metal oxides and observed that the exchange rate is dominated by the mobility of surface oxygen species and/or defects at higher temperatures, and as temperature decreases, the rate becomes dominated by the actual exchange of adsorbed oxygen with lattice oxygen [7,8]. These two reactions, which will be referred to as surface mobility and surface exchange, match the qualitative and quantitative results observed in Figure 1. This suggests that as the temperature decreases, the oxygen exchange rate on  $\text{CeO}_2$  will transition from superionic conductivity to surface mobility to surface exchange.

Both the surface mobility and surface exchange reactions have a very strong dependence on the SSA of the material [7,8]. The -325 mesh material has a fairly low SSA of  $4.23 \text{ m}^2 \cdot \text{g}^{-1}$ , explaining why it transitioned into a surface mobility dominated regime long before the 70-100 nm material, which had a SSA =  $26.94 \text{ m}^2 \cdot \text{g}^{-1}$ .

Interestingly, the SSA of the materials studied appeared to be influenced by exposure to high temperatures. Sequential oxygen exchange experiments were performed on a single sample of the 70–100 nm material at 1000, 900, 800, 700, 650, and 600 °C, in descending order. As can be seen in Figure 1, the mechanism governing the exchange rate for this material changed at 700 °C (open squares). This new mechanism has an  $E_a$  that is nearly identical to the surface mobility  $E_a$  measured on the -325 mesh material. Howev-

er, when a fresh sample of 70–100 nm material that was never exposed to high temperatures was tested at 700, 650, 625, and 600, the results continued to follow the superionic conductivity trend (full squares).

This suggests that the thermal exposure from the high temperature exchange experiments caused a decrease in the SSA, which impacted the mechanism governing the exchange reaction. This result is somewhat surprising since the phenomenon of SSA reduction is not generally expected until the temperature is  $\sim$ half the melting point (i.e. 1200 °C). It does explain, however, why other researchers have had such difficulty obtaining stable and reliable results for exchange reactions that occurred at temperatures above 700 °C. These researchers were probably operating in the range where the exchange was dominated by the surface mobility or surface exchange reactions. Exposure to the exchange temperatures would then cause a dynamic change in the SSA and the reaction rate during the experiment. This would produce confusing results that would be very difficult to interpret correctly.

Though the data on the oxygen exchange process on  $\text{PuO}_2$  is very limited, the results presented here are very similar to the data that has been previously published on  $\text{PuO}_2$  [9]. This suggests that the chemical and kinetic behaviors observed on  $\text{CeO}_2$  here are indicative of the behavior of  $\text{PuO}_2$ , and since all of the known actinide dioxides form the fluorite atomic space grouping, it is likely that the results obtained here will be representative of the behavior in all actinide dioxides.

#### References:

- [1] Sazonov L. A., Sokolovsky V. D., and Borskov G. K. (1966) *Kinet. Katal.*, 7, 521. [2] Kharton V. V., Yaremchenko A. A., Naumovich E. N., and Marques F. M. B. (2000) *J. Solid State Electrochem.*, 4, 243-266. [3] Whiting C. E., Cremeans B. M., Barklay C. D., and Kramer D. P. (2013) *Proc. NETS 2013*, 6765. [4] Whiting C. E., Barklay C. D., and Kramer D. P. (2013) *UDR-TR-13-187*. [5] Gross M. S., Ulla M. A., and Querini C. A. (2012) *J. Mol. Catal.*, 352, 86-94. [6] Vayas, S. (2005) *Thesis*, Univ. of London. [7] Winter E. R. S. (1968) *J. Chem. Soc. A*, 9, 2889-2902. [7] Winter E. R. S. (1958) *Adv. Catal.*, Vol. X, 196-241. [8] Deaton R. L. and Wiedenheft C. J. (1972) *J. Inorg. Nucl. Chem.*, 34, 3419-3425.