Mechanisms and Kinetics of the Oxygen Exchange Reaction with CeO₂ at High Temperatures

Christofer E. Whiting^{}, Chadwick D. Barklay, Daniel P. Kramer, Emily A. Kaufman, and John M. Douglas*

University of Dayton – Research Institute, 300 College Park, Dayton, OH 45469-0172

Contact Information:

^{*} corresponding author; +01 937 229 2570; chris.whiting@udri.udayton.edu

Abstract

Bulk isotopic oxygen exchange reactions with CeO₂ appear to be dominated by a non-diffusion based internal chemical reaction at ≥ 1000 °C when the specific surface area is ≥ 2 m²/s. This internal chemical reaction is correlated to the isotopic redistribution of oxygen ions, but independent of the rate of oxygen motion through the lattice. As temperature decreases, exchange kinetics eventually become dominated by the surface mobility of active species/defects and then by the surface exchange of adsorbed oxygen. Transitioning between these three rate limiting mechanisms appears to be a complex function of parameters including at least temperature and specific surface area. Exposure to high temperatures induces a reduction in the specific surface area, which could cause a dynamic change in the exchange rate and mechanism during experimentation. Activation energies for the internal chemical reaction, surface mobility, and surface exchange mechanisms were measured to be 11.0, 29.1, and 114 kJ/mol, respectively. This report is the first study examining the internal chemical reaction mechanism and the activation energy for the surface mobility reaction. This data helps elucidate the high temperature oxygen mobility mechanism on CeO₂ and will help inform future oxygen exchange experiments on ²³⁸PuO₂.

Keywords: cerium (IV) oxide, oxygen exchange, kinetics, activation energy, plutonium (IV) oxide

Non-standard Abbreviations: RPS – radioisotope power system

1 Introduction

CeO₂ is a material of interest primarily because of its highly labile oxygen ions. This extraordinary flexibility is the source of the material's large oxygen storage capacity, which, in turn, is the reason why CeO₂ is useful as a catalyst support, catalytic surface, and as an electrolyte for solid oxide fuel cells. Studying the oxygen exchange reaction between solid CeO₂ and the gas phase is one method that is used to help better understand the thermodynamics and reaction kinetics that govern these useful properties. Until recently, however, there were no very high temperature studies (≥ 700 °C) of the bulk

oxygen exchange behavior on pure CeO₂ powders. Previous reports have studied the oxygen exchange behavior at lower temperatures (350-520 °C),¹⁻⁴ at higher temperatures for doped CeO₂ (up to ~1000 °C),⁵⁻⁷ or specifically studied only the surface exchange reaction at very high temperatures (800–1300 °C).⁸ The reason for this lack of information most likely stems from a classic report published almost 50 years ago that observed, "...an extremely high but unstable activity of cerium oxide powder quenched after annealing in vacuum at 970 K..." during a study of the oxygen exchange rate on CeO₂.^{1,9} This is what has most likely led to the following common wisdom: in order to obtain stable results from oxygen exchange experiments on CeO₂ powders, the material must be thermally pre-treated at temperatures much higher than the experimental temperature and experimental temperatures should be kept below 700 °C.

Previously, we reported extremely rapid and consistent oxygen exchange behavior on a wide variety of CeO₂ powders at 1000 °C, and observed that the exchange is independent of oxygen partial pressure, total pressure, and most particle characteristics, including specific surface area (SSA).¹⁰ The results from this report are intriguing for two reasons. First, stable and consistent results are obtained at temperatures above 700 °C without thermal pretreatment and without a stabilizing agent. Second, prevailing theories regarding the oxygen exchange behavior on CeO₂ suggest that the rate limiting step in the exchange reaction occurs at the material surface, and therefore, will have a very strong dependence on SSA. In Winter's classic work on the oxygen exchange behavior of metal oxides, he suggests that at high temperatures the exchange rate is dominated by the surface mobility of active species/defects, and that as temperature decreases the dominant reaction will shift to the exchange of adsorbed surface oxygen with lattice oxygen ions.^{2,11} Other reports indicate that oxygen from the gas phase interacts with CeO₂ as an adsorbed superoxide (O₂⁻) or peroxide species (O₂²⁻), and that these species are generally agreed to incorporate into the CeO₂ lattice via the following set of generic reactions:¹²⁻¹⁴

Equation 1 and Winter both agree that the surface reactions described in these works are necessarily strongly dependent on the SSA of the material. The fact that the exchange rate becomes independent of

SSA at 1000 °C suggests that the rate is limited by an internal chemical reaction that is occurring through the bulk and not at the material surface. This internal chemical reaction has not been studied previously and was not reported in Winter's extensive work on the exchange behavior of metal oxides. It is likely that the internal chemical reaction represents a step in the exchange reaction that has never been evaluated in CeO₂ systems previously because it has never been isolated for study. Experiments in our previous work were relegated to evaluating the rate law at a single exchange temperature of 1000 °C, so despite observing this new stage in the reaction, we were not able to conclusively fit this step in the reaction into our overall understanding of the oxygen exchange behavior on CeO₂.

It is interesting to note that ThO₂^{2,15} exhibits oxygen exchange behavior similar to CeO₂ at lower temperatures while PuO₂¹⁶⁻¹⁹ exhibits oxygen exchange behavior similar to CeO₂ at 1000 °C.¹⁰ Similarities in these systems raises an intriguing question: is this novel oxygen exchange behavior the result of chemical similarities between these systems, similarities in the solid state ionic structure, or some combination of chemistry and structure? All of the known actinide dioxides form the fluorite atomic space grouping (*Fm* $\bar{3}$ *m*; #225), and one major reason why CeO₂ is a common surrogate material for the actinide dioxides is because it is the only chemically stable, non-radioactive, pure binary metal oxide that also takes on the fluorite space grouping under benign conditions.²⁰ Understanding the origins of this high temperature oxygen exchange behavior on CeO₂ may help improve our understanding of the chemistry and structure of the actinide dioxides. This may have value for improving both our fundamental knowledge of the complicated *f*-elements as well as the practical understanding of the actinide dioxides in the nuclear fuel cycle and in the environment.

While it is unlikely that the actinide dioxides will ever see practical use as catalysts or electrolytes in solid oxide fuel cells, some of the actinide dioxides require the practical application of an oxygen exchange reaction for safety purposes. U.S. radioisotope power systems (RPS) employed in space exploration utilize ²³⁸PuO₂ as a heat source to generate electricity using various forms of energy conversion technology, with development of an americium-241 oxide based heat source underway in

Europe.²¹⁻²⁸ The heat generating α radiation produced by these heat sources undergoes an (α ,n) reaction with the naturally occurring ^{17}O and ^{18}O isotopes in the oxide. This (α ,n) reaction can induce an increase in the more dangerous neutron radiation coming from the radioactive fuel, particularly for $^{238}\text{PuO}_2$ based heat sources.^{16-19,29,30} Performing an isotopic exchange reaction between $^{17}\text{O}/^{18}\text{O}$ and ^{16}O helps minimize neutron emission rates and provides a safer working environment for both the people and the spacecraft involved in any RPS project. Therefore, a more complete understanding of the oxygen exchange reaction on CeO_2 may help improve our understanding of the oxygen exchange reaction on the actinide dioxides, and help RPS users develop oxygen exchange procedures, adapt to processing changes, and understand currently unexplained phenomena without the need for extensive developmental work.

The report presented here investigates the rate limiting mechanisms for oxygen exchange reactions on CeO_2 between 600 and 1100 °C and shows how these mechanisms fit into our overall understanding of the oxygen exchange reaction. This information helps improve our understanding of the unique oxygen behavior in CeO_2 ; helps improve our understanding of the role CeO_2 plays as a catalyst and electrolyte for solid oxide fuel cells; and may provide additional insight into the chemistry of the actinide dioxides, particularly for RPS users.

2 Materials and Methods

2.1 Reagents and Services

CeO_2 powder with a nominal particle size of 70–100 nm was obtained from Alfa Aesar (Ward Hill, MA), -325 mesh (i.e. $\leq 44\ \mu\text{m}$) CeO_2 powder was obtained from Materion (Milwaukee, WI), and $> 5\ \mu\text{m}$ nominal particle size CeO_2 powder was obtained from Sigma-Aldrich (St. Louis, MO). All CeO_2 powders were $\geq 99.5\%$ purity, determined on a rare-earth metals basis. Specific surface area (SSA) and particle size distribution data were obtained from a commercial laboratory, Particle Technology Labs (Downers Grove, IL) and performed by a 3-point BET (SSA) and laser diffraction analysis (particle size distribution). Grain sizes were determined visually from images obtained using transmission electron

microscopy (TEM). 50% isotopically enriched ^{18}O gas was obtained from Isotech, Inc. (Miamisburg, OH) and packaged as a 1:4 mixture with N_2 to minimize pure oxygen safety concerns. Ultra Zero Air, a high purity grade of synthetic air containing only N_2 and O_2 in natural isotopic abundances, was obtained from AirGas (Radnor, PA).

2.2 Instrumentation and Methodology

Our previous report describes in detail the in-house constructed fused silica reaction chamber with on-line sampling and residual gas analyzer (RGA) mass spectrometric detection that was used to perform all of the oxygen exchange experiments.¹⁰ While this same report also describes the experimental procedure in detail, an abbreviated version of the procedure is also given here. A target mass of ~20 mg of CeO_2 was placed into a high purity alumina boat with the control thermocouple placed in direct contact with the alumina boat and inserted into a fused silica reaction tube with a nominal volume of 290 mL. The sample was then allowed to come to equilibrium with the desired temperature. Then, the system was flushed a minimum of three times with ~760 torr Ultra Zero Air. The reaction chamber was then evacuated before adding ~760 torr of the $^{18}\text{O}/\text{N}_2$ gas mixture. Gas phase isotopic ratios were then monitored via RGA. Upon completion of the exchange reaction, the tube was evacuated and re-filled to ~760 torr with Ultra-Zero Air so that a “reverse” reaction could be observed between the ^{16}O in the gas phase and the ^{18}O enriched CeO_2 . Previous results showed that identical exchange rates were obtained with ^{18}O and ^{16}O ,¹⁰ so we will not differentiate between any ^{18}O and ^{16}O based exchanges. The RGA continuously monitored the signals at $m/z = 7, 18, 28, 32, 34, \text{ and } 36, \text{ and } 40$ with a 5 second sampling rate. Conditions for these experiments were selected to keep the amount of exchange material larger than the amount of O found in the solid sample, to help maximize the amount of O that is exchanged out of the solid sample for detection by the RGA.

While a detailed description of the methods used to analyze this data were also discussed previously,¹⁰ we feel it is important to review some of the salient details. First, the derived rate law is:

$$\text{Rate} = k * F \quad (2)$$

where F is the fraction of reaction remaining. Second, the rate only has units of s^{-1} , meaning that this derivation of the rate law is independent of sample size. Finally, this rate law expresses the apparent rate of reaction, as described by the change in the ratio of oxygen isotopes in the gas phase. Technically, the true rate of the exchange reaction never changes since the sample is constantly exchanging oxygen with the gas phase and the chemical composition of the system does not change with time, despite changes in the isotopic composition. Equation 2 describes this apparent rate, and is derived from the true rate constant (k) as modified by a set of probability constants, which are summarized by F . Factors that influence the true rate of reaction can therefore be determined by observing how those experimental parameters (e.g. SSA) influence k .

3 Results and Discussion

3.1 Activation Energies of High Temperature Exchange Mechanisms

Figure 1 shows that the effect of temperature on the oxygen exchange rate for CeO_2 is actually quite complex. When the temperature is ≥ 1000 °C, both the -325 mesh and 70–100 nm samples produce identical rate constants and have an activation energy (E_a) of 11.0 ± 0.4 kJ/mol (0.114 eV). This high temperature, low E_a reaction observed was previously determined to be independent of oxygen partial pressure, total pressure, and most particle characteristics including particle size and SSA; leading to the conclusion that the rate is dominated by an internal chemical reaction that is occurring through the bulk and not at the surface of the material.¹⁰ As the temperature decreases below 1000 °C, the reaction governing the rate of exchange changes for the -325 mesh sample with an $E_a = 29.1 \pm 1.2$ kJ/mol (0.287 eV). Below 800 °C, the reaction governing the -325 mesh sample changes again with an $E_a = 114 \pm 8$ kJ/mol (1.18 eV). Meanwhile, the reaction governing the 70–100 nm sample is the same at all temperatures studied (600–1100 °C).

Figure 1. Arrhenius plots of the oxygen isotopic exchange reactions with CeO_2 showing three distinct rate limiting reactions. (■) 70–100 nm material. (□) 70–100 nm material after thermal treatment. (x) -325 mesh material.

Single column image

The reason for the drastic differences in exchange behavior on these two samples below 1000 °C is most likely due to their differences in SSA. Both samples are reported to be 99.5+% pure and produce identical powder x-ray diffraction patterns (Supplementary Information Figure S1), suggesting that any changes in bulk chemistry or structure are small and not capable of producing the changes observed here. Previous reports showed that this lot of the 70–100 nm material has a much broader distribution of particle sizes with more very large and very small particles than this lot of the -325 mesh material, suggesting that particle size does not play a role in these reactions.¹⁰ TEM images show that the grain sizes for the 70–100 nm and > 5 μm powders were determined to be 20 ± 8 nm and 105 ± 73 nm, respectively, with example TEM images are provided in Supplementary Information Figures S2 and S3. Our previous report shows that these two powders exhibit identical exchange rates at 1000 °C,¹⁰ suggesting that the exchange mechanism at this temperature is also independent of grain size. Thus, the surface characteristics of the material are one of the only major remaining factors that could impact the exchange rate. Since SSA for the -325 mesh sample ($4.23 \text{ m}^2/\text{g}$) is over six times smaller than the 70–100 nm sample ($26.94 \text{ m}^2/\text{g}$), even a relatively small dependence on SSA would cause a large change in the exchange rate and could explain the differences observed in Figure 1.

These conclusions are corroborated by several classical reports written by Winter on the oxygen exchange behavior of metal oxides. In this work, Winter concluded that the reaction limiting the exchange rate is typically the exchange of surface adsorbed oxygen with lattice oxygen ions at moderately

high temperatures (e.g. $\sim 200\text{--}400\text{ }^{\circ}\text{C}$), and that as temperature increases, the exchange rate will eventually become dominated by the surface migration of defects and/or active oxygen species.^{2,11} Winter makes it clear that both reactions will have a very strong dependence on the SSA of the material. Similarly, Equation 1 predicts that the exchange reaction will have a strong dependence on SSA since the amount of adsorbed oxygen will necessarily have a strong dependence on SSA. Winter also shows that E_a for the surface exchange on metal oxides typically falls within 80-160 kJ/mol, while the surface mobility reaction occurs at higher temperatures with a typical $E_a \leq 40\text{ kJ/mol}$.¹² Several reports have concluded that the reaction dominating the oxygen exchange rate for bulk CeO_2 at low temperatures (i.e. $350\text{--}520\text{ }^{\circ}\text{C}$) was the surface exchange and measured the E_a to be 122,¹ 109,² 122,³ 91³¹ kJ/mol in four separate studies, while one high temperature ($800\text{--}1300\text{ }^{\circ}\text{C}$) study specifically measured only the surface exchange and obtained an $E_a = 136\text{ kJ/mol}$.⁸ E_a values obtained here match the observations by Winter and others on both a quantitative level (i.e. 29.1 and 114 kJ/mol for the surface mobility and surface exchange reactions, respectively) and on a qualitative level. This suggests that surface mobility and surface exchange are the middle and low temperature exchange reactions observed on the -325 mesh sample, and that the differences in the exchange rates between the samples presented in Figure 1 are the result of differences in SSA. While the surface exchange reaction has been studied in detail previously, we are not aware of any previous studies that were able to obtain the E_a for the surface mobility reaction on CeO_2 .

It is interesting to note that the surface mobility and surface exchange reactions observed on the -325 mesh material are visibly competitive over the 700 to 800 $^{\circ}\text{C}$ range. Figure 2 presents first order rate law plots that show how the exchange rate for the -325 mesh material transitions with temperature. At 900 $^{\circ}\text{C}$, the exchange rate does not appear to be significantly influenced by these competing reactions, which makes sense because Figure 1 predicts that the surface mobility and surface exchange will produce the exact same rate at 890 $^{\circ}\text{C}$ on the -325 mesh material. As the temperature decreases, the surface exchange becomes more prominent. At 800 $^{\circ}\text{C}$ it is possible to obtain k for the surface mobility from the early sections of the plot and k for the surface exchange from the later sections of the plot. By 700 $^{\circ}\text{C}$, the

influence of the surface exchange is large enough that it is no longer possible to extract k for the surface mobility from the early plot, but its influence is still observed through a significant curvature in the data. It is still possible, however, to obtain k for the surface exchange reaction from the later portions of the plot. Finally, at 600 °C the surface exchange completely dominates the exchange rate. This gradual transition over the course of several hundred degrees is interesting because it suggests that the surface mobility and surface exchange have different dependencies on the same fundamental particle characteristic, and since we know that the surface mobility and surface exchange are both dependent on the SSA, it would seem reasonable to hypothesize that these reactions have different dependencies on SSA. The -325 mesh material has broad, bi-modal distribution of particle sizes ($\sim 0.1\text{--}5\text{ }\mu\text{m}$), which implies a range of SSA.¹⁰ Assuming that the surface mobility and surface exchange reactions have a different dependence on SSA, particles on one end of the SSA spectrum would transition into the surface exchange reaction before particles on the other end of the spectrum, creating a rate law plot with a curved transition in the region where the two reactions are competitive.

Figure 2. -325 mesh samples experience a competitive reaction mechanism influenced by both surface mobility and surface exchange. At 900 °C the rates of the two reactions are identical with surface exchange completely dominating at 600 °C.

2 Column Image

One of the well-known properties of CeO_2 is its ability to become partially reduced at high temperatures and low oxygen pressures, and the presence of Ce(III) could have a significant impact on the exchange rates. Fortunately, the oxygen partial pressure in the exchange experiments presented here are quite high (~ 150 torr), so the anticipated amount of reduction is very small. The literature predicts that the stoichiometry of cerium dioxide will be approximately $\text{CeO}_{1.9997}$ at 1100°C under the conditions presented here, with the stoichiometry approaching a true value of 2.00 as the temperature decreases.³² Therefore, even if the presence of Ce(III) can influence the exchange rate, the quantity of Ce(III) is expected to be small enough that it will not produce a significant impact on these experiments.

3.2 Impact of Thermal Treatment on Exchange Rate

Determining the exact mathematical effect of SSA on the surface mobility and surface exchange rates is much more challenging than it would appear. CeO_2 samples will have radically different SSA values depending on the exact thermal treatments experienced during production, and it has been observed that thermal treatment at high temperatures can induce a reduction in SSA, particularly if the thermal treatment temperature is higher than any production temperatures (e.g. calcination temperature).³³⁻³⁶ It is likely this sensitivity of SSA to thermal treatment contributed to the common wisdom regarding preparing CeO_2 powders, which suggests that samples need to undergo a thermal pretreatment in order to obtain consistent results. While the justification for this wisdom is not widely discussed in the literature, the implication would appear to be that thermal treatment at temperatures significantly higher than the experimentation temperature creates samples with SSA values that are unlikely to change during experimentation. Table 1 shows that both the 70–100 nm and -325 mesh samples experience significant, time-dependent reductions in SSA as a result of extended exposure to 1000°C , indicating that exposure to very high exchange temperatures may induce a change in SSA during the experiment. Reduction in SSA is most likely due to a reduction in the surface texture and porosity of the powders studied. Figure S4 in the supplementary information shows an example SEM image of the

70–100 nm powder, which clearly has a significant amount of surface texture and porosity. While attempting to determine the exact mathematical impact of SSA on the surface mobility and surface exchange rates when the experiment causes SSA to change is not impossible, it is also not trivial and beyond the scope of this work.

Table 1. Effect of Thermal Treatments at 1000 °C on Specific Surface Area (m²/g)

Treatment	70–100 nm	-325 mesh
None	26.94	4.23
2 h	8.90	2.17
8 h	4.28	1.88

While samples used in this report never underwent any specific thermal pretreatment, the testing was generally performed on a single sample of material in descending temperature order. In other words, a single sample of -325 mesh material was tested at 1000, 900, 800, 700, and then finally at 600 °C, with a minimum of 4 experiments being performed at each temperature. The exceptions to this are the experiments performed at 1100 °C, which were always executed with a fresh sample and were discarded after all replicate experiments were completed. Therefore, even though the samples were not “pretreated” *per se*, they underwent thermal treatment for ~2 hours during the 1000 °C experiments (~30 min per experiment). After the 1000 °C experiments, further exposure to lower temperatures did not appear to cause significant changes to the exchange rate (i.e. consistent replicate measurements). This supports the conclusion that the proposed internal chemical reaction is not a surface based reaction, since the changing SSA would have caused the rate of the 1000 °C experiments to change during replicate runs. It also suggests that the internal chemical reaction is not related to the porosity of the material, since it is anticipated that the open porosity of the material is actively being closed off during these experiments as a result of exposure to the exchange temperatures.

Interestingly, Figure 1 shows that this sample of -325 mesh material transitioned from the internal chemical reaction to the surface mobility dominated rate at about 1000 °C, and Table 1 predicts that the

SSA for this sample was $\sim 2 \text{ m}^2/\text{g}$. Therefore, despite the challenges in obtaining the exact mathematical impact of SSA on the exchange rate, it is possible to provide a set of guidelines regarding the transition from the internal chemical reaction to the surface mobility limited rate. When exchange temperatures are $\geq 1000 \text{ }^\circ\text{C}$ and $\text{SSA} \geq 2 \text{ m}^2/\text{g}$, samples will have exchange rates that will be limited by the internal chemical reaction. When the SSA for a sample is large, the sample will have faster surface mobility and surface exchange reactions, so the exchange rate is more likely to be limited by the internal chemical reaction. Likewise, when the exchange temperature is high, the surface mobility and surface exchange reactions are likely to be faster than the internal chemical reaction. As either of these values decrease, it is anticipated that eventually the surface mobility reaction will eventually become slow enough to dominate the exchange rate.

Evidence of the exchange reaction altering the SSA was also observed when a sample of 70–100 nm material was tested at 1000, 900, 800, 700, 650, and 600 $^\circ\text{C}$; in descending temperature order. Exchange rates followed the internal chemical reaction from 1000–800 $^\circ\text{C}$, but below 800 $^\circ\text{C}$ the exchange rates decreased drastically and produced an $E_a = 31.1 \text{ kJ/mol}$ (Figure 1, open squares), very similar to the E_a obtained for the surface mobility reaction observed on the -325 mesh material. Subsequent results obtained on a new sample of 70–100 nm material that had never experienced high temperature treatment produced rates that continued to follow the internal chemical reaction curve when the only exchange temperatures tested were 700, 650, 625, and 600 $^\circ\text{C}$ (Figure 1, closed squares). This data suggests that the sample exposed to higher exchange temperatures experienced a reduction in SSA, which subsequently caused the exchange to transition into the surface mobility limited rate at a higher temperature. Meanwhile, the sample that was not exposed to higher exchange temperatures had a larger SSA, which led to a faster surface mobility rate and resulted in an exchange that was still limited by the internal chemical reaction at lower temperatures.

3.3 Novel Non-Diffusion Based Internal Chemical Reaction

The high temperature, low E_a internal chemical reaction observed in this report represents a step in the exchange reaction that has not been evaluated in CeO_2 systems previously because it has not been isolated for study. Since the first observation of, "...an extremely high but unstable activity of cerium oxide powder..." reported almost 50 years ago,^{1,9} most exchange studies on pure CeO_2 claims that experiments need to be kept below 700 °C with proper thermal pretreatment in order to obtain reliable results. No study of this "extremely high but unstable activity" on CeO_2 has been reported before now, and we hypothesize that the reason for this is that previous high temperature exchange experiments were causing a change in the SSA of the sample during the experiment. Changes in SSA during the experiment could cause a dynamic change in the exchange rate and possibly even in the exchange mechanism, which would make the empirical data very difficult to interpret, or to quote the previous work, "unstable."

As discussed previously, the internal chemical reaction described here is independent of nearly all particle characteristics and atmospheric conditions, including SSA.¹⁰ Thus, it seems clear that the rate limiting reaction must be a reaction that is occurring in the bulk of the material. Current theories that describe the oxygen exchange reaction (e.g. Equation 1) suggest that the entire exchange occurs at the surface of the material. This further suggests that the internal reaction proposed is most likely not a major step in the exchange reaction proper, but instead relates to the isotopic redistribution of lattice oxygen throughout the material.

It then seems logical to assume that isotopic redistribution rates are related to the ionic mobility of the lattice oxygen ions within the material, but the rate of exchange also appears to be independent of ionic mobility. Ionic mobility is defined as a function of the ionic diffusivity of the material, which means that the mechanism of ionic mobility is diffusion based.³⁷⁻³⁹ Our previous report clearly establishes that the reaction being observed is limited by a chemical reaction and not by diffusion because the data does not fit the equations used to evaluate a diffusion based mechanism.¹⁰ Additionally, rates based on a diffusion mechanism will have a second-order dependence on the size of the system (e.g. particle size, grain size, and/or SSA), while rates of ionic motion in the presence of a potential (e.g. voltage) will have

a first-order dependence on the size of the system.³⁸ Previous results on four different CeO₂ powders indicate that the exchange rate at 1000 °C is independent of particle size and SSA,¹⁰ and this report shows that the exchange rate is also independent of grain size. This corroborates the conclusion that the isotopic redistribution rate is not limited by diffusion, which, in turn, suggests that the isotopic redistribution rate is independent of ionic mobility.

One hypothesis that would explain this particular observation is the motion of an oxygen ion between its normal lattice position and the vacant interstitial space found at the center of the fluorite space grouping. The presence of oxygen ions in, or near, the interstitial space is commonly observed, or suspected, in many fluorite based metal oxides including: CeO₂,⁴⁰ ThO₂,⁴¹ UO₂,⁴² UO_{2+x},^{39,41,43} and PuO_{2+x}.^{44,45} Movement of lattice oxygen ions towards the interstitial spaces would produce vacancies at the normal lattice positions and create a channel for oxygen ions to move through the structure and reach lattice positions that were previously inaccessible. Since the rate of oxygen ion motion through the lattice is determined by the rate of oxygen ions moving between lattice positions, this shift into the interstitial space should not influence the actual rate of ionic motion, but it would influence the ability of the ¹⁸O exchange material to reach all of the lattice positions and promote isotopic equilibrium.

At this point, it is important to briefly discuss the semantics of the oxygen exchange reaction. As discussed previously, the actual exchange of oxygen ions between the gas phase and the solid material never actually changes, and this exchange nominally occurs at the surface of the material. Therefore, one could make the argument that the “true exchange rate” is actually the surface exchange rate, and that the redistribution of oxygen ions throughout the bulk of the material is unrelated to the exchange rate. Thus, some might consider an apparent rate that is limited by an internal chemical reaction through the bulk not a measure of the actual exchange rate, since the exchange is still occurring at the surface of the material independent of the isotopic redistribution rates. Since our goal with this discussion is not to be pedantic or to argue the validity of this opinion, we will simply state that we acknowledge this point of view. However, we justify referring to the bulk redistribution as a part of the overall exchange rate because the

goal of this experiment was complete isotopic exchange with the gas phase, which would include isotopic redistribution as a critical stage in the reaction.

It is also important to note that these conclusions are tied to the particle properties of the system studied here. In addition to SSA, the exchange kinetics and rate limiting reactions are expected to be dependent on both particle and grain size. As we discussed in our previous report, the powders studied here had a typical particle size ranging from submicron to $\leq 44\ \mu\text{m}$, and we anticipate that as particle size increases, grain boundary diffusion will eventually take over and become the rate limiting mechanism.¹⁰ Similarly, as grain size increases, we expect that lattice diffusion will eventually take over and become the rate limiting mechanism. We anticipate that transitioning into these diffusion based rate limiting mechanisms will be a complex function of particle properties (i.e. SSA, particle size, and/or grain size) and temperature. Therefore, it is important to consider the influence of particle properties when comparing other data to the results presented here.

3.4 Consequences for $^{238}\text{PuO}_2$ Oxygen Exchange Reactions

Finally, since our previous report showed that the oxygen exchange reaction on CeO_2 is very similar to PuO_2 at $1000\ ^\circ\text{C}$,¹⁰ it is likely that PuO_2 will exhibit oxygen exchange behavior similar to the results presented here. This will help inform the RPS community and help guide future experimentation on $^{238}\text{PuO}_2$ for purposes of reducing the detrimental (α, n) reaction from the naturally occurring ^{17}O and ^{18}O . Since CeO_2 is also a surrogate material for AmO_2 , the results presented here may prove to be useful studies for potential (α, n) reduction in a European RPS as well.²¹⁻²⁸

4 Conclusions

Empirical evidence presented here allows us to conclude that the very high temperature activity observed during the oxygen exchange of pure CeO_2 is related to the ability of oxygen ions to move through the CeO_2 structure but not related to the speed with which these ions move. A potential reason

why this stage in the exchange reaction has never been studied before is due to the significant changes in SSA that can occur in CeO_2 systems at high temperatures. High temperature oxygen exchange experiments are likely to produce a reduction in the specific surface area of the CeO_2 powder, which means that performing the exchange reaction could cause a change in the exchange rate and/or rate limiting step if the exchange is operating in or near the surface mobility or surface exchange limited rates. These changes in SSA could cause a dynamic change in the exchange rate and/or rate limiting reaction, which could cause data obtained from such experiments to appear unstable and difficult to interpret. In many ways, we were fortunate that our initial operational temperature of 1000 °C was just barely high enough that the internal chemical reaction was still the dominant mechanism observable in all samples, and that any reductions in SSA caused by the experimentation were not enough to change the rate limiting mechanism during testing or for replicate experiments. As temperature decreases, the rate becomes limited by the mobility of active surface species followed by the surface exchange of adsorbed oxygen with oxygen ions in the lattice. The transition between these rate limiting steps was observed to be a complex function including at least temperature and SSA. In this work we report the E_a for the surface exchange, surface mobility, and internal chemical reaction observed in the oxygen exchange reaction on CeO_2 .

Acknowledgements

This work was funded under the U.S. Department of Energy contract #: DE-NE0000422. The authors would like to acknowledge the help of Dr. Robert Ellefson from Mound Technologies, Inc., for discussions regarding sampling methodologies. Additional discussions with David Armstrong at Los Alamos National Laboratory, Dr. Robert Wham at Oak Ridge National Laboratory, and Dirk Cairns-Gallimore at the U.S. Department of Energy were particularly helpful for designing experiments that would provide data useful to the $^{238}\text{PuO}_2$ community. Barbara Miller is gratefully acknowledged for obtaining the TEM images.

References

1. Sazonov, L. A.; Sokolovskii, V. D.; Boreskov, G. K. *Kinet. Katal.*, **1966**, 7, 521.
2. Winter, E. R. S. *J. Chem. Soc. A*, **1968**, 9, 2889-2902.
3. Gorelov, G. P.; Kurumchin, E. Kh. *Kinet. Katal.*, **1986**, 27, 1346.
4. Anan'ev, M. V.; Kurumchin, E. Kh.; Vdovin, G. K.; Bershitshaya, N. M. *Russ. J. Electrochem.*, **2012**, 48, 871-878.
5. Manning, P. S.; Sirman, J. D.; Kilner, J. A. *Solid State Ionics*, **1997**, 93, 125-132.
6. Ruiz-Trejo, E.; Sirman, J. D.; Baikov, Y. M.; Kilner, J. A. *Solid State Ionics*, **1998**, 113-115, 565-569.
7. Lane, J. A.; Kilner, J. A. *Solid State Ionics*, **2000**, 136-137, 927-932.
8. Kamiya, M.; Shimada, E.; Ikuma, Y.; Komatsu, M.; Haneda, H. *J. Electrochem. Soc.*, **2000**, 147, 1222-1227.
9. Kharton, V. V.; Yaremchenko, A. A.; Naumovich, E. N.; Marques, F. M. B. *J. Solid State Electrochem.*, **2000**, 4, 243-266.
10. Whiting, C. E.; Douglas, J. M.; Cremeans, B. M.; Barklay, C. D.; Kramer, D. P. *J. Solid State Chem.*, **2014**, 218, 116-123.
11. Winter, E. R. S. "The Reactivity of Oxide Surfaces," in *Advances in Catalysis*, vol. X 196-241; Eley, D. D.; Frankenburg, W. G.; Komarewsky, V. I. Eds.; Academic Press, Inc.: New York, NY, 1958.
12. Li, C.; Domen, K.; Maruya, K.; Onishi, T. *J. Catal.*, **1990**, 123, 436-442.
13. Binet, C.; Daturi, M.; Lavalley, J. C. *Catal. Today*, **1999**, 50, 207-225.
14. Gross, M. S.; Ulla, M. A.; Querini, C. A. *J. Mol. Catal. A*, **2012**, 352, 86-94.
15. Winter, E. R. S. *J. Chem. Soc.*, **1950**, 1170-1175.
16. Rutherford, W. M.; Huffman, G. N.; Coffey, D. L. *Nucl. Appl.*, **1967**, 3, 366.
17. Miles, J. C.; Deaton, R. L.; Wiedenheft, C. J., *MLM-1891*, **1972**.

18. Deaton R. L.; Wiedenheft, C. J. *J. Inorg. Nucl. Chem.*, **1972**, 34, 3419-3425.
19. Porter, J. A.; Thompson, M. C. *DP-1153*, **1968**.
20. Morss, L. R.; Edelstein, N. M.; Fuger, J. Eds., *The Chemistry of the Actinide and Transactinide Elements*, 4th Ed.; Springer: Dordrecht, The Netherlands, 2010.
21. Summerer L.; Stephenson, K. *Proc. IMechE, Part G: J. Aerospace Eng.*, **2011**, 225, 129-143.
22. Tinsley, T. P.; Sarsfield, M. J.; Cordingley, L.; Stephenson, K. *NETS 2012*, **2012**, 3028.
23. Tinsley, T. P.; Clough, M.; Rhodes, C.; Sarsfield, M. J.; Stephenson, K. *NETS 2012*, **2012**, 3029.
24. Ambrosi, R. M.; Williams, H. R.; Samara-Ratna, P.; Bannister, N. P.; Vernon, D.; Crawford, T.; Bickness, C.; Jorden, A.; Slade, R.; Deacon, T.; Koenig, J.; Jaegle, M.; Stephenson, K. *NETS 2012*, **2012**, 3043.
25. Sarsfield, M. J.; Bell, K.; Maher, C. J.; Carrott, M. J.; Gregson, C.; Brown, J.; Woodhead, D. A.; Baker, S. R.; Cordingly, L.; Taylor, R. J.; Tinsley, T. P.; Rice, T. G.; Rhodes, C. J.; Clough, M. *NETS 2013*, **2013**, 6750.
26. Ambrosi, R. M.; Williams, H. R.; Samara-Ratna, P.; Jordan, A.; Slade, R.; Bannister, N. P.; Sykes, J.; Deacon, T.; Stephenson, K.; Simpson, K.; Reece, M.; Ning, H.; Stuttard, M.; Rice, T.; Tinsley, T.; Sarsfield, M.; Jaegle, M.; Koenig, J.; Edgington, A.; Lerman, H. *NETS 2013*, **2013**, 6780.
27. Sarsfield, M. J.; Bell, K.; Maher, C. J.; Carrott, M. J.; Gregson, C.; Brown, J.; Woodhead, D. A.; Baker, S. R.; Taylor, R. J.; Tinsley, T. P.; Rice, T. G.; Rhodes, C. J.; Clough, M.; Stephenson, K. *NETS 2014*, **2014**, 1001.
28. Ambrosi, R. M.; Williams, H. R.; Samara-Ratna, P.; Bannister, N. *NETS 2014*, **2014**, 1014.
29. Hyde, E. K.; Perlman, I.; Seaborg, G. T. *The Nuclear Properties of the Heavy Elements II*; Prentice Hall: Englewood Cliffs, NJ, 1964.
30. Plymale, D. L. *J. Inorg. Nucl. Chem.*, **1968**, 30, 886-890.

31. Antoshin, G. V.; Guinh, N. Q.; Minachev, Kh. M.; Kondrat'ev, D. A. *Izv. Akad. Nauk SSSR, Ser. Khim*, **1971**, *10*, 2346-2348.
32. Tuller, H. L. and Nowick, A. S. *J. Electrochem. Soc.*, **1979**, *126*, 209-217
33. de Leitenburg, C.; Trovarelli, A.; Llorca, J.; Cavani, F.; Bini, G. *Appl. Catal. A*, **1996**, *139*, 161-173.
34. Stark, W. J.; Mädler, L.; Maciejewski, M.; Pratsinis, S. E.; Baiker, A. *Chem. Commun.*, **2003**, *39*, 588-589.
35. Stark, W. J.; Grunwaldt, J. D.; Maciejewski, M.; Pratsinis, S. E.; Baiker, A. *Chem. Mater.*, **2005**, *17*, 3352-3358.
36. Stark, W. J.; Maciejewski, M.; Mädler, L.; Pratsinis, S. E.; Baiker, A. *J. Catal.*, **2003**, *220*, 35-43.
37. Shoko, E.; Smith, M. F.; McKenzie, R. H. *J. Phys. Chem. Solids*, **2011**, *72*, 1482-1494.
38. Gellings, P. J.; Bouwmeester, H. J. M. *Catal. Today*, **1992**, *12*, 1-105.
39. Kümmerle, E. A.; Heger, G. *J. Solid State Chem.*, **1999**, *147*, 485-500.
40. Mamontov, E.; Egami, T. *J. Phys. Chem. Solids*, **2000**, *61*, 1345-1356.
41. Colmenares, C. A. *Prog. Solid State Chem.*, **1975**, *9*, 139-239.
42. Auskern, A. B.; Belle, J. *J. Nucl. Mater*, **1961**, *3*, 267-276.
43. Andersson, D. A.; Baldinozzi, G.; Desgranges, L.; Conradson, D. R.; Conradson, S. D. *Inorg. Chem.*, **2013**, *52*, 2769-2778.
44. Haschke, J. M.; Allen, T. H.; Morales, L. A. *Science*, **2000**, *287*, 285-287
45. Petit, L.; Svane, A.; Szotek, Z.; Temmerman, W. M. *Science*, **2003**, *301*, 498-501.