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# POTENTIOMETRIC SENSOR FOR REAL-TIME MONITORING OF MULTIVALENT ION CONCENTRATIONS IN MOLTEN SALT

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## ABSTRACT

Electrorefining of metallic spent nuclear fuel in high temperature molten salt systems is a core technology in pyroprocessing, which in turn plays a critical role in advanced fuel cycle technologies. In electrorefining, spent nuclear fuel is electrochemically processed to separate uranium, noble metals, and active metals, which include the transuranics. The accumulation of the active metals in a LiCl-KCl eutectic molten salt electrolyte occurs at the expense of the  $\text{UCl}_3$ -oxidant concentration in the electrolyte, which must be periodically replenished. Our interests lie in the accumulation of active metals in the molten salt electrolyte. The real-time monitoring of actinide concentrations in the molten salt electrolyte is highly desirable for controlling electrochemical operations and assuring material safeguards. However, real-time monitoring is not possible with current methods for sampling and chemical analysis. A new solid-state electrochemical sensor is being developed for real-time monitoring of actinide ion concentrations in a molten salt electrorefiner. The ultimate function of the sensor is to monitor plutonium and other actinide concentrations during electrorefining operations. In this work gadolinium was employed as a surrogate material for plutonium. In a parametric study, polycrystalline Na- $\beta''$ -alumina precursor discs and tubes were subject to vapor-phase exchange with  $\text{Gd}^{3+}$  using a  $\text{GdCl}_3$ -containing salt to produce exchanged Gd- $\beta''$ -alumina samples. Electrochemical impedance spectroscopy and microstructural analysis were performed on the ion-exchanged discs to determine the relationship between ion exchange and  $\text{Gd}^{3+}$  ion conductivity. A sensor design and model are proposed for configuring the ion-exchanged tubes as potentiometric sensors in order to monitor real-time  $\text{Gd}^{3+}$  ion concentrations in mixtures of  $\text{GdCl}_3$  and LiCl-KCl eutectic molten salts through measurement of the potential difference between a reference and working electrode.

## INTRODUCTION

The concept of a ceramic actinide sensor is based on relatively mature technology. Solid electrolytes and solid-state ionic devices have been used as sensors in molten media for over 40 years. Molten state and gas phase sensors are commercially available. Solid electrolyte based sensors have material properties that are advantageous when used in pyroprocessing, and several solid ionic conducting materials show sufficient conductivity in the operating temperature range. Solid electrolyte compounds are generally stable and can withstand the harsh environment of a molten chloride. When configured as potentiometric sensors, these materials have precise, near real-time ionic conductivity and sensitivity. These traits make solid electrolyte based sensors well suited to electrorefining applications. This technique additionally produces no sample waste and would be more cost effective than conventional sampling and analysis methods for measuring ion concentrations in the molten salt.

One candidate material for a solid state electrolyte is sodium beta double-prime alumina (Na- $\beta''$ -alumina;  $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$ ). Na- $\beta''$ -alumina and sodium beta-alumina (Na- $\beta$ -alumina) are used as solid state sensor materials for molten metal applications<sup>1</sup>. Ion exchange with other elements whose ions are mobile in Na- $\beta''$ -alumina can enable the sensor to detect these other elements. This versatility of the  $\beta''$ -aluminas presents an additional challenge, as multiple mobile ions can produce a potential across the electrolyte. In addition, Na- $\beta$ -alumina is known to respond to changes in oxygen partial pressure ( $pO_2$ ), and other elements with thermodynamic activity in solution, even when those elements have not been exchanged into the  $\beta''$ -alumina electrolyte<sup>1,2</sup>.

It is well reported that up to 100% of the monovalent sodium ( $Na^+$ ) ion content of Na- $\beta''$ -alumina can be replaced through ion exchange with monovalent, divalent, or trivalent cations<sup>3,4,5</sup>. Beta double-prime alumina is primarily an ionic conductor, with an electronic conductivity of less than  $10^{-11}$  S/cm at 25°C<sup>6</sup>. The versatility and high ionic conductivity of  $\beta''$ -alumina is due to its crystal structure, which is made up of spinel-type blocks of close-packed oxygen, separated at every fifth layer by a conduction plane, where three-quarters of the oxygen ions are missing. In Na- $\beta''$ -alumina, the excess sodium ions lie in these planes and have a relatively high mobility due to their smaller radius compared to the surrounding oxygen ions<sup>7</sup>. Electroneutrality is maintained by substitution of aluminum ions ( $Al^{3+}$ ) with magnesium ( $Mg^{2+}$ ) or lithium ( $Li^+$ ) ions in the spinel blocks. Ion exchange is accomplished either by immersing the  $\beta''$ -alumina crystal in a molten salt or by exposing the crystal to the salt vapor. Once exchanged, the  $\beta''$ -alumina crystal is primarily an ionic conductor of the exchanged ion.

The goal of this research is to create a sensor that responds to a single actinide element concentration in a molten salt electrorefiner, where there are many cations present that are known to be able to exchange into  $\beta''$ -alumina. Understanding the degree to which  $\beta''$ -alumina can be modified to select for a specific species under such conditions is essential, but only lightly addressed in the literature. Larose et al found that the presence of higher valence cations did not affect a potential across a pure Na- $\beta''$ -alumina electrolyte<sup>2</sup>, while Teitz and Urland suggest that the presence of trivalent ions in the conduction plane block the conduction pathways of the  $Na^+$  ions<sup>8</sup>. This suggests that exchanged  $\beta''$ -alumina may at least select for ions with similar valence to the primary conducting ion. By thoroughly exchanging specific ions into  $\beta''$ -alumina, we hope to create a sensor that responds to changes in the concentration of that ion, while not being significantly affected by changes in the chemical potentials of other species in the melt.

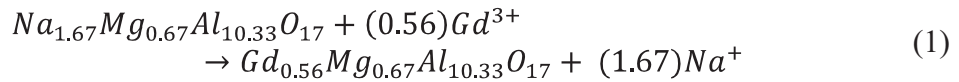
Inspired by sensors for use in molten metals<sup>2</sup>, a potentiometric sensor design is considered using  $\beta''$ -alumina tubes exchanged with trivalent gadolinium ( $Gd^{3+}$ ) ions. A model is also proposed for using ion-exchanged  $\beta''$ -alumina to monitor ion concentrations in LiCl-KCl eutectic molten salts through measurement of the potential difference between a reference and working electrode.

## **THEORY**

Gadolinium ion exchange into Na- $\beta''$ -alumina has been performed in the past, with 100% exchange reported in 5 hours at 615°C by immersion of Na- $\beta''$ -alumina single crystals into molten  $GdCl_3$  ( $T_m=609^\circ C$ )<sup>5</sup>. The exchanged single crystals yielded relatively low gadolinium ionic conductivity ( $\sim 10^{-11}$  S/cm at 25°C,  $\sim 8 \times 10^{-5}$  S/cm at 400°C)<sup>9,10</sup> compared to  $Na^+$  ion conductivity in the precursor

Na- $\beta''$ -alumina ( $2 \times 10^{-3}$  S/cm at 25°C,  $3.8 \times 10^{-1}$  S/cm at 400°C)<sup>11</sup>. It is generally understood that the increase in Coulombic forces produced by the substitution of trivalent ions for monovalent ions is the cause of the decrease in conductivity and increase in activation energy<sup>12</sup>. This effect may be caused in part by the contraction of the *c* lattice parameter due to the smaller ionic radius of Gd<sup>3+</sup> ions compared to Na<sup>+</sup> ions<sup>13,14</sup>. The Gd<sup>3+</sup> ion conductivity, while low, is expected to be sufficient to provide reasonable sensitivity to the range of concentrations present in an electrorefiner.

Single-crystal X-ray diffraction studies have shown that Na<sup>+</sup> ions occupy both Beevers-Ross (BR), anti-Beevers-Ross (aBR), and mid-oxygen (mO) sites in the conduction plane<sup>7</sup>, while Gd<sup>3+</sup> ions are found primarily on the mO sites<sup>10</sup>. To maintain electroneutrality, for each Gd<sup>3+</sup> ion that enters the crystal, three Na<sup>+</sup> ions must exit<sup>15</sup>. This charge balance is shown by the exchange reaction in Equation 1. The decrease in the number of conducting ions is also understood to contribute to lower conductivity in higher valence  $\beta''$ -aluminas<sup>16</sup>.



Ionic conduction in Na- $\beta''$ -alumina occurs through a vacancy mechanism, where approximately 17% of the available sodium sites are vacant<sup>17</sup>. Exchanging three Na<sup>+</sup> ions for a single Gd<sup>3+</sup> ion increases the vacancy concentration, but the number of available hopping sites decreases due to the strong preference of the Gd<sup>3+</sup> ions for eightfold coordinated mO sites<sup>18</sup>. The large hopping distance between the mO sites may contribute to the higher activation energy and lower conductivity. Previous studies have found that there is significant ordering of mobile ions in the conduction plane, which may also affect the transport properties of mobile ions through the material<sup>19</sup>. Other research indicates that trivalent ion mobility has a significant temperature dependence, which can affect mobile cation site preference and distribution<sup>20</sup>. In general, it is observed that conductivity of divalent and trivalent cations is significantly lower in  $\beta''$ -alumina than monovalent cations. For cations capable of multiple valence states, which includes many of the actinides, heat treatment in low pO<sub>2</sub> environments may affect the valence state preference of exchanging ions<sup>15,21</sup>. Additionally, exposing  $\beta''$ -alumina to low pO<sub>2</sub> at high temperature is known to cause reversible oxygen loss from the conduction plane. Indicators of oxygen loss include changes in color and ionic conductivity<sup>22,23</sup>.

Many studies have utilized Electrochemical Impedance Spectroscopy (EIS) to measure the total conductivity of single crystals of Na- $\beta''$ -alumina and derivatives of Na- $\beta''$ -alumina, where the Na<sup>+</sup> ions have been exchanged for other monovalent, divalent, and trivalent cations.<sup>4,5,6,24</sup> In some cases, multivalent- $\beta''$ -aluminas have been used as the exchange precursor material. Trivalent cations are found to readily exchange with each other at rates similar to those at which Na<sup>+</sup> ions can be exchanged by trivalent cations.<sup>15</sup> In this work, Gd<sup>3+</sup> ions were used as a surrogate species and exchanged into Na- $\beta''$ -alumina discs and tubes. EIS was performed on exchanged discs to determine their conductivity as a function of exchange parameters and temperature. It is understood that the measured ionic conductivity may be due to the ionic contributions of several ionic species, especially where exchange was not 100% complete. It is expected that even under ideal conditions, contrary to reports in the literature, Na- $\beta''$ -alumina cannot be 100% completely exchanged with Gd<sup>3+</sup> ions, though multiple exchanges in separate batches of pure salt may produce very high levels of exchange. It is assumed that the electronic conductivity of  $\beta''$ -alumina is several orders of

magnitude lower than the ionic conductivity, and thus is negligible, so that the measured total conductivity corresponds to the ionic conductivity of the material.

It should be noted that the majority of published  $\beta''$ -alumina ion exchange and conductivity research has focused on single crystal studies. In this application, a sensor will likely take the form of a tube made from polycrystalline  $\beta''$ -alumina. Where polycrystalline  $\beta''$ -alumina has been studied in the literature, the ionic conductivity is found to be significantly lower than in single crystals<sup>25,26,27</sup>. These differences are largely attributed to the grain boundaries, and suggest that grain size and orientation have a considerable effect on the polycrystalline  $\beta''$ -alumina ionic conductivity. It has also been observed that for ion exchange in polycrystalline  $\beta''$ -alumina, it is necessary to have a substituting ion with a radius that is similar to or smaller than the starting conducting species<sup>27</sup>. In this specific case, exchange from  $\text{Na}^+$  to  $\text{Gd}^{3+}$ , or  $\text{Na}^+$  to  $\text{Pu}^{3+}$  would meet that requirement. The effective ionic radii of select species are given in Table 1.

Table 1. Ionic radii. Radii correspond to eightfold coordination based on  $r(\text{VI}\text{O}^{2-}) = 1.40 \text{ \AA}$ <sup>14</sup>

Ion	Effective Ionic Radii (Å)
$\text{Na}^+$	1.16
$\text{Gd}^{3+}$	1.06
$\text{Pu}^{3+}$	0.96

Once exchanged,  $\beta''$ -alumina tubes would be filled with a reference electrode with a fixed, known mobile cation (M) activity,  $a_M(\text{ref})$ , and submerged in a molten salt with unknown mobile cation activity,  $a_M(\text{WE})$ . This system can be described as a galvanic cell written according to Equation 2,



where (M = Na, Gd, Pu). In this case, where the electronic conductivity is many orders of magnitude smaller than the ionic conductivity<sup>6</sup>, the cell potential can be written using the Nernst equation according to Equation 3,

$$E = E^0 + \left(\frac{RT}{ZF}\right) \ln \left[ \frac{a_M(\text{ref})}{a_M(\text{WE})} \right] \quad (3)$$

where R is the gas constant, T is the temperature in K, Z is the charge of the transporting ion (1 for  $\text{Na}^+$ , 3 for  $\text{Gd}^{3+}$  and  $\text{Pu}^{3+}$ ), F is faraday's constant, and  $E^0$ , the standard electrode potential for the cell, is a constant for a given system. Since the activity of the ion being sensed at the reference electrode is fixed, this can be rewritten as Equation 4,

$$E = E^0 - \left(\frac{RT}{ZF}\right) \ln[a_M(\text{WE})] + A \quad (4)$$

where A represents the constant reference electrode potential. Given that Pu concentration in electrorefiner salt is likely to be on the order of a few weight percent<sup>28</sup>, in this model M can be assumed to be dilute in the molten salt, and thus  $a_M = \gamma_M^0 \cdot X_M$  where  $X_M$  is the mole fraction of

species M and  $\gamma_M^0$ , the Henry's law constant, is the activity coefficient for the species M, and is understood to be independent of concentration in a dilute solution. Equation 4 can be rewritten as Equation 5,

$$E = E^0 - \left(\frac{RT}{ZF}\right) \ln[\gamma_M^0(WE)] - \left(\frac{RT}{ZF}\right) \ln[X_M(WE)] + A \quad (5)$$

and it can be seen that at a given temperature a plot of potential as a function of  $\ln[X_M(WE)]$  for a purely Nernstian potential cell yields a straight line of slope,  $-\left(\frac{RT}{ZF}\right)$ . In reality, we expect deviation from this linear behavior due to non-Nernstian effects at the cell electrodes. These effects can include electron conduction and significant electrode polarization in comparison to the polarization of the electrolyte<sup>29</sup>. In our application, non-Nernstian behavior may additionally include the effects of the chemical potentials of other species in the molten electrorefiner salt across the electrolyte.

The choice of reference electrode can have a profound effect on sensor response, sensitivity and stability, and is still in progress<sup>30</sup>. Larose et al found that a polycrystalline Na- $\beta''$ -alumina tube configured with a Na reference could be used to detect the Na content of molten Al to parts per million precision by measuring the cell potential<sup>2</sup>. The present work focused on the preparation and characterization of gadolinium exchanged Na- $\beta''$ -alumina in order to determine if it is sufficiently conductive and stable for use as an actinide sensor in a molten salt.

## EXPERIMENT

Polycrystalline Na- $\beta''$ -alumina crystal discs and tubes (Ionotec Ltd, England) were suspended in a tantalum crucible above GdCl<sub>3</sub> (Alfa Aesar, 99.99%). Care was taken to keep all components under a dry argon atmosphere (~50 ppm O<sub>2</sub>) to prevent hydration of the  $\beta''$ -alumina samples and chloride salts, and to avoid formation of oxychlorides that might affect ion exchange. Any minor hydration that occurred during  $\beta''$ -alumina manufacturing or preparation was assumed to be reversible and to have not permanently affected the  $\beta''$ -alumina ionic conductivity<sup>31</sup>. The crucible was heated to 700°C and kept at temperature for 48-72 hours to allow vapor-phase exchange of Gd<sup>3+</sup> ions for Na<sup>+</sup> ions in the  $\beta''$ -alumina structure. Gadolinium trichloride melts at 609°C, and the vapor pressure at 700°C is approximately  $1 \times 10^{-6}$  bar. After exchange was complete, the discs were removed from the argon atmosphere, and had a non-uniform grayish-blue appearance, and any loose deposited material was wiped from the surface. Several exchanged discs were annealed at 500°C for 24 hours in argon atmosphere to allow the exchanged ions to diffuse throughout the conduction planes and to remove any residual moisture incorporated during cleaning.

Two methods were employed to verify the percent of ion exchange. After vapor deposits were removed by wiping the sample, the weight change was measured with a balance accurate to 1 mg. Any weight change was attributed to the reaction shown in Equation 1. A 100% exchange of Gd<sup>3+</sup> ions for Na<sup>+</sup> ions should correspond to an 8% increase in weight, assuming that each Gd<sup>3+</sup> ion replaces three Na<sup>+</sup> ions. Weight change is known to be an imprecise indicator of exchange, particularly in the case of multivalent ion exchange<sup>15</sup>, therefore scanning electron microscopy (SEM) quantitative energy dispersive X-ray (EDX) analysis (JEOL JSM-7000F SEM, Oxford INCAx-sight EDAX) was subsequently performed to confirm the extent and distribution of cation



exchange<sup>32,33</sup>. A SEM backscattered electron (BSE) photomicrograph of the cross section of a partially exchanged disk is shown in Figure 1. The exchanged part of the sample is visible by a change in brightness and coarser texture of the material. The dashed line in the figure indicates the location of an EDX line scan. The line scan yielded intensities of gadolinium and sodium present in each sample, which were compared with background and theoretical atomic percents to determine the extent of exchange, shown in Figure 2.

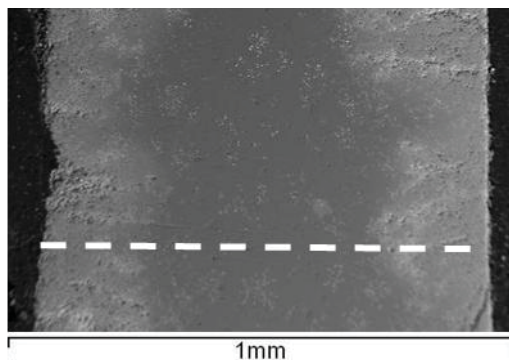


Figure 1. SEM BSE Micrograph of partially exchanged Gd- $\beta''$ -alumina.

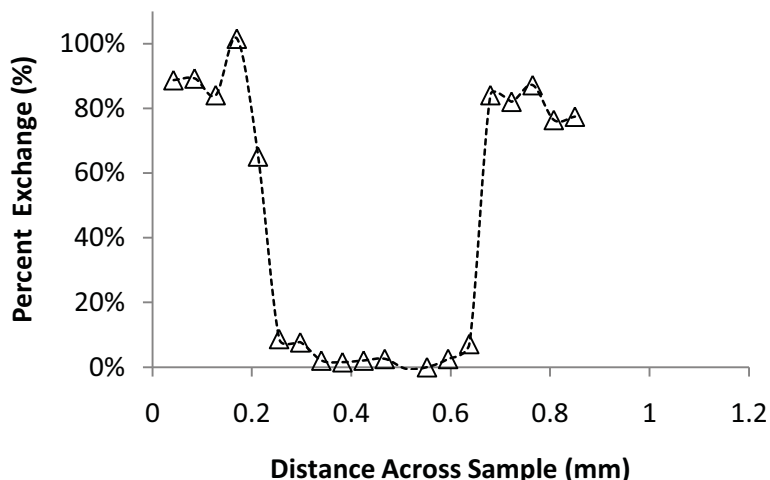


Figure 2. Plot of percent exchange as a function of distance across sample.

The absolute value of the EDX measurements is not expected to be precise, due to background noise and instrument error, however, there is good correlation between the visible effects of exchange and the relative levels of  $Gd^{+3}$  and  $Na^{+}$  ions present as measured with EDX.

Standard powder x-ray diffraction (XRD) was performed with a Bruker D8 X-ray Diffractometer on crushed samples. Lanthanum hexaboride ( $LaB_6$ ) was used as a standard to detect any shift in lattice parameters as a result of exchange.

The ionic conductivity was measured as a function of temperature using AC impedance spectroscopy (Solartron SI 1287 Electrochemical System and 1255 Frequency Response Analyzer). Electrode contact was achieved by sputtering Au/Pd onto masked  $\beta''$ -alumina discs and then painting platinum

(SPI-Chem Platinum Paint) onto the sputtered layer. In order to apply the sputtered layer, the discs were briefly exposed to an air environment. The discs were subsequently fired between 750°C and 900°C. Both un-exchanged (sodium conducting) and gadolinium exchanged discs were tested as a function of temperature in a low humidity, high purity argon atmosphere.

## RESULTS AND DISCUSSION

Ion exchange was found to be extremely sensitive to salt concentration and other impurities. EDX of some pellets showed over 90% of the sodium content was exchanged with gadolinium, up to and exceeding 100% of the theoretical amount of gadolinium expected. Analysis of sample weight change corresponded well with EDX results for samples with high amounts of exchange, but as expected only provided a rough, average estimate of the percent exchange where EDX showed that exchange was incomplete and not uniform across the samples. Annealing the discs after exchange had little effect on the exchange distribution. Figure 3 illustrates the grey discoloration that the discs acquired during Gd exchange (left), which disappeared after annealing (right), such that the discs appeared white.

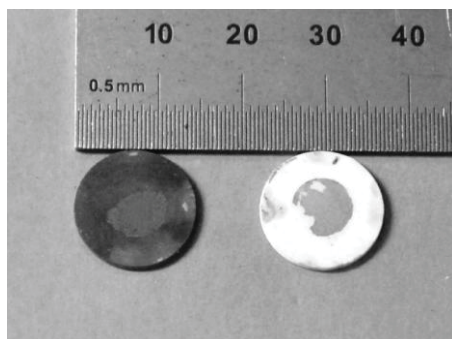


Figure 3. Gd-exchanged  $\beta''$ -alumina discs; after Gd exchange (left) and after annealing (right). The grey spot in the center is platinum paint applied for conductivity testing.

Gadolinium vapor exchanged samples showed minor cracking ( $\sim 100$ - $200\ \mu\text{m}$  long, after a 64 hour exchange) at the sample edges, indicating that the  $\text{GdCl}_3$  has a corrosive effect on  $\beta''$ -alumina, and a sensor might require a thicker  $\beta''$ -alumina substrate in order to be mechanically sound for practical use as a sensor. The low ionic conductivity of Gd-  $\beta''$ -alumina poses a potential problem, as a thicker electrolyte will have higher resistance and a subsequently lower response time. Chlorine was also detected by EDX along the inner crack surfaces, suggesting that the  $\text{GdCl}_3$  deposited into the cracks during exchange.

X-ray diffraction patterns obtained by crushing the discs after exchange were consistent with the SEM EDX results. Un-exchanged and very lightly exchanged samples yielded clear crystalline patterns that closely matched the published pattern definition file (PDF) for Na- $\beta''$ -alumina, while highly-exchanged sample peaks shifted towards higher values of 2-theta. This is consistent with the idea that the unit cell shrinks as a result of exchange with a higher valence ion, and there was good agreement between the shifted peaks and a published pattern definition file (PDF) for Gd- $\beta''$ -alumina. The exchanged patterns indicate that the  $\beta''$ -alumina structure may have become less crystalline during exchange, which can be seen in Figure 4 as a broadening of the peaks.



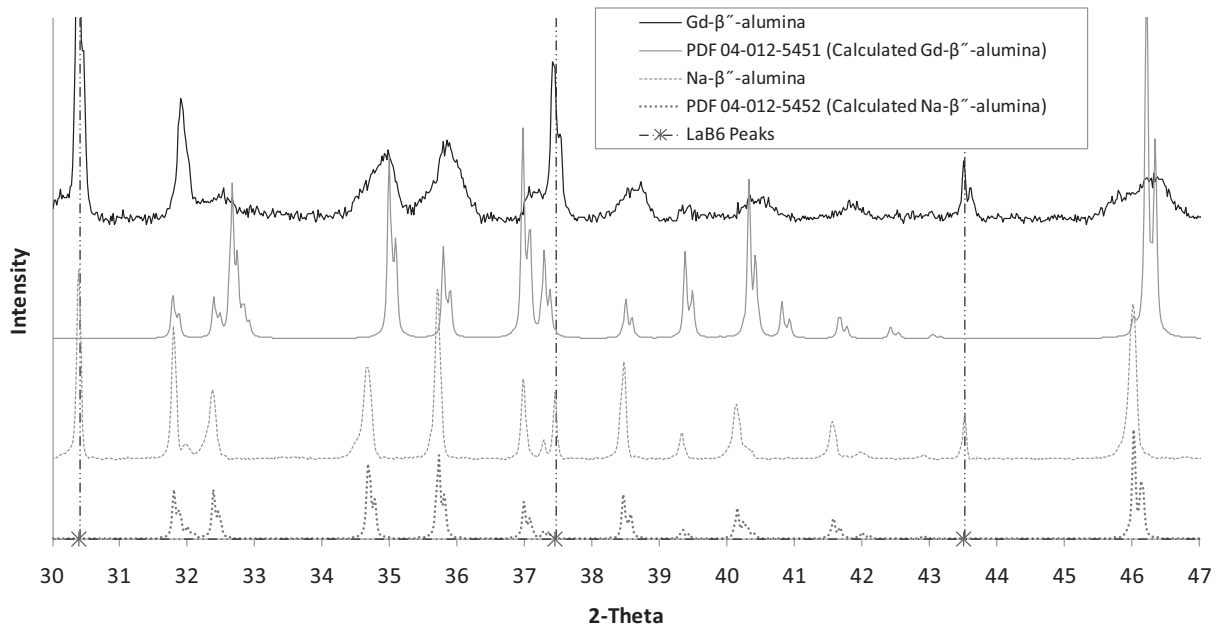


Figure 4. X-ray diffraction pattern showing a Gd-exchanged disc, a calculated PDF pattern for Gd-β''-alumina, an un-exchanged disc, a calculated PDF pattern for Na-β''-alumina, and LaB<sub>6</sub> standard peaks.

Conductivity results of as-received Na-β''-alumina were found to be slightly lower than published Na<sup>+</sup> ionic conductivity values and values provided by the manufacturer. This may be due to contact resistance between the platinum and Au/Pd electrodes and Na-β''-alumina disc surface.

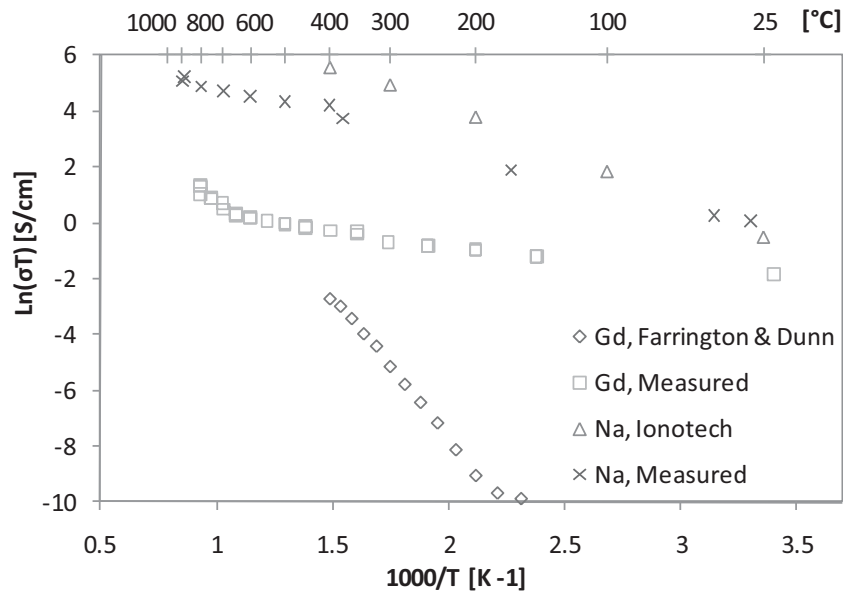


Figure 5. Measured and published values of the ionic conductivity for Na-β''-alumina and Gd-β''-alumina.

Conductivity of vapor-phase gadolinium exchanged samples were consistently higher than the published results from Dunn and Farrington<sup>5</sup>. Figure 5 shows that comparison, which was contributed to incomplete ion exchange and later confirmed by SEM. The activation energy ( $E_a$ ) of our results (0.09 eV) was noticeably lower than the published values for Gd- $\beta''$ -alumina (0.82 eV), and are closer to the activation energy for Na- $\beta''$ -alumina ( $\sim$ 0.25 eV), consistent with incomplete exchange.

## CONCLUSIONS

EIS data yielded values for the ionic conductivity of Na- $\beta''$ -alumina that were consistently, albeit slightly lower than the values supplied by the manufacturer, but within the range of values found in the large volume of literature on the conductivity of Na- $\beta''$ -alumina. Gadolinium ions were exchanged into Na- $\beta''$ -alumina, and the measured conductivity was lower than the ionic conductivity of Na- $\beta''$ -alumina.

It was evident from SEM EDX that 100% exchange of  $Gd^{3+}$  ions into Na- $\beta''$ -alumina did not occur, and future work will include efforts to increase the completeness of exchange and compare the conductivity of those materials with earlier published results. SEM BSE images showed that Gd exchanged Na- $\beta''$ -alumina developed minor cracks and microstructural coarsening during exchange, suggesting that trivalent ion exchange into Na- $\beta''$ -alumina might cause stress sufficient to weaken the material and make fabrication of a physically stable sensor difficult. Future work will investigate the possibility of exchanging an ion with intermediary size and valence to reduce that strain and resulting damage.

A design and model for an exchanged Na- $\beta''$ -alumina potentiometric sensor in molten salt was proposed based on existing sensor designs similar to those used in the aluminum industry. To the authors' knowledge, the use of exchanged  $\beta''$ -alumina for potentiometric measurements in a molten salt electrorefiner is unprecedented and based on these results warrants further research.

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