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The ionic resistance and chemical stability of polycrystalline K- β'' alumina in aqueous solutions at room temperature



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ABSTRACT

Interfaces between alkali metal solid state electrolytes and aqueous solutions are often unstable. In particular, the use of β/β'' alumina superionic conductors is generally limited to conditions absent of liquid water due to their well-known sensitivity to water vapor. However, the degradation mechanism upon exposure to aqueous solutions is not well understood. Using impedance spectroscopy, infrared spectroscopy, and chemical analysis, we studied the mechanism of ionic impedance rise for K⁺-ion-conducting, polycrystalline K- β'' alumina membranes in room temperature aqueous solutions. By using a non-blocking Fe²⁺/Fe³⁺ couple in a symmetric aqueous impedance cell with different concentrations of LiOH, NaOH, KOH, CsOH, and KBr, we find that the rate of resistance rise of the membrane is highly dependent on the pH and K⁺ concentration in the solution. We find the rate decreases from ~50–200 Ω cm² h⁻¹ in neutral pH solutions to ~0.1–1 Ω cm² h⁻¹ in alkaline solutions or solutions with high K⁺ concentrations. Characterization results are consistent with ion exchange of K⁺ for hydrated protons as the mechanism of resistance rise.

1. Introduction

The use of solid electrolytes in aqueous solutions is not common in devices today due to the significant challenge of maintaining their stability. Further, understanding the interface between ceramic solid electrolytes and aqueous solutions could result in the development of new electrochemical devices such as sensors, ion pumps, and energy storage devices. This interface is particularly important for alkali-air secondary batteries, where water is sometimes used on the positive electrode to dissolve large amounts of alkali hydroxides [1].

When exposed to water, solid electrolytes undergo many chemical interactions, such as ion exchange, dissolution, and surface reactions, which are briefly reviewed here. One of the most common interactions is the exchange of the alkali-metal ions in the solid with protons from the solution. For some Li+-ion-conducting ceramics, such as Li₇La₃Zr₂O₁₂, Li⁺ exchanges with protons without changing the crystal structure or lattice parameters of the ceramic [2]. When NASICONstructured Na₃Zr_{1.88}Y_{0.12}Si₂PO₁₂ is immersed in water, hydronium ions slowly exchange with Na⁺, forming a new phase with a larger lattice constant, and lower ionic conductivity [3]. Beyond ion exchange, many studies find evidence of chemical reactions between water and the host lattice or impurity phases. For example, Li_{0.44}La_{0.52}TiO₃ and $Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$ have been reported to dissolve in acidic and alkaline solutions, respectively [4,5]. For NASICON (Na superionic conductor), dissolution of impurity phases, such as amorphous phases at grain boundaries [6-8] was observed. Both ion exchange and

chemical reactions can also lead to the formation of hydroxides on the surface of the ceramic which, when exposed to air, form carbonate species [9]. The large variety of possible interactions of solid electrolytes with aqueous solutions necessitates the use of multiple techniques to isolate the degradation mechanism for a given material.

In this work, we study the degradation mechanism of the K⁺ superionic conductor K-β" alumina when exposed to aqueous solutions of a variety of compositions. Degradation in this context is defined as the impedance degradation (i.e. the change in impedance with time). We carefully examine the chemical interactions of the material in solutions of LiOH, NaOH, KOH, CsOH, and KBr by using impedance spectroscopy to probe the interfacial resistance of the material in solution. This particular solid electrolyte was chosen for the study because we have recently discovered that it is stable against Na-K alloy [10], a liquid metal at room temperature. Such stability provides motivation to study K-B" alumina in a variety of liquid environments for application as a membrane in flow batteries. In addition, this work can help the community understand how various β/β'' alumina compounds degrade in liquid water. Since β/β'' alumina is a well-studied system, we now review its relevant properties as well as the literature on its interaction with water.

Briefly, β/β'' alumina is a class of 2-D ionic conductors that transports H⁺, Li⁺, Na⁺, K⁺, Ag⁺, Pb²⁺, and other cations [11]. β and β'' alumina have the nominal compositions $M_{1.55}Al_{11}O_{17.28}$ and $M_{1.67}Al_{10.66}Li_{0.3}O_{17}$, respectively, where M is a monovalent cation. However, the composition of the phase can vary depending on alkali

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Table 1 Conductivity at 25 °C (S cm⁻¹) for various β/β'' alumina compounds.

Mobile ion	β single crystal	β'' single crystal	β" polycrystal
Li Na K	3×10^{-3} [34] 1.4 × 10 ⁻² [12] 6.5 × 10 ⁻⁵ [12]	1.0×10^{-1} [12] 1.3×10^{-1} [12]	2.0×10^{-2} [27] ~1 × 10 ⁻³ [35]

metal content and doping. The crystal structure consists of alternating layers of spinel-like aluminum oxide blocks and conduction planes which contain the mobile ions. β and β'' have similar layered structures [11], though the β'' phase has a higher concentration of mobile ions which is accommodated via substitution of Al^{3+} ions with lower valence ions (e.g. Mg^{2+} or Li^+). Single crystalline K- β'' alumina has room temperature conductivities as high as $0.13 \, \mathrm{S \, cm^{-1}}$ [12], which is among the highest of any ceramic alkali-ion solid electrolyte reported to date. We note that K- β'' alumina single crystals have a significantly higher K⁺ conductivity than the β phase, summarized in Table 1. The extensive amount of research on the conduction of ions in β'' alumina makes it a model system for the study of solid state ion conductors.

The interaction of β/β'' alumina with water vapor is well characterized, but only a few studies have been performed with aqueous solutions. Multiple studies show that the affinity for water vapor depends on the alkali metal ion [13–15]. Li- β alumina has the most negative enthalpy of hydration followed by Na- β alumina. K- β alumina, on the other hand, does not absorb measurable amounts of water from air [13,16]. The interaction of the β'' phase with water vapor is less studied. One such study by Bates et al. examined the hydration thermodynamics of Na- β'' alumina single crystals by careful mass and infrared spectroscopy measurements [17].

The conductivity of β/β'' alumina compounds was also investigated largely in terms of exposure to water vapor, air, and, to some extent, liquid water. Will [18] found that the magnitude of the impedance of polycrystalline Na-β alumina at 0.1 MHz remained nearly constant with time, while the impedance at 1 Hz increased by an order of magnitude after exposure to liquid water for 2 h and air for 330 h. The impedance rise was attributed to H_3O^+ incorporation in the grain boundaries. However, as pointed out by Farrington et al. [19], the low frequency impedance rise could be due to the formation of hydronium-ß alumina which is present near the surface as a separate phase. In another study, Dunbar et al. found that the tracer diffusion coefficients were unchanged after exposing single crystals and polycrystals of Na-ß alumina to boiling water [20]. On the other hand, Kaneda et al. reported that exposing Na-β alumina crystals to boiling water did not cause water incorporation based on infrared spectroscopy data [21]. Interestingly, Will and Mitoff observed that polycrystalline Na-ß alumina membranes could be used in primary batteries with water on the positive electrode side and exhibited only slow increases in resistance [22].

The impact of water vapor on the conductivity of Na- β'' alumina has also been studied. Dunn [23] as well as Armstrong and Sellick [24] investigated the effect of water vapor on Na- β'' polycrystals. Both studies found that exposure to air caused significant increases in the ionic resistance. Interestingly, Armstrong found that under saturated water partial pressure, the resistance of the samples decreased over time, which was attributed to a liquid-like phase forming in grain boundaries or microcracks [24]. More recently, Koh et al. have claimed that NaAlO₂ phases at grain boundaries formed during liquid phase sintering can be susceptible to attack by water [25]. However, Na- β'' alumina produced by a vapor phase method to prevent the formation of NaAlO₂ still show significant impedance degradation when exposed to aqueous solutions while operated in a flow battery [26].

In summary, while most studies show that water has a negative impact on the conductivity of β/β'' alumina compounds, the literature is not entirely consistent. Furthermore, the mechanism for this degradation has yet to be fully determined. In the case of K- β'' alumina,

there are no reports of its stability or conductivity in aqueous solutions. By examining K- β'' alumina with a host of analytical techniques, we aim to determine the degradation mechanism of this material in aqueous solutions and to provide additional data on the degradation of β'' alumina compounds in general. Preventing the degradation of β'' alumina compounds in aqueous solutions could enable many electrochemical applications. This is especially true for flow batteries, where a separator with minimal crossover is required.

2. Materials

Li-doped K- β'' alumina membranes of nominal composition K_{1.67}Li_{0.67}Al₁₁O₁₇ were produced via vapor ion exchange from fully dense Na- β'' alumina discs by Ionotec Ltd. The density of the disks was > 99% of theoretical density. The β'' volume phase fraction was > 0.85, determined by powder X-Ray diffraction (XRD) combined with Rietveld refinement. Approximately 0.5 wt% of the sample is ZrO₂, a strengthening additive. Trace Na is also present. All experiments were conducted on either K- β'' alumina discs or powders crushed from these discs with a mortar and pestle. Discs were 23 mm in diameter and between 1.5 and 3 mm in thickness. Powders were sieved using 4 different mesh sizes: 500, 350, 250, and 180 µm. The resulting average particle sizes were 590, 440, and 290 µm, quantified using scanning electron microscopy (SEM). All solution chemistry utilized Milli-Q deionized water with a resistivity > 18 MΩ cm.

3. Methods

3.1. Electrochemical impedance spectroscopy (EIS)

To measure the transport properties of K-β" membranes in aqueous solutions, a symmetric cell was used (Fig. 1). Biologic SP-200 and SP-300 potentiostats recorded the impedance spectra. Specifically, potentiostatic impedance spectroscopy was measured at a perturbation amplitude of 20 mV, between 0.1 Hz and 3 MHz. For all tests, a membrane area of 1.26 cm² was in contact with the aqueous solutions (as defined by o-ring diameter). Our cell is designed in order to examine the K⁺ ion transport through the membrane by utilizing the electrochemical couple $K_3Fe(CN)_6/K_4Fe(CN)_6$ (0.05/0.05 M) on Au electrodes. This couple changes between the Fe^{2+}/Fe^{3+} states which forces K^+ ions to flow between the two sides of the membrane when a bias is applied. Blocking electrodes (i.e. electrodes which do not allow for Faradaic reactions) were not used because they obscure changes in lowfrequency impedance components if the capacitance of the blocking electrode is smaller than the capacitance of the ionic conductor. The charge transfer resistance of the Faradaic reactions was $< 10 \Omega$, and therefore can be neglected from the analysis. Furthermore, baselines performed on blank cells over multiple days showed no changes of any





Fig. 1. Schematic of electrochemical impedance spectroscopy cell.



Fig. 2. (A) Equivalent circuit diagram used for analyzing aqueous impedance data. Circuit elements defined in the text. (B) Initial Nyquist plot of impedance cell with K-β" alumina membrane in 1 M KOH. Membrane area = 1.26 cm^2 . Membrane thickness = 0.2 cm. (C) Impedance of K-β" alumina using gold blocking electrodes as the contact.

impedance feature impedance within $\pm 5 \Omega$. Buffers and supporting electrolyte were not used in order to eliminate any unwanted interactions between species in solution and the membrane. Using this symmetric cell, we measured the resistance of the membrane exposed to a variety of aqueous solutions as a function of time. Experiments in alkaline solutions of concentration > 0.1 M were conducted in a temperature controlled environmental chamber at 30 \pm 0.1 °C to more accurately quantify the degradation rate.

3.2. Materials characterization methods

SEM was conducted with an FEI XL30 Sirion (5 keV). Transmission electron microscopy (TEM) images were taken with an FEI Tecnai G2 F20 X-TWIN (200 keV). TEM samples were prepared by mechanical grinding to 20 µm thickness followed by 1 h of Ar ion milling with a Gatan PIPs II at 5 keV and 5° incident beam angle. To examine bulk reactions between K-β" alumina and water, XRD (Bruker D8-Advanced, Cu Ka X-rays) and Rietveld refinement (TOPAS) were carried out. Four phases were assumed: K- β'' alumina (ICSD 200993, with Li in place of the Mg dopant), K-β alumina (ICSD 298), tetragonal ZrO₂ (ICSD 66781), and monoclinic ZrO₂ (ICSD 26488). To gain insight into chemical reactions taking place between the membrane and water, powders of K- β'' alumina were immersed in water and the solution composition measured using inductively coupled plasma optical emission spectroscopy (ICP-OES). A Thermo Scientific ICAP 6300 Duo View Spectrometer was used for the ICP-OES measurements. The concentration of K⁺ dissolved in the solution was measured as a function of time and normalized by surface area based on SEM images of K- β'' powders. pH was measured using a Mettler Toledo FiveEasy Plus pH meter with LE422 pH electrode in a three-neck glass flask, bubbled with N2 through a rubber septum and stirred to ensure atmospheric CO2 did

not affect the measurement. Fourier transform infrared spectroscopy in attenuated total reflectance mode (ATR-FTIR) was used to examine water content in the membrane. A polished K- β " alumina disk was exposed to DI water for various lengths of time, removed and blown dry with N₂. Subsequently, FTIR-ATR measurements were taken with a diamond ATR element using a single bounce of the IR beam at a 45° incident angle. Finally, atomic force microscopy (AFM) images were taken with an Asylum Research Cypher AFM; a K- β " membrane was first imaged after being polished and thermally etched at 1200 °C for 1 h to reveal the grain structure, and then imaged again after the sample was immersed in 5% acetic acid for 330 h.

4. Results

4.1. Electrochemical impedance spectroscopy

The ionic resistance of a membrane is the most important figure of merit for a solid electrolyte, which was measured for K- β'' alumina in a symmetric cell using EIS as described above. Fig. 2B shows a Nyquist plot for a pristine membrane. The high frequency intercept with the real axis corresponds to the sum of the aqueous solution resistance and the intragrain resistance of the K- β'' alumina, labeled as $R_g + R_s$. We attribute the high frequency arc with a characteristic frequency of $\sim 10^2$ kHz to the grain boundary of pristine β alumina, with a resistance of R_{gb} . We also measured the impedance of membranes with Au blocking electrodes, which is shown in Fig. 2C. We observed a similar impedance response at $\sim 10^2$ kHz using these blocking electrodes. However, the data in Fig. 2C also show another arc at slightly lower frequencies. This feature is attributable to the contact between the gold blocking electrodes and the sample. This low frequency arc is not attributable to the membrane because others have noted that the low



Fig. 3. Typical Nyquist plots showing evolution of impedance between 0 and 16 h for membrane in aqueous solutions of $0.05 \text{ M K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$. Membrane area = 1.26 cm^2 . Membrane thickness = 0.2 cm. Fits are for the circuit model shown in Fig. 2.



Fig. 4. Resistance of the "water impurity" feature from impedance data, $R_{\rm w}$ over time. Top: membrane in 0.05 M K₃Fe(CN)₆/K₄Fe(CN)₆, pH \sim 8.5, with no additional salts added. Nyquist plots shown in Fig. 3. Bottom: membrane in the same solution with 1 M cesium hydroxide. Lines are linear least squares.

frequency features are dependent on the type of contact [27]. This low frequency feature is also not present for pristine membranes in our aqueous cells. For our aqueous impedance data at the lowest frequencies, we see an infinite Warburg-type response, which corresponds to ferro/ferricvanide diffusion in the aqueous solutions, which was verified by testing the impedance cell without a beta alumina membrane. The resistances of the Faradaic reactions are negligible relative to the other resistances in the system, and therefore are not included in the impedance circuit. All of the features remain invariant with time, except for the one between 10^2 and 10^3 Hz, which grows significantly. We define this feature as the "water impurity" feature, with a resistance Rw. Both grain boundary and water impurity features were modeled using constant phase elements. Nyquist plots are shown in Fig. 3 as a function of time exposed to an aqueous solution of ferro/ferricvanide. The electrochemical cell was modeled using the equivalent circuit shown in Fig. 2, and the area-specific resistance (ASR) and effective capacitance of the water impurity feature were tracked as a function of time.

We find that the evolution of the resistance depends strongly on the concentration and type of salt (LiOH, NaOH, KOH, CsOH, and KBr), and that the membrane degradation rate can be tuned by several orders of magnitude based on salt concentration alone. For exposure < 50 h, the resistance vs. time curves are approximately linear (Fig. 4), and the slope gives the ASR rate of change, dR_w/dt. The resistance vs time curve is also approximately linear for all of the solution compositions examined here. Fig. 5 shows how the concentration of various salts affects this quantity. These data are representative of both pristine membranes and those which were mechanically polished before each measurement. Specifically, for solutions at near neutral pH, the ASR rates of change is significant, between 50 and $200 \,\Omega \,\text{cm}^2 \,\text{h}^{-1}$. For solutions with pH between 11 and 14, the ASR rate of change decreased between two to three orders of magnitude relative to that of neutral-pH solutions, to ~0.1–1 Ω cm² h⁻¹. Consistently, this degradation rate is similar to the degradation rate found during 300 h cycling of batteries at $1.9 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ using the same solution at the negative electrode and NaK liquid metal at the positive electrode [10]. As a reference, a pristine membrane with 2 mm thickness and zero interfacial resistance has an ASR of about $50\,\Omega\,\mathrm{cm}^2$. Based on this value, the normalized degradation rate is 100–400% h^{-1} for neutral pH solutions and 0.2–2% h^{-1} in high pH solutions. In general, we find no consistent trends in changes of the effective capacitance over time. Beyond the significant tunability demonstrated, comparison of the degradation rate between the various



Fig. 5. Resistance rate of change of water impurity feature for various solution chemistries. The pH of the alkali hydroxide solutions increases linearly with the log of concentration. The pH of the KBr solutions is approximately constant with KBr concentration. Error bars are ± 2 standard deviations of log(dr/rt) from [KOH] = 10^{-6} M tests. Membrane area is 1.27 cm², membrane thickness is between 2 and 3 mm. Fits are guides to the eye.

salts suggests cation interaction with the membrane is taking place. This is seen from the data in Fig. 5. The ASR rate of change is over an order of magnitude higher at 1 M concentrations for LiOH and NaOH compared to KOH and CsOH, despite having similar pH.

To explore the effect of K^+ ions on the degradation of the membrane, we also examined solutions with KBr. Using KBr allows us to examine the effect of K^+ concentration on the degradation rate because the pH of these solutions does not change significantly with the KBr concentration. KBr also has a high solubility and does not react with the ferro/ferricyanide in solution. We find that the ASR rate of change decreased sharply with K^+ concentration, with a pH of approximately 6–7 (Fig. 5). It is interesting to note that the log scale degradation rate vs concentration slope is much greater for KBr (~1) than for KOH (~0.5) in the high salt concentration regime. Furthermore, only very high concentrations of K^+ ions in neutral pH water appear to lower the



Fig. 6. (A) Effect of mechanical grinding on reversal of impedance. All impedance experiments were performed in $0.05 \text{ M} \text{ K}_3 \text{Fe}(\text{CN})_6/\text{K}_4 \text{Fe}(\text{CN})_6$. (B) Effect of heat treatment on resistance rise. Top: resistance of pristine sample as a function of exposure to aqueous solution. Bottom: resistance of the same sample after heat treatment at 1000 °C in air for 1 h.

degradation rate, in contrast to hydroxide ions. We note that the highest concentrations of KBr reported here correspond to saturated solutions of KBr.

Finally, the reversibility of the impedance rise was also studied. Polishing away $< 10 \,\mu$ m of the degraded membrane restores the ASR to close to the pristine state (Fig. 6A). This result indicates that the effect of exposure to aqueous solution is limited to near the surface of the membrane. Other processes also partially reverse the degradation. These include heat treatment at 1000 °C, immersion in solutions of KOH and methanol, and immersion in molten salts such as KOH, KNO₃, or KCl. However, these regeneration procedures significantly affect the degradation rates in subsequent measurements, as shown in Fig. 6B for the case of heat treatment. The specific reasons for these results are unknown. However, other researchers have found changes in conductivity of \beta'' alumina compounds after heat treatments because of claimed changes in the host structure of the material [28]. These structural changes may also change the degradation rate in water. The cause of this hysteresis in reversibility is interesting and merits further study.

4.2. Characterization and discussion

We now discuss the possible mechanisms for impedance degradation of K- β'' alumina membranes in aqueous solutions. We will discuss three categories of possible degradation mechanisms (Fig. 7): (A) ion exchange between K⁺ in the solid and hydrated protons in the liquid; (B) chemical reactions or dissolution of grain boundary phases such as $KAlO_2$ -type phases, or phases containing impurity elements; (C) formation of liquid/solid interphase, such as AlOOH from the reaction of the oxide with water, or carbonates from dissolved CO_2 .

We first discuss mechanism (A), ion exchange, which we believe is the most likely cause of degradation. The proposed ion exchange reaction is given below:

$$K_{\beta''}^+ + 2 H_2 O_1 \leftrightarrow H_3 O_{\beta''}^+ + K_{aq}^+ + OH_{aq}^-$$

$$\tag{1}$$

where the subscript β'' indicates species in K- β'' alumina conduction planes. The inverse correlation of the impedance rate of change with pH and K⁺ concentration in solution is consistent with hydronium ion exchange as the primary cause of impedance degradation. Additional confirmation comes from ICP-OES analysis of K⁺ concentration in solution. Fig. 8 shows that K⁺ concentration increases with time, with a power law scaling of 0.37. This remains true for different particle sizes, consistent with the diffusion length in the particle being much smaller than the length of the particles themselves. Consistent with ICP-OES data, pH measurements show that the concentration of H₃O⁺ in solutions decreases concomitantly with a similar power law scaling, also shown in Fig. 8. These power law scalings indicate a sub-diffusive process consistent with hydronium ion exchange, though they do not rule out dissolution of impurity phases containing K, a point that we will return to later.

We also observed that K- β'' alumina degradation in solutions of LiOH and NaOH at pH > 10 increases, rather than decreases with pH. Moreover, the degradation in these solutions is faster than in solutions



Fig. 7. Possible mechanisms for impedance degradation in K- $\beta^{\prime\prime}$ alumina.



Fig. 8. Results of ICP-OES (A) and pH analysis (B) of K dissolution for K- β " alumina particles immersed in DI water. Powder surface area is projected surface area estimated from SEM images,with average particle size shown in legend A. Fits (orange) are linear least squares fits of log-log data. Errors listed are standard deviation from fits. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of CsOH and KOH at the same pH. One possible explanation for this observation is that hydrated Na⁺ or Li⁺ ions exchange with K⁺ in the lattice at high concentrations, lowering the conductivity due to the highly immobile nature of hydrated ions in the crystal, which is also claimed for H_3O^+ - β'' alumina [29]. Indeed, the fact that CsOH shows significantly lower degradation than LiOH and NaOH at high concentrations appears to support this hypothesis, since Cs⁺ is too large to intercalate into K- β'' alumina. It is possible that mixed alkali effects occur in high concentration alkali hydroxide solutions, but this mechanism would need additional data to verify.

To directly assess water uptake by K- β'' alumina, FTIR-ATR measurements were carried out on a polished disc immersed in aqueous solutions for various lengths of time (Fig. 9, trace C, D, E). Over time, four peaks above 2000 cm⁻¹ wavenumber grow in intensity for samples exposed to DI water. Bates et al. also observed these peaks for β'' alumina exposed to CO₂ and water vapor [30] (Fig. 9, trace A). Immersion



Fig. 9. FTIR-ATR spectra of K- β'' alumina membranes. (A) Polycrystalline Na- β'' alumina exposed to water vapor and CO₂ from reference [35]. (B) Single crystal H₃O⁺ β'' alumina from reference [30]. (C) polished K- β'' alumina exposed to DI water for 78 h, (D) Exposed to 2 M KOH for 300 h, (E) pristine K- β'' alumina (traces C–E are from this work).

in 2 M KOH solution results in significantly lower rates of peak growth (Fig. 9, trace D). It is useful to compare our measurements with previous measurements of hydronium- β'' alumina, which is produced by immersing single crystals of β'' alumina in concentrated acid at elevated temperatures for several days [29]. Previous infrared measurements of this compound [31] show a clear peak at 3000 cm⁻¹ (Fig. 9, trace B), which is absent in our measurement and the measurement by Bates et al. This could be because the degree of proton exchange causes different peaks to emerge (e.g., hydronium-hydronium interactions). Alternatively, it could mean that water is absorbed at grain boundaries rather than into the conduction planes, where the local bonding environment for hydrated protons could be different. Peaks at 1124 and 1237 cm⁻¹ are close to those reported for Al–OH bonds [32], possibly indicating the hydration of Al–O spinel block surfaces after exposure to water.

For completeness, we also carried out XRD on K- β'' alumina before and after DI water exposure. Fig. 10 shows that there are no statistically significant changes in lattice parameters for both discs of 2 mm and powders with average particle size of 290 µm (1000 h exposure). While the thermodynamics of hydronium ion exchange have not been reported, if all K⁺ ions exchange with hydronium, the lattice parameter should be comparable to hydronium β'' alumina. The only reported c lattice parameter for this compound [31] corresponds to a 0.8% expansion compared to K- β'' alumina. This discrepancy is likely explained by the shallow hydronium penetration (estimated to be < 10 µm based on polishing experiments discussed above) relative to the characteristic X-ray attenuation length (~60 µm for Cu K α X-rays at $\theta = 30^\circ$).

Turning to mechanism (B), chemical reactions or dissolution of grain boundary phases, we tested this hypothesis by examining ICP-OES and TEM data. Chemical analysis of the solution indicates that a notable amount of K⁺ is leached from the material over time (Fig. 8). However, even after 1000 h of immersion, only $\sim 1\%$ of the K⁺ ions have been leached from the K- β'' alumina for the particle sizes examined here. Since the reaction never reaches equilibrium, we are unable to determine the thermodynamic properties of the exchange. To rule out dissolution of impurity phases, we conducted additional ICP-OES measurements to determine if elements other than K are dissolved in the solution. The data shown in Fig. 11 reveals that the ratio of leached Na, Al, and Si to K is significantly < 1 (< 0.07). Therefore, dissolved phases, if any, cannot be silicates, specifically KAlO₂, NaAlO₂, or the β'' alumina host lattice. Consistently, XRD measurements did not detect crystalline NaAlO₂ or KAlO₂ phases in the pristine solid, although the volume fraction of these phases might be too small to resolve. Another possibility is the dissolution of amorphous K₂O type phases at grain boundaries, with the reaction given below:



 $K_2O_{\beta''} + H_2O_1 \leftrightarrow 2K_{aq}^+ + 2OH_{aq}^-$

(2)

To examine the possibility of amorphous grain boundary phases present in K- β'' alumina, we imaged pristine K- β'' alumina using TEM, as shown in Fig. 12. No secondary phases were observed at grain boundaries. Beam sensitivity of the sample prevented the determination of composition of the grain boundaries by energy dispersive X-ray spectroscopy. The high beam sensitivity is likely due to the high mobility of K⁺ ions, leading to knock-on damage. Our results are consistent with previous TEM studies of Na- β and β'' alumina which did not detect amorphous Na₂O, or NaAlO₂ phases [33]. Based on the above observations, we conclude that mechanism B is unlikely.

Finally, mechanism (C), formation of liquid/solid interphase, was directly examined using SEM and AFM imaging. The microstructure of membrane surfaces after exposure to water for 1200 h remains unchanged, as shown by SEM images in Fig. 13. From this data, we can deduce that any new phases that form must be conformal and thin. To directly probe the possible formation of such surface layers, AFM images were taken of the surface in identical regions before and after



Fig. 11. ICP-OES analysis of DI water containing 0.1 g of K- β'' alumina powder for 330 h at room temperature. Statistics from 4 measurements. Error bars are \pm 2 standard deviations.

Fig. 10. Powder XRD plots for K-β" alumina discs before (A) and after (B) operated symmetric cells for 50 h in DI water. Data is shown in blue and Rietveld refinement is shown in orange. Difference plot ×10 shown in green. Refined lattice parameters for the β" phase are also shown. Error in fits is from TOPAS bootstrapping algorithm. Similar results observed for powder samples immersed in DI water for 1000 h. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 12. TEM images of grain boundaries in pristine K-β" alumina.

exposure to 5% acetic acid for 330 h. Acetic acid was used to accelerate the kinetics of the degradation process. The topography is shown in Fig. 14. From these AFM images, it is clear that no major topographical changes occur at the surface, within the resolution of the AFM. Consistent with AFM, ATR-FTIR results do not indicate carbonate or boehmite layers on the surface. Based on the above evidence, it is unlikely that the degradation observed is due to the formation of surface layers. Finally, because the AFM and SEM images look essentially unchanged, we conclude that there is no appreciable change in surface area over the course of the exposure to aqueous solutions.

5. Conclusions

In this work, we have reported the stability of K- β'' alumina in aqueous solutions. By using a Fe²⁺/Fe³⁺ electrochemical couple in a symmetric impedance cell, we are able to measure the K⁺ ion transport across K- β'' alumina membranes at room temperature. Our results indicate that the impedance of K- β'' alumina increases by 50–200 Ω cm²h⁻¹ in water at neutral pH but increases by only ~0.1–1 Ω cm²h⁻¹ in solutions of high concentration K⁺ or pH around 11–12. Material characterization reveals that this behavior is likely due to a sub-diffusion-limited ion exchange reaction occurring between K⁺ in the solid and hydrated protons in solution.

We note that the degradation mechanism for K- β " alumina in aqueous solutions could be different than the Na⁺ and Li⁺ analogs. The impedance studies here can be extended to both other forms of β "



Fig. 13. SEM images of K- β'' alumina membrane surface exposed to different solution chemistries.



Fig. 14. AFM images of the surface of K-β" membranes (A) before and (B) after exposure to 5% acetic acid for 330 h. Images show the same regions. Displayed areas are all 2.9 × 2.9 μm.

alumina and different classes of solid electrolytes in order to quantify the aqueous degradation process. This study shows promise for use of K- β'' alumina as a membrane in K⁺ ion shuttling devices utilizing alkaline solutions such as flow batteries.

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References

- M.A. Rahman, X. Wang, C. Wen, High energy density metal-air batteries: a review, J. Electrochem. Soc. 160 (10) (2013) A1759–A1771.
- [2] M. Cheng, E. Rangasamy, C. Liang, J. Sakamoto, K.L. More, M. Chi, Excellent stability of a lithium-ion-conducting solid electrolyte upon reversible Li⁺/H⁺ exchange in aqueous solutions, Angew. Chem. Int. Ed. 54 (1) (2015) 129–133.
- [3] R.O. Fuentes, F. Figueiredo, F.M.B. Marques, J.I. Franco, Reaction of NASICON with water, Solid State Ionics 139 (3-4) (2001) 309–314.
- [4] T. Durán, E. Climent-Pascual, M.T. Pérez-Prior, B. Levenfeld, A. Varez, I. Sobrados, J. Sanz, Aqueous and non-aqueous Li⁺/H⁺ ion exchange in Li_{0.44}La_{0.52}TiO₃ perovskite, Adv. Powder Technol. 28 (2) (2017) 514–520.
- [5] S. Hasegawa, N. Imanishi, T. Zhang, J. Xie, A. Hirano, Y. Takeda, O. Yamamoto, Study on lithium/air secondary batteries—stability of NASICON-type lithium ion conducting glass-ceramics with water, J. Power Sources 189 (1) (2009) 371–377.
- [6] F. Mauvy, E. Siebert, P. Fabry, Reactivity of NASICON with water and interpretation

of the detection limit of a NASICON based Na $^+$ ion selective electrode, Talanta 48 (2) (1999) 293–303.

- [7] M. Guin, S. Indris, M. Kaus, H. Ehrenberg, F. Tietz, O. Guillon, Stability of NASICON materials against water and CO₂ uptake, Solid State Ionics 302 (2017) 102–106.
- [8] A. Ahmad, T. Wheat, A. Kuriakose, J. Canaday, A. Mcdonald, Dependence of the properties of NASICONs on their composition and processing, Solid State Ionics 24 (1) (1987) 89–97.
- [9] O. Bohnke, Q.N. Pham, A. Boulant, J. Emery, T. Šalkus, M. Barré, H⁺/Li⁺ exchange property of Li₃XLa_{2/3}·XTiO₃ in water and in humid atmosphere, Solid State Ionics 188 (1) (2011) 144–147.
- [10] A.C. Baclig, G. McConohy, A. Poletayev, A. Michelson, N. Kong, J.H. Lee, W.C. Chueh, J. Rugolo, High-voltage, room-temperature liquid metal flow battery enabled by Na-K|K-β"-alumina stability, Joule 2 (2018) 1287–1296.
- [11] J.L. Sudworth, A.R. Tilley, Sodium Sulfur Battery, Chapman and Hall, New York, 1985
- [12] J. Briant, G. Farrington, Ionic conductivity in Na⁺, K⁺, and Ag⁺ beta"-alumina, J. Solid State Chem. 33 (1980) 385–390.
- [13] V. Berbenni, G. Flor, A. Marini, V. Massarotti, R. Riccardi, On the dehydration enthalpies of some beta-aluminas, J. Therm. Anal. 34 (2) (1988) 457–463.
- [14] G. Flor, A. Marini, V. Massarotti, M. Villa, Reactivity of beta-aluminas with water, Solid State Ionics 2 (3) (1981) 195–204.
- [15] J.B. Bates, N.J. Dudney, G.M. Brown, J.C. Wang, R. Frech, Structure and spectra of H₂O in hydrated β-alumina, J. Chem. Phys. 77 (10) (1982) 4838–4856.
- [16] A. Marini, Hydration and carbonation of beta alumina powders, J. Electrochem. Soc. 132 (5) (1985) 1250.
- [17] J.B. Bates, J.C. Wang, N.I. Dudney, W.E. Brundage, Hydration of beta"-alumina, Solid State Ionics 9–10 (PART 1) (1983) 237–243.
- [18] F.G. Will, Effect of water on beta alumina conductivity, J. Electrochem. Soc. 123 (6) (1976) 834.
- [19] G.C. Farrington, J.L. Briant, M.W. Breiter, W.L. Roth, Ionic conductivity in H₃O + beta alumina, J. Solid State Chem. 24 (1978) 311–319.
- [20] B.J. Dunbar, S. Sarian, Introduction, I. Effect of H₂O on Na⁺ diffusivity in beta alumina, Solid State Commun. 21 (1977) 729–731.
- [21] T. Kaneda, J.B. Bates, J.C. Wang, H. Engstrom, Effect of H₂O on the ionic conductivity of sodium beta-alumina, Mater. Res. Bull. 14 (8) (1979) 1053–1056.
- [22] F.G. Will, S.P. Mitoff, Primary sodium batteries with beta-alumina solid electrolyte, J. Electrochem. Soc. 122 (4) (1975) 457.
- [23] B. Dunn, The effect of air exposure on the resistivity of sodium beta, Aluminas 64 (3) (1981) 2–5.
- [24] R.D. Armstrong, D.P. Sellick, A study into the effect of water vapour on sodium βaluminas, Electrochim. Acta 25 (9) (1980) 1199–1204.
- [25] J.H. Koh, N. Weber, A.V. Virkar, Synthesis of lithium-beta-alumina by various ionexchange and conversion processes, Solid State Ionics 220 (2012) 32–38.

- [26] C. Liu, J.S. Shamie, L.L. Shaw, V.L. Sprenkle, An ambient temperature molten sodium-vanadium battery with aqueous flowing catholyte, ACS Appl. Mater. Interfaces 8 (2) (2016) 1545–1552.
- [28] P.K. Davies, F. Garzon, T. Feist, C.M. Katzan, Effects of thermal history upon the behavior of crystalline fast ionic conductors, Solid State Ioncs (1986) 1120–1128.
- [29] G.C. Farrington, J.L. Briant, Hydronium beta alumina: a fast proton conductor, Mater. Res. Bull. 13 (8) (1978) 763–773.
- [30] J.B. Bates, D. Dohy, R.L. Anderson, Reaction of polycrystalline Na β "-alumina with CO₂ and H₂O and the formation of hydroxyl groups, J. Mater. Sci. 20 (9) (1985)

3219-3229.

- $\mbox{[31]}$ P. Colomban, A. Novak, Infrared study of $H^+(H_2O)_n$ beta" alumina, Solid State Commun. 32 (1979) 467–471.
- [32] A.B. Kiss, G. Keresztury, L. Farkas, Raman and i.r. spectra and structure of boehmite (γ-AlOOH). Evidence for the recently discarded D¹⁷2h space group, Spectrochim. Acta A: Mol. Spectrosc. 36 (7) (1980) 653–658.
- [33] L.C. De Jonghe, Grain boundaries and ionic conduction in sodium beta alumina, J. Mater. Sci. 14 (1) (1979) 33–48.
- [34] J. Briant, G. Farrington, Ionic conductivity in lithium and lithium sodium beta alumina, J. Electrochem. Soc. 128 (9) (1981) 1830–1834.
- [35] G.M. Crosbie, G.J. Tennenhouse, Potassium beta"-alumina membranes, J. Am. Ceram. Soc. 65 (4) (1982) 187–191.