Comparing Proton Conduction in Potassium and Ammonium Borosulfate—Isostructural Inorganic Polyelectrolytes Exhibiting High Proton Mobility

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A scalable new method for the synthesis of borosulfate compounds in sulfuric acid providing control over product crystallite size is reported as an alternative to traditional methods requiring slow growth from oleum. This new synthetic approach is used to prepare three isostructural, 1D borosulfates: one containing only ammonium cations, another containing only potassium cations, and the third sample with a solid solution of 1:1 ammonium–potassium. Proton conduction in polycrystalline pellets of these borosulfate electrolytes is compared by electrochemical impedance spectroscopy (EIS) and ab initio molecular dynamics (AIMD) simulations. For a given cation (e.g., NH4⁺), conductivity decreases by three orders of magnitude with decreasing particle size while maintaining constant activation energy, indicating that proton conduction is not primarily a grain-boundary process. AIMD simulations show that excess proton mobility in \( \text{KB(SO}_4\text{)}_2 \) is in line with that of \( \text{NH}_4\text{[B(SO}_4\text{)]}_2 \), being a backbone (not cation) mediated process. Although \( \text{KB(SO}_4\text{)}_2 \) achieves comparable conductivity to \( \text{NH}_4\text{[B(SO}_4\text{)]}_2 \) samples, which is attributable to hydrolytic \( \text{B–O–H} \) defects being the common source of mobile protons in these materials.

1. Introduction

Hydrogen fuel cells have characteristic temperatures of operation dictated by the properties of the electrolyte material around which the fuel cell is designed. Polymer electrolyte membrane fuel cells (PEMFCs) operate at comparatively low temperatures (≤100 °C) due to relying upon liquid water for proton (H⁺) conduction, while solid oxide fuel cells (SOFCs) are limited to high-temperature operation (500–1000 °C) due to poor oxide anion (O²⁻) conduction in ceramic oxide electrolytes at lower temperatures.[13] Accessing an intermediate temperature regime (100–400 °C) is challenging, as H⁺ conduction in a dry (i.e., waterless) electrolyte is difficult and O²⁻ conduction in ceramics has a high activation energy barrier. However, the ability to run a hydrogen fuel cell in this intermediate temperature range is technologically attractive as it has the potential to simplify (or eliminate) water management subsystems (a bulky component of PEMFCs) while still allowing for the use of standard engineering materials in cell construction (whereas SOFCs rely on ceramics and high-temperature seals).[11] Achieving operation at 100–400 °C relies upon an electrolyte exhibiting high ionic conductivity (H⁺ or O²⁻) and good thermo-oxidative and mechanical stability at these temperatures under fuel cell operating conditions. Solid acids were demonstrated to be effective proton conductors in this temperature range over 20 years ago and were subsequently proposed for use as fuel cell electrolytes.[2–4] Since then, the Haile group and others have continued to advance solid acid fuel cell (SAFC) technology.[5–13]

Of the solid acid electrolytes reported over the past two decades, CsH2PO4 has emerged as the material of choice for high-performance SAFCs. While CsH2PO4 is functional, it possesses characteristics that complicate its use as an electrolyte. One such characteristic, intrinsic to many solid acids, is that good H⁺ conduction occurs only above a “superprotonic transition,” which for most compounds occurs at an elevated temperature where the hydrogen bonding network in the crystal structure is broken and the protic species (e.g., HSO4⁻, H₂PO4⁻) becomes rotationally disordered, allowing proton exchange between neighboring units.[5–9] In the case of CsH₂PO₄, its superprotonic transition occurs at ≈225 °C, where the effective proton conductivity improves by three orders of magnitude in the span of just a few degrees. In practice, this means that below the superprotonic transition temperature, a fuel cell utilizing this electrolyte cannot function effectively. Another complicating characteristic of

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CsH₂PO₄ is, like many phosphate materials, its tendency to decompose by dehydration in the absence of water.\(^{[14]}\) The combination of high superprotonic transition temperature and tendency to dehydrate above 200 °C means that CsH₂PO₄ requires active humidification in a narrow operational temperature window (≈225–245 °C). Therefore, it presents engineering challenges that, although possible to overcome, make SAFCs utilizing a CsH₂PO₄ electrolyte more complicated and costly.

Significant gains in SAFC performance may be possible with the discovery of electrolyte materials that exhibit effective proton conduction in a wider temperature range with good stability regardless of the presence of water. Recently, we identified ammonium borosulfate (NH₄[B(SO₄)₂], Figure 1) as a promising new solid acid proton-conducting polyelectrolyte displaying characteristics that improve some of the properties of CsH₂PO₄.\(^{[15]}\)

We originally identified the potential for NH₄[B(SO₄)₂] to be a good proton conductor based on the structural characteristic that it exhibits hydrogen bonding along 1D chains of borosulfate oriented in the crystallographic c-axis. EIS measurements on NH₄[B(SO₄)₂] pellets exhibit ionic conductivity up to 7 mS cm⁻¹ at 180 °C, which is on par with CsH₂PO₄ above its superprotonic transition. Unlike CsH₂PO₄, however, NH₄[B(SO₄)₂] is thermally stable (i.e., exhibiting no mass loss during thermogravimetric analysis) up to 320 °C in dry air, potentially expanding the window of feasible operating temperature compared to CsH₂PO₄ with a possible opportunity to achieve this in the absence of active humidification. Ab initio molecular dynamics (AIMD) simulations showed that NH₄⁺ exhibits an order–disorder transition analogous to a superprotonic transition; however, unlike in CsH₂PO₄, where the superprotonic transition occurs at elevated temperatures, the onset of NH₄⁺ disorder in NH₄[B(SO₄)₂] was found to occur at the cryogenic temperature of ≈140 K. Examining H⁺ motion in cells deficient in, or bearing excess, protons showed that the NH₄⁺ does not actively participate in proton locomotion. Instead, local backbone ([B(SO₄)₂]ₙ⁻ chain) motion and an extrinsic source of “free” protons appear to be critical to the high proton conduction that was observed in NH₄[B(SO₄)₂].\(^{[15]}\)

Determining the origin of mobile H⁺ concentration in these materials, and whether conduction is predominantly a bulk or a grain-boundary-mediated process, is generally challenging due to the difficulty of controlling for the many variables involved. In this study, we report a new synthetic approach to prepare NH₄[B(SO₄)₂] and K[B(SO₄)₂] that specifically allows for a direct comparison of the behavior of NH₄[B(SO₄)₂] as compared to its isostructural and (nominally) aprotic analog K[B(SO₄)₂]. The originally reported borosulfates were synthesized utilizing 60% oleum (i.e., fuming sulfuric acid) as the solvent, which poses significant challenges in handling.\(^{[16]}\) Our new synthetic approach utilizes common reagents (e.g., sulfuric acid, boric acid, sulfate salts) and readily available equipment (e.g., glassware, Schlenk lines, etc.) to prepare these materials safely, on a multi-gram scale, and with access to a range of crystallite sizes. Synthesizing NH₄[B(SO₄)₂] of varying crystallite size, its aprotic analog K[B(SO₄)₂], and a 1:1 solid solution of the two borosulfates (K₀.₅(NH₄)₀.₅[B(SO₄)₂]), we compare the behavior of these materials to identify a common mechanism of proton transport therein. In the process, we find that NH₄[B(SO₄)₂] is only one of a family of 1D borosulfate compounds that exhibit excellent proton mobility, expanding the possible set of borosulfate proton-conducting electrolytes available for developing electrochemical devices that operate at intermediate temperatures.

![Figure 1](image)

**Figure 1.** The structure of ammonium borosulfate represented as: A) a ball-and-stick crystallographic model viewed along the c-axis (white = H, pink = B, purple = N, red = O, yellow = S) and B) a polymeric structure consisting of the NH₄[B(SO₄)₂] repeat unit.

2. Results and Discussion

2.1. Synthesis and Crystallite Size

This method of synthesizing 1D borosulfates (e.g., NH₄[B(SO₄)₂], K[B(SO₄)₂]) can be thought of as the dehydration-driven condensation of sulfuric acid with boric acid under the simultaneous action of heating and dynamic vacuum to form infinite polyanionic chains of [B(SO₄)₂]⁻, as illustrated in Figure 1b, per Equation (1).
In the absence of another cation, protons serve to charge balance the borosulfate chains. In this form, products remain soluble in sulfuric acid as a viscous solution. When a suitable source of alternative cations, such as K₂SO₄, is added to the reaction mixture, H₂SO₄-insoluble products with higher lattice energy, such as K[B(SO₄)₂], precipitate from the reaction mixture. In this manner, this method of synthesizing borosulfates relies upon the solubility of starting materials and insolubility of products in the concentrated H₂SO₄ solvent, as well as the ability to remove water formed over the course of the reaction to drive the reaction toward completion.

Viewing the synthesis of borosulfates in terms of Equation (1) also leads us to another innovation: since the reaction is driven in part by precipitation of a poorly soluble, polymeric product, crystallite size can be controlled by changing reaction conditions to affect nucleation and growth. The slow (1–3 day), evaporative process used in the oleum-based synthesis of NH₄[B(SO₄)₂] yields millimeters to centimeters long needles,[16] while transitioning to forced, rapid (3–16 h) dehydration with mechanical stirring yielded sub-mm length crystallites (product 1a, see Figure S1, Supporting Information, for optical images) that are more amenable to powder processing. Nucleation can be made even more rapid (and crystallites even smaller) by choosing a cation source that exhibits sparing solubility in H₂SO₄, and therefore causing concerted nucleation only once a critical concentration of cation is reached in solution. We found that ammonium sulfamate (NH₄SO₃NH₂) worked well in this capacity, causing rapid precipitation of NH₄[B(SO₄)₂] as a fluffy, white powder (product 1b, see Figure S2, Supporting Information, for optical images) after the dissolution of a critical amount of sulfamate. These three methods of preparing the same material (NH₄[B(SO₄)₂]) to give chemically and structurally identical products, as confirmed by IR spectroscopy and powder X-Ray diffraction (PXRD), provided a suitable subset of materials to investigate how grain boundaries affect the conductivity of sintered borosulfate pellets.

2.2. Grain Boundary Effects on Conduction

The source of “free” protons in NH₄[B(SO₄)₂] was a major unresolved question from the original discovery of proton conductivity in this material.[15] From AIMD simulations, it was determined that excess protons coordinated to the borosulfate chain are exceptionally mobile, while those on NH₄⁺ are unlikely to be dissociated as the source of mobile protons; the activation energy found computationally for dissociation of NH₄⁺ (≈83 kJ mol⁻¹) is much higher than the activation energy for conduction measured by impedance spectroscopy (EIS, ≈35 kJ mol⁻¹).[15] This leaves two likely scenarios: 1) charge carriers arise primarily from defects at grain boundaries; or 2) charge carriers originate from defects within the crystal lattice. We postulated that proton defects are likely to be the result of hydrolysis, as depicted schematically in Figure 2. The formation of these defects may be considered the inverse of the dehydration process used to synthesize NH₄[B(SO₄)₂]. Due to the ladder structure of the borosulfate chain, single hydrolytic point defects should not destabilize the backbone, although they may interfere with crystallinity.

Sintered pellets of NH₄[B(SO₄)₂] were prepared by pressing 100–200 mg of 1a (larger crystallites) or 1b (smaller crystallites) at ≈240 MPa in a 12.7 mm diameter tungsten carbide die in a Carver press with platen heated to 100 °C for 16 h. The resulting pellets were opaque but were measured to be at ≈95% of the crystal density of NH₄[B(SO₄)₂] (2.337 g cm⁻³) and thus relatively well-consolidated. These pellets were subsequently mounted in an aluminum test fixture (illustrated in Figure S10, Supporting Information) between spring-loaded, porous, Au sputter-coated, stainless steel electrodes and heated to 200 °C for ≈16 h under a low flow of dry air to ensure samples were equilibrated prior to performing EIS. Impedance spectra were collected on cooling from 200 °C to room temperature under dry airflow over the course of ≈8 h, from which conductivity was calculated by fitting the data to a modified Randles circuit (Figure S11, Supporting Information) and dividing the cell constant (k = thickness/1.228 cm²) by the extracted electrolyte resistance (R) at each temperature. The results are plotted in Figure 3 (full Bode plots in Figure S12 [1a] and S13 [1b], Supporting Information) alongside prior results from a pellet made of large (mm-sized) NH₄[B(SO₄)₂] crystallites synthesized by the originally reported synthesis in oleum.[15]

If defects are localized primarily at grain boundaries, where access to atmospheric moisture is greatest and the lattice is unconstrained, pellets pressed from materials with smaller crystallites should contain more protic defects and thus exhibit higher conductivity. Instead, conductivity was observed to decrease with decreasing crystallite size, dropping by several orders of magnitude from the largest (several mm length) to smallest (≈10 μm length) crystallites. This is excellent evidence that the proton defects providing mobile proton concentration cannot be primarily a grain boundary phenomenon. If either proton transport is primarily grain-boundary-mediated or proton concentration results primarily from grain boundary defects (as in many metal oxides), any increase in the area of grain

n B(OH)₃ + 2n H₂SO₄ → 3n H₂O + n H⁺ + [B(SO₄)₂]⁻₂n⁻ (1)
Knowing that conduction in NH₄[B(SO₄)₂] is not a grain-boundary-mediated process, our next goal was to determine if the ammonium cation form is unique in promoting proton conduction in borosulfates. Although comparing prior AIMD results with the experimental activation energy for conduction in NH₄[B(SO₄)₂] \( (E_a \approx 34 \text{ kJ mol}^{-1}) \) showed that dissociation of the NH₄⁺ cation \( (E_a \approx 83 \text{ kJ mol}^{-1}) \) is unlikely to take part in the generation of charge carriers, the hydrogen bonding of NH₄⁺ to the borosulfate chain could still be critical to facilitating proton conduction. To test this, we performed AIMD simulations on NH₄[B(SO₄)₂] and the isostructural, aprotic borosulfate K[B(SO₄)₂] to assess proton mobility in both these structures.

Compared to the AIMD simulations presented in our prior work, the simulation box in this study was enlarged to 8 unit cells \( (2 \times 2 \times 2) \) containing a total of 32 cations (NH₄⁺ or K⁺).

One to four (1–4) excess protons were added to each super-cell, along with a homogeneous negative background to maintain charge neutrality. By using a variable number of excess protons, it is possible to determine whether results are being affected by Coulombic interactions between nearby protons in the simulation volume. As previously observed in similar calculations for NH₄[B(SO₄)₂], the excess proton in both NH₄[B(SO₄)₂] and K[B(SO₄)₂] exists in its lowest energy state when attached to one of the two tetrahedral corners of the SO₄ unit that are not attached to the BO₄ tetrahedral backbone. The oxygen atoms at the corners of distinct but adjacent SO₄ units are, on average, \( \approx 3.2 \text{ Å} \) apart in both compounds at 900 K, which is too far for facile proton hopping. However, the SO₄ units are extremely flexible; proton hopping occurs when phonons twist and stretch the SO₄ units such that the distance between two oxygen atoms sufficiently decreases so as to allow a low energy site-to-site hop. In our calculations, hops occur when the O...O distance is \( < 2.5 \text{ Å} \) and when the proton rotates around its current "host" atom to reside as close as possible to the next oxygen atom.

The change in mean square displacements (msd) of atoms over time can be used to approximate diffusivity (units of \( \text{m}^2 \text{s}^{-1} \)) over long times. Tracking msd of the excess protons from their initial, energy minimized positions over 20 ps at 900 K (Figure 4) shows that the diffusivity of excess protons should be comparable in K[B(SO₄)₂] to NH₄[B(SO₄)₂]. It is useful to compare calculated proton diffusivities (\( D_{H^+} \)) in borosulfates to other proton conductors, such as water, for example. Linear regressions (not shown) to the data in Figure 4 give \( D_{H^+} \) at 900 K from which diffusivities at lower temperatures can be calculated per Equation (2), assuming that conduction is an Arrhenius process over the 900 K to 300 K (23 °C) interval.

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**Figure 3.** Conductivity versus inverse temperature plotted for sintered pellets prepared from NH₄[B(SO₄)₂] with large crystallites (Oleum synthesis, red circles), intermediate crystallites (1a, blue diamonds), and small crystallites (1b, green squares). Arrhenius fits (colored lines) and the activation energies calculated from these fits are also shown.

**Figure 4.** Mean squared displacement (msd) of excess protons diffusing through ammonium borosulfate (top) and potassium borosulfate (bottom) lattices of 8 unit cells containing 1–4 excess H⁺ per simulated volume. The derivative of msd with respect to time (averaged over long times) equals the proton diffusivity \( (1 \text{ Å}^2 \text{ps}^{-1} = 10^{-5} \text{m}^2 \text{s}^{-1}) \).
$$D_1 = D_2 e^{-\frac{E_a}{RT}}$$

(2)

From the data in Figure 4, we calculate $D_{\text{H}^+}$ at 900 K to be $(1.3 \pm 0.5) \times 10^{-8} \text{m}^2 \text{s}^{-1}$ in NH$_4$[B(SO$_4$)$_2$] and $(1.6 \pm 0.6) \times 10^{-8} \text{m}^2 \text{s}^{-1}$ in K[B(SO$_4$)$_2$]. The activation energy for proton hopping in K[B(SO$_4$)$_2$] is unknown, but for NH$_4$[B(SO$_4$)$_2$] this value was previously determined by simulations to be $\approx 12.5 \text{kJ mol}^{-1}$. Therefore, at 25 °C in NH$_4$[B(SO$_4$)$_2$] (assuming Arrhenius behavior), $D_{\text{H}^+} \approx (4.6 \pm 1.8) \times 10^{-10} \text{m}^2 \text{s}^{-1}$, which is only one order of magnitude lower than the diffusivity of a proton in water at 25 °C ($D_{\text{H}^+} = 9.8 \times 10^{-9} \text{m}^2 \text{s}^{-1}$). Despite ammonium borosulfate being a crystalline solid. Additionally, protons appear to not interact with each other significantly at these concentrations (0.03–0.12 per formula unit), as msds appear to be independent of proton concentration.

To test whether proton conduction analogous to that exhibited by NH$_4$[B(SO$_4$)$_2$] can be measured experimentally in K[B(SO$_4$)$_2$], we synthesized K[B(SO$_4$)$_2$] via the same preparative method as described earlier for NH$_4$[B(SO$_4$)$_2$] (1a) by substituting K$_2$SO$_4$ for (NH$_4$)$_2$SO$_4$ as a starting material. In theory, a perfect K[B(SO$_4$)$_2$] crystal should bear no free protons to display ionic conduction, but in practice, we expect it to contain the same type of hydrolytic defects (Figure 2) as NH$_4$[B(SO$_4$)$_2$]. Interestingly, the crystallites of K[B(SO$_4$)$_2$] (2, Figure S3, Supporting Information) synthesized using K$_2$SO$_4$ as the potassium source are of comparable size to the smaller NH$_4$[B(SO$_4$)$_2$] crystallites (1b, Figure S2, Supporting Information) prepared using the poorly soluble NH$_4$SO$_3$NH$_2$ ammonium source. In light of the crystallite size-dependent conductivities illustrated in Figure 3, this makes 1b and 2 well-matched for a direct comparison of proton conductivities between NH$_4$[B(SO$_4$)$_2$] versus K[B(SO$_4$)$_2$] (Figure 5).

The most readily apparent result of comparing conduction in polycrystalline NH$_4$[B(SO$_4$)$_2$] and K[B(SO$_4$)$_2$] pellets having comparable crystallite sizes is that the activation energy for conduction in K[B(SO$_4$)$_2$] ($E_a = 60.6 \pm 2.0 \text{kJ mol}^{-1}$) is almost twice that of NH$_4$[B(SO$_4$)$_2$] ($E_a = 33.1 \pm 1.5 \text{kJ mol}^{-1}$). Despite the higher activation energy, proton conductivity in K[B(SO$_4$)$_2$] approaches that of NH$_4$[B(SO$_4$)$_2$] above 200 °C. The difference in the activation energies observed for conduction in K[B(SO$_4$)$_2$] and NH$_4$[B(SO$_4$)$_2$] could arise from either a difference in the ease of transport across grain boundaries or from differences in backbone motion resulting from hydrogen bonding (or lack thereof) to the cation.

We subsequently tested whether this trend holds in mixed-cation borosulfates by synthesizing K$_{0.5}$(NH$_4$)$_{0.5}$[B(SO$_4$)$_2$] (3) using a 1:1 mixture of K$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$ as starting materials. The resulting crystallite sizes (see Figure S4, Supporting Information) are in line with both 1b and 2, and PXRD on (see Figure S9, Supporting Information) shows that the product is a solid solution of the two cations, not a mixture of independent NH$_4$[B(SO$_4$)$_2$] and K[B(SO$_4$)$_2$] crystallites. Interestingly, the temperature-dependent conductivity of the mixed cation borosulfate is not an average (in either magnitude or activation energy) of the mono-cationic borosulfates. The conductivity of 3 is a factor of 3–4 higher than pure NH$_4$[B(SO$_4$)$_2$] with an activation energy ($E_a = 28.9 \pm 0.8 \text{kJ mol}^{-1}$) slightly lower than the pure compound (Figure 5). Although definitive conclusions cannot be drawn from these data, we believe this is likely due to the mixed compound sintering better than the single cation compounds.

2.4. Evidence for Bulk Hydrolytic Defects as the Source of “Free” H$^+$

We had previously hypothesized that hydrolytic defects (see Figure 2) are the source of the “free” protons that contribute to ionic conduction in borosulfates. As shown by the comparable degrees of conduction measured in NH$_4$[B(SO$_4$)$_2$] and K[B(SO$_4$)$_2$] (Figure 5), this hypothesis remains in line with these experimental results. Such protic defects are unlikely to be confined to surfaces or grain boundaries, as crystallite size-dependent measurements of conductivity (Figure 3) show decreasing conductivity with increasing surface area of crystallites. Unfortunately, many analytical techniques are limited in their ability to resolve the excess protons resulting from partial hydrolysis, especially at low levels of doping. Direct measurement with X-Ray analytical techniques, while useful for heavier elements, is essentially impossible for hydrogen. Further, the local chemical environments of sulfur and boron are unlikely to be very different between hydrolyzed borosulfate chains and perfect crystals to be resolvable by these methods. However, the IR spectra of ammonium and potassium borosulfate (Figure 6) do provide critical insight due to the sensitivity of vibrational spectroscopies to the large dipole moment and highly polarizable O—H bond.

As shown in Figure 6, the IR spectra of ammonium (1b) and potassium (2) borosulfate below 1500 cm$^{-1}$ are almost identical. Above 1500 cm$^{-1}$, the only major feature is a peak at 3200–3300 cm$^{-1}$ that was initially attributed to N—H stretching in NH$_4^+$, but clearly must be originating from another species in K[B(SO$_4$)$_2$]. These peaks are present even after samples have
been dried extensively at 200 °C under a dynamic vacuum, indicating that they cannot originate from surface moisture. Likewise, washing these samples with isopropanol gives a neutral (pH 7) filtrate, indicating that free H₂SO₄, which would be dissolved into the alcohol, is not present. Based on the hydrolysis mechanism postulated in Figure 2, this stretching mode could therefore be either the sulfate O–H stretch (S–O–H) or borate O–H stretch (B–O–H). The acidity of a hydroxyl group and its hydrogen bonding environment affects its stretching frequency quite significantly,[18] however, the frequencies of a prototypical sulfate O–H stretch (3500 cm⁻¹)[19] and borate O–H stretch (3200 cm⁻¹)[20] are quite far apart. Since the peak in K[B(SO₄)₂] is so close to the O–H stretch in boric acid, we attribute this stretching mode (in both ammonium and potassium samples) to hydrolytic B–O–H point defects in the crystal lattice, and not to a residual sulfate hydroxyl group. In NH₄[B(SO₄)₂], hydrogen bonding with the ammonium cations causes these peaks to overlap and show up closer to 3300 cm⁻¹ with a stronger relative absorbance. The lack of hydroxyl stretching modes corresponding to residual sulfates has caused us to revise our hypothesis of the structure of hydrolytic defects in 1D borosulfates. While the initial steps of hydrolysis probably proceed according to Figure 2, the dangling borosulfate is likely susceptible to either further cleavage by water (and loss of H₂SO₄) or to irreversible loss of gaseous SO₃, resulting in a structure with two dangling, proximal B–O–H units, illustrated in Figure 7. Based on the observed evidence, these acidic borate units are the most likely a source of mobile protons for conduction without significantly disrupting the overall structure and crystallinity of the borosulfate.

3. Summary and Conclusions

We present a new, general method of borosulfate synthesis that uses sulfuric acid, rather than oleum, and is, therefore, less hazardous and more amendable to scale-up than syntheses previously reported in the literature. This method provides the means to not only produce a variety of borosulfate salts but also control the product crystallite size. In turn, this has afforded us the materials necessary to elucidate the roles of grain boundaries and hydrolytic defects on proton conduction in 1D borosulfates, which at this point we believe to be a general characteristic of this structural family of compounds.

The ionic conductivity previously observed in NH₄[B(SO₄)₂] is demonstrated to also be present in another isostructural 1D borosulfate, K[B(SO₄)₂], confirming that this phenomenon is not tied to the protic nature of the NH₄⁺ cation in ammonium borosulfate, but instead is enabled by the movement of the 1D borosulfate chain, and therefore is likely to be present in other similar compounds. The activation energies for the Arrhenius conduction process (over 50–200 °C) vary significantly between the pure ammonium and potassium compounds, increasing from 33.1 ± 1.5 kJ mol⁻¹ for NH₄[B(SO₄)₂] to 60.6 ± 2.0 kJ mol⁻¹ for K[B(SO₄)₂]. Increased activation energy for conduction in K[B(SO₄)₂] is likely the result of either differing ease of transport at the grain boundaries or differences in backbone mobility due to hydrogen bonding to the interstitial cations. Further investigations into these phenomena are certainly warranted.

Infrared spectra strongly suggest that B–OH hydrolytic defects in the backbone generate “free” acidic protons enabling proton conductivity in these materials regardless of the identity of the cation. AIMD simulations show high proton mobility for free protons in both NH₄[B(SO₄)₂] and K[B(SO₄)₂], with diffusivity for NH₄[B(SO₄)₂] at room temperature of only 1 order of magnitude lower than that of H⁺ in water. Crystallite size-dependent conductivity studies show that these defects are likely distributed not at grain boundaries, but rather throughout the bulk of the crystallites. In fact, the conductivity of sintered polycrystalline pellets decreases with decreasing powder crystallite size, indicating that grain boundary conduction is likely to be the limiting process in these materials. It is our conclusion that future work focused on the improvement of the performance of borosulfate materials as proton-conducting electrolytes should focus on minimizing the interfacial resistance of these grain-to-grain contacts.

4. Experimental Section

All reagents were purchased from Fisher Scientific and used as received. Procedures were performed in air, but products were stored in sealed vials under inert (N₂) atmosphere to prevent absorption of moisture over time.

Figure 6. Attenuated total internal reflectance (ATR) IR spectra of: 1b, green line) NH₄[B(SO₄)₂] and 2, magenta line) K[B(SO₄)₂] after washing with isopropanol to neutral pH and drying under vacuum.

Figure 7. Revised hypothesized structure of hydrolytic defects giving rise to “free” protons in 1D borosulfates. Hydroxyl groups in red should have a stretching mode at ≈3500 cm⁻¹, whereas groups in blue should have a stretching mode at ≈3200 cm⁻¹.
**General Method:** Boric acid was dissolved as a 5–15 wt% solution in concentrated (98%) H2SO4, to which an approximately equimolar amount of sulfate salt (e.g., (NH4)2SO4, K2SO4) was added. The reaction mixture was then allowed to distillate the apparatus in which a desiccant (e.g., isopropanol, sulfolane), and dried in vacuo to isolate the borosulfate product.

To clear the colorless reaction mixture slowly became viscous, then rapidly precipitated white solid, and the mixture cooled to room temperature. The white solids were suction filtered off the mother liquor on a fritted filter funnel, washed with isopropanol, and dried under vacuum at 230 °C for 1 h. The solids were weighed at 36.128 g (91% isolated yield). Crystals were measured by optical microscopy to be needles averaging 8 μm long by 2 μm wide (see Figure S5, Supporting Information).

**Supporting Information:** (0.15 mmHg) was applied to the system, the reaction vessel was immersed in an oil bath, and the reaction was heated to 200 °C with magnetic stirring for 16 h. The solids were weighed at 11.132 grams (48.1% yield). Crystalline size was too small to successfully perform single-crystal X-ray diffraction (XRD) on the product, but PXRD confirms that only a single phase is present, which is isostructural with both $\text{K}_0.5(\text{NH}_4)_0.5(\text{B}[\text{SO}_4]_2)[3]$ and $\text{K}[\text{B}(\text{SO}_4)_4][3]$. Since the lattice parameters of $\text{NH}_4[\text{B}(\text{SO}_4)_4]$ and $\text{K}[\text{B}(\text{SO}_4)_4]$ are different, if the product was a physical mixture of phase pure ammonium and potassium borosulfates, rather than a single, phase pure compound, the difference in diffraction peaks would instead be visible. Crystals were measured by optical microscopy to be needles averaging 15 μm long by 1 μm wide (see Figure S4, Supporting Information).

**Further details:** To confirm the identity and phase purity of the products, PXRD, IR spectroscopy, and X-ray photoelectron spectroscopy (XPS) were utilized. PXRD was performed on the products of each synthesis using a Rigaku Smartlab Diffractometer and Cu Kα radiation (λ = 1.5406 Å). These powder X-ray diffraction patterns were compared to simulated powder patterns of the known ammonium and potassium species generated from their single crystal structures using the Mercury software package. Full diffraction patterns are provided in Supporting Information (Figure S6). Single crystal XRD was not possible on samples synthesized in the previous literature, [16] may be obtained from the Fachinformationszentrum Karlsruhe, 76 344 Eggenstein-Leopoldshafen (Germany), quoting the depository number CSD-428 004.

**Crystallographic Data:** Single crystals were obtained from a solution of borax and potassium sulfate in isopropanol, and dried under vacuum at 230 °C for 16 h. The solids were weighed at 36.128 g (91% isolated yield). Crystals were measured by optical microscopy to be needles averaging 8 μm long by 2 μm wide (see Figure S5, Supporting Information).

**Additional Data:** (0.15 mmHg) was applied to the system, the reaction vessel was immersed in an oil bath, and the reaction was heated to 200 °C with magnetic stirring for 16 h. The solids were weighed at 11.132 grams (48.1% yield). Crystalline size was too small to successfully perform single-crystal X-ray diffraction (XRD) on the product, but PXRD confirms that only a single phase is present, which is isostructural with both $\text{K}_0.5(\text{NH}_4)_0.5(\text{B}[\text{SO}_4]_2)[3]$ and $\text{K}[\text{B}(\text{SO}_4)_4][3]$. Since the lattice parameters of $\text{NH}_4[\text{B}(\text{SO}_4)_4]$ and $\text{K}[\text{B}(\text{SO}_4)_4]$ are different, if the product was a physical mixture of phase pure ammonium and potassium borosulfates, rather than a single, phase pure compound, the difference in diffraction peaks would instead be visible. Crystals were measured by optical microscopy to be needles averaging 15 μm long by 1 μm wide (see Figure S4, Supporting Information).

**Further details:** To confirm the identity and phase purity of the products, PXRD, IR spectroscopy, and X-ray photoelectron spectroscopy (XPS) were utilized. PXRD was performed on the products of each synthesis using a Rigaku Smartlab Diffractometer and Cu Kα radiation (λ = 1.5406 Å). These powder X-ray diffraction patterns were compared to simulated powder patterns of the known ammonium and potassium species generated from their single crystal structures using the Mercury software package. Full diffraction patterns are provided in Supporting Information (Figure S6). Single crystal XRD was not possible on samples synthesized via these methods as the crystallites were not of suitable size. Attenuated total internal reflection (ATR) IR spectra were acquired from 4000 to 525 cm⁻¹ on a Nicolet iS50 spectrometer using a single-bounce diamond ATR crystal and averaging over 256 scans. A two-point linear baseline was applied to each spectrum after referencing the bare ATR crystal (i.e., air). XPS was performed on a Thermo Scientific Nexsa spectrometer. Samples were prepared for XPS by loading loose powders into a copper well plate
and tamping them down with a clean glass rod to prevent surface contamination. Spectra were collected under flood gun (Ar+)) irradiation to minimize charging. All spectra were fit with Shirley backgrounds without calibrating binding energies. B1s, N1s, O1s, S2p, and K2p spectra were fit with symmetrical 30% Gaussian–70% Lorentzian (G–L) peaks, where full width at half maximum (FWHM) was constrained to be equal for any peaks for the same element. Elemental compositions are reported as weight percentages converted from the atomic percentages measured by XPS. Full XPS spectra for 1b, 2, and 3 are provided in Supporting Information (Figure S17 through Figure S19, Supporting Information).

Disc-shaped pellets of each sample 300–700 μm thick were prepared by pressing 100–200 mg of each material in a 12.7 mm tungsten carbide die press to ≈240 MPa between platens of a Carver press heated to 100 °C for 16 h. The bulk density of these pellets (1.2668 cm² area) was measured using a digital micrometer to determine the thickness of each pellet and an analytical balance to determine its weight. Bulk densities were compared with single crystal densities to determine the fraction of theoretical density/extent of consolidation as ρi = ρbulk/ρsingle-crystal.

The ionic conductivity was calculated from electrochemical impedance spectra (EIS) acquired on a Gamry Reference 3000 potentiostat. For EIS, pellets were sandwiched between two 12.7 mm diameter gold-coated (50 nm by sputtering) porous sintered steel discs as electrical contacts allowing gas permeability. The assembly of sample and porous contacts was mounted in a machined aluminum cell (Figure S10, Supporting Information) through which dry air was passed over both sides of the sample during heating and cooling cycles. Impedance spectra were collected on cooling after holding for ≈16 h at 200 °C under flowing, dry air. Bode plots of the raw impedance data along with fits to a modified Randles circuit (Figure S11, Supporting Information) are provided in Supporting Information (Figure S12–S15, Supporting Information). Conductivities were extracted from these fits by the equation: \( \sigma = \frac{t}{\pi A^2} \), where \( t \) is the pellet thickness, \( A \) is its area (1.228 cm²), and \( R \) is the electrolyte resistance calculated from the circuit model.

To calculate proton diffusivity, an NRL-developed formulation[21] with input forces and energies imported from the Vienna Ab Initio Simulation Program VASP[22] using the Perdew–Burke–Ernzerhof (PBE) approximation to the exchange-correlation functional was used.[23] All calculations began by creating \( 2 \times 2 \times 2 \) supercells of \( \text{NH}_4[\text{B(SO}_4)_2] \) and \( \text{K}[\text{B(SO}_4)_2] \), comprising 32 formula units. 1–4 excess H atoms were added and converted to protons by subtracting an electron and adding a negative uniform background to obtain a charge-neutral cell. Each cell at each proton concentration was fully relaxed at \( T = 0 \), with a very high energy cutoff of 670 eV to ensure accurate stresses for lattice relaxation. Subsequently, MD simulations of the initially relaxed cells were run for 100 ps with time steps of 0.5 fs at 900 K to evaluate proton diffusivity. The mean-squared displacement (MSD), which gives a measure of the diffusivity.

**Data Availability Statement**

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords**

borosulfates, fuel cells, polyelectrolytes, proton conductivity

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