Proton-Conducting Films of Nanoscale Ribbons Formed by Exfoliation of the Layer Perovskite H$_2$SrTa$_2$O$_7$

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Thin films of nanoscale ribbons derived from the layer perovskite H$_2$SrTa$_2$O$_7$ were grown and characterized as solid-state proton conductors. The ribbons, made by exfoliation of the parent solid with tetra(n-butyl)ammonium hydroxide, were typically 500 nm long, 40 nm wide, and 3 nm thick, with the short axis corresponding to the layer axis of H$_2$SrTa$_2$O$_7$. Powder X-ray diffraction and high-resolution transmission electron microscopy confirmed that the ribbons had similar a-axis unit cell parameters (3.98 ± 0.05 Å) to H$_2$SrTa$_2$O$_7$ (3.87 ± 0.02 Å) and the defect perovskite SrTa$_2$O$_6$ (3.92 ± 0.01 Å) which is the dehydration product of H$_2$SrTa$_2$O$_7$. By using inductively coupled plasma atomic emission spectroscopy, X-ray photoelectron spectroscopy, and energy-dispersive X-ray spectroscopy, the ribbons were found to have a lower Sr/Ta ratio than H$_2$SrTa$_2$O$_7$. Thin films of these ribbons were grown by layer-by-layer assembly and by spin-coating, and in both cases the long axis had a preferred orientation parallel to the substrate. Electrochemical impedance measurements were done on pellets of H$_2$SrTa$_2$O$_7$ and SrTa$_2$O$_6$ and on films of oriented ribbons measured perpendicular and parallel to the plane of their long axis. At 25 °C, the proton conductivities in humidified air were 1.5 × 10$^{-4}$ and 1.7 × 10$^{-5}$ S/cm for pellets containing randomly oriented grains of H$_2$SrTa$_2$O$_7$ and SrTa$_2$O$_6$. The measured conductivities of oriented films of the ribbons were 1.3 × 10$^{-3}$ and 2.4 × 10$^{-2}$ S/cm in the perpendicular and parallel directions, respectively, indicating a high proton conductivity along the ribbon axis and very high conductivity anisotropy.

Introduction

Solid-state proton conductors—both polymeric and inorganic—are of great current interest for their applications in fuel cells. Polymer electrolyte membranes (PEMs) have been the most thoroughly studied class of electrolytes for low-temperature (20–200 °C) fuel cells. While PEMs have many attractive properties, including mechanical flexibility and manufacturability, a major drawback is their loss of conductivity and chemical decomposition at intermediate temperatures (250–400 °C). Fuel cells that operate in this temperature range, which can be maintained with waste heat from the cell, could employ low- or non precios-metal electrocatalysts on both the anode and cathode sides of the cell. In addition, such intermediate temperature fuel cells could eliminate the final stages of fuel purification to remove traces of carbon monoxide, thereby reducing the overall system cost. The realization of such fuel cells is now limited by the availability of suitable electrolytes for this temperature range.

Several kinds of inorganic membrane materials, including alkali phosphate salts, transition metal phosphates, perovskites, and layer perovskites, are good proton conductors in the intermediate temperature regime, but so far there are few reports of their use in fuel cells.10 Most of these materials are brittle ceramics that cannot form mechanically strong, thin membranes.11 The exceptions are pellicular membranes made from layered materials such as exfoliated zirconium phosphate.12 Unfortunately, the proton conductivity in these membranes, as in most lamellar inorganic proton conductors,13 is highly anisotropic. Within the plane of the sheets, conductivities approaching those of PEMs have been observed, but perpendicular to this plane (in the direction of

proton transport in the fuel cell), the conductivity is orders of magnitude lower. It is therefore interesting to consider inorganic proton conductors in other forms (such as nano-tubes, ribbons, or fibers) that might be assembled into mechanically robust membranes with higher proton conductivity in the transverse direction.

Layered perovskites, which are ternary transition metal oxides, are capable of undergoing a variety of structural conversions through soft chemical reactions.\(^{14-19}\) By using ion-exchange reactions,\(^{20-22}\) their interlayer alkali cations can be easily replaced by protons. The protonated form can be neutralized by strong or weak bases that contain bulky cations, causing the layers to exfoliate and form base-stable neutralized forms of exfoliated sheets into mesoporous “house of cards” ion-exchange reactions,\(^{20-22}\) their interlayer alkali cations can be easily replaced by protons. The protonated form can be neutralized by strong or weak bases that contain bulky cations, causing the layers to exfoliate and form base-stable neutralized forms of exfoliated sheets into mesoporous “house of cards” structures.\(^{23-25}\) Thin films of these exfoliated materials have been grown layer-by-layer (LBL) using electrostatic interactions with a polyelectrolyte,\(^{26}\) or by casting directly from colloidal suspensions.\(^{12,17}\) The proton-exchanged forms of the membranes can be easily replaced by protons. The protonated form can be neutralized by strong or weak bases that contain bulky cations, causing the layers to exfoliate and form base-stable neutralized forms of exfoliated sheets into mesoporous “house of cards” ion-exchange reactions,\(^{20-22}\) their interlayer alkali cations can be easily replaced by protons. The protonated form can be neutralized by strong or weak bases that contain bulky cations, causing the layers to exfoliate and form base-stable neutralized forms of exfoliated sheets into mesoporous “house of cards” structures.\(^{23-25}\) Thin films of these exfoliated materials have been grown layer-by-layer (LBL) using electrostatic interactions with a polyelectrolyte,\(^{26}\) or by casting directly from colloidal suspensions.\(^{12,17}\) The proton-exchanged forms of

Experimental Section

Synthesis of \(K_2SrTa_2O_7\) and \(H_2SrTa_2O_7\). \(K_2SrTa_2O_7\) was synthesized from KOH (Aldrich, 99.99%), \(SrCO_3\) (Aldrich, 99.94%), and \(Ta_2O_5\) (Aldrich, 99.99%) by grinding stoichiometric amounts of these solids with an additional 30% KOH to compensate for volatilization. The reactant mixture was heated to 800 °C at a ramp rate of 5 °C/min, held at 800 °C for 30 min, then heated to 1100 at 10 °C/min, and held there for 30 min. The products were analyzed by X-ray powder diffraction (XRD), and the results were compared to literature XRD patterns.\(^{19}\) If the products were not single phase, they were reground and reheated to 1100 °C using the same ramp sequence. Typically, three heating cycles were needed to obtain a phase pure product. The \(K_2SrTa_2O_7\) product was then filtered, rinsed with water, and allowed to dry under ambient conditions. Pellets of \(H_2SrTa_2O_7\) for impedance measurements were prepared by pressuring 0.5 g in a 13 mm die at 2 t, yielding pellets typically 0.95 mm thick. 100 nm Pt films were then sputtered onto both faces of the pellets to serve as electrodes.

Exfoliation of \(H_2SrTa_2O_7\) and Purification of Fibers. \(H_2SrTa_2O_7\) (0.5 g) was exfoliated using 100 mL of 0.5 M aqueous tetra(n-butyl)ammonium hydroxide (TBAOH). Since exfoliation to fibers or ribbons is only partial, the fibers were isolated by first centrifuging 25 mL of the supernatant from the TBAOH colloid mixture at ~5000 rpm to precipitate unexfoliated bulk material and exfoliated sheets. Subsequent centrifugation of the resulting supernatant at 14 000 rpm precipitated typically 10–50 mg of the fibers. AEM samples of the fibers were prepared by rinsing in water and resuspending in 10 mL of ethanol, followed by casting on a spin-coater (500–1000 rpm), with alternating drops of PDDA (5 wt %) and the colloidal solution. AEM showed that a film created in this way was typically 20 nm thick.

In-Plane Measurements. Films for in-plane conductivity measurements were prepared by a layer-by-layer deposition on patterned glass substrates. The patterns on glass were first defined by using Shipley 1813 photoresist and MF312 developer. 10 nm of chromium and 20 nm of gold were then evaporated onto the resist. As the resist was removed with acetone and piranha solution (30% \(H_2O_2/\)concentrated \(H_2SO_4\); caution: this solution can react violently with organic substances), the Au/Cr layers on the photoresist also conveniently lifted off. The Au layer was finally covered by electroplating with Pt using a Technic platinum TP plating solution at ~0.355 V vs SCE for 30 min, using a Pt counter electrode. The gap defined by lithography is 35 nm deep (based on AEM measurements), 800 µm wide between the two metal electrodes, and 6.25 mm long.

The H$_2$SrTa$_2$O$_7$ films for in-plane measurements were deposited layer-by-layer using a poly(diallyldimethylammonium) chloride/\(\text{TBABr} \) (5 wt \% PDDA, 0.05 M TBABr) solution as the polycation source. Initially, the substrate was placed in 2–5 mL of the PDDA/TBABr solution and agitated on an orbital shaker for 5 min and then rinsed with water and blown dry with nitrogen. The process was repeated using the fiber colloidal suspension and the PDDA solution until the desired film thickness was obtained.

Since the prepared films contain PDDA, this polymer was removed by calcination in order to obtain samples that would have similar compositions to the other materials derived from H$_2$SrTa$_2$O$_7$. To determine a calcination temperature adequate to oxidize the polymer but low enough to avoid sintering or irreversible dehydration of the fibers, a bulk sample of PDDA/fibrous H$_2$SrTa$_2$O$_7$ was prepared by flocculating a suspension of H$_2$SrTa$_2$O$_7$ with PDDA, followed by centrifuging to wash away excess PDDA. TGA-MS was then done to determine the temperature at which the generation of gaseous oxidation products CO (28 amu) and CO$_2$ (44 amu) was complete (see Supporting Information).

Measurements across the Film (Cross-Plane Measurements). Substrates of Pt/Au/Cr glass were prepared in an analogous manner, but without patterning. Thick films (2 \(\mu\)m as measured by AFM) of fibrous H$_2$SrTa$_2$O$_7$ were deposited by spin-coating alternating drops of the colloid in methanol and acidified methanol. A top contact was made by sputtering a round spot of Pt (6 mm diameter) on the deposited film.

Instrumentation. X-ray diffraction (XRD) patterns were obtained on a Phillips X-Pert MPD diffractometer using monochromatized Cu K\(\alpha\) (\(\lambda = 1.5418 \ \text{Å}\)) radiation, in \(\theta - \theta\) geometry. Thermogravimetric analysis (TGA) was performed on a TA Instruments 2050 instrument. Mass spectrometry (MS) was obtained in tandem with TGA on a Pfeiffer quadrupole mass spectrometer. Atomic force microscopy (AFM) images were obtained on a Nanoscope IIIA AFM in tapping mode with aluminum-coated silicon cantilevers. Transmission electron microscopy (TEM) was performed on a JEOL 1200EXII microscope at an accelerating voltage of 80 kV. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on a Leeman Laboratories PS3000UV spectrophotometer, with acidified aqueous fluoride standards of potassium, strontium, and tantalum, on solids collected from supernatants of colloids in TBAOH, and on H$_2$SrTa$_2$O$_7$. Samples were dissolved in 48% HF with agitation on an orbital shaker and then diluted to within standard ranges. X-ray photoelectron spectroscopy (XPS) was done on a Kratos Analytical Axis Ultra photoelectron spectrometer using Al K\(\alpha\) radiation with an approximate sampling depth of 25 Å. High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL 2010F field-emission microscope operated at 200 kV. Ellipsometry was performed on a Gaertner Scientific Corp. LSE Stokes ellipsometer, set at a 70° angle of incidence and recorded at 632.8 nm. Electrochemical impedance spectra were obtained with a Solatron 1255B frequency response analyzer with a Solatron 1287 electrochemical interface. Two-point measurements were done with no dc bias and ac amplitudes ranging between 50 and 200 mV. Samples were placed in a flow-through cell, and the sample chamber was heated by a hot air gun placed \(\sim 15\) cm away to avoid electrical interference. Frequencies were typically varied from 1 MHz to 0.005 Hz. Humidified atmospheres were produced by aspirating the carrier gas though water, which was held at ambient temperature. The temperature of the sample was monitored by using a thermocouple within the cell.

Results and Discussion

Structural Analysis of K$_2$SrTa$_2$O$_7$ and H$_2$SrTa$_2$O$_7$. The starting material K$_2$SrTa$_2$O$_7$ was found to be phase pure by XRD (Figure 1a). Refinement of lattice parameters in space group \(I4/mmm\), using CELREF,\(^{(39)}\) yielded \(a = 3.980(2) \ \text{Å}\) and \(c = 21.7351(3) \ \text{Å}\), in agreement with previously published results.\(^{(39)}\) The proton-exchanged form of this compound (H$_2$SrTa$_2$O$_7$) matched previously reported XRD patterns (Figure 1b).\(^{(27,41)}\) The pattern of the proton-exchanged material could be fitted to either a body-centered or primitive tetragonal cell with unit cell parameters \(a = 3.84(5) \ \text{Å}\), \(c = 19.524(4) \ \text{Å}\) or \(a = 3.87(2) \ \text{Å}\), \(c = 9.761(1) \ \text{Å}\), respectively. Either choice of Bravais lattice leaves one unindexed reflection, \(d = 2.253\) and 1.746 Å, respectively, for the primitive and body-centered cells. The unindexed reflection in the case of the body-centered lattice corresponds well to the (111) reflection of a 3-dimensional perovskite impurity phase. Heating H$_2$SrTa$_2$O$_7$ results in its topochemical dehydration to the 3-dimensional defect perovskite SrTa$_2$O$_6$.\(^{(27)}\) The XRD pattern of H$_2$SrTa$_2$O$_7$ heated to 410 °C is shown in Figure 1c. This temperature was determined from TGA (see Supporting Information) in order to avoid the conversion to the tungsten bronze phase.\(^{(16,27)}\) The diffraction pattern of the resulting 3-dimensional perovskite was fit to a primitive cubic cell with \(a = 3.92(1) \ \text{Å}\), which agrees with previous observations.\(^{(27)}\) A layer line from residual H$_2$SrTa$_2$O$_7$ is visible in the XRD pattern.

Colloidal Ribbons Made by Exfoliation of H$_2$SrTa$_2$O$_7$. When H$_2$SrTa$_2$O$_7$ was exfoliated by reaction with excess tetra-(n-butylammonium) hydroxide, colloids with a fibrous ribbon morphology were obtained (Figure 2). This morphology was unexpected because exfoliation of layer perovskites typically gives sheet colloids or, in some cases, scrolled sheets.\(^{(19)}\) AFM images of these colloids deposited on silicon wafers after two cycles of layer-by-layer growth (see

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\(^{(40)}\) Laugier, J.; Bochu, B. LMGP-SuiteSuite of Programs for the interpretation of X-ray Experiments; ENSP/Laboratoire des Matériaux et du Génie Physique; BP 46, 38042 Saint Martin d’Hères, F., CELREF. 
Supporting Information) show that the height and width of a typical ribbon are 3 ± 1 and 40 ± 20 nm, respectively. The height is consistent with exfoliation to the level of 1–3 layers of an \( n \) = 2 layered perovskite. The ribbons are typically 500 nm in length. Ribbons are easily distinguishable from scrolled sheets, which have similar length, because in the latter case the diameter (and height in AFM images) is typically tens of nanometers.24,29,31 Additionally, cross-sectional TEM images of these colloids imbedded in resin did not show any indication of scrolling.

HRTEM images of the ribbon colloids are shown in Figures 3–5. Figure 3 shows low- and high-magnification images of a partially exfoliated sample deposited on the TEM grid from a methanol suspension. The electron diffraction pattern corresponding to the high-magnification image (Figure 3b) was indexed to a tetragonal cell viewed along the \( c \)-axis, with \( a = 3.77 \pm 0.09 \) Å. Lattice fringe measurements from Figure 4b gave a similar spacing (\( a = 3.97 \pm 0.08 \) Å), indicating that the image is a view down the \( c \)-axis of the layer perovskite. These lattice dimensions correspond well with those measured by XRD for \( \text{H}_2\text{SrTa}_2\text{O}_7 \) and \( \text{SrTa}_2\text{O}_6 \) (3.84(5) and 3.92(1) Å, respectively). Figure 5 shows an image of a ribbon that is partially splintered by exfoliation. Lattice fringes can be seen spanning the full width of the particle in the upper part of the image. A Fourier transform of a section of one of the lower splinters in the image is shown in the inset of Figure 4. The spot pattern in the Fourier transforms can also be indexed to a tetragonal unit cell viewed along the \( c \)-axis. As expected, the Fourier transforms and lattice fringes yielded consistent results (3.98 ± 0.05 and 3.8 ± 0.2 Å, respectively). These cell parameters are again in agreement with the those of \( \text{H}_2\text{SrTa}_2\text{O}_7 \) and \( \text{SrTa}_2\text{O}_6 \), as viewed along the \( c \)-axis.

<table>
<thead>
<tr>
<th>sample</th>
<th>O</th>
<th>K</th>
<th>Ta</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>fibers</td>
<td>51.6 ± 1.5</td>
<td>2.0 ± 0.2</td>
<td>37.2 ± 0.5</td>
<td>9.2 ± 0.3</td>
</tr>
<tr>
<td>( \text{H}_2\text{SrTa}_2\text{O}_7 )</td>
<td>57.3 ± 1.4</td>
<td>2.2 ± 0.2</td>
<td>30.9 ± 0.4</td>
<td>9.6 ± 0.3</td>
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* Elemental ratios were normalized to exclude carbon and oxygen.

![Figure 2](image2.png) **Figure 2.** TEM image of exfoliated \( \text{H}_2\text{SrTa}_2\text{O}_7 \).

![Figure 3](image3a.png) ![Figure 3](image3b.png) **Figure 3.** HRTEM images of (a) a partially exfoliated \( \text{H}_2\text{SrTa}_2\text{O}_7 \) particle and (b) a magnified region of the particle with (inset) electron diffraction pattern.

![Figure 4](image4.png) **Figure 4.** HRTEM image of a split ribbon of exfoliated \( \text{H}_2\text{SrTa}_2\text{O}_7 \) and (inset) a Fourier transform of the image.

![Figure 5](image5.png) **Figure 5.** HRTEM of small exfoliated particles.

![Figure 6](image6.png) **Figure 6.** Ellipsometric thickness measured following adsorption steps of ribbon colloid (○) and PDDA (●) during layer-by-layer growth on a silicon substrate.
Figure 7. EIS spectra of a pellet of H$_2$SrTa$_2$O$_7$ in humidified hydrogen (C) and air (D) at (a) 23, (b) 35, and (c) 50 °C.

Figure 8. Model circuit used in fitting impedance data. Only the parallel arrangement of $R_0$ and CPE$_{dl}$ was used for fitting data in Figure 7a.

Table 2. Parameters Derived from Fits to Impedance Spectra of H$_2$SrTa$_2$O$_7$ and SrTa$_2$O$_6$ Pellets Measured in Humidified Air

<table>
<thead>
<tr>
<th></th>
<th>23 °C</th>
<th>35 °C</th>
<th>50 °C</th>
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<tbody>
<tr>
<td>H$_2$SrTa$_2$O$_7$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{ionic}$</td>
<td>6.7 kΩ·cm (fixed)</td>
<td>404 kΩ·cm</td>
<td>214 kΩ·cm</td>
</tr>
<tr>
<td>$C_{geom}$</td>
<td>42.9 nF/cm$^2$</td>
<td>143 nF/cm$^2$</td>
<td></td>
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<tr>
<td>$R_{ele}$</td>
<td>157 kΩ·cm</td>
<td>7.70 MΩ·cm</td>
<td>747 kΩ·cm</td>
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<tr>
<td>$C_{dl}$</td>
<td>222 µF/cm$^2$</td>
<td>48.7 µF/cm$^2$</td>
<td>51.9 µF/cm$^2$</td>
</tr>
<tr>
<td>$p_{ct}$</td>
<td>0.748</td>
<td>0.545</td>
<td>0.414</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SrTa$_2$O$_6$</th>
<th></th>
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</tr>
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<tbody>
<tr>
<td>$R_{ionic}$</td>
<td>58.3 kΩ·cm</td>
<td>2.88 MΩ·cm</td>
<td>6.70 MΩ·cm</td>
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<tr>
<td>$C_{geom}$</td>
<td>2.26 nF/cm$^2$</td>
<td>1.52 nF/cm$^2$</td>
<td>1.22 nF/cm$^2$</td>
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<tr>
<td>$R_{ele}$</td>
<td>0.8</td>
<td>0.748</td>
<td>0.75</td>
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<tr>
<td>$C_{dl}$</td>
<td>1.72 MΩ·cm</td>
<td>3.17 MΩ·cm</td>
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<tr>
<td>$p_{ct}$</td>
<td>0.719</td>
<td>0.729</td>
<td>0.73</td>
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</table>

Exfoliated samples of ribbons were deposited on silicon by spin-casting a suspension in methanol at 400 rpm. XRD of these films (~2 µm thick, as measured by AFM) indicated a layered material with spacing (10.97 Å) slightly larger than that observed for H$_2$SrTa$_2$O$_7$ (9.77 Å, Figure 1d). The increased layer spacing can be rationalized in terms of the presence of residual TBA$^+$ cations and/or water in the restacked colloid.

Electrochemical Impedance Spectroscopy. Bulk Measurements. The proton conductivity of H$_2$SrTa$_2$O$_7$ samples was measured in humidified hydrogen and in air. The measurements in hydrogen atmosphere are relevant to use of solid electrolytes in fuel cell but can be complicated (especially in the case of reducible B-site cations such as Ti and Nb) by the onset of electronic conduction. In humidified hydrogen, however, electronic conductivity can be suppressed via the reverse of (1), which is the reaction of hydrogen with lattice oxygen to create oxygen vacancies and conduction band electrons.

$$H_2(g) + O^\circ + 2e^- = V^{\circ} + H_2O(g)$$  \hspace{1cm} (1)

Pressed pellet samples of H$_2$SrTa$_2$O$_7$ with Pt electrodes generally exhibit impedance spectra with two semicircles, although the visibility of each relaxation depends upon

some HRTEM images, very small ribbons were observed (lengths of 5–10 nm and widths of 1.0 ± 0.1 nm) (Figure 5). The lattice fringes of these particles have spacings (7.9 ± 0.1 Å) corresponding to a double layer of TaO$_6$ octahedra (8.0 Å), and the images may therefore be a view along the a-axis. The gap between these small particles is much larger that that expected for an intercalated interlayer, suggesting that the particles are not bonded together.

ICP-AES analysis of the exfoliated colloids indicates that they contain less strontium than H$_2$SrTa$_2$O$_7$ or SrTa$_2$O$_6$. This analysis gives a Ta:Sr ratio of 3.0 ± 0.2. EDS of the individual ribbons suggests lower strontium content than that of a H$_2$SrTa$_2$O$_7$ reference sample, although quantification was not possible due to some overlap of peaks in the spectrum. XPS analysis of the precipitated colloids (Table 1) gave a Ta:Sr ratio of 2.5 ± 0.1, consistent with the ICP-AES analysis. These analyses suggest that splintering the sheets along the a-axis involves dissolution of Sr$^{2+}$ ions at the edges of the ribbons.
humidity is zero at 23°C illustrates the very large resistance when the relative humidity is provided by a room temperature bubbler due to the differences in relative humidity. Since the difference between 35°C and 50°C temperature and elevated temperature is much higher than that between 23°C and 35°C, this increases dramatically to a few hundred kΩ·cm. A separate run (shown in Figure 7a) illustrates the very large resistance when the relative humidity is zero at 23°C. These experiments show that over the temperature range of 23–50°C the relative humidity, rather than temperature, is the dominating factor. Adsorbed liquid water at 23°C would also inhibit hydrogen transfer across the Pt electrode/air surface, which explains why the Nyquist plot for the spectrum obtained under H₂ at 23°C (inset, Figure 7a) shows a diagonal tail/onset of a large semicircle.

Figure 9 shows the impedance spectra obtained after the H₂SrTa₂O₇ pellet has been dehydrated in situ to SrTa₂O₆. The general trends remain the same; ionic conductivity remains highest at 100% relative humidity and drops dramatically once the relative humidity drops below 100%. Overall, the resistivities are higher, and this may be due to a number of reasons. Structurally, the pellet may have slightly sintered, offering less surface area for water adsorption; the unprotonated surface of SrTa₂O₆ may have a smaller water adsorption capacity; and finally, the lack of interlayer protons and water in SrTa₂O₆ may also contribute to the lower protonic conductivity.

**Thin Film Measurements.** Thin film samples of H₂SrTa₂O₇ ribbons were calcined in air at 450°C; this temperature was chosen on the basis of TGA data for the ribbon–PDDA composite (see Supporting Information). The impedance spectra from in-plane conductivity measurements are shown in Figure 10a. The general shape remains similar to that obtained from pellet samples. Fitting to the same model circuit yields the R_{ionic} = 1.5–1.6 MΩ for both H₂ and air atmospheres. Taking the thickness of the conductive portion of the film to be the same as the thickness of the electrodes (35 nm), this corresponds to a resistivity of only 42 Ω·cm, which is 4 orders of magnitude lower than the resistivity observed in pellet samples. Similar anisotropic conductivity effects have been observed with lamellar solid-state ionic conductors. We also see that the semicircle at higher frequency tends to be less depressed; this is also likely to be a consequence of well-aligned fibers along the platinum electrode surface.

Conductivity measurements through the film gave the impedance spectra shown in Figure 10b. The high-frequency response normally seen as a semicircle in the other spectra is barely visible in the H₂ experiment and essentially nonexistent in the air experiment. The visible semicircle is depressed, and its real axis intercept (~550 kΩ) implies a very high resistivity of ~780 MΩ·cm. It is likely that the depressed semicircle is due to an

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inhomogeneous film/electrode interface. Poor hydration (because the conducting portion of the film is by platinum on both sides) may contribute to the very high resistance that is measured across the film.

The order of ionic conductivity of the four samples can be explained from a structural point of view. The thin film sample, prepared from layer-by-layer assembly of the ribbons, measured parallel to the direction of orientation was the most conductive ($2.4 \times 10^{-2}$ S/cm). This was expected since this geometry requires proton to travel along the fiber axis. The pellet of hydrated H$_2$SrTa$_2$O$_7$ with its randomly grains was the next most conductive ($1.5 \times 10^{-4}$ S/cm), although 2 orders of magnitude lower than the thin film measured in plane. The conductivity of the SrTa$_2$O$_6$ pellet ($1.7 \times 10^{-5}$ S/cm) was 1 order of magnitude lower than that of the H$_2$SrTa$_2$O$_7$ pellet. This is expected due to the loss of conductive pathways of the interlayers. Finally, the thin film sample measured perpendicular to the ribbon axis had the lowest conductivity, several orders of magnitude lower than that of SrTa$_2$O$_6$ ($1.3 \times 10^{-9}$ S/cm). While the conductivity in the direction perpendicular to the ribbon axis is likely to be low, other factors such as poor hydration of the film may contribute to the resistance in this case.

Conclusions

Exfoliation of H$_2$SrTa$_2$O$_7$ yields a novel ribbon material, which appears to maintain its parent perovskite block structure, although with loss of some A-site Sr$^{2+}$ cations. Oriented films of these ribbons can be grown layer-by-layer, by alternate adsorption of ribbons and polycations, or by spin-coating. The proton conductivity of these films is highly anisotropic, and in the plane that contains the ribbon axis it is $\sim$2 orders of magnitude higher than that of randomly oriented grains of hydrated H$_2$SrTa$_2$O$_7$. We are currently investigating the possibility of using the diamagnetic anisotropy of H$_2$SrTa$_2$O$_7$ and related materials to orient fibers and sheets with their conductive directions perpendicular to substrates by means of strong magnetic fields. The results of these experiments will be reported in a future publication.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-0616450. We thank Jeff Shallenberger, Bob Hengstebeck, Vince Bojan, and Henry Gong for assistance with the XPS, ICP-AES, and EDS measurements.

Supporting Information Available: TGA data for dehydration of H$_2$SrTa$_2$O$_7$ and thermal decomposition of colloids flocculated with PDDA, AFM images of colloidal ribbons grown as layer-by-layer thin films, and schematic diagram showing measurement geometry for thin films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure 10. EIS of films of exfoliated H$_2$SrTa$_2$O$_7$ in humidified hydrogen (○) and air (●) measured (a) parallel and (b) perpendicular to the plane of the film.