# Proton-Conducting Films of Nanoscale Ribbons Formed by Exfoliation of the Layer Perovskite H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>

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Thin films of nanoscale ribbons derived from the layer perovskite H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> 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<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>. Powder X-ray diffraction and high-resolution transmission electron microscopy confirmed that the ribbons had similar *a*-axis unit cell parameters (3.98)  $\pm$  0.05 Å) to H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> (3.87  $\pm$  0.02 Å) and the defect perovskite SrTa<sub>2</sub>O<sub>6</sub> (3.92  $\pm$  0.01 Å) which is the dehydration product of H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>. 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<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>. 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  $H_2SrTa_2O_7$  and  $SrTa_2O_6$ 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  $1.5 \times 10^{-4}$  and  $1.7 \times 10^{-5}$  S/cm for pellets containing randomly oriented grains of H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> and SrTa<sub>2</sub>O<sub>6</sub>. The measured conductivities of oriented films of the ribbons were  $1.3 \times 10^{-9}$  and  $2.4 \times 10^{-2}$  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-precious-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,<sup>1–8</sup> but so far there are few reports of their use in fuel cells.<sup>9,10</sup> Most of these materials are brittle ceramics that cannot form mechanically strong, thin membranes.<sup>11</sup> The exceptions are pellicular membranes made from layered materials such as exfoliated zirconium phosphate.<sup>12</sup> Unfortunately, the proton conductivity in these membranes, as in most lamellar inorganic proton conductors,<sup>13</sup> 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

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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 nanotubes, 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.<sup>14-19</sup> By using ion-exchange reactions,  $2^{20-22}$  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 anionic colloids.<sup>23–25</sup> Thin films of these exfoliated materials have been grown layer-by-layer (LBL) using electrostatic interactions with a polycation<sup>26</sup> or by casting directly from colloidal suspensions.<sup>12,17</sup> The proton-exchanged forms of layered perovskites can also undergo a topochemical dehydration reaction, collapsing the layers and leaving A-sitedeficient three-dimensional perovskites.<sup>21,27,28</sup> Recently, several groups have observed scrolling of layer perovskites into tubular morphologies,<sup>29,30</sup> scrolling of related nonperovskite niobium<sup>31</sup> and vanadium<sup>32</sup> oxides, and restacking of exfoliated sheets into mesoporous "house of cards" structures.<sup>33,34</sup> Rod-shaped and tubular perovskites have also been synthesized by direct hydrothermal methods.<sup>35–38</sup> These new forms are particularly interesting as intermediate temperature proton conductors because of the possibility of

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proton conductors in the plane but relatively poor conductors in the transverse direction.

orienting the sheet, tube, or rod axis transverse to the plane

and ambient temperature proton conductivity of colloidal

films derived from the layer perovskite K<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>. Interest-

ingly, we find that the colloid is composed of ribbonlike

fibers rather than sheets or scrolls. When cast as thin films or grown layer-by-layer with alternating polycation adsorp-

tion steps, these ribbons orient parallel the substrate plane.

As expected, these electronically insulating ribbons are good

In this paper we report the exfoliation, thin film assembly,

of the membrane.

## **Experimental Section**

Synthesis of K<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> and H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>. K<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> was synthesized from KOH (Aldrich, 99.99%), SrCO<sub>3</sub> (Aldrich, 99.9+%), and Ta<sub>2</sub>O<sub>5</sub> (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.<sup>39</sup> 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<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> product was ion exchanged with 4 M HNO<sub>3</sub>, and the solution was replaced several times over the course of 1 week to obtain H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>. Completion of the proton exchange reaction was verified by XRD. The product was then filtered, rinsed with water, and allowed to dry under ambient conditions. Pellets of H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> for impedance measurements were prepared by pressing 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<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> and Purification of Fibers.** H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> (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. AFM 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. AFM 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<sub>2</sub>O<sub>2</sub>/ concentrated H<sub>2</sub>SO<sub>4</sub>; *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 Technnic 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 AFM measurements), 800  $\mu$ m wide between the two metal electrodes, and 6.25 mm long.

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#### Proton-Conducting Films of Nanoscale Ribbons

The  $H_2SrTa_2O_7$  films for in-plane measurements were deposited layer-by-layer using a poly(diallyldimethylammonium) chloride/ 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  $H_2SrTa_2O_7$ . 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  $H_2SrTa_2O_7$  was prepared by flocculating a suspension of  $H_2SrTa_2O_7$  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<sub>2</sub> (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<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> 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 $\alpha$  ( $\lambda = 1.5418$  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<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>. Samples were dissolved in 48% HF with agitation on an orbital shaker and were then diluted to within standard ranges. X-ray photoelectron spectroscopy (XPS) was done on a Kratos Analytical Axis Ultra photoelectron spectrometer using Al Ka 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.



**Figure 1.** X-ray powder diffraction patterns of (a)  $K_2SrTa_2O_7$ , (b)  $H_2SrTa_2O_7$  with reflection assignments for both P-centered and (I-centered) unit cells, (c)  $SrTa_2O_6$ , and (d) spin-cast exfoliated fibers.

#### **Results and Discussion**

Structural Analysis of K<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> and H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>. The starting material K<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> was found to be phase pure by XRD (Figure 1a). Refinement of lattice parameters in space group I4/mmm, using CELREF,<sup>40</sup> yielded a = 3.980(2) Å and c = 21.7351(3) Å, in agreement with previously published results.<sup>39</sup> The proton-exchanged form of this compound (H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>) matched previously reported XRD patterns (Figure 1b).<sup>27,41</sup> 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) Å, c =19.524(4) Å or a = 3.87(2) Å, c = 9.761(1) 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<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> results in its topochemical dehydration to the 3-dimensional defect perovskite SrTa<sub>2</sub>O<sub>6</sub>.<sup>27</sup> The XRD pattern of H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> 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.<sup>16,27</sup> The diffraction pattern of the resulting 3-dimensional perovskite was fit to a primitive cubic cell with a = 3.92(1) Å, which agrees with previous observations.<sup>27</sup> A layer line from residual H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> is visible in the XRD pattern.

**Colloidal Ribbons Made by Exfoliation of H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>.** When H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> 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.<sup>19</sup> AFM images of these colloids deposited on silicon wafers after two cycles of layer-by-layer growth (see

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500 nm

Figure 2. TEM image of exfoliated H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>.



Figure 3. HRTEM images of (a) a partially exfoliated  $H_2SrTa_2O_7$  particle and (b) a magnified region of the particle with (inset) electron diffraction pattern.

Supporting Information) show that the height and width of a typical ribbon are  $3 \pm 1$  and  $40 \pm 20$  nm, respectively. The height is consistent with exfoliation to the level of 1-3layers 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.<sup>24,29,31</sup> Additionally, crosssectional 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  $H_2SrTa_2O_7$  and  $SrTa_2O_6$  (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



**Figure 4.** HRTEM image of a split ribbon of exfoliated  $H_2SrTa_2O_7$  and (inset) a Fourier transform of the image.



Figure 5. HRTEM of small exfoliated particles.

Table 1. Elemental Ratios from XPS Spectra of  $H_2SrTa_2O_7$  and Exfoliated  $H_2SrTa_2O_7$ 

sample	0	Κ	Та	Sr
fibers	$51.6 \pm 1.5$	$2.0 \pm 0.2$	$37.2 \pm 0.5$	$9.2 \pm 0.3$
HaSrTaaOr	57.3 ± 1.4	2.2 ± 0.2	$30.9 \pm 0.4$	9.6 ± 0.3

<sup>a</sup> Elemental ratios were normalized to exclude carbon and oxygen.



**Figure 6.** Ellipsometric thickness measured following adsorption steps of ribbon colloid ( $\bullet$ ) and PDDA ( $\diamond$ ) during layer-by-layer growth on a silicon substrate.

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  $\pm$  0.05 and 3.8  $\pm$  0.2 Å, respectively). These cell parameters are again in agreement with the those of H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> and SrTa<sub>2</sub>O<sub>6</sub>, as viewed along the *c*-axis. In



Figure 7. EIS spectra of a pellet of  $H_2SrTa_2O_7$  in humidified hydrogen (O) and air () at (a) 23, (b) 35, and (c) 50 °C.



**Figure 8.** Model circuit used in fitting impedance data. Only the parallel arrangement of  $R_{ct}$  and CPE<sub>dl</sub> was used for fitting data in Figure 7a.

Table 2. Parameters l	Derived from Fi	ts to Impeo	lance Spectra of
H <sub>2</sub> SrTa <sub>2</sub> O <sub>7</sub> and SrT	a <sub>2</sub> O <sub>6</sub> Pellets Me	asured in H	Iumidified Air

H <sub>2</sub> SrTa <sub>2</sub> O <sub>7</sub>	23 °C	35 °C	50 °C
Rionic	6.7 k $\Omega$ · cm (fixed)	404 kΩ•cm	214 kΩ•cm
$C_{\text{geom}}$		42.9 nF/cm <sup>2</sup>	143 nF/cm <sup>2</sup>
$p_{\text{geom}}$		0.695	0.613
$R_{\rm ct}$	157 kΩ•cm	9.70 MΩ•cm	747 kΩ•cm
$C_{ m dl}$	$222 \ \mu \text{F/cm}^2$	48.7 $\mu$ F/cm <sup>2</sup>	51.9 $\mu$ F/cm <sup>2</sup>
$p_{ m dl}$	0.748	0.545	0.414
SrTa <sub>2</sub> O <sub>6</sub>	23 °C	35 °C	50 °C
Rionic	58.3 kΩ•cm	2.88 MΩ•cm	6.70 MΩ•cm
$C_{\text{geom}}$	2.26 nF/cm <sup>2</sup>	1.52 nF/cm <sup>2</sup>	1.22 nF/cm <sup>2</sup>
$p_{\text{geom}}$	0.8	0.748	0.75
R <sub>ct</sub>	1.72 MΩ•cm	3.17 MΩ•cm	4.88 MΩ•cm
$C_{ m dl}$	95.6 $\mu$ F/cm <sup>2</sup>	64.9 $\mu$ F/cm <sup>2</sup>	21.7 $\mu$ F/cm <sup>2</sup>
$p_{\rm dl}$	0.719	0.729	0.73

some HRTEM images, very small ribbons were observed (lengths of 5–10 nm and widths of  $1.0 \pm 0.1$  nm) (Figure 5). The lattice fringes of these particles have spacings (7.9  $\pm$  0.1 Å) corresponding to a double layer of TaO<sub>6</sub> 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<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> or SrTa<sub>2</sub>O<sub>6</sub>. This analysis gives a Ta:Sr ratio of  $3.0 \pm 0.2$ . EDS of the individual ribbons suggests lower strontium content than that of a H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> 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  $2.5 \pm 0.1$ , consistent with the ICP-AES analysis. These analyses suggest that splintering the sheets along the *a*-axis involves dissolution of Sr<sup>2+</sup> ions at the edges of the ribbons.

Layer-by-Layer Deposition and Spin-Casting of Oriented Films. Layer-by-layer film growth was accomplished by submerging a substrate into poly(diallyldimethylammonium) chloride (PDDA) solution, forming a positively charged surface. After rinsing with water, the substrate was then immersed in a suspension of the polyanionic colloidal ribbons. The cycle of alternating polycation and polyanion adsorption leads to stepwise growth of a multilayer film with a bilayer thickness of  $\sim 20$  Å, as shown in Figure 6. There is a slight downward curvature to the plot, and the first deposition step leads to the largest increase in film thickness. This suggests that the affinity of the anionic ribbons for the PDDA-covered surface decreases as the surface roughens after the first cycle. AFM images (see Supporting Information) show that the ribbons aggregate and create a rough surface.

Exfoliated samples of ribbons were deposited on silicon by spin-casting a suspension in methanol at 400 rpm. XRD of these films (~2  $\mu$ m thick, as measured by AFM) indicated a layered material with spacing (10.97 Å) slightly larger than that observed for H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> (9.77 Å, Figure 1d). The increased layer spacing can be rationalized in terms of the presence of residual TBA<sup>+</sup> cations and/or water in the restacked colloid.

**Electrochemical Impedance Spectroscopy.** *Bulk Measurements.* The proton conductivity of  $H_2SrTa_2O_7$  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.<sup>42,43</sup> 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.

$$H_2(g) + O_0^x = 2e' + V_0^{\bullet \bullet} + H_2O(g)$$
 (1)

Pressed pellet samples of H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> with Pt electrodes generally exhibit impedance spectra with two semicircles, although the visibility of each relaxation depends upon

<sup>(42)</sup> Sato, M.; Abo, J.; Jin, T.; Ohta, M. J. Alloys Compd. 1993, 192, 81-3.

<sup>(43)</sup> Thangadurai, V.; Weppner, W. Solid State Ionics 2004, 174, 175–183.



Figure 9. EIS spectra of a pellet of SrTa<sub>2</sub>O<sub>6</sub> in humidified hydrogen (O) and air () at (a) 23, (b) 35, and (c) 50 °C.

various conditions. Such spectra, as shown in Figure 7, are qualitatively reminiscent of those reported for structurally related layer perovskites,<sup>5,34</sup> where the higher frequency (inner) semicircle is assumed to be due to ionic conduction and the outer circle is a response from the electrode/electrolye interface. A general model circuit is shown in Figure 8. Here,  $R_{\text{ionic}}$  refers to the ionic conductivity of the electrolyte and  $R_{\rm ct}$  reflects the resistance associated with charge transfer, as the Pt electrodes are semipermeable to hydrogen. Constant phase elements CPE<sub>geom</sub> and CPE<sub>dl</sub> represent the overall geometric capacitance and double-layer capacitance at the electrode/electrolyte interface, respectively. Constant phase elements, rather than simple capacitors, are used since they account for the depression of the semicircles, which is reflective of the distribution of the RC constant, which in turn stems from the rough nature of the electrode/electrolyte interface. In general, impedance data obtained under hydrogen lose the pronounced lower frequency semicircle since  $R_{\rm ct}$  has decreased and the electrodes, which were semiblocking, become nonblocking to hydrogen.

Table 2 summarizes the various parameters obtained after performing least-squares fits to the spectra.  $R_{\text{ionic}}$  is generally close to the Z intercept of the inner semicircle of the Nyquist plot. At 23 °C, the ionic resistivity of  $H_2SrTa_2O_7$  is 6.7 k $\Omega$ ·cm; when the temperature is increased to 35 or 50 °C, this increases dramatically to 200–400 k $\Omega$  · cm. The difference in  $R_{\text{ionic}}$  between ambient temperature and elevated temperature is much higher than the difference between 35 and 50 °C. This is most likely due to the differences in relative humidity. Since the humidity is provided by a room temperature bubbler upstream of the cell, at 23 °C the relative humidity at the sample is 100%; at 35 °C it is 50%, and at 50 °C it is only 23%. At 23 °C, the surface of the H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> grains are saturated with adsorbed water, and this leads to the relatively high conductivity. Raising the temperature even slightly lowers the relative humidity, removing the adsorbed water, and resistivity rises abruptly to a few hundred k $\Omega$ ·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  $H_2$  at 23 °C (inset, Figure 7a) shows a diagonal tail/onset of a large semicircle.

Figure 9 shows the impedance spectra obtained after the  $H_2SrTa_2O_7$  pellet has been dehydrated in situ to  $SrTa_2O_6$ . 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  $SrTa_2O_6$  may have a smaller water adsorption capacity; and finally, the lack of interlayer protons and water in  $SrTa_2O_6$  may also contribute to the lower protonic conductivity.

Thin Film Measurements. Thin film samples of H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> 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  $R_{\text{ionic}} = 1.5-1.6 \text{ M}\Omega$  for both H<sub>2</sub> 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  $\Omega \cdot cm$ , 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.<sup>34,44,45</sup> 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 H<sub>2</sub> experiment and essentially nonexistent in the air experiment. The visible semicircle is depressed, and its real axis intercept ( $\sim$ 550 k $\Omega$ ) implies a very high resistivity of  $\sim$ 780 M $\Omega$ •cm. It is likely that the depressed semicircle is due to an

<sup>(44)</sup> Hutchison, J. C.; Bissessur, R.; Shriver, D. F. Chem. Mater. 1996, 8, 1597–1599.

<sup>(45)</sup> Lutkenhaus, J. L.; Olivetti, E. A.; Verploegen, E. A.; Cord, B. M.; Sadoway, D. R.; Hammond, P. T. *Langmuir* 2007, 23, 8515–8521.



Figure 10. EIS of films of exfoliated H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> in humidified hydrogen (O) and air () measured (a) parallel and (b) perpendicular to the plane of the film.

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  $(2.4 \times 10^{-2} \text{ S/cm})$ . This was expected since this geometry requires proton to travel along the fiber axis. The pellet of hydrated H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> with its randomly grains was the next most conductive  $(1.5 \times 10^{-4} \text{ S/cm})$ , although 2 orders of magnitude lower than the thin film measured in plane. The conductivity of the  $SrTa_2O_6$  pellet  $(1.7 \times 10^{-5} \text{ S/cm})$  was 1 order of magnitude lower than that of the H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> 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  $SrTa_2O_6$  (1.3  $\times$  10<sup>-9</sup> 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  $H_2SrTa_2O_7$  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-bylayer, 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 ~2 orders of magnitude higher than that of randomly oriented grains of hydrated H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub>. We are currently investigating the possibility of using the diamagnetic anisotropy of H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> and related materials to orient fibers and sheets with their conductive directions perpendicular to substrates by means of strong magnetic fields. The resuls of these experiments will be reported in a future publication.

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**Supporting Information Available:** TGA data for dehydration of H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> and thermal decomposition of colloids flocculated wth 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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