

# Synthesis, Exfoliation, and Electronic/Protonic Conductivity of the Dion–Jacobson Phase Layer Perovskite HLa<sub>2</sub>TiTa<sub>2</sub>O<sub>10</sub>

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## **(5)** Supporting Information

**ABSTRACT:** Electrochemical impedance spectroscopy was used to study the transport properties of the three-layer Dion–Jacobson phase  $HLa_2Ti_2TaO_{10}$  in the temperature range of interest (250–475 °C) for intermediate temperature fuel cells. The compound was prepared by proton exchange of  $RbLa_2Ti_2TaO_{10}$ , which in turn was made by direct solid state synthesis or by an organic precursor-based method. When prepared by the precursor method,  $HLa_2Ti_2TaO_{10} \cdot nH_2O$  (n = 1-2) could be exfoliated by tetrabutylammonium hydroxide to produce rectangular sheets with ~30 nm lateral dimensions.  $HLa_2Ti_2TaO_{10} \cdot nH_2O$  lost intercalated water at temperatures between 100 and 200 °C, but X-ray diffraction patterns up to 500 °C did not show evidence of collapse of the interlayer galleries that has been observed with the structurally similar compound  $HCa_2Nb_3O_{10}$ . Under humid hydrogen atmosphere, the conductivity of  $HLa_2Ti_2TaO_{10}$  followed Arrhenius behavior with an activation energy of 0.9 eV; the conductivity was in the range of  $10^{-9}$  to  $10^{-5}$  S cm<sup>-1</sup> depending on the preparation



conditions and temperature. Modification of the stoichiometry to produce A-site or B-site (vacancy or substitution) defects decreased the conductivity slightly. The conductivity was approximately 1 order of magnitude higher in humid hydrogen than in humid air atmospheres, suggesting that the dominant mechanism in the intermediate temperature range is electronic. A-site substitution ( $Sr^{2+}$  for  $La^{3+}$ ) beyond the Ruddlesden–Popper phase limit converted the layered pervoskite to a cubic perovskite  $Sr_{2,5}\square_{0.5}Ti_2TaO_9$  with 2 orders of magnitude higher conductivity than  $HLa_2Ti_2TaO_{10}$  at 475 °C.

# ■ INTRODUCTION

Electrochemical energy conversion technologies are becoming increasingly important as the global energy economy evolves toward higher efficiency and sustainability. The development of these technologies is to a large extent driven by the discovery of higher performing and lower cost materials. In the case of fuel cells, which are devices that electrochemically oxidize fuels to produce electrical energy, the current technology is dominated by low temperature (<150 °C) and high temperature (>600 °C) devices that contain polymer and solid oxide electrolytes, respectively.<sup>1</sup> A gap exists in the intermediate temperature regime (250-450 °C) where there are reasons to expect that fuel cells could be made more efficient and less expensive. The loading of precious metal anode and cathode catalysts could be substantially decreased because of the higher activity of catalysts at higher temperature. Also, carbon-containing species such as CO, which poison noble metal catalysts in polymer fuel cells, are easily oxidized at the anode at intermediate temperatures. However, the development of intermediate temperature fuel cell technology is hampered by the lack of electrolyte materials that have sufficiently high proton conductivity in the temperature range of interest.<sup>2</sup>

Experiments on intermediate temperature fuel cells have employed ceramic proton conductors that include  $C_{sH_2PO_4}$ ,<sup>4</sup> Ba( $Ce_{1-x}Zr_x$ )<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3</sub>,<sup>5</sup> and indium-doped tin pyrophosphate.<sup>6,7</sup> In general, low current densities have been obtained because relatively thick (and thus highly resistive) membranes

are needed for mechanical integrity. However, much thinner films of inorganic proton conductors can be used in hybrid electrolyte membranes in which an electronically insulating proton conductor is supported on a flexible metal hydride foil.<sup>8–10</sup> In this configuration, materials with proton conductivities in the range of  $10^{-2}$  to  $10^{-1} \Omega^{-1} \text{ cm}^{-1}$  might be used as films of ~10  $\mu$ m thickness without incurring major resistive loss in the fuel cell.

Among the inorganic materials that show promise as intermediate temperature proton conductors, oxides derived from the perovskite (ABO<sub>3</sub>) structural family are particularly interesting. The perovskite structure can accommodate anion vacancies, which filled by oxygen atoms from water molecules; protons in the resulting OH groups can be mobile in the lattice.<sup>11–14</sup> By using early transition metal B-site cations that resist reduction, perovskites can be electronically insulating even in hydrogen atmospheres. For example, BaZr<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3- $\delta$ </sub> (BZY20) films made by pulsed laser deposition have a proton conductivity of 0.11  $\Omega^{-1}$  cm<sup>-1</sup> at 500 °C.<sup>15</sup> Polycrystalline BZY20 synthesized by a precursor-based route has a reported conductivity of ~0.01  $\Omega^{-1}$  cm<sup>-1</sup> at 450 °C.<sup>16</sup>

In addition to simple  $ABO_3$  perovskites, layer perovskites can be made with intergrown A'O or A'\_2O layers (A' = alkali or

Received: June 4, 2013 Revised: December 20, 2013

Published: December 29, 2013

alkali earth) between the  $A_{n-1}B_nO_{3n}$  perovskite blocks. If A' is an alkali metal, ion exchange with acid affords a layered proton conductor. Some of these materials, including HLa<sub>2</sub>Ti<sub>2</sub>NbO<sub>10</sub> and HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>, have conductivities in the range of  $10^{-4}$ - $10^{-3} \Omega^{-1}$  cm<sup>-1</sup> at 450 °C, although it has not been established that the conductivity is purely ionic.<sup>17</sup> Under similar conditions, the two-layer Dion–Jacobson phases  $MLaNb_2O_7$  (M = H, Li, Na, and K) have shown conductivities in the range of  $10^{-5}$ - $10^{-4} \ \Omega^{-1} \ cm^{-1} \ ^{18}$  Although layer perovskites generally have lower conductivity than three-dimensionally bonded perovskites, their conductivity can be significantly increased by soft chemical reactions.<sup>19</sup> For example, films of hydrated H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> made by exfoliation and restacking have a proton conductivity parallel to the sheets of 2.4  $\times$  10<sup>-2</sup>  $\Omega^{-1}$  cm<sup>-1</sup> at 25 °C. By comparison, the proton conductivity of the same material in pellet form with random grain orientation is  $1.4 \times 10^{-4} \ \Omega^{-1}$ cm<sup>-1,20</sup> Recent experiments have shown that it is possible to orient layer perovskite microcrystals with their layer planes parallel to the field lines of a ~1 T magnet, exploiting the diamagnetic anisotropy of the sheets.<sup>21</sup> In principle, this method could be used to make films of these materials several micrometers thick, with the lattice directions of highest proton conductivity oriented perpendicular to a metal hydride membrane support.

Layer perovskite structures are highly adaptable to nonstoichiometry. Gopalakrishnan and co-workers have shown that it is possible to tune the composition continuously between the Dion-Jacobson  $(A'A_{n-1}B_nO_{3n+1})$  and Ruddlesden-Popper  $(A'_2A_{n-1}B_nO_{3n+1})$  limits, to obtain materials with interstitial ions or vacancies on the A' sites.<sup>22</sup> Proton exchange of these nonstoichiometric layer perovskites could yield materials with excess protons or oxygen vacancies at high temperature, which could lead to increased ionic conductivity. The goal of this study was to investigate the effect of this kind of nonstoichiometry on the intermediate temperature proton conductivity of the Dion-Jacobson phase layer perovskite HLa2TaTi2O10.nH2O.23 We chose Ta- rather than Nbcontaining compounds because earlier work had shown that the two-layer Dion-Jacobson phase HLaNb<sub>2</sub>O<sub>7</sub> is susceptible to reduction in hydrogen atmospheres.<sup>24</sup> In this study, the Tacontaining compounds were made by conventional solid state synthesis and also by a molecular precursor-based route to examine the effect of particle size on conductivity. A series of nonstoichiometric RbLa2TaTi2O10 compounds was made by partial substitution of Sr for La and by adjusting the La:Ta:Ti ratios in the synthesis. These compounds were ion-exchanged to their proton forms, and their conductivity in oxidizing and reducing atmospheres was measured by electrochemical impedance spectroscopy.

#### EXPERIMENTAL SECTION

Solid-State Synthesis and Proton Exchange of RbLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>. The parent compound RbLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> and its nonstoichiometric derivatives were made by solid-state reaction of the appropriate oxides and carbonates. The starting materials were Rb<sub>2</sub>CO<sub>3</sub> (Alfa Aesar), La<sub>2</sub>O<sub>3</sub> (Alfa Aesar), TiO<sub>2</sub> (Aldrich), and Ta<sub>2</sub>O<sub>5</sub> (Alfa Aesar). Excess Rb<sub>2</sub>CO<sub>3</sub> (25 mol %) was added to compensate for volatilization of Rb<sub>2</sub>O. In addition to the parent compound the target stoichiometries included those with A-site vacancies, Rb<sub>1+x</sub>La<sub>2-x</sub>TaTi<sub>2</sub>O<sub>10</sub> ( $0 \le x \le 0.08$ ), A-site substitution, Rb<sub>1+x</sub>Sr<sub>x</sub>La<sub>2-x</sub>TaTi<sub>2</sub>O<sub>10</sub> ( $0 \le x \le 1.50$ ), B-site vacancies, Rb<sub>1+5</sub>xLa<sub>2</sub>Ta<sub>1-x</sub>Ti<sub>2</sub>O<sub>10</sub> and Rb<sub>1+4y</sub>La<sub>2</sub>TaTi<sub>2-y</sub>O<sub>10</sub> ( $0 \le x, y \le 0.08$ ), and B-site substitution, Rb<sub>1+x</sub>La<sub>2</sub>Ta<sub>1-x</sub>Ti<sub>2+x</sub>O<sub>10</sub> ( $-0.08 \le x \le 0.08$ ). These materials were prepared by mixing appropriate amounts of

 $Rb_2CO_3$ ,  $La_2O_3$ ,  $TiO_2$ , and  $Ta_2O_5$ . The powders were ground together in ethanol and then calcined at 1100 °C for 12 h in alumina crucibles. After calcination, the products were washed with water to remove residual Rb oxide or hydroxide.  $RbLa_2Ti_2TaO_{10}$  and its nonstoichiometric derivatives were proton exchanged by mixing them with nitric acid (1 M) for 2 days (30 mL/g-solid). The nitric acid solution was replaced each day to promote complete proton exchange. The  $HLa_2Ti_2TaO_{10}$ · $nH_2O$  product and its derivatives were isolated by centrifugation, washed with water, and then dried at 60 °C under reduced pressure overnight. Samples made by the solid state synthetic route are hereafter designated as SS.

Molecular Precursor-Based Synthesis of RbLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>. The stock solutions for molecular precursor-based synthesis were rubidium carbonate (Rb<sub>2</sub>CO<sub>3</sub> dissolved in 0.1 M HNO<sub>3</sub>), lanthanum acetate hydrate ((CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>La·H<sub>2</sub>O dissolved in 0.1 M HNO<sub>3</sub>), titanium isopropoxide (diluted in ethanol), and tantalum citrate (Ta2O5 dissolved in citrate solution).<sup>25</sup> In a typical synthesis (0.5 g,  $\sim 6.25$  $\times$  10^{-4} mole of final product), a stoichiometric amount of Rb\_2CO\_3 (with 30% excess to compensate for volatilization of Rb<sub>2</sub>O during calcination) and the La and Ta precursor solutions, along with 0.2 g of hydroxypropyl cellulose ( $M_w$  80,000, Aldrich) and 0.2 g of polyethylene glycol 20 000 (Mr 16 000-24 000, Fluka) were added to 10 mL of deionized water. Then, 20 mL of toluene and a stoichiometric amount of the Ti precursor solution were added with vigorous stirring (stirring at 80 °C helps with dissolution). The asobtained orange mixture was heated to 130 °C on a hot plate stirrer to evaporate excess solvent and to promote esterfication. The viscous orange mixture obtained after 30-45 min was transferred to an Al<sub>2</sub>O<sub>3</sub> crucible and calcined immediately at 1100 °C for 12 h. (Caution: volatilization of the organic components produces odors during calcination.) Samples made by the precursor-based method are hereafter designated as PB. Proton exchange of the PB compounds was carried out with nitric acid as described above for SS-RbLa2Ti2TaO10.

**Exfoliation of HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·***n***H<sub>2</sub>O. Exfoliation of HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>.** *n***H<sub>2</sub>O (from the acid-exchanged Rb precursors made by either the SS or the PB method) was carried out by intercalating aqueous tetra(***n***-butyl)ammonium hydroxide (TBA<sup>+</sup>OH<sup>-</sup>, Aldrich, 40 wt % in H<sub>2</sub>O) at ambient temperature. A total of 50 mg of HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·***n***H<sub>2</sub>O was mixed with 1 mL of deionized water and 0.1 mL of TBA<sup>+</sup>OH<sup>-</sup> solution, ultrasonically dispersed for 30 min, and then agitated on an orbital shaker for one day, resulting in a milky suspension containing exfoliated HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·***n***H<sub>2</sub>O particles remained in the mixture, TEM specimens were prepared by collecting supernatant colloids after the mixture had settled for five minutes.** 

**Conductivity Measurements.** Pellets of HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·nH<sub>2</sub>O and its nonstoichiometric derivatives were prepared for impedance measurements by ambient temperature pressing 0.5 g of the powdered sample in a 13 mm die at 3 t, yielding pellets that were typically 1.0 mm thick ( $d = 3.77 \text{ g/cm}^3$ ). The porosity ( $28 \pm 5\%$ ) of the pellets was obtained from their dimensions and the calculated density of the unit cell. The 100 nm thick Pt films were then sputtered onto both faces of the pellets to make circular contacts. These films were continuous (see Supporting Information), and two-point measurements gave resistances in the range of 1–40  $\Omega$  across the face of the pellets. Impedance spectra were collected by using a Solartron 1255B Frequency Response Analyzer with a Solartron 1287 Electrochemical Interface at zero dc bias and an ac voltage amplitude of 100-200 mV. Impedance data were recorded at frequencies ranging from 1 MHz to 5 mHz, depending on the sample. Measurements were made under humid air or humid hydrogen (5% in argon) at ambient temperature (23 °C) and in the temperature range of 250–475 °C. Both heating and cooling cycles were recorded. Since the differences between heating and cooling were not significant, values presented in this study were the average values. Samples were equilibrated at each measurement temperature for 10-20 min in the appropriate atmosphere. All impedance spectra were collected in triplicate, and thus the exposure time of each sample was 70-100 min under each set of conditions. Gases were humidified by bubbling through water at 25  $^{\circ}C$  ( $P_{\rm H2O}$  = 0.031 atm). Measurements were also made under dry air and dry hydrogen/Ar atmospheres. Analysis of the impedance spectra was carried out by using ZView 3.2c software (Scribner Associates Inc.).

**Other Characterization.** Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'pert MPD diffractometer with a scan range between 2 and 80 degrees  $2\theta$ , using Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) at 40 kV and 40 mA. HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·nH<sub>2</sub>O particles and exfoliated sheets were imaged by field emission scanning electron microscopy (FESEM, JEOL 6700F) and transmission electron microscopy (TEM, JEOL 1200EXII). BET surface areas were determined from nitrogen adsorption isotherms at liquid nitrogen temperature using a Micromeritics ASAP 2020 instrument. Thermogravimetric analyses (TGA) were performed on a TA Instruments 2050 under a nitrogen atmosphere at a heating rate of 10 °C/min. Atomic force microscopy (AFM) images were obtained on Digital Instruments Nanoscope IIIA in tapping mode.

## RESULTS AND DISCUSSION

Structure and Morphology of RbLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>. X-ray powder diffraction patterns of RbLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> made by the SS and PB methods are shown in Figure 1. The pattern of SS-RbLa2Ti2TaO10 was indexed in tetragonal space group P4/ mmm using CELREF<sup>26</sup> with a = 3.838(4) and c = 15.286(10)Å, in good agreement with values obtained in earlier studies.<sup>23,27</sup> For PB-RbLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> the lattice parameters were a = 3.838(2) and c = 15.256(10) Å. The 0.03 Å difference in the c-axis parameters between the SS- and PBmaterials was slightly outside the error of the refinement. A simulated XRD pattern generated by PowderCell 2.4, based on the refined lattice parameters, is also shown for comparison in Figure 1. The XRD patterns show that both the SS and the PB synthetic methods resulted in phase pure RbLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>. The proton-exchanged compounds, SS- and PB-HLa2Ti2TaO10.  $nH_2O$ , could be indexed with slightly larger *a*-axis lattice constants (3.841(3) and 3.845(5) Å, respectively) relative to RbLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> and an expanded *c*-axis spacing (16.068(20) and 16.072(20) Å, respectively), consistent with a water content  $n \approx 1.5 - 1.7$  determined in an earlier study by Matsuda et al.<sup>23</sup> In the proton-exchanged materials, no Rb was found by EDS analysis, which has a detection limit in the range of 3-5%. This is in contrast to the results of Matsuda et al., who found ~15% residual Rb after acid exchange.

The XRD patterns of proton-exchanged SS-HLa2Ti2TaO10.  $nH_2O$  in a heating cycle (up to 500 °C and then back down to 25 °C) are also shown in Figure 2. The sample was prepared by dispersing SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·nH<sub>2</sub>O in ethanol and allowing the suspension to dry on the platinum heating stage of the diffractometer. All diffraction patterns were obtained in dry air. There are subtle changes in the heating cycle, most notably the broadening of high angle lines and a slight shift to higher angle that is consistent with contraction of the c-axis spacing from 16.07 to 14.47 Å for SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·nH<sub>2</sub>O (Figure 2). In contrast, the variation in the a-axis dimension is negligible (<0.02 Å). These small changes indicate that  $HLa_2Ti_2TaO_{10}$ retains its layered structure at temperatures up to 500 °C. A caxis contraction of 1.6 Å is observed between 100 and 200 °C, consistent with the loss of weakly bound water molecules. Between 200 and 500 °C, the anhydrous SS-HLa2Ti2TaO10 undergoes an additional contraction of only 0.08 Å. In contrast,  $HCa_2Nb_3O_{10}$  topochemically collapses to  $Ca_4Nb_6O_{19}$  above 300 °C with a c-axis contraction of 1.4 Å,  $^{28}$  and the two-layer Dion Jacobson phase oxide H<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub> contracts by 1.9 Å in its transformation to the three-dimensional perovskite  ${\rm SrTa_2O_6}^{.20}$ 



Figure 1. (Top) XRD patterns of SS- and PB-RbLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> and proton-exchanged derivatives; a simulated XRD pattern of RbLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> is shown for comparison. (Bottom) XRD patterns for the A-site substituted Rb<sub>1+x</sub>Sr<sub>x</sub>La<sub>2-x</sub>TaTi<sub>2</sub>O<sub>10</sub> derivatives made by the SS-method.

Thus the dehydration of  $HLa_2Ti_2TaO_{10}\cdot nH_2O$  does not involve the formation of B–O–B (B = Ti, Ta) linkages between layers below 500 °C.

Results of N<sub>2</sub>–BET surface area measurements and TGA analysis are also shown in Figure 2. The BET surface areas of SS- and PB-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·nH<sub>2</sub>O are both low (3 and 4 m<sup>2</sup>/g, respectively) indicating that neither compound has significant porosity. TGA of samples that were equilibrated overnight at ambient temperature in air at 100% relative humidity are also shown in Figure 1d. Between 100 and 600 °C, PB- and SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·nH<sub>2</sub>O lose about 3 and 6%, respectively, of their total weight. The calculated stoichiometry of this weight loss as water at 600 °C is 1.3 and 2.0 mol of H<sub>2</sub>O per mole of PB- and SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·nH<sub>2</sub>O, respectively. These values are roughly consistent with the *c*-axis contraction observed by XRD (Figure 2a). Consistent with the TGA data, there is a more pronounced *c*-axis contraction for SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·nH<sub>2</sub>O.



Figure 2. (Top) XRD patterns of SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·nH<sub>2</sub>O from a heating cycle. (Middle) Lattice parameters obtained from heating cycles of SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·nH<sub>2</sub>O. (Bottom) N<sub>2</sub>-BET adsorption-desorption curves. Inset panel shows the TGA weight loss data recorded at a heating rate of 10 °C/min.

Taken together the data suggest that 1-2 lattice water molecules are lost, with the most dramatic change in the *c*-axis parameter occurring between 100 and 200 °C. The weight loss observed in the TGA plot over a broader temperature range may simply be a consequence of the relatively rapid heating rate (10  $^{\circ}\mathrm{C/min})$  used in the TGA experiments.

The morphologies of as-synthesized and exfoliated  $HLa_2Ti_2TaO_{10}\cdot nH_2O$  particles are shown in Figure 3. Both



Figure 3. SEM images of unexfoliated compounds and the corresponding TEM images of exfoliated sheets (insets) of (a) SS- $HLa_2Ti_2TaO_{10}$ · $nH_2O$  and (b) PB- $HLa_2Ti_2TaO_{10}$ · $nH_2O$ .

SS- and PB-HLa2Ti2TaO10·nH2O have the crystal texture expected for layered materials, and no porosity is evident in the FESEM images, which explains the low surface area found by BET. Exfoliated HLa2Ti2TaO10 sheets are shown in the inset panels of Figure 3. The lateral dimensions of the SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> sheets are about 300-400 nm, whereas those of PB-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> are ~30 nm. EDS analysis confirmed that the rectangular exfoliated sheets contained La, Ti, Ta, and O, and the electron diffraction pattern of the sheets shows the expected tetragonal symmetry and a-axis spacing of the layer perovskite structure (Figure 4). Interestingly, the size distribution of the rectangular PB-HLa2Ti2TaO10 nanosheets is quite narrow. By averaging 277 nanosheets measured from five different TEM images, the lateral dimensions were found to be  $30.4 \pm 11.2$  nm. While there are well established techniques for growing size- and shape-controlled nanocrystals of ABO3 perovskites, such as  $PbTiO_3$  and  $CaTiO_3^{29-31}$  for more complicated layered structures, nanocrystal growth techniques almost always result in irregular shapes.<sup>32–34</sup> The formation of the layered structure requires a high calcination temperature, and thus it is difficult to control nucleation and growth separately by either the PB- or SS- methods. With twodimensionally bonded materials, microstructural defects such as dislocations, twin boundaries, antiphase boundaries, and stacking faults can make morphology control difficult.<sup>35</sup> To



Figure 4. EDS data, bright field HRTEM image, and the corresponding electron diffraction pattern of  $HLa_2Ti_2TaO_{10}$ · $nH_2O$ . Cu signals are due to fluorescence from the Cu support grid.

our knowledge, this is the first time that a layer perovskite has been made in the form of nanocrystals with a narrow distribution of lateral dimensions. Nanosheets derived from these crystals may be useful as building blocks of organized layer-by-layer assemblies, and their well-defined edge and corner sites may also be of interest for anchoring specific ligands or catalyst particles. It has been reported that the surface chemistry at the edge, corner, and faces of layered perovskites is different, which can lead to interesting effects in photoinduced electron transfer and photocatalysis.<sup>32</sup>

Electronic and lonic Conductivity of  $HLa_2Ti_2TaO_{10}$ ·  $nH_2O$  Made by the Solid State Reaction and Precursor-Based Methods. Perovskites made by the PB method often possess higher surface area than the same compounds made by the solid-state reaction. To examine the effects of these parameters on the conductivity,  $HLa_2Ti_2TaO_{10}$ · $nH_2O$  prepared by both methods was pressed into pellets and impedance spectra were measured both at ambient temperature and at 275–475 °C. Representative impedance spectra are shown in Figures 5 and 6, where the imaginary part of the impedance, -Z'', is plotted against the real part, Z' (Nyquist plot).

At ambient temperature (23 °C), a high frequency semicircle is observed for both the PB and SS samples, and in the case of the PB sample, which has lower impedance, a low frequency tail that begins to curve into a second semicircle is also observed. Earlier impedance studies of layer perovskite tantalates<sup>18,20,24</sup> have attributed the relaxation at high frequency to grain surface conduction and the low frequency tail to electrode polarization. Conductivity within the bulk grains of the solid is likely to be small relative to ionic conductivity arising from water adsorbed to the surface of the grains. Consistent with this hypothesis, Sato et al. found that the conductivity of the layer perovskite HLaNb<sub>2</sub>O<sub>7</sub>·0.5H<sub>2</sub>O increased with the amount of adsorbed water.<sup>18</sup> We also find substantially increased conductivity for SS- and PB-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·*n*H<sub>2</sub>O in humidified air relative to dry air (Figure 5).

Dehydration of the solid occurs at temperatures higher than 200  $^{\circ}$ C, and at higher temperatures the impedance spectra



Figure 5. Ambient temperature Nyquist plots for (a) SS- $HLa_2Ti_2TaO_{10}\cdot nH_2O$  and (b) PB- $HLa_2Ti_2TaO_{10}\cdot nH_2O$  in dry and humidified air. The equivalent circuit used to obtain fits to the data (solid lines) is shown in part a.

consist of a single arc (Figure 6), the radius of which is expected to be a function of the internal resistance of the grains.<sup>36,37</sup> The lack of a low frequency tail usually means that the interfacial capacitance is shunted by electronic current and thus the contribution of charge carrier diffusion is not resolved.<sup>15</sup> When the equivalent circuit shown in Figure 5a was used to fit the data in Figure 6a,b, values of  $C_{\text{geom}}$  and  $C_{\text{dl}}$  were typically in the nF range (see Supporting Information) and physically reasonable values of the dielectric constant were obtained from  $C_{\text{geom}}$  and the dimensions of the samples.

In Figures 5 and 6, the observed arcs for  $HLa_2Ti_2TaO_{10}$  (formulated as the anhydrous compound at 300–450 °C) are depressed rather than perfect semicircles. This shape is often observed in impedance spectra of solid electrolytes. Depressed semicircles can be interpreted as a distribution of relaxation times,<sup>36</sup> which implies that there is more than one kind of charge carrier or that the charge carriers move in a number of different physicochemical environments. One can model the depressed semicircle either as a linear combination of a series of semicircles (i.e., in terms of a combination of components that each have a resistor in parallel with a capacitor) or as a constant phase element (CPE). In this analysis, we adopt the CPE to



Figure 6. Representative impedance spectra and corresponding fits to the data for SS- (a) and PB-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> (b) under wet air conditions.

describe depressed semicircles because it avoids the introduction of additional components that do not have a clear physical meaning. We use  $R_{series}$  to represent the resistance of the entire sample and  $R_{ct}$  for the charge transfer resistance between the sample and the contacting electrodes. The CPE<sub>dl</sub> parallel to  $R_{ct}$ represents the capacitance at the interface of the two contacting electrodes and the relatively insulating sample. The circuit element CPE<sub>geom</sub> describes the capacitance across the pellet. *P*values derived from fits to the data (see Supporting Information) were in the range of 0.7–0.9, which are typical values for constant phase elements.<sup>35</sup>

The conductivity (the reciprocal of the total resistivity  $\rho_{\rm series} + \rho_{\rm ct}$ ) is shown as a function of temperature for SS- and PB-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> in Figure 7a,b, respectively. For SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>, the conductivities under dry hydrogen and wet hydrogen conditions are very comparable. The conductivities under dry air and wet air are also very close to each other, and both are about 1 order of magnitude lower than under the hydrogen atmosphere. On the other hand, the conductivity of PB-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> is much higher in a dry hydrogen environment, about 1 order of magnitude higher than under wet hydrogen or dry air conditions, and 2 orders of magnitude higher than under a wet air environment. In addition, PB-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> always has about 1 order of magnitude higher conductivity than SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> under the same conditions.

While the oxygen partial pressure can affect the ionic conductivity of oxides, the effect on electronic conductivity is typically much larger. Holes and electrons can be generated



Figure 7. Arrhenius plots of the conductivity of (c) SS- and (d) PB- $HLa_2Ti_2TaO_{10}$ . Except as noted, all samples had Pt contacts.

under oxidizing and reducing conditions according to reactions 1 and 2, respectively:<sup>38</sup>

$$\frac{1}{2}O_2(g) \Leftrightarrow O_i'' + 2h^{\bullet}$$
(1)

$$O_0 \Leftrightarrow \frac{1}{2}O_2(g) + V_0^{\bullet\bullet} + 2e'$$
<sup>(2)</sup>

Here the subscripts *i* and *o* refer to interstitial and oxygen lattice positions, respectively. Under oxygen-rich conditions such as dry/wet air, if oxygen reacts with  $HLa_2Ti_2TaO_{10}\cdot nH_2O$  it can diffuse to interstitial sites, and at the same time two holes are produced per  $O_i$ . In contrast, under oxygen-deficient environments such as dry/wet hydrogen conditions, an oxygen vacancy along with two electrons can be produced. The latter effect is especially important if the oxide contains reducible elements such as Ti or Nb and results in significant electronic conductivity in the case of the layered perovskite proton conductor  $HLaNb_2O_7 \cdot 0.5H_2O$ .<sup>24</sup> However, the presence of water suppresses the formation of electrons via equilibrium 3.<sup>20</sup>

$$H_2O(g) + V_0^{\bullet\bullet} + 2e' \Leftrightarrow H_2(g) + O_0$$
(3)

The formation of electrons according to reaction 2 is consistent with the oxygen pressure-dependent conductivity of SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>, i.e., the higher conductivity under hydrogen. Oxides with n-type conductivity often display a power law dependence of electronic conductivity on oxygen partial pressure with an exponent of -1/6 or -1/4.<sup>39</sup> In such a case, we would expect a greater conductivity difference at high temperatures between the hydrogen and oxygen atmospheres than that observed in Figure 7. This implies that, in oxygencontaining atmospheres, the total conductivity is dominated by the ionic component. In addition, we note that equilibria 1-3are not sufficient to interpret the conductivity under wet atmosphere at high temperature since water should suppress the formation of electrons. We postulated that the platinum contact could play a role in modulating the electronic conductivity of  $SS-HLa_2Ti_2TaO_{10}$  under these conditions. Catalytically active platinum can split hydrogen molecules to form protons and electrons, which can then diffuse into or over the SS-HLa2Ti2TaO10 surface and result in electron doping. This phenomenon, known as hydrogen spillover, is important in the charging and discharging of hydrogen storage materials.<sup>40-42</sup> As long as the catalytic reaction is fast enough to compensate for the loss of electrons via equilibrium 3, the electronic conductivity can be high under humid hydrogen conditions.

To test this hypothesis, the conductivity of PB- $HLa_2Ti_2TaO_{10}$  was compared under wet hydrogen with gold and platinum contacts as shown in Figure 7b. Under identical conditions the catalytic activity of platinum results in a fivefold increase in conductivity, confirming that under hydrogen atmosphere, electronic conductivity dominates with platinum contacts. Because intermediate temperature fuel cells are run under conditions where the hydrogen partial pressure is high on the anode side of the cell, this electronic conductivity will compromise the utility of  $HLa_2Ti_2TaO_{10}$  as the fuel cell membrane.

The activation energy of the electronic conductivity can be calculated from the slope of the Arrhenius plots (Figure 7). We found the activation energy for both SS- and PB-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> under the conditions studied to be ~0.86 eV. We note from the TGA data that there is less water loss with PB- than with SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·*n*H<sub>2</sub>O. The higher degree of hydration of the SS compound may be a consequence of a more defective oxygen sublattice. According to reaction 3, increasing the number of oxygen vacancies should inhibit electron doping of the solid. This is consistent with the lower conductivity of SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> and with electronic conduction as the dominant transport mechanism.

Structure and Conductivity of Nonstoichiometric Derivatives of HLa2Ti2TaO10·nH2O. Because of the important role of interstitial and vacancy sites in the transport properties of intermediate temperature proton conductors, we investigated different nonstoichiometric compositions in order to vary the concentrations of vacancies or interstitial ions in the interlayer galleries of RbLa2Ti2TaO10. A series of compositions intended to produce A-site substitution of Sr for La and structures spanning the Dion-Jacobson (x = 0) and Ruddlesden-Popper (x = 1) range in Rb<sub>1+x</sub>Sr<sub>x</sub>La<sub>2-x</sub>TaTi<sub>2</sub>O<sub>10</sub> was prepared. XRD patterns of these compounds are shown in Figure 1, and patterns of the proton-exchanged compounds are shown in Figure S-1 (see Supporting Information). The layered phase is evident in the XRD pattern for x values below 0.20 in  $Rb_{1+x}Sr_xLa_{2-x}TaTi_2O_{10} \cdot nH_2O$ , but at x = 0.50 and higher there is a concurrent marked loss in intensity of the 00l, hk0, and hkl reflections, and a new three-dimensional perovskite phase

begins to dominate the pattern. This strong 110 reflection of this new phase is not visible at x = 0.05 but can be seen at x = 0.10 and above. Above the Ruddlesden–Popper limit (x = 1.0), the lines of the layered phase disappear completely. The proton-exchanged compounds show a similar trend. At x = 1.50, the patterns can be indexed to a simple cubic perovskite unit cell with a = 3.90(6) Å. EDS of an acid-washed sample prepared by the SS method gave an approximate Ti:Ta:Sr atomic ratio of 10:5:5. No Rb or La was detected by EDS. This compound was thus formulated as  $Sr_{2.5}\square_{0.5}Ti_2TaO_{9}$ , where  $\square$  indicates an A-site vacancy.

Interestingly, the defective 3D perovskite  $Sr_{2.5}\square_{0.5}Ti_2TaO_9$ shows 2 orders of magnitude higher conductivity than the parent compound SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> under a wet hydrogen atmosphere. Figure 8 compares the conductivity of



**Figure 8.** Arrhenius plots of the conductivity of SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>.  $nH_2O$ , Sr<sub>2.5</sub> $\Box_{0.5}Ti_2TaO_{9}$ , and previously studied Dion–Jacobson phase compounds under (a) wet air and (b) wet hydrogen atmospheres.

 $Sr_{2.5}\square_{0.5}Ti_2TaO_9$  to that of SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> and to HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> and HLaTa<sub>2</sub>O<sub>7</sub>, which have been studied in detail previously.<sup>17,43</sup> The conductivities of the titanotantalates follow the sequence of cubic > two-layer > three-layer structure. The conductivity of the 3D tantalate perovskite is higher than that of any of the layered niobates or tantalates, even though the activation energy for conduction (1.76 eV) is much higher.

This implies a much higher carrier density in the 3D perovskite phase. The conductivity of this compound is also substantially increased in wet  $H_2$  relative to wet air, indicating again that the dominant charge transport mechanism under reducing conditions is electronic. Thus none of the compounds studied appear to be viable candidates as proton conducting electrolytes for intermediate temperature fuel cells, because their conductivities are low and because they have appreciable electronic conductivity under reducing conditions.

## CONCLUSIONS

The conductivity of HLa2Ti2TaO10 and nonstoichiometric derivatives was investigated by impedance spectroscopy. Under reducing atmospheres, the dominant transport mechanism in HLa2Ti2TaO10 and its derivatives is electronic, with activation energies in the range  $\sim 0.9-1.1$  eV. HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> made by the precursor-based method has higher conductivity by about 1 order of magnitude than the same compound made by solidstate reaction. A-site substitution of Sr for La gave single-phase compounds up to about 5% Sr incorporation, and at higher levels led to the formation of a cubic perovskite phase,  $Sr_2 \prod_{i=1}^{n} Ti_2 TaO_0$ . This defective tantalate perovskite had the highest conductivity of any of the compounds studied. However, its conductivity is predominantly electronic under reducing conditions. Thus it appears that none of the compounds in this series can be useful solid electrolytes in intermediate temperature fuel cell applications.

The precursor-based synthesis results in the formation of RbLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub> microcrystals that can be acid-exchanged and then exfoliated in TBA<sup>+</sup>OH<sup>-</sup> solutions to uniform rectangular sheets with ~30 nm lateral dimensions. This morphology is rather rare among layer perovskites, which typically form as much larger sheets. Because the acidity of the three-layer Dion–Jacobson structure can be tuned by adjusting the Nb/Ta ratio<sup>44</sup> and because exfoliated sheets in this structural family can be restacked to give three-dimensionally ordered solids,<sup>45</sup> these rectangular nanosheets may be interesting building blocks for layer-by-layer assemblies with tunable compositions and properties.

## ASSOCIATED CONTENT

## **S** Supporting Information

XRD patterns and conductivity data for proton-exchanged Asite substituted nonstoichiometric derivatives of SS-HLa<sub>2</sub>Ti<sub>2</sub>TaO<sub>10</sub>·nH<sub>2</sub>O, images of samples used for conductivity measurements and fitting parameters for impedance spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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# Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant CHE-0910513. T.H.W. gratefully acknowledges the support of the National Science Council, Taiwan, Grant NSC-98-2917-I-564-120.

## ABBREVIATIONS

XRD, X-ray powder diffraction; SS, solid-state; PB, precursorbased; FESEM, field-emission scanning electron microscopy; TEM, transmission electron microscopy; BET, Brunauer– Emmet–Teller surface area analysis; TGA, thermogravimetric analysis; AFM, atomic force microscopy; CPE, constant phase element; BZY, barium zirconium yttrium oxide

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