Protonic and electronic conductivity of the layered perovskite oxides HCa$_2$Nb$_3$O$_{10}$ and Ca$_4$Nb$_6$O$_{19}$

Thomas I. Draskovic$^1$, TsingHai Wang$^2$, Camden N. Henderson, Thomas E. Mallouk*

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

**Article Info**

- **Article history:** Received 24 December 2013
- **Received in revised form:** 30 December 2013
- **Accepted 4 January 2014
- **Available online 1 February 2014

**Keywords:**
- Layer perovskite
- Solid electrolyte
- Mixed valence
- Electronic conductivity
- Intermediate temperature fuel cell

**Abstract**

The structural and electrical properties of the Dion–Jacobson series layer perovskite HCa$_2$Nb$_3$O$_{10}$ were investigated. Within the intermediate temperature range (200–475 °C), the compound undergoes topochemical dehydration to Ca$_4$Nb$_6$O$_{19}$ and, under reducing atmospheres, partial reduction of Nb(V) to Nb(IV). These changes occur upon heating and are not reversed on cooling. Analysis of impedance data shows that the conductivity of Ca$_4$Nb$_6$O$_{19}$ is predominantly electronic under reducing atmospheres, consistent with the behavior of other structurally related mixed-valence niobates.

**1. Introduction**

Intermediate temperature proton conductors are of interest for possible applications in all-inorganic fuel cells. Compared to low temperature polymer electrolyte fuel cells and high temperature solid oxide fuel cells (SOFC), fuel cells that operate in the intermediate temperature range (200–450 °C) offer several advantages, such as greater immunity to catalyst poisoning, higher catalyst activity, and fewer engineering issues stemming from the high temperature of operation of SOFCs. Perovskite oxides are often used as oxide ion conductors in SOFCs and have been the focus of much research on intermediate temperature proton conductors [1–3]. Recently, Pergolesi et al. reported that thin films of the anion-defective perovskite BaZr$_{0.8}$Y$_{0.2}$O$_{3-δ}$ have a conductivity of 0.11 Ω$^{-1}$ cm$^{-1}$ at 500 °C [4]. In principle, thin films of such electronically insulating proton conductors on hydrogen-permeable metallic foils [5–7] could serve as low resistance membranes for intermediate temperature fuel cells.

Many of the best intermediate temperature proton conductors are perovskites that contain defects on oxygen atom sites in the lattice [8]. Layer perovskites are intergrowths of the ABO$_3$ perovskite structure with other metal oxide

---

**Abbreviations:** XRD, X-ray powder diffraction; SOFC, solid oxide fuel cell.

* Corresponding author. Tel.: +1 814 863 9637; fax: +1 814 865 2925.

E-mail address: tem5@psu.edu (T.E. Mallouk).

1 Present address: Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210, USA.

2 Present address: Nuclear Science and Technology Development Center, National TsingHua University, Hsinchu 300, Taiwan.

0360-3199/$ – see front matter Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

http://dx.doi.org/10.1016/j.ijhydene.2014.01.017
structures. Compounds in the Ruddlesden-Popper \( (A'_{2n-1}B_{n}O_{3n+1}) \) [9,10] and Dion–Jacobson series \( (A'_{n}BO_{3n+1}) \) \( A' = \text{alkali metal} \) [14–16], can undergo intercalation, ion exchange, exfoliation, and condensation reactions, which provide synthetic routes to unique ceramic materials and thin films. The structural and electrical properties of the three-layer Dion–Jacobson phase compounds \( A'_{n}BO_{3n+1} \) \( A' = \text{K, Rb, Cs} \) and their proton-exchanged derivatives have been studied since their discovery in the early 1980s [11–18]. Early investigations by Thangadurai et al. into the potential proton conductivity of \( \text{H} \text{Ca}_{2n} \text{Nb}_{n} \text{O}_{2n} \) were promising, as high conductivity \( (10^{-4} - 10^{-3} \text{ S cm}^{-1}) \) was observed below 450 °C [15]. Although protonic conduction was proposed as the dominant transport mechanism, the exact origins of the high conductivity were not clearly established. We subsequently observed that the structurally similar two-layer Dion–Jacobson phase niobate \( \text{H} \text{LaNb}_{2} \text{O}_{7} \$ 0.5 \text{H}_{2} \text{O} \) underwent partial reduction in wet or dry hydrogen atmospheres [19]. In this compound and the related two-layer Dion Jacobson oxyfluoride \( \text{H}_{1-x} \text{Rb}_{x} \text{LaNb}_{2} \text{O}_{6} \text{F}_{x} \), impedance measurements established that the conductivity is predominantly electronic [20]. This has prompted us to re-examine the conductivity of \( \text{HCa}_{2n} \text{Nb}_{n} \text{O}_{2n} \) and its lamellar intermediate temperature condensation product \( \text{Ca}_{2n} \text{Nb}_{n} \text{O}_{19} \) in oxidizing and reducing atmospheres, to address the question of the potential utility of layer perovskite niobates as proton conductors for intermediate temperature fuel cells and related applications.

2. Experimental section

2.1. Synthesis and proton exchange of \( \text{KCa}_{2n} \text{Nb}_{n} \text{O}_{19} \)

The Dion–Jacobson compound \( \text{KCa}_{2n} \text{Nb}_{n} \text{O}_{19} \) was prepared by grinding together \( \text{K}_{2} \text{CO}_{3} \) (Aldrich, 99.99%) (20% excess), \( \text{CaCO}_{3} \) (Aldrich, 99.995%), and \( \text{Nb}_{2} \text{O}_{5} \) (Aldrich, 99.99%) and firing the mixture in air at 1100 °C for 24 h [5]. Proton exchange of the \( \text{KCa}_{2n} \text{Nb}_{n} \text{O}_{19} \) product was carried out by constant shaking at room temperature, using an excess of nitric acid (1 M) for at least 3 days with daily centrifugation and replacement of the acid solution. The product was isolated by centrifugation, washing, and drying at 60 °C under reduced pressure. The identity and purity of the product phases were confirmed by X-ray powder diffraction (XRD).

2.2. Structural characterization and impedance measurements

XRD patterns were obtained using a Philips X’Pert MPD diffractometer with monochromatized Cu Kα radiation. Pelleted samples of \( \text{HCa}_{2n} \text{Nb}_{n} \text{O}_{2n} \) 0.5\( \text{H}_{2} \text{O} \) were prepared by pressing 0.5 g of powder in a cylindrical die at 3 metric tons, yielding pellets 13 mm in diameter and typically 1 mm thick. Pellets were coated on both sides with 100 nm thick films of Pt by sputtering to produce circular contacts. Because \( \text{HCa}_{2n} \text{Nb}_{n} \text{O}_{2n} \) 0.5\( \text{H}_{2} \text{O} \) loses its water of hydration below 200 °C, the compound is formulated in the discussion below as \( \text{HCa}_{2n} \text{Nb}_{n} \text{O}_{19} \) at the start of the impedance measurements, which were carried out between 200 and 475 °C. Two-point impedance measurements were obtained using a Solartron 1255B Frequency Response Analyzer with a Solartron 1287 Electrochemical Interface, zero DC bias, and an AC voltage amplitude of 100 mV. Maximum frequencies ranged from 1 MHz to 5 mHz, depending on the sample. Subsequent heating and cooling cycles were performed, allowing for sample equilibration at each temperature in the range 200–475 °C. Measurements were conducted under humidified air and humidified \( \text{H}_{2} \) (5%, balance Ar) atmospheres, produced

---

**Fig. 1** – (a) Simulated and (b) experimental X-ray powder diffraction patterns of \( \text{KCa}_{2n} \text{Nb}_{n} \text{O}_{19} \) (indexed in space group Cmcm, \( a = 3.858(9) \) Å, \( b = 29.36(6) \) Å, \( c = 7.708(13) \) Å), (c) its proton-exchanged derivative \( \text{H} \text{Ca}_{2n} \text{Nb}_{n} \text{O}_{19} \) 0.5\( \text{H}_{2} \text{O} \) (P4/mmb, \( a = 5.461 \) Å, \( c = 14.424 \) Å), and (d) the dehydration product \( \text{Ca}_{2n} \text{Nb}_{n} \text{O}_{19} \) (P4/mmm, \( a = 3.846 \) Å, \( c = 12.611 \) Å).
by bubbling the carrier gas through water at 25 °C (P_{H_2O} = 23 torr).

3. Results and discussion

3.1. Dehydration and reduction of HCa_2Nb_3O_{10}·0.5H_2O under reducing atmospheres

X-ray diffraction patterns of KCa_2Nb_3O_{10} and its proton-exchanged derivative HCa_2Nb_3O_{10}·0.5H_2O were in agreement with prior literature reports [11–13,21]. Previous studies on HCa_2Nb_3O_{10} have shown that upon heating above 300 °C, a metastable dehydration product Ca_4Nb_6O_{19} is formed by topochemical collapse of the interlayer galleries [16]. In addition, it is known that Nb(V) in the Dion–Jacobson series AA’_{n–1}Nb_nO_{3n–1} can be partially reduced to Nb(IV) by heating in a H_2 atmosphere [17–19,22]. The reduced niobium is relatively stable towards oxidation in air and has little effect on the lattice structure. Exposure of a HCa_2Nb_3O_{10}·0.5H_2O sample to dry H_2 (5%, balance Ar) for 3 h at 450 °C was performed to confirm that dehydration and reduction could occur in the intermediate temperature range of interest. The powder sample changed from white to bluish gray in color and XRD analysis gave a diffraction pattern consistent with that of Ca_4Nb_6O_{19} (Fig. 1). The change in color can be attributed to partial reduction of niobium and the likely formation of a mixed valence state. This color change was retained upon cooling to ambient temperature in the same gas mixture.

These reactions in the intermediate temperature range are problematic for applications as solid electrolytes, because mixed valent niobates are typically electronic conductors. The metastable Ca_4Nb_6O_{19} is semiconducting and has higher electronic conductivity than the parent compound HCa_2Nb_3O_{10} [16].

3.2. Impedance measurements in humidified air and hydrogen

Previous studies have established that the introduction of water can suppress the reduction of Nb(V) to Nb(IV) in layer perovskites [19]. Under humidified hydrogen, the equilibrium pO_2 is orders of magnitude higher than under dry hydrogen. Accordingly, experiments were done under humidified conditions. Impedance spectra of HCa_2Nb_3O_{10} recorded in humidified air and H_2 atmospheres are shown in Figs. 2 and 3, respectively. A previously developed brick-layer model [23], which includes both grain and grain boundary conduction pathways, was used to analyze the data. The equivalent circuit in this model is shown in Fig. 4. Because the ionic and electronic conductivity act in parallel within the crystal grains, they are represented together as R_{series} = (1/R_{elec} + 1/R_{ionic})^{-1}. The charge transfer resistance (R_{ct}) represents the real part of the impedance at the grain boundaries. Fits of the impedance data improve when cell and grain boundary capacitances are replaced by constant phase elements (CPE).
this case, $R_{\text{series}}$ and $R_{\text{ct}}$ no longer correspond strictly to grain and grain boundary values, but their series combination still represents the low frequency impedance of the circuit.

When HCa$_2$Nb$_3$O$_{10}$ is heated in an atmosphere of humidified air, both the series component of the resistance $R_{\text{series}}$ and the charge transfer resistance $R_{\text{ct}}$ decrease with increasing temperature. Nyquist plots recorded between 200 and 475 °C (Fig. 2) are strikingly similar in the heating and cooling directions. At 200 °C, $R_{\text{series}}$ and $R_{\text{ct}}$ are both in the range of $10^8$ Ω and drop to ~$10^6$ Ω upon heating to 475 °C. At the lower end of the temperature range, only one semicircle can be resolved in the Nyquist plots, but at higher temperature, where $R_{\text{ct}}$ exceeds $R_{\text{series}}$, a second low-frequency semicircle begins to emerge. These changes in impedance are consistent with an activated conduction process, but they do not differentiate between electronic hopping conduction and protonic conduction.

Under humidified hydrogen, the impedance behavior of HCa$_2$Nb$_3$O$_{10}$ is quite different. Fig. 3 shows Nyquist plots recorded upon heating and cooling. Initially, at 200 °C, the values of $R_{\text{ct}}$ and $R_{\text{series}}$ are slightly lower (by a factor of ~2) than they are in humidified air. As the temperature is increased, $R_{\text{ct}}$ and $R_{\text{series}}$ drop by four and three orders of magnitude, respectively. In contrast to the behavior in humidified air, cooling from 475 to 200 °C results in an increase of only one order of magnitude in both $R_{\text{ct}}$ and $R_{\text{series}}$.

These features in the impedance spectra can be rationalized in terms of the known phase behavior of HCa$_2$Nb$_3$O$_{10}$. In the heating part of the cycle, HCa$_2$Nb$_3$O$_{10}$ undergoes irreversible dehydration to Ca$_4$Nb$_6$O$_{19}$. The changes in $R_{\text{series}}$ and $R_{\text{ct}}$ upon heating and cooling in air are consistent with thermally activated electronic conductivity of semiconducting Ca$_4$Nb$_6$O$_{19}$, and/or with thermally activated protonic conductivity. The more pronounced drop in resistance under humid hydrogen can be interpreted as arising from partial reduction of Nb(V) to form a mixed-valent electronic conductor. This material remains partially reduced (and therefore electronically conducting) as the temperature is lowered under the H$_2$ atmosphere.

Total conductances of the samples were obtained by fitting the impedance data shown in Figs. 2 and 3 to the equivalent circuit in Fig. 4. The total impedance in the low frequency limit corresponds to the sum of the series and charge transfer resistances, $R_{\text{total}} = R_{\text{series}} + R_{\text{ct}}$. The values of $R_{\text{total}}$ obtained in this way were, as expected, very close to the Z’-axis intercepts of the Nyquist shown in Figs. 2 and 3. The corresponding total conductivity values are plotted as a function of temperature and atmosphere in Fig. 5. In air during the heating part of the cycle, the conductivity remains fairly constant until 350 °C. Below this temperature, protonic conductivity is likely the dominant transport mechanism [19]. Mobile protons are created by hydration of oxide ion vacancies, according to the following mechanism:

$$\text{H}_2\text{O}(g) + v_0 + O_0^- = 2\text{OH}_0$$

(1)

Above 350 °C, there is a sharp jump in conductivity as the material dehydrates to the semiconducting Ca$_4$Nb$_6$O$_{19}$ phase. Past this point, the conductivity follows an Arrhenius relation with an apparent activation energy of 0.59 ± 0.03 eV on the subsequent cooling cycle. In the reducing hydrogen atmosphere, the initial conductivity is close to that in humidified air. However there is a more rapid increase upon heating between 200 and 350 °C, consistent with reduction of Nb(V) to Nb(IV), which occurs prior to the phase transition to Ca$_4$Nb$_6$O$_{19}$. The conductivity in the humid hydrogen atmosphere decreases upon cooling with an apparent activation energy of 0.35 ± 0.04 eV. Comparing the cooling cycles, the similar activation energies suggest that electronic hopping conduction dominates in both atmospheres. If this interpretation is correct, the different intercepts indicate a 20–30 fold increase in the density of charge carriers in a reducing atmosphere.

4. Conclusions

An early conductivity study of HCa$_3$Nb$_3$O$_{10}$ in hydrogen atmospheres suggested that the high conductivities observed were likely to be protonic in origin [15]. Reproducible conductivity measurements were presented from the second and
subsequent heating/cooling cycles. The conductivity followed linear Arrhenius behavior, much like that observed after the initial heating cycle in our experiments. However that study was conducted before the phase transition from HCa₄Nb₆O₁₉ to Ca₄Nb₆O₁₉ had been characterized and also prior to much of the literature on the formation of mixed valent Nb(V/IV) compounds among Dion–Jacobson phase niobates. We conclude from this study that these niobates have significant electronic conductivity under intermediate temperature conditions, especially in reducing humid atmospheres, and thus they are unlikely to be useful as proton conductors in intermediate temperature fuel cells. It is important to note that isostructural Dion–Jacobson phase tantalates are known, and it is possible that some of those compounds will be less susceptible to reduction, and also may not undergo the same phase transition that eliminates mobile protons in HCa₄Nb₆O₁₉.

Acknowledgment

This work was supported by the National Science Foundation under grant CHE-0910513.

REFERENCES