

Soft chemistry routes for the synthesis of
 $\text{Sr}_{0.02}\text{La}_{0.98}\text{Nb}_{0.6}\text{Ta}_{0.4}\text{O}_4$ proton conductor

A.B. Santibáñez-Mendieta^a, E. Fabbri^b, S. Licoccia^a,
E. Traversa^{a,b}

a. Department of Chemical Science and Technologies
University of Rome Tor Vergata.
Via della Ricerca Scientifica 1, 00133 Rome Italy.

b. International Center for Materials Nanoarchitectonics
(MANA), National Institute for Materials Science
(NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

High temperature proton conducting (HTPC) oxides allow lowering the solid oxide fuel cell (SOFC) operating temperature, reducing SOFC costs. Furthermore, in protonic SOFCs water is generated at the cathode side, without diluting the fuel and thus reducing the cell efficiency. SrCeO_3 and other perovskite-type oxides have been studied in detail by different research groups [1-3]. Alternative to these materials, the ortho-niobates and ortho-tantalates have been recognized as promising HTPCs since they show good chemical stability [4-6]. Sr-doped LaNbO_4 and Ca-doped LaTaO_4 show a total conductivity at 800 °C of 4×10^{-4} and $1.5 \times 10^{-4} \text{ Scm}^{-1}$, respectively. At around 500 °C, LaNbO_4 phase changes from fergusonite to scheelite structure, which results into different conductivity behavior and different thermal expansion coefficients for each phase, deriving in problems for the cell design [5,6]. A way to avoid this phase transition is using the solid-solution containing 40 % of Ta, $\text{LaNb}_{0.6}\text{Ta}_{0.4}\text{O}_4$, which shows the phase transformation at 800 ± 10 °C [7]. This will allow operating fuel cells based on $\text{Sr}_{0.02}\text{La}_{0.98}\text{Nb}_{0.6}\text{Ta}_{0.4}\text{O}_4$ electrolytes below this temperature.

Good quality electrolyte materials can be attained from wet chemistry synthesized powders, co-precipitation and sol-gel based procedures. The latter methods had proven for niobates to be successful in yielding homogeneous morphology and a low sintering temperature, by using chelating agents such as oxalates, malates and citrates [8]. However, for all these synthesis techniques two main challenges arise; first, to acquire the tantalum cation solution, and second, to combine the niobium and tantalum solution with the rare earth compounds.

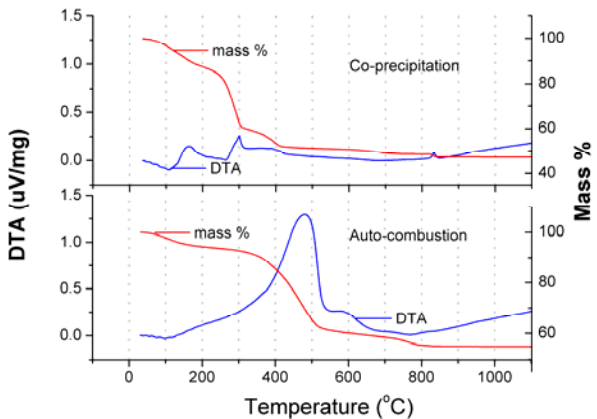
On these grounds, the aim of this work is to prepare $\text{Sr}_{0.02}\text{La}_{0.98}\text{Nb}_{0.6}\text{Ta}_{0.4}\text{O}_4$ powders using auto-combustion and co-precipitation methods, and comparing with conventional solid-state reaction.

Water solutions of all the cations are needed for the co-precipitation method. In this case, strontium nitrate, lanthanum nitrate and niobium oxalate are commercially available and already water soluble. Tantalum oxalate was prepared from as-purchased tantalum chloride, used to allow $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ precipitating in ammonia solution, which was then filtrated and dissolved in ammonium oxalate solution. Once prepared, the four solutions were mixed and dripped in ammonia solution to form a precipitate, which was filtered and dried to form the precursor powder of $\text{Sr}_{0.02}\text{La}_{0.98}\text{Nb}_{0.6}\text{Ta}_{0.4}\text{O}_4$.

Regarding the auto-combustion method, commercial strontium and lanthanum nitrates were used. To prepare tantalum citrate solutions, $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was produced and then dissolved in citric acid. Niobium citrate was prepared from niobium oxalate precipitation in ammonia solution to form the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, which was then filtered and later

dissolved in citric acid. The four solutions were mixed and pH was adjusted to 7. The solvent was then evaporated and the obtained gel was ignited and burned until ashes were formed, which were heated as precursor powder of the desired oxide.

The precursor materials were investigated by TGA and DTA to establish the heating treatment. With this results the calcination conditions –temperature, time and rate– were established and the material was produced. Then the structural characterization was performed followed by morphology investigation. After observing the sintering behavior, conductivity measurements were performed to assess the suitability of the studied material as a proton conducting electrolyte.



References

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