



Development of all-solid-state pH and reference electrodes based on lithium lanthanum titanium oxide (LLTO) using Spark Plasma Sintering (SPS) for the long-term monitoring of nuclear waste disposal

Djouhar Aoubida^{1,3}, Quoc Nghi Pham³, Stéphanie Betelu¹, Johan Bertrand², Nita Dragoe³ and Ioannis Ignatiadis¹

¹BRGM (French Geological Survey), Orleans, France

²ANDRA (French national radioactive waste management agency), Châtenay-Malabry, France

³ICMMO (Institute of Molecular Chemistry and Materials), Orsay, France

* d.aoubida@externe.brgm.fr

In France, Callovo-Oxfordian geological formation (Cox) has been identified to host the future deep geological disposal facility for isolation of nuclear waste in innovative reversible storage. The Cox is a water-saturated clayey environment with extremely low permeability, porosity and hydraulic conductivity. In order to monitor the evolution of the near-field around radioactive wastes, the implementation of reliable all-solid-state pH and reference electrodes turn out to be useful to support safety and reversibility. pH and redox potential are among the parameters to be monitored, because they easily characterize physical, chemical and electrochemical (redox) transformations.

This work aims to develop innovative all-solid-state pH and reference electrodes based on ceramic oxide membranes (LLTO) using Spark Plasma Sintering (SPS), which is a great novelty in the fabrication of ceramic all-solid-state-sensors.

The lithium lanthanum titanates of the series $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO), where A = Li, La and B = Ti, are ABO_3 type perovskites, which have received considerable attention in recent years due to their high lithium conductivity ($\sigma = 10^{-3} \text{ S.cm}^{-1}$ at 25°C , $x=0.10$) linked to their crystallographic structure [1]. Depending on the sintering temperature, LLTO can exhibit either pH sensitivity [2] or pH insensitivity [3]. This property is correlated with the sintering temperature.

In this work, LLTO powder was synthesized using the solid-state reaction method from La_2O_3 , TiO_2 , and Li_2CO_3 (99.9%) in stoichiometric amounts [4]. The weighed powder was planetary milled using zirconia balls. The mixtures were pressed into pellets, heated in air for 4 h at 850°C to remove carbon dioxide [5], and then heated at 1050°C for 12 h at a heating rate of 5°C.min^{-1} . The blends were subsequently cooled to ambient temperature at a cooling rate of 5°C.min^{-1} . Another grinding step was carried out using the same conditions as before, and then the mixtures were pressed into pellets and heated in air for 12 h at 1100°C . The LLTO powder was characterized (Fig. 1 (a), (b)) by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM, including EDS analysis) before and after SPS. The prepared LLTO powders were pressed into pellets and sintered using SPS under varying parameters. Using the FullProf program, we conducted refinement on the data to determine



the crystallographic structure and composition of the obtained material (Fig. 1(a)). The result is in good agreement with the literature [5]. The crystallite size of LLTO powder was also estimated by SEM and is approximately 5 μm .

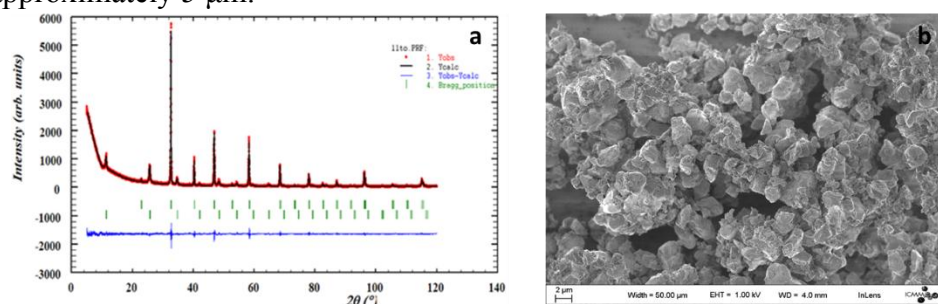


Figure 1: (a) XRD patterns of the LLTO powder before SPS, (b) SEM images of the LLTO powder before SPS

SEM analyses performed on different samples, under various SPS sintering conditions, showed that grain size influences the response of the electrodes (pH or reference). Impedance measurements revealed that the grain conductivity, approximately $10^{-3} \text{ S}\cdot\text{cm}^{-1}$, does not seem to affect the pH properties of the LLTO ceramic. However, the conductivity of the grain boundaries plays a significant role: the more compact the material, the higher the grain boundary resistance, and the more pH-sensitive the material is. Potentiometric measurements were carried out in air and in a glove box using Cox water, demonstrating the robustness of these electrodes. Finally, XPS analyses were conducted to explain the working mechanisms of our electrodes.

Work is in progress to demonstrate the robustness of the LLTO RE in actual Cox pore water over a long period.

References

- [1] Y. Inaguma, L. Chen, M. Itoh, and T. Nakamura, « Candidate compounds with perovskite structure for high lithium ionic conductivity », *Solid State Ionics*, vol. 70- 71, p. 196- 202, 1994, doi: 10.1016/0167-2738(94)90309-3.
- [2] Cl. Bohnke, H. Duroy, and J.-L. Fourquet, « pH sensors with lithium lanthanum titanate sensitive material: applications in food industry », *Sensors and Actuators B: Chemical*, vol. 89, n° 3, p. 240- 247, 2003, doi: 10.1016/S0925-4005(02)00473-2.
- [3] S. Lorant, O. Bohnke, J. Brévière, and C. Bohnke, « All- Solid- State pH Sensor Used in Oil Drilling Mud », *Electroanalysis*, vol. 25, n° 1, p. 223- 229, 2013, doi: 10.1002/elan.201200367.
- [4] J.L. Fourquet, H. Duroy, and M.P. Crosnier-Lopez, « Structural and Microstructural Studies of the Series $\text{La}_{2/3-x}\text{Li}_3\text{x}\square_{1/3-2x}\text{TiO}_3$ », *Journal of Solid State Chemistry*, vol. 127, n° 2, p. 283- 294, 1996, doi: 10.1006/jssc.1996.0385