

Lithium lanthanum titanate ceramic as sensitive material for pH sensor: Influence of synthesis methods and powder grains size

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Abstract

The lithium lanthanum titanate (LLTO), prepared by two different methods (solid state reaction and sol–gel), has been studied as sensitive element for detecting the pH variations in aqueous solutions when used as a potentiometric sensor. This property is dependent on mechanical and thermal treatments of the synthesised powder. A screening design was performed with the material obtained by solid state reaction. Several parameters (grinding time, heating rate for sintering process. . .) have been optimized. The main step, which increases the sensitivity, is the grinding of the powder before a heat treatment when the LLTO is synthesised by solid state reaction. We suppose that a small grains size of the powder is favourable to the pH variations sensitivity. A comparison with LLTO synthesised by the sol–gel route without grinding is also shown. The sensitivities of these two materials to the pH variations are very similar.

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1. Introduction

The lithium lanthanum titanates of the series $\text{Li}_{3-x}\text{La}_{2/3-x}\square_{1/3-x}\text{TiO}_3$ (LLTO), where \square refers to a vacancy, is a fast Li^+ conductor owing to its crystallographic structure.^{1–6} Kunigi et al.⁷ have shown that this material, as a separator, could be applied to the electrochemical selective recovery of lithium ions and to the isotope separation for lithium ions, ^6Li and ^7Li , by electrolysis in aqueous solution. Generally, pure ionic ceramics are good candidate to be sensitive element in potentiometric sensors in reason of the fast ion exchange than can occur between the ions in solution and the ions of the ceramic membrane. Surprisingly, we found an application in the use of this oxide ceramic in an ion selective electrode for pH detection as showed by our previous paper.⁸ Furthermore, in a second paper,⁹ impedance measurements were performed which reveal a reaction at the grain boundaries/buffer solutions interface. We conclude this reaction as adsorption reaction, as suggested by Noguera.¹⁰ The ceramic was obtained

by solid state reaction (SSR) with Li_2CO_3 , TiO_2 and La_2O_3 as starting materials. Finally, we introduce a new step in the fabrication of sensitive elements for pH measurements: a mechanical grinding, followed by pressing and a thermal treatment of the LLTO samples at temperatures between 1100 and 1350 °C. The most important parameters for a good pH response were studied with a screening design and it was mainly the grinding of LLTO powders before the thermal treatment of the samples.¹¹ Recently, we used the sol–gel synthesis route in order to obtain low grain sizes and to increase the grain boundaries dimensions.¹² In this paper, the LLTO has been prepared by both conventional solid state reaction and by modified Pechini method (sol–gel). The performances of the preparations of pH sensors are showed.

2. Experimental

- (i) The LLTO samples has been prepared by solid state reaction and the detailed procedure is reported elsewhere.⁵ Synthesised powder was ball-milled in a planetary grinder Fritsch Pulverisette 7 with ethyl alcohol in zir-

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conium oxide jars with zirconium oxide balls. The grain size distributions were measured with a Coulter LS 320 laser granulometer in water using the Fraunhofer model. After isostatic pressing under 500 MPa, the pellets were heated at 1200 °C for 8 h.

- (ii) Samples obtained by the sol–gel route were prepared by the reactions described in.¹³ They were pressed under 500 MPa with an isostatic press. They were heated at 1200 °C for 8 h, with a heating rate of 5 °C/min.
- (iii) These conditions obtained after a screening design are chosen for a better pH response of the samples.¹¹ SEM studies on the pellets were performed with a HITACHI S-2300 scanning electron microscope.

The pellets were fixed with two-component Araldite™ glue (CIBA-GEIGY) on the end side of a glass tube. The surface area in contact with the liquid electrolyte under test was ~0.196 cm². The internal reference was built with a calomel electrode (RADIOMETER) in contact with a saturated KCl solution buffered at pH = 7. The external reference was a RedRod™ electrode (RADIOMETER). The potential of this electrode is independent on temperature variations. The electrochemical cell is described by:

Ag/AgCl/saturated KCl (aqueous) pH 7/LLTO/solution under test/external reference.

The potential of the pH-sensors versus the external reference electrode was measured with a MINISIS 8000™ Millivoltmeter (TACUSSEL) connected to an AGILENT 34970A. Potential and temperature were recorded as a function of time in different buffer solutions. Solutions under test were magnetically stirred and thermostated at 25 °C. Temperature was controlled with a HUBER thermostat.

Solutions: the solutions under test were commercial buffer solutions (RADIOMETER and CARLO ERBA) for pH from 2 to 12. Nitric acid and sodium hydroxide (RP from CARLO ERBA) were prepared with deionised water.

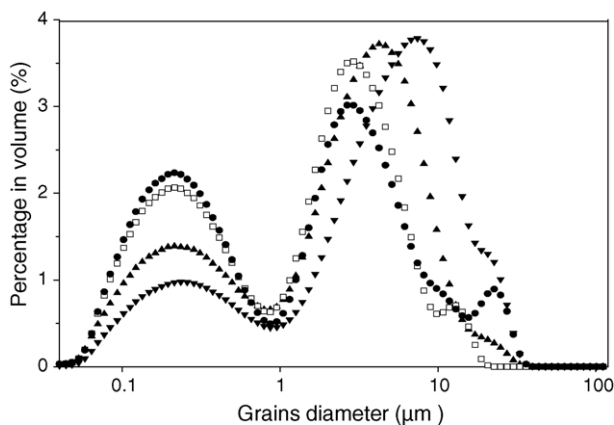


Fig. 1. Grain size percentage in volume after four different grinding times at 3500 rpm in a planetary grinder. (●) 5 h, (□) 1 h, (▲) 30 min and (▼) 10 min.

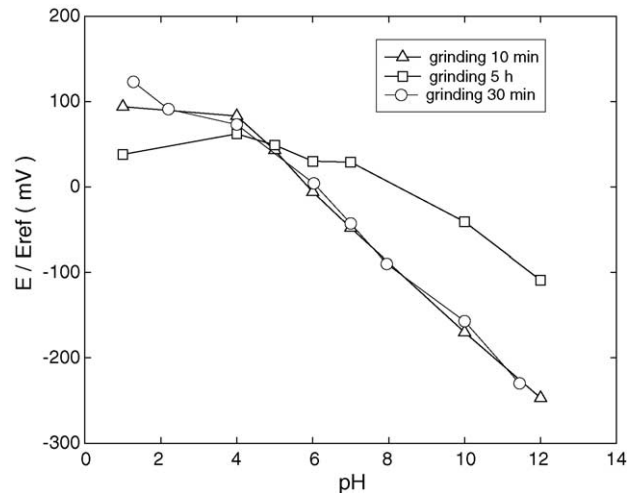


Fig. 2. E vs. pH curve of three samples of SSR-LLTO after sintering of powder grinded at three different times 10 min, 30 min and 5 h.

3. Results and discussion

3.1. pH measurements with LLTO obtained by solid state reaction

After grinding, the grain dimensions, as shown in Fig. 1, are statically distributed with two peaks at ~0.2 and ~5 µm values for four different grinding durations, at the same speed (3500 rpm). The difference resided only on the distribution population between these two dimensions. After the thermal treatment at 1200 °C for 8 h, we obtain different responses to the pH in buffer solutions at 25 °C (Fig. 2). We observed a poor response for a long grinding duration, whereas, durations of 10 and 30 min give an equivalent sensitivity. Long grinding times are well known to induce an amorphisation of materials and thus can be the reason of the poor response. The ΔE variation in function of pH is $280 - 41.3 \times \text{pH}$ in mV at 25 °C for the grinding time of 30 min. As a result, the grind-

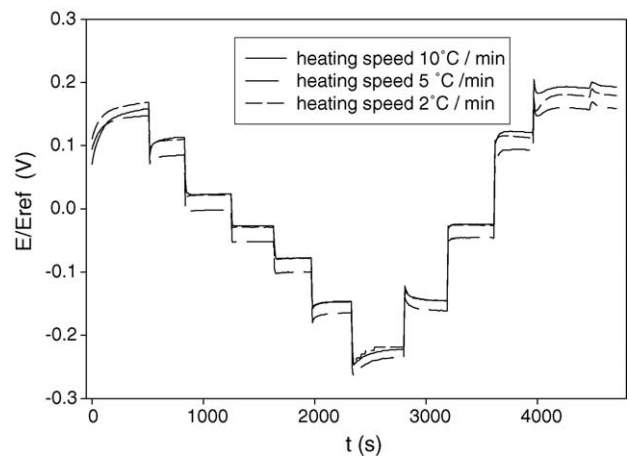


Fig. 3. Response of SSR-LLTO grinded 30 min and heated at 1200 °C for 8 h at three heating speeds: 2, 5 and 10 °C/min.

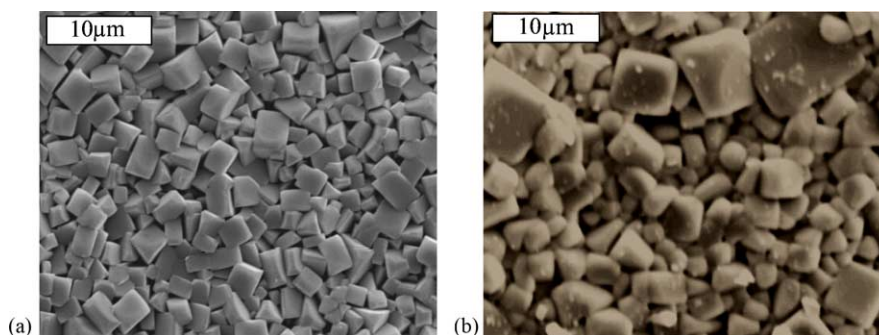


Fig. 4. SEM picture of LLTO, obtained by solid state reaction (a) and sol-gel (b), after grinding and a heat treatment at 1200 °C for 8 h.

ing time of 30 min was chosen for studying the influence of heating speed on LLTO samples, which, may be, modify the morphology (closed porosity) during the sintering step. We observed a good sensitivity (40–50 mV/pH unit) and a fast response time and a good reproducibility (Fig. 3). The difference between the curves is not significant and is not linked to the variations of heating speed. For these three samples, a SEM picture shows a very typical octahedral morphology of the grains (Fig. 4a).

3.2. pH measurements with LLTO obtained with the sol-gel route

LLTO material was prepared by using the polymerizable precursor method derived from the Pechini method.^{12,13} The samples were treated at 1200 °C, after isostatic pressing for 8 h as for SSR-LLTO. The SEM pictures are very closed in both cases, however, the grain dimensions obtained in this

case are not as homogeneous as the one obtained by SSR method and the grains are less sharp octahedrons (Fig. 4b). The compacity of SSR samples is about 95 and 90% for the sol-gel samples. The response of the pH sensor has been measured with two different samples and found to yield good results. The slope of the response curve ΔE versus pH has been found to be 42 mV/pH unit for the measurements at RT, as shown in Fig. 5. The results of SSR-LLTO for two sintering heating rates are also showed. It must be noticed a low sensitivity in acidic medium (lower than pH 4). Further, preliminary trials with as prepared samples (just isostatically pressed and without heat treatment) failed to give good sensitivity to the pH variations.

4. Conclusions

The lithium lanthanum titanate can be used as sensitive element in industrial pH sensors. Several previous experiments indicate that the sensitivity of the electrode is linked to the granulometric distribution of the material before a heat treatment at 1200 °C for 8 h. Two synthesis methods were used: solid state reaction following by a grinding in planetary grinder or sol-gel method. The first one allows to obtain reproducible and sensitive electrodes but needs about 5 days of preparation. A long grinding time decrease the sensitivity to the pH variations and the heating speed during sintering has no influence on the pH sensitivity. The second leads to a very comparable sensitivity of the electrodes but the synthesis time is shorter (about 5 h) and permits to obtain pure and great quantity of LLTO.

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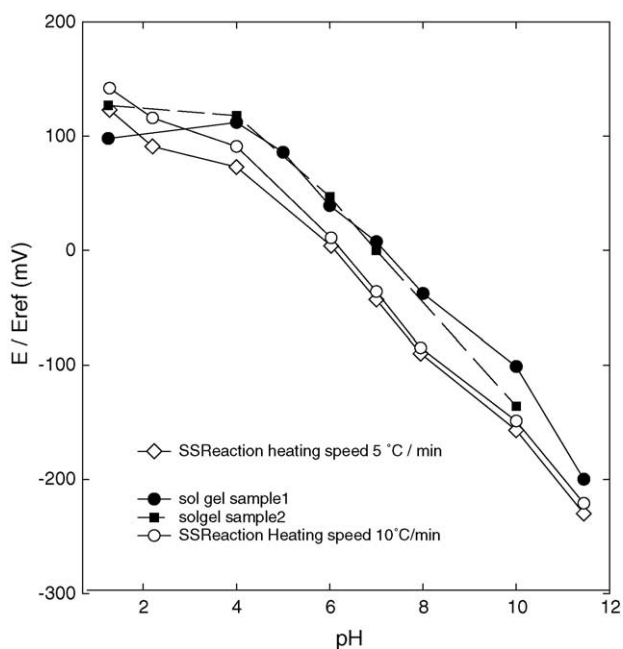


Fig. 5. E vs. pH curve of two samples of SG-LLTO and two samples of SSR-LLTO treated at 1200 °C for 8 h.

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