

pH sensors with Lithium Lanthanum Titanate ceramic sensitive material

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Abstract

The lithium lanthanum titanates of the series $\text{Li}_{3x}\text{La}_{2/3-x}\square_{1/3-2x}\text{TiO}_3$ (LLTO), where \square refers to cation vacancy, are studied in our Laboratory in reason of their high lithium conductivity linked to their crystallographic structure. A maximum value of conductivity ($\sigma = 10^{-3} \text{ S cm}^{-1}$ at 300 K) has been reported for the composition $x = 0.10$. One practical application of an ionic conductor can be its use in an ion selective electrode i.e. LaF_3 for the detection of Fluoride ion in aqueous solution. Here the detection of Lithium ion in aqueous solution is not well achieved but we have found an other property : the sensors built with these materials react to the variations of pH in aqueous solutions like a glass electrode but with a SubNernstian slope (about 43 mV / pH unit at RT). The measurements domain is between pH=2 to pH=12. These type of sensors are interesting for the industrial control where the glass electrode can not be used in reason of its weakness. Like the glass electrode , the variation of the redox potential has no influence on the response of these sensors A thermal treatment analogue to a sintering permit to obtain more or less response to the pH variations. During the last two years, the influence of twelve different parameters was studied and we can obtain a good or no response to the pH variations. This second property permit to built ceramic-based reference electrode. The materials were prepared by solid state reaction or the sol-gel route. We present the mains results obtained in our Laboratory since four years with these new pH ceramic sensors.

Keyword : perovskite, Lithium ion conductor , sol-gel method, pH sensor

Introduction

The lithium lanthanum titanates of the series $\text{Li}_{3x}\text{La}_{2/3-x} \text{TiO}_3$ (LLTO), where x refers to a vacancy, have received a considerable attention in recent years [1-6] in view of their high lithium conductivity linked to their crystallographic structure. A maximum value of conductivity ($\sigma = 10^{-3} \text{ S.cm}^{-1}$ at 300 K) has been reported for the composition $x = 0.1$ by Inaguma et al [2]. Kunigi et al 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 [7]. Another application could be the use of this oxide ceramic as an ion selective electrode for pH detection as showed by our previous paper[8]. The ceramic was obtained by solid state reaction with LiCO_3 , TiO_2 and La_2O_3 as starting materials. Further, in a second paper [9], impedance measurements were performed and which reveals a reaction at the grain boundaries/buffer solutions interface. We conclude this reaction as adsorption reaction as suggested by Cl.Noguera [10]. Finally, we introduce a new step in the fabrication of sensitive elements for pH measurements: the heating of the LLTO samples at temperature between $1100 \text{ }^\circ\text{C}$ to 1350°C . The most important parameters for a good pH response were studied with a screening design. New important factors was discovered for the detection of pH and it was mainly the grinding of LLTO powder before the thermal treatment of the samples [11]. The use of the sol-gel route synthesis well know to yields lower grain dimensions and can increase the grain boundaries dimensions which in turn offers adsorption reaction. The LLTO has been prepared by both conventional solid state reaction and by modified Pechini Method (sol-gel).

EXPERIMENTAL

- (i) The LLTO samples has been prepared by solid state reaction and the detailed procedure is reported elsewhere [5]. Powder of this material was ball-milled in a planetary grinder (Fritsch Pulverisette 7) with ethyl alcohol in zirconium oxide jars with zirconium oxide balls. After pressing isostatically under 500 Mpa with water , the pellets were heated at 1200°C during 8 hours.
- (ii) Samples obtained by the sol-gel route were obtained by the reactions described in[12]. They were pressed under 500 Mpa in water with a isostatic press (TOP Industrie) . They were heated at 1200°C during 8 hours
- (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 a two components 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 of 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. The data were recorded in function of time. Solutions under test were magnetically stirred and thermostated at 25°C and 62°C. Temperature was controlled with a HUBER thermostat. Potential and temperature were recorded in function of time in different buffer solutions

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

RESULTS AND DISCUSSION

(i) pH measurements with LLTO obtained by solid state reaction. After a thermal treatment , the samples have the morphology showed on figure 1. We observe regular grains with octahedral form with dimensions less of 5 μ m.

The results of figure 2 are related to the influence of grinding on the sensitivity on the pH of LLTO ceramic. Different durations of grinding were performed and after thermal treatment , we observe different response to the pH in buffer solutions at 25 °(figure 2) The E versus pH (= ΔE) equation is 347-41.3pH at 25 °C for a grinding time of 30 min . The grinding time of 30 min was chosen for the study of the influence of heating speed of LLTO samples on the pH sensitivity. We observe a good sensitivity (40 to 50 mV by pH unit) , good response time and a good reproducibility.

(ii) pH measurements with LLTO obtained with the sol-gel route :LLTO material was obtained with a polymerizable precursor method derived from the Pechini method [12][13]. The samples were treated same as of SSR-LLTO . The SEM pictures are very close in both cases, however grains obtained with the Sol-Gel method are slightly smaller than the SSR method material. The response of the pH sensor with the sol-gel prepared material has been tested with two different samples and found to yield good results . The slope of the response curve ΔE vs pH has been found to be 42 mV for room temperature measurements . It must be noted a bad sensitivity in acidic medium (lower than pH 4) . Further , preliminary trials with as prepared samples (just isostically pressed and without heat treatment failed to give good sensitivity to the pH variations .

CONCLUSION The Lithium Lanthanum Titanate can be used as sensitive element in industrial pH sensors. The sensitivity of the electrode is linked to the grains dimensions of the

material before an heat treatment at 1200°C during 8 hours . Two synthesis methods were used : solid state reaction and grinding in planetary grinder or sol-gel method . The first permit to obtain reproducible and sensitive electrodes but its long (about five days). The second leads to less sensitive electrodes but the synthesis time is short (about five hours) and permit to obtain pure and great quantity of LLTO.

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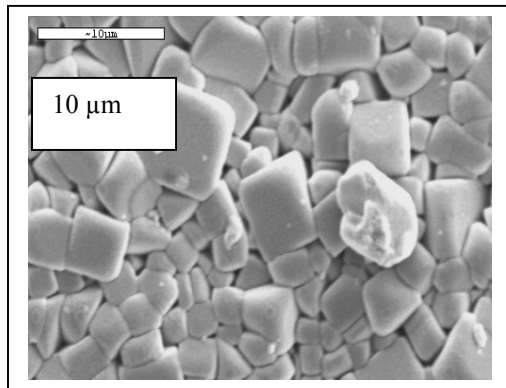


Figure 1: SEM picture of LLTO obtained by Solid State Reaction grinded and heated at 1200°C during 8 hours

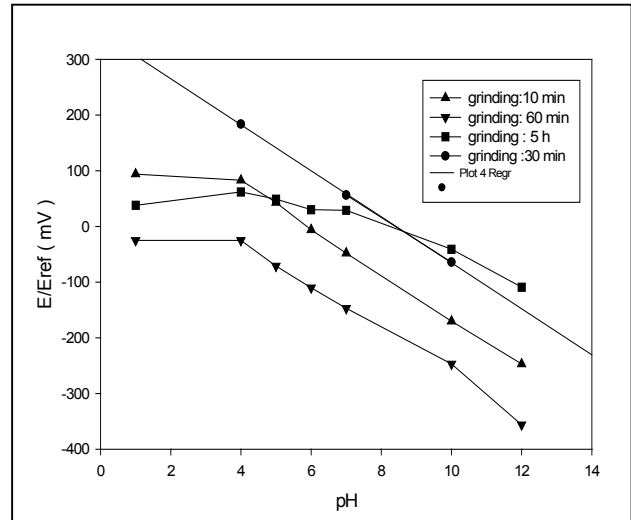


Figure 2: Influence of the grinding time on the response of the SSR-LLTO electrode

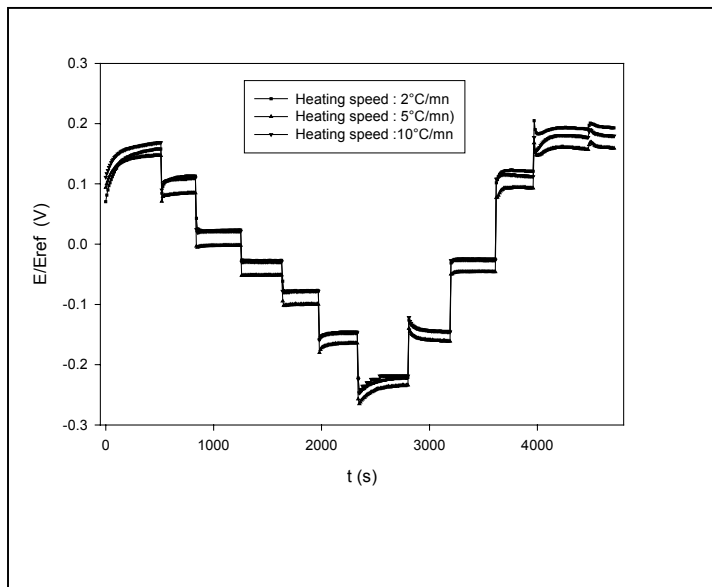


FIGURE 3 : Response of SSR-LLTO grinded 30 min and heated at 1200°C during 8 hours with different heating speed in different buffer solutions pH1.25;4;6;7;8;10;11.45;10;7;4;2;1.25

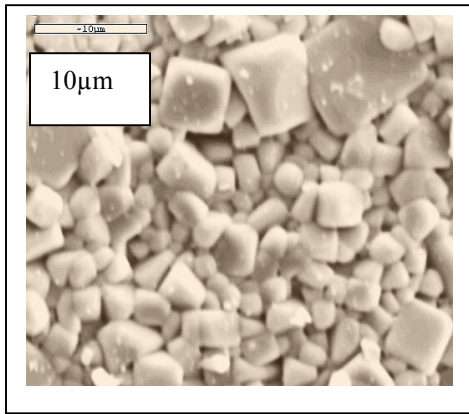


Figure 4: SEM picture of LLTO obtained by sol-gel after heat treatment at 1200°C during 8 hours

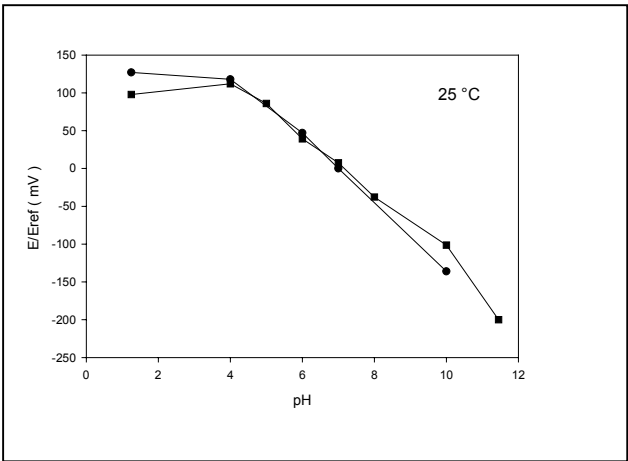


Figure 5 : E vs pH curve of two samples of SG-LLTO treated at 1200 °C during 8 hours

