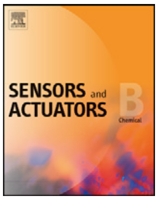
Sensors and Actuators B 138 (2009) 193–200

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb



Investigation of the perovskite ceramic $Li_{0.30}La_{0.56}TiO_3$ by Pulsed Force Mode AFM for pH sensor application

Mickaël Roffat[a], Olivier Noël[b], Olivier Soppera[c], Odile Bohnke[a,*]

[a] *Laboratoire des Oxydes et Fluorures UMR 6010 CNRS, Institut de Recherche en Ingénierie Moléculaire et Matériaux Fonctionnels (FR 2575 CNRS), Université du Maine, Avenue O. Messiaen 72085 Le Mans Cedex, France*
[b] *Laboratoire de Physique de l'Etat Condensé UMR 6087 CNRS, Institut de Recherche en Ingénierie Moléculaire et Matériaux Fonctionnels (FR2575 CNRS), Université du Maine, Avenue O. Messiaen 72085 Le Mans Cedex, France*
[c] *Département de Photochimie Générale UMR 7525 CNRS, E.N.S.C.Mu, 3 rue A. Werner, 68093 Mulhouse Cedex, France*

ARTICLE INFO

Article history:
Received 28 October 2008
Received in revised form
26 November 2008
Accepted 9 December 2008
Available online 25 December 2008

Keywords:
Atomic force microscopy
Ceramics
Ionic conductors
pH sensors
Perovskite

ABSTRACT

Depending on the sintering temperature, $Li_{0.30}La_{0.56}TiO_3$ ceramics are either sensitive or insensitive to the pH of aqueous solutions. These ceramics may then be used as pH sensor and reference electrode in an all solid state combined pH electrode device. To shed some light on the mechanism of the ceramics pH sensitivity or insensibility, we have studied the surface properties of both types of ceramics, at a local scale. We have performed adhesion and topographic surface images by means of an atomic force microscope (AFM) in the Pulsed Force Mode (PFM). The interpretation of the AFM images is discussed in terms of both surface roughness and capillary force. In particular, adhesive surface property images show that the sensitive ceramics exhibit higher hydrophilic surface properties than the insensitive ones. Such hydrophilic character can be attributed to the basic hydroxyl –OH groups present at the surface of the sensitive ceramics. Finally, some attempts are given to understand the mechanism of the pH behaviour of these oxides.

1. Introduction

The lithium lanthanum titanates of the series $(Li_{3x}La_{2/3-x}\square_{1/3-2x})TiO_3$ (called LLTO), where $\square$ refers to a vacancy, are fast Li^+ conductors [1–6]. In addition, it is well known that pure ionic conductor ceramics are good candidates for sensitive elements in potentiometric sensors. This feature is generally attributed to the fast ion exchange that can occur between the ions in solution and the ions of the ceramic membrane. In previous studies, we demonstrated the potential application of the LLTO oxide ceramics for both Li^+ detection in non-aqueous solutions and pH detection in aqueous media [7–9]. Such sensitive ceramics are usually prepared by conventional solid state reaction (SSR) method. This method requires a three steps procedure including a mechanical grinding of the powder, followed by a uniaxial pressing and finally a thermal treatment of the LLTO pellets between 1000 and 1350 °C. However, our group has proposed important improvements of the synthesis process. They consisted in decreasing significantly both the synthesis temperature and time, and in avoiding the time consuming grinding step by using the modified Pechini method [10]. Such prepared ceramic membranes are still sensitive to pH (about 35–45 mV per pH unit). In controlling the sintering temperature, it is possible to prepare either pH sensitive or insensitive (called reference) ceramic electrodes [11]. Our assumption to explain the behaviour of such ceramics is based on an enhancement of the acido-basic surface properties of the ceramic by heat-treatment. In particular, basic hydroxyl groups ($-OH_{basic}$) may be present on the surface of the ceramic [12,13]. Such active hydroxyl groups, which are reactive to protons, have a higher electronegativity than non-active hydroxyl groups, which are not sensitive to protons. Moreover, these active hydroxyl groups should exhibit higher hydrophilic surface properties than the non-active ones. Reference ceramics are obtained when the heat-treatment is not efficient to create these active hydroxyl groups.

The analysis of surface chemistry is thus of valuable importance to describe the pH behaviour of the electrodes. Many tools are available at the macroscale to investigate the chemical composition of a surface. At the micro- and sub-microscale, atomic force microscopy (AFM) has proved to be a powerful instrument for investigations of surface properties at a local scale. In particular, this gives access to topographical imaging of the surfaces and to physico-chemical surface properties as hydrophilic character, with a nanometer spatial resolution.

In this paper, we have performed adhesion surface and topographic surface images with an AFM using Pulsed Force Mode (PFM). All AFM experiments are done at room temperature, under

---

* Corresponding author.
E-mail address: odile.bohnke@univ-lemans.fr (O. Bohnke).

0925-4005/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2008.12.031

air with a constant relative humidity (RH). These measurements are done on sensitive and reference LLTO ($x = 0.1$) ceramic surfaces. The influence of surface roughness and capillary forces on the PFM measurements is discussed. Finally, on the basis of the AFM measurements, we propose a mechanism able to explain the pH behaviour of LLTO ceramics.

2. Experimental

2.1. Oxide synthesis

The synthesis of $Li_{0.30}La_{0.56}TiO_3$ has been carried out from Ti powder (purity of 98.5% – Fluka), and Li_2CO_3 (purity of 99% – Merck), and La_2O_3 (purity of 99.999% – Rhone-Poulenc). Before synthesis, La_2O_3 has been heated for 10 h at 1000 °C in air to remove lanthanum hydroxide. Efficiency of the heat treatment has been checked by powder X-ray diffraction (XRD) that confirms the absence of lanthanum hydroxide. The water traces and adsorbed gases were removed from Li_2CO_3 by keeping it in an oven at 120 °C before use. Control of both Li:Ti and La:Ti ratios was obtained by weighting, immediately after the above mentioned heat-treatments, the reagents cooled at room temperature. In one hand, the titanium solution was prepared in dissolving the Ti powder into hydrogen peroxide solution (purity of 30% from Merck) and ammonia solution (purity of 35% – Prolabo). On the other hand, lithium carbonate and lanthanum oxide were dissolved in a diluted nitric acid solution obtained from an extra pure HNO_3 (65% from Riedel de Haën). The polymer precursor was prepared from the above solutions in adding citric acid powder (CA, purity of 99.5%) and ethylene glycol solutions (EG, purity of 99% Aldrich). The molar ratios CA/EG = 1:4 and CA/M = 12:1 (where M is the total number of cations Ti, Li and La) were used. The detailed synthesis procedure, which leads to the synthesis of LLTO powder, has been described previously [14].

2.2. XRD characterisation

Powder XRD pattern has been recorded at room temperature with a PANalytical X'Pert PRO diffractometer (Cu Kα radiation), equipped with the X'Cellerator detector, in the 2θ range from 10° to 70° with an interpolated step of 0.067°.

2.3. pH and reference electrodes preparation

To prepare the pH electrodes, the LLTO powder was mechanically grounded (with a Retsch apparatus) then pressed under 5000 bars and heated (heating rate 5 °C/min) at high temperature for 2 h in air and, finally cooled with the same rate as heating rate, to obtain pellets of 5 mm of diameter. Their thickness was around 1 mm. Heating temperature was 1000 °C to obtain the non-sensitive electrode (or reference electrode) and 1150 °C to obtain the sensitive to pH electrode (or sensitive electrode) [7,15]. It has to be noticed that the side of the pellets in contact with air during the sintering process is more sensitive to pH than the other side which is in contact with Pt crucible. Therefore, we polished the side which is not in contact with air during the heat treatment and used this surface as internal reference of the electrode and the non-polished side as active surface of the electrode. Afterwards, the pellet was fixed with two components Araldite glue (DIL) on the end of an epoxy tube (Weber Metaux). An Ag wire (Strem Chemicals) of 0.5 mm of diameter was modified by electroxidation to obtain an Ag/AgCl wire. The internal reference was made of this Ag/AgCl wire in contact with a saturated KCl solution buffered at pH 7 in contact with the polished surface of the pellet. The external reference was an Ag/AgCl electrode (Radiometer). The electrochemical cell could then be described as follows:

Cu/Ag/AgCl/KCl(aqueous)pH7/LLTO/solutionundertest//
saturatedKCl/AgCl/Ag/Cu

The voltage between the two Cu wires was measured with a 3510 pHmeter (Jenway). During the measurements, solutions under test were stirred and thermally stabilized at 25 °C (supplier is La Crosse Technology). The voltage was recorded as a function of pH of different buffer solutions ranging from 4 to 10 (Riedel de Haen). Depending on the sintering temperature of the LLTO pellet, the above electrochemical cell was either a pH electrode (when sintering temperature is 1150 °C) or a reference electrode (when sintering temperature is 1000 °C).

2.4. Topography images and adhesive properties determined by PFM

2.4.1. Principle

In the Pulsed Force Mode (PFM WITec Wissenschaftliche Instrumente und Technologie, Ulm, Germany) a sinusoidal z-modulation was used to perform force versus distance curves (called force curves) by continuously bringing the tip into contact with the surface up to a given force value and withdrawing it again. Thus the PFM was one of the so-called intermittent contact modes in AFM. The PFM operation mode represents a powerful tool since it provides a simultaneous characterisation of the topography, the adhesion and the stiffness properties [16]. For our experiments, typically, the cantilever of the AFM in the PFM has been brought into contact at a rate of 0.5 kHz and amplitude ranging from 10 to 500 nm.

In Fig. 1, it is reported the typical probe response during one excitation cycle. At step 1, the tip snaps into contact with the sample surface. Then, the force acting on the tip increases as the z-piezo pushes the tip further on the surface. At step 3, a maximum force (F_{max}) is reached before withdrawing the tip from the surface. The maximum force (or set point) is set as the feedback parameter for topographic imaging. At step 4, the tip pulls off the surface sample and comes back to its equilibrium state (baseline). This pull off force defines the adhesion force between the tip and the surface. Meanwhile, free oscillations of the cantilever are damped. At step 5, the next cycle starts. The slope between step 2 and step 3 in Fig. 1 was recorded for mapping the stiffness properties of the surface. A detailed description is given in reference [18].

The PFM had been successfully used to investigate the surface properties of various materials like polymers [16,17] and hybrid sol–gel materials [19]. In the case of hybrid sol–gel materials, the correlation between OH functionalities and adhesion forces was clearly established.

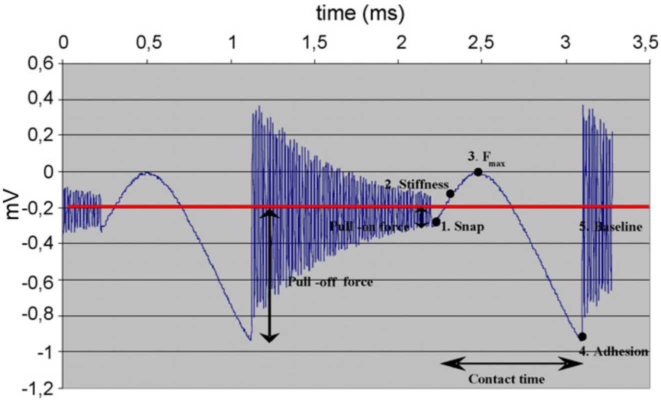


Fig. 1. Principle of Pulsed Force Mode AFM (PFM/AFM).