



Zeta potential measurement on lithium lanthanum titanate nanoceramics



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ARTICLE INFO

Article history:

Received 2 August 2014

Received in revised form

21 November 2014

Accepted 4 December 2014

Available online 9 April 2015

Keywords:

Titanate

Nanoparticles

Zeta potential

Colloidal suspension

ABSTRACT

The zeta potential, isoelectric point, and agglomeration of $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (LLTO) nanoparticles dispersed in aqueous media at different ionic strengths have been studied. The zeta potential was determined from electrophoretic mobility measurements, according to Smoluchowski's equation, for $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ suspensions in NaCl and KCl electrolytes with ionic strengths of 1, 10, and 100 mmol/dm^3 . The isoelectric point (IEP), zeta potential (ζ), and the agglomeration were shown to strongly depend on the ionic strength of the $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ aqueous colloidal suspension in both NaCl and KCl electrolytes, which allows the determination of the effects of environmental conditions for $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ manipulation in aqueous colloidal systems. The suspensions of $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ nanoparticles reach the IEP in the pH range of 3–5. The ζ of $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ nanoparticles varied from positive to negative values with a pH increase, which allows for the control of the surface charge depending on the purpose. The pH range of 7–8 and an ionic strength $\leq 1 \text{ mmol}/\text{dm}^3$ are recommended as the most suitable conditions for both the LLTO colloidal shaping techniques application and the LLTO-based nanocomposite formation.

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Introduction

The $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ perovskite material pertains to the lithium lanthanum titanates ceramic systems, known as LLTO (Stramare, Thangadurai, & Weppner, 2003; Knauth, 2009). These materials are being intensively studied owing to their high lithium diffusion coefficient at room temperature (Stramare et al., 2003). There have already been interesting reports which focused on the behavior of LLTO as a solid electrolyte and cathode-active material for lithium batteries (Antoniassi, González, Fernandes, & Graeff, 2011; Milian Pila et al., 2012). In addition, as a result of the nanoparticles' capacity to dissociate water on their grain surface and then to exchange protons for lithium ions both in pure water and in acidic medium at 25 °C, LLTO particles have been studied as proton

sensors (Bohnke et al., 2011). Some of these applications require very dense ceramics or fine layers, which can be prepared from nanometric powders by colloidal shaping techniques, such as the casting process (Ferrari & Moreno, 2010). For other applications, it is essential to control the surface chemical interactions between nanometric LLTO particles and diverse additives, such as electroactive polymers (Milian Pila et al., 2012). These tailoring processes are strongly related to the surface charge on the LLTO particles and to its stability in different media, where aqueous media are preferred owing to environmental considerations.

The zeta potential (ζ) versus pH dependence is an important measurement of a colloidal system, since flocculation (at low ζ) is expected at pH values where van der Waals forces predominate, while deflocculation (at high ζ) occurs at pH values above which the particles are removed from aggregates, according to DLVO theory (Derjaguin & Landau, 1941; Verwey & Overbeek, 1948). DLVO theory is the classical explanation of the stability of colloids in suspension. This theory assumes a balance between two opposite forces: electrostatic repulsion and van der Waals attraction in the colloidal medium. In many cases, the colloidal particle

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environment can be altered by either increasing or decreasing these two forces, for example by changing the pH or the counterion valence/concentration, which can be observed by the zeta potential measurements.

There have been a number of reports relating to ζ measurements on mixed oxides (Kirby & Hasselbrink, 2004) under different conditions, such as BaTiO₃ (Lopez, Rand, & Riley, 2000) and Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O₃ (Li, Zhang, Yang, & Zou, 2009). These studies showed that ceramic oxides generally have a well-defined and characteristic isoelectric point (IEP) value, where the electrophoretic mobility is zero. However, variations in the material preparation have resulted in the changes in the ζ measurement conditions, which are responsible for the spread in the reported values (Kirby & Hasselbrink, 2004; Kosmulski, 2009). However, to the best of our knowledge, experiments of this kind are yet to be reported for LLTO particles.

In the present study, we report for the first time the electrophoretic measurements of the ζ versus pH, IEP, and particle agglomeration for nanometric Li_{0.5}La_{0.5}TiO₃ dispersed in aqueous media with different ionic strengths.

Experimental

Sample preparation

The Li_{0.5}La_{0.5}TiO₃ nanoceramic was synthesized by the combustion method described by Milian Pila et al. (2014) to prepare nanoparticles of the LLTO system. This method is based on the thermal decomposition at 350 °C of a Li–La–Ti–citrate/ammonium nitrate solid precursor.

Characterization

The characterization for the as-prepared Li_{0.5}La_{0.5}TiO₃ was carried out 24 h after its synthesis. The X-ray diffraction (XRD) pattern was recorded in a diffractometer (Model 7000, Shimadzu, Kyoto, Japan) under the following conditions; Cu K α 1 ($\lambda = 1.5406$) radiation with a $\Delta 2\theta = 0.02^\circ$ step width in the $10^\circ < 2\theta < 90^\circ$ range. The phase identification was carried out by Hanawalt's method using the PDF-2002 and ICSD-2008 databases. The infrared (IR) spectra were recorded using a spectrometer (model FTLA-2000, ABB Company, Zurich, Switzerland) in the 400–4000 cm⁻¹ region. High magnification images were obtained using a scanning electron microscope (SEM; JSM 6360LV, JEOL, USA) and a transmission electron microscope (TEM; JEM-2200FS, JEOL, USA). The electrophoretic measurements were carried out using a Zetasizer system (Model ZEN 3600, Malvern Instruments, Malvern, UK). Very dilute aqueous suspensions (1 wt%) of the nanometric Li_{0.5}La_{0.5}TiO₃ (previously washed with acetic acid and then heated at 120 °C) in KCl and NaCl electrolytes (at 100, 10, and 1 mmol/dm³ counterion concentrations) were prepared under ultrasonic irradiation in an ultrasonic cleaner (Model 8891, Cole-Parmer, Vernon Hills, USA). The pH of the nanoparticle suspensions in NaCl electrolyte was adjusted between 2 and 8 using HCl (0.25 mol/dm³) or NaOH (0.25 mol/dm³) solutions and then stored at 4 °C for 24 h. The pH was readjusted just before each measurement. The pH of the nanoparticles suspensions in KCl was automatically adjusted by the ZEN 3600 Zetasizer analyzer (working in the titration mode) between three and eight using HCl (0.25 mol/dm³) or KOH (0.25 mol/dm³) solutions. The pH of individual samples was varied in one direction (from neutral toward either low or high pH), in order to avoid the addition of acid and base to the same sample, which would have altered the saline concentration. The ζ of Li_{0.5}La_{0.5}TiO₃ nanoparticles in aqueous media was determined

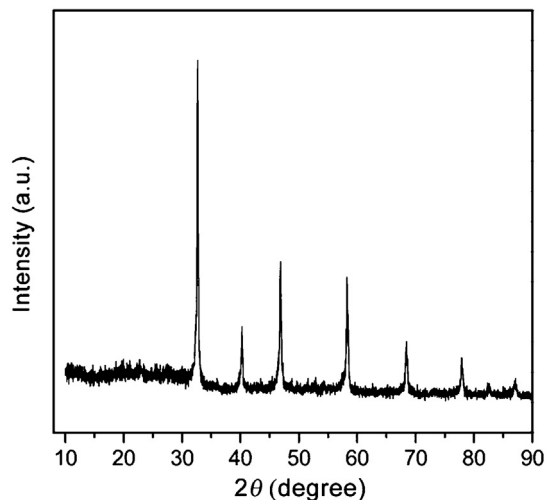


Fig. 1. The XRD pattern of the as-prepared Li_{0.5}La_{0.5}TiO₃ nanoceramic.

from its electrophoretic mobility according to Smoluchowski's equation (Hunter, 1981). The size and aggregation of the dispersed particles were carried out by the dynamic light scattering (DLS) method coupled to the ZEN 3600 Zetasizer system. The error in the zeta potential measurement was 1% and the DLS particles' size was registered with a polydispersity index of 0.3 nm for the stable measurements.

Results and discussion

Structural and morphological characterization

The XRD pattern of the as-prepared oxide (Fig. 1) shows both the peak positions and their relative intensities in good agreement with *Pm3m* cubic structure reported in the PDF 89-4928 database for the Li_{0.5}La_{0.5}TiO₃ composition. No additional diffraction peaks associated with impurities were resolved.

The SEM and HRTEM images (Fig. 2) of the as-prepared Li_{0.5}La_{0.5}TiO powder reveal spherical particles with sizes ranging from 20 to 50 nm. These nanoparticles are agglomerated forming grains of about 200 nm.

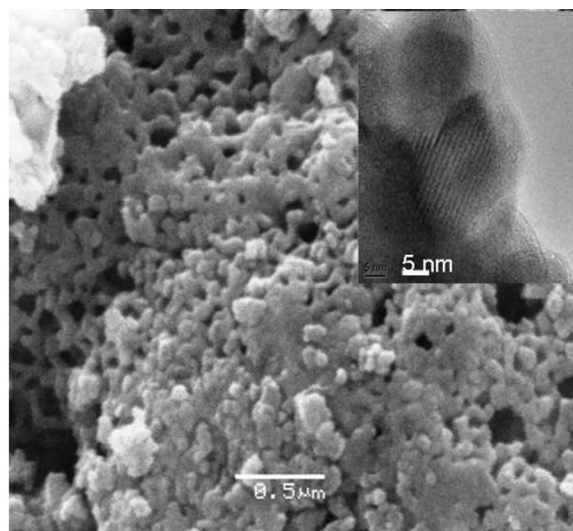


Fig. 2. The SEM image of the as-prepared Li_{0.5}La_{0.5}TiO₃ nanoceramic. The inset corresponds to the HRTEM picture of Li_{0.5}La_{0.5}TiO₃ particles aggregates.

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