



Enhancement of lithium conductivity and evidence of lithium dissociation for LLTO-PMMA nanocomposite electrolyte

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ARTICLE INFO

Article history:

Received 17 November 2015

Received in revised form

4 February 2016

Accepted 24 February 2016

Available online 26 February 2016

Keywords:

Lithium

Electrolyte

Polymer

Nanocomposite

Confocal Raman spectroscopy

ABSTRACT

We report the effect of $\text{La}_{0.57}\text{Li}_{0.3}\text{TiO}_3$ (LLTO) nanoparticles addition, with different crystallite size, on the lithium conductivity of LLTO-PMMA nanocomposites. X-ray powder diffraction and differential scanning calorimetry analyses showed a moderate increase of the disorder on the polymer chains with the addition of LLTO nanoparticles. Confocal Raman spectroscopy analysis evidenced lithium nitrate dissociation for both LLTO-loaded and unloaded polymer. Additionally, this technique also revealed that the free nitrate anions are mostly located in the proximity of LLTO nanoparticles interface, thus evidencing its participation in the lithium dissociation on these nanocomposites. An enhancement in the lithium conductivity in more than one order of magnitude was observed for all nanocomposites, in respect to LLTO-unloaded polymer, showing a maximum lithium conductivity of $\sigma_{\text{total}} \sim 1.13 \times 10^{-4} \text{ S/cm}$ at room temperature, for a 50 nm LLTO crystallite mean size addition.

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1. Introduction

Solid polymer electrolytes are being studied as promising materials for lithium batteries because of its flexibility, safety and light weight [1–5]. These solid polymer electrolytes are basically composed by a polymer, such as poly(ethyleneoxide) (PEO) [1,2], poly(methylmethacrylate) (PMMA) [3,4] or poly(acrylonitrile) (PAN) [5], and a lithium salt such as LiClO_4 , LiBF_4 or LiCF_3SO_3 . The improvement of the performance of these polymer electrolytes is usually associated to the reducing crystallinity of the polymer, decreasing glass transition temperature and improving the capacity of lithium ion dissociation. PMMA is usually preferred as a solid polymer electrolyte host because of its great degree of amorphousness (> 96%), capability of coordination to lithium through carbonyl group, high transparency and light weight [6–11]. In order to improve the room temperature conductivity of lithium, several studies have been made by adding ceramic nanoparticles such as passive materials Al_2O_3 [12], SiO_2 [13], TiO_2 [14,15], or active materials LiAlO_2 [16], Li_2N [17], $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ [18], in the last three, participating in the lithium conduction. In all cases, the nanoparticle fillers not only enhance the mechanical properties, but also favor the plasticization by kinetically inhibiting the polymer crystallization at room temperature and the

interaction with ionic species of the lithium salt [19]. Recently, Liu et al. [20] showed that the addition of $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$ (LLTO) nanofibers leads to a remarkable increase in the lithium conductivity of LLTO-PAN polymer nanocomposite.

In the present report, we study the effects in the addition of LLTO nanoparticles with different sizes and its consequences on the LLTO-PMMA nanocomposites lithium conductivity. The crystallinity of nanocomposites was studied by X-ray powder diffraction (XRPD) and differential scanning calorimetry (DSC) and both the microstructure and chemical composition by means of confocal Raman spectroscopy. Using this technique, we show a full characterization of nanocomposites including the polymer matrix, LLTO nanoparticles and the interphase of PMMA and LLTO nanoparticles. Finally, we performed electrochemical impedance spectroscopy (EIS) analysis to characterize the Li-conductivity for all nanocomposites at room temperature.

2. Materials and methods

LLTO nanoparticles with different particle sizes were prepared by the sol-gel method in acetic medium under different annealing temperature treatments. Poly(methyl methacrylate) (PMMA) 15,000 Mw and lithium nitrate (LiNO_3) 99.9%, both purchased from Sigma-Aldrich, were dissolved separately in anhydrous tetrahydrofuran (THF) and stirred during 1 h at room temperature. Both solutions were mixed and kept stirring during 3 h in a (LiNO_3 /PMMA)=0.07 wt ratio to obtain the Li-PMMA precursor solution.

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Equal quantities of LLTO nanoparticles (0.15 g) with different mean crystallite sizes $D \sim 10, 50$ and 100 nm were suspended separately in 10 mL THF and sonicated for 15 min using SONICS Vibracell 130 W 20 kHz Ultrasonic device. The LLTO suspensions were added separately to the Li-PMMA precursor solutions in a fixed (LLTO/PMMA)=0.15 wt ratio and kept stirring at room temperature until dryness. In addition, a reference material without LLTO nanoparticles was also prepared using the same experimental conditions. The nanocomposite samples were pressed into pellets at ~ 50 kN pressure for 10 min and simply named as LiPMMA-LX with $X=0, 1, 2$ and 3 , for no LLTO, LLTO with $D \sim 10, 50$ and 100 nm, respectively.

X-ray powder diffraction (XRPD) was performed using Rigaku Ultima IV diffractometer with $\text{CuK}\alpha$ radiation in the $2\theta = 10\text{--}80^\circ$ range using 2θ steps of 0.02° with a 5 s integration time per step. Differential scanning calorimetry (DSC) was performed using Shimadzu DSC-60 with $10^\circ\text{C}/\text{min}$ ramp rate in the $T = 30\text{--}120^\circ\text{C}$ temperature range. Initial heating at 120°C was performed in order to erase the prior thermal history of the sample, and then fictive temperature (T_f) was determined from heating run using the Moynihan method [21], as an approximation to the glass transition temperature (T_g) [22]. Confocal Raman spectroscopy was performed using WITec Alpha 300-R confocal Raman spectrometer with a 532 nm laser wavelength. The laser power used was ~ 30 mW and confocal Raman spectra were obtained by averaging a set of 5 spectra of 0.05 s integration time. The confocal Raman microscopy images were obtained for a $20 \times 20 \mu\text{m}$ zone with a ~ 265 nm pixel resolution, by filtering the well-defined peaks of both the LLTO and PMMA components. Electrochemical impedance spectroscopy (EIS) measurements were performed on LiPMMA-LX pellets (diameter=1.2 cm, thickness=0.15 cm) at room temperature using a Gamry Reference 3000 impedance analyzer in the 0.15 Hz to 1 MHz frequency range with a 10 mV AC amplitude. Gold blocking electrodes were homogeneously deposited on both sides of the LiPMMA-LX pellets using the sputtering technique. Data processing was performed using Echem Analyst software.

3. Results and discussion

X-ray powder diffraction patterns for PMMA (Fig. 1a) showed

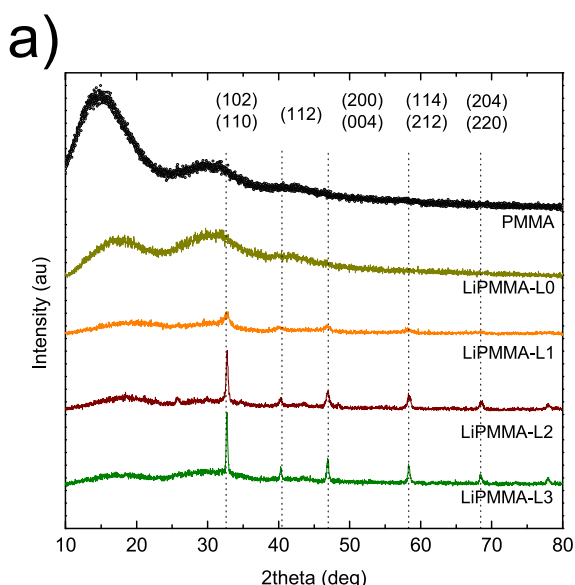


Table 1
Mean crystallite size of LLTO particles (D_{LLTO}) and fictive temperature (T_f) for PMMA and LiPMMA-LX with $X=0, 1, 2$ and 3 .

	D_{LLTO} (nm)	T_f ($^\circ\text{C}$)
PMMA	–	85(2)
X=0	–	82(1)
X=1	11.81(21)	87(2)
X=2	43.14(5)	81(1)
X=3	91.95(6)	79(1)

D_{LLTO} mean crystallite sizes were estimated from XRD data using the Scherrer equation and T_f was extracted from DSC data using the Moynihan method.

the presence of three broad peaks at $2\theta \sim 16, 30$ and 42° , ascribed to the typical PMMA mean coherence distances [23]. LiPMMA-LX with $X=0$ showed a notorious decrease in the intensity and broadening of the peak located at $2\theta \sim 16^\circ$ associated to the increase of the disorder on the polymer chains caused only by the simply addition of LiNO_3 salt. LiPMMA-LX with $X=1, 2$ and 3 , showed the presence of diffraction peaks ascribed to LLTO perovskite in a tetragonal structure with $P4/mmm$ spacegroup, in addition to the PMMA broad peaks at $2\theta \sim 18$ and 30° .

Both the broadening and decrease in the intensity of PMMA peaks in XRD patterns suggested that the addition of LLTO nanoparticles lead to a moderate increase in the disorder on the polymer chains of PMMA. The LLTO diffraction peaks showed a remarkable broadening with decreasing X , as expected for lower crystalline size in LLTO. The mean crystallite size (D), applying the Scherrer equation, showed $D \sim 10, 50$ and 100 nm, for $X=1, 2$ and 3 , as it is shown in Table 1.

DSC analysis (Fig. 1b) for PMMA showed a fictive temperature $T_f \sim 85(3)^\circ\text{C}$, in good agreement with the T_g usually observed for low molecular weight PMMA. LiPMMA-LX nanocomposites showed $T_f = 82(1), 87(2), 81(1)$ and $79(1)^\circ\text{C}$ for $X=0, 1, 2$ and 3 , respectively [24]. Raman spectra for sample references and LiPMMA-LX with $X=0, 1, 2$ and 3 are shown in Fig. 2a–e. LiPMMA-LX with $X=0, 1, 2$ and 3 spectra (Fig. 2b–e) showed the presence of typical peaks ascribed to PMMA and no evidence of polymer decomposition due to the preparation treatment was observed, as already observed for similar nanocomposites prepared under ultrasonic conditions [25].

PMMA peaks observed at $605, 817, 990, 1475$ and 1720 cm^{-1} are attributed to $\nu(\text{C}=\text{C})$ stretching, $\delta(\text{O}=\text{C}=\text{O})$ deformation,

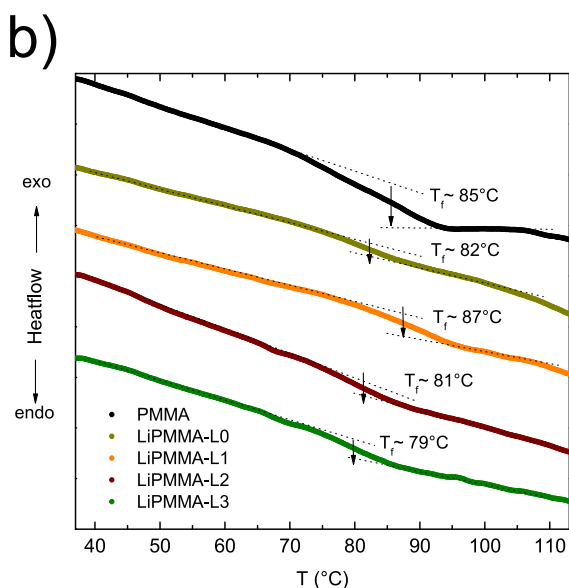


Fig. 1. X-ray powder diffraction patterns (a) and DSC profiles (b) for PMMA and LiPMMA-LX with $X=0, 1, 2$ and 3 .

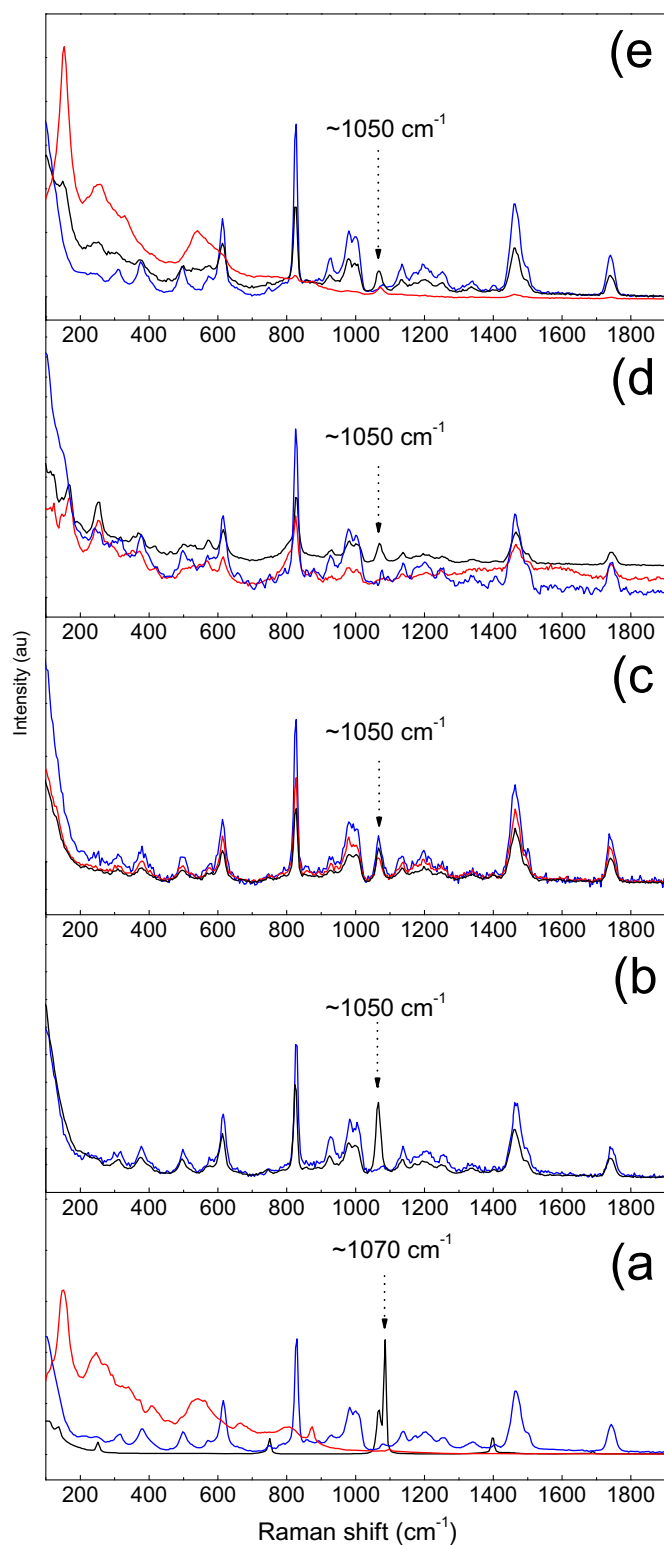


Fig. 2. Confocal Raman spectroscopy for LLTO (red), PMMA (blue) and LiNO_3 (black) sample references (a) and LiPMMA-LX with $X=0$ (b), 1(c), 2(d) and 3(e). Raman spectra ascribed to LLTO-rich, PMMA-rich and LLTO-PMMA interface zones are associated to the zones marked in Fig. 3, represented with red, blue and black lines, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$\nu(\text{O}-\text{CH}_3)$ stretching, $\delta(\text{H}-\text{C}-\text{H})$ deformation and $\nu(\text{C}=\text{O})$ stretching modes, respectively [25]. LiPMMA-L0 spectra (Fig. 2b) also showed a peak at $\sim 1050 \text{ cm}^{-1}$ attributed to the nitrate symmetric stretching. The peak ascribed to nitrate coordinated to lithium for

LiNO_3 salt is expected to be located at $\sim 1070 \text{ cm}^{-1}$, as it is shown in the Raman spectra in Fig. 2a. The shift of nitrate stretching mode toward lower wavenumber at $\sim 1050 \text{ cm}^{-1}$ is suggesting lithium nitrate dissociation [26], probably promoted by the lithium interaction with the polymer carbonyl groups, as it was observed in similar reports [27,28]. LiPMMA-L1 spectra (Fig. 2c) showed almost no differences respect to $X=0$ spectra for all zones analyzed, but only a low intensity shoulder at $\sim 145 \text{ cm}^{-1}$ ascribed to the LLTO A_{1g} mode, associated to the red spots shown in the confocal Raman image (Fig. 3). Moreover, the nitrate peak at $\sim 1050 \text{ cm}^{-1}$ was observed in all zones analyzed for $X=1$, suggesting that nitrate is homogeneously distributed and mostly uncoordinated to lithium. LiPMMA-L2 spectra (Fig. 2d) showed, in addition to PMMA peaks, the presence of well defined peaks at ~ 145 , 230 and 520 cm^{-1} ascribed to the LLTO A_{1g} , E_g and analogous E_g modes, respectively. The LLTO-rich zone, associated to red spots in Fig. 3, is more defined than for $X=1$ samples due to the higher Raman intensity of larger LLTO nanoparticles. The nitrate peak at $\sim 1050 \text{ cm}^{-1}$ was observed mostly at the LLTO-rich and LLTO-PMMA interface zones. The higher intensity of the nitrate peak at the LLTO-PMMA interphase is suggesting that LLTO nanoparticles are interacting with nitrate anions favoring the lithium dissociation in these nanocomposites. LiPMMA-L3 spectra (Fig. 2e) showed the presence of larger red spots in Fig. 3, ascribed to the larger size and clustering of LLTO nanoparticles. Raman spectra for the LLTO-rich zone showed the presence of peaks at ~ 145 , 230 and 520 cm^{-1} , already described previously.

Electrochemical impedance spectra in the Nyquist plane form are shown in Fig. 4. In all cases, the impedance spectra is composed by an arc circle at high frequencies related to the parallel combination of a resistance (R) and constant phase element (CPE), as a result of lithium migration in the nanocomposites. At lower frequencies, a typical straight line is observed related to the lithium diffusion-limited process usually modeled with the Warburg element (W). EIS analysis showed an enhancement in the lithium conductivity for all the different additions of LLTO nanoparticles respect to unloaded LiPMMA polymer, which usually shows a 10^{-7} – 10^{-5} S/cm lithium conductivity [29–31]. The total lithium conductivity (σ_{total}), obtained directly from the inverse of total impedance (Z_{total}), for all nanocomposites is shown in Table 2. As it is observed, an enhancement of one order of magnitude was evidenced for LLTO-PMMA nanocomposites respect to unloaded LiPMMA polymer. A maximum in the lithium total conductivity ($\sigma_{\text{total}} \sim 1.13 \times 10^{-4} \text{ S/cm}$) was observed for $X=2$, in which the LLTO crystallite size is $D \sim 50 \text{ nm}$. This large enhancement in the lithium conductivity was also observed recently in LLTO-PAN nanocomposites by Liu et al. [20]. In the before mentioned report, the large enhancement of lithium conductivity was mostly ascribed to the stronger affinity between the ClO_4^- anions and the nano-oxide surface, supplying a fast pathway for lithium mobility. In our work, we show empirical evidence of enhancement of lithium dissociation by means of confocal Raman spectroscopy supporting the idea that this mechanism is the responsible of the lithium-enhanced conductivity. Moreover, the addition of nanoparticles does not lead to relevant variations in the disorder on the polymer chains of the PMMA, respect to LLTO-unloaded PMMA. In this case, the dissociation of NO_3^- anions, probably enhanced by its interaction with the LLTO nanoparticles surface, leads to a remarkable increase in the lithium dissociation. For this reason, the Li ion conductivity enhancement reaches a maximum value of $\sigma_{\text{total}} \sim 1.13 \times 10^{-4} \text{ S/cm}$ at room temperature, for nanocomposites with a $D \sim 50 \text{ nm}$ LLTO crystallite size addition.

Z_{total} values are associated to the R value obtained from the model shown in Fig. 4.

In spite of the fact that the smaller crystallite size nanoparticles ($D \sim 10 \text{ nm}$), that could be associated to the highest surface area,

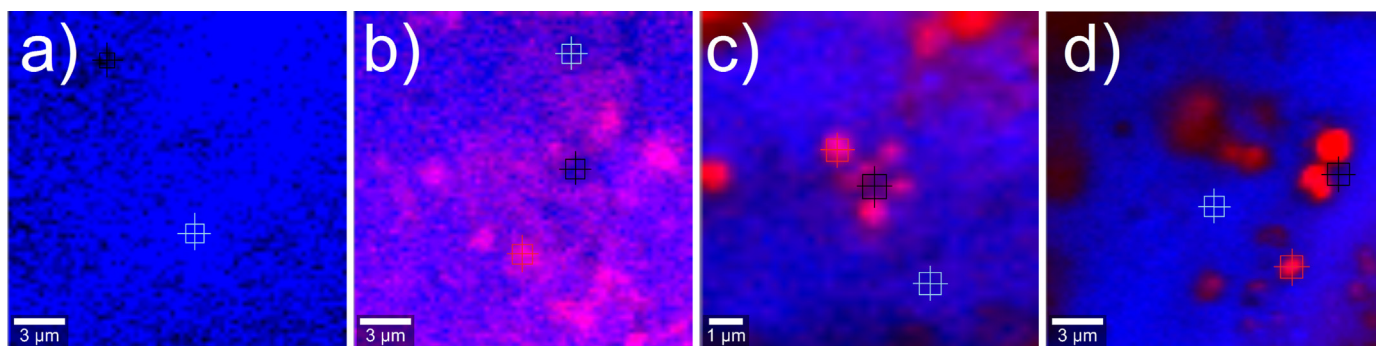


Fig. 3. Confocal Raman microscopy for LiPMMA-LX with X=0(a), 1(b), 2(c) and 3(d). The filtering of the LLTO A_{1g} mode at $\sim 145 \text{ cm}^{-1}$ and the PMMA $\nu(\text{C}=\text{O})$ mode at $\sim 1725 \text{ cm}^{-1}$ are shown in red and blue, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

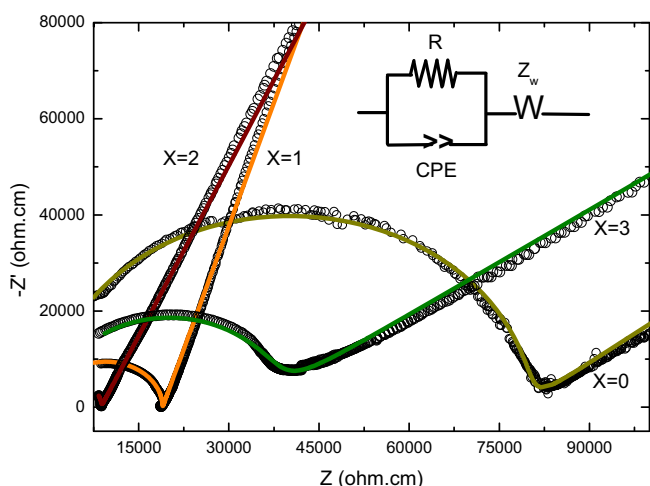


Fig. 4. Electrochemical impedance spectroscopy for LiPMMA-LX with X=0, 1, 2 and 3. Total impedance (Z_{total}) is marked with a dotted line.

Table 2

Total impedance (Z_{total}) and lithium conductivity (σ_{total}) for LiPMMA-LX with X=0, 1, 2 and 3.

	Z_{total} (ohm cm)	σ_{total} (S/cm)
X=0	$83,039 \pm 106$	$(1.204 \pm 0.002) \times 10^{-5}$
X=1	$19,262 \pm 23$	$(5.192 \pm 0.006) \times 10^{-5}$
X=2	8781 ± 17	$(1.139 \pm 0.002) \times 10^{-4}$
X=3	$42,460 \pm 65$	$(2.355 \pm 0.004) \times 10^{-5}$

the best lithium conductivity was not observed for this crystallite size but for larger LLTO crystallite size nanoparticles ($D \sim 50 \text{ nm}$) addition. This could be suggesting that smaller LLTO nanoparticles, with higher surface area, could be causing extra resistance to the total lithium migration through the polymer matrix. On the other hand, for larger LLTO crystallite size addition ($D \sim 100 \text{ nm}$), the lithium dissociation declines leading to a decrease in the conductivity. This is probably a consequence of the lower LLTO surface area, which leads to a declining in its interaction with nitrate anions and thus leading to less global dissociation of lithium, in relation to $D \sim 50 \text{ nm}$ LLTO addition.

4. Conclusions

We report the preparation and characterization of LLTO-PMMA nanocomposites with different crystallite sizes of LLTO nanoparticles. XRPD and DSC analyses showed a moderate increase in the disorder on the chains of PMMA of both LLTO loaded and

unloaded nanocomposites. Confocal Raman spectroscopy evidenced the lithium nitrate dissociation due to the increase of the Raman signal associated to free nitrate, especially in the proximities of LLTO-PMMA interface. For this reason, we conclude that the presence of LLTO nanoparticles favors the lithium dissociation in the polymer matrix. An enhancement in the lithium conductivity of more than one order of magnitude was observed for all LiPMMA-LX nanocomposites respect to LLTO unloaded LiPMMA polymer. The major lithium conductivity ($\sigma_{\text{total}} \sim 1.13 \times 10^{-4} \text{ S/cm}$) was observed for the nanocomposites with LLTO nanoparticles whose crystallite mean size was $D \sim 50 \text{ nm}$.

Acknowledgments

The authors wish to thank the Uruguayan funding institutions CSIC, ANII and PEDECIBA. We would like to thank financial support of ANII-POSNAC-2013-1-11169 PhD grant, ANII-FSE-1-2011-1-6458 and EQC-X-2012-1-14 research projects.

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