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Aqueous and non-aqueous Li^+/H^+ ion exchange in $Li_{0.44}La_{0.52}TiO_3$ perovskite

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ABSTRACT

The topotactic Li^+/H^+ exchange in $Li_{0.44}La_{0.52}TiO_3$ has been studied in different aqueous and non-aqueous media with different acidity. With this purpose, aqueous hydrochloric and nitric acid solutions and benzoic acid/ethanol solution were employed. The pristine and exchanged samples have been characterized by ^1H and ^7Li MAS-NMR, TGA and XRD techniques. Aqueous hydrochloric and nitric acid solutions produce the powders degradation and the subsequent formation of Li_2TiO_3 and $La_2Ti_2O_7$ phases. A detailed analysis of the ^1H MAS NMR spectra of exchanged samples indicate that Li^+/H^+ exchange reaction in pure water produced formation of LiOH at the particles surface, band at 0 ppm, that could subsequently carbonated after exposition in air. Furthermore the presence of other OH signals at 8, 6 and 2 ppm has been related to differences on octahedral Ti-O distances, produced by La/vacancy ordering in alternating planes of perovskites. In samples immersed into benzoic acid/ethanol solution results are similar, however the amount of LiOH species in particle surface is considerable lower. The exchange degree improved when increasing exchange temperature. The mechanical grinding of powders decreases the particle size improving exchange reactions; however, grinding treatments eliminated specific NMR bands of perovskite. In ground materials new ^1H NMR bands at 6 and 4 ppm were ascribed to an amorphous phase.

1. Introduction

The low working temperature is the main disadvantage of commercial Proton Exchange Membrane Fuel Cells (PEMFCs) devices. Much effort has been done to develop new proton conducting materials for intermediate temperatures (100–300 °C) ceramic fuel cells [1,2]. In this sense, Li^+/H^+ topotactic exchange reactions has been performed in Li ion conductors, such as $Li_2Ti_3O_7$ [3], $Li_2Ti_6O_{13}$ [4], $Li_4Ti_5O_{12}$ [5], $Li_{0.5}La_{0.5}TiO_3$ [6], $Li_5La_3Nb_2O_{12}$ [7] for preparing new proton solid electrolytes. In the case of the $LiMn_2O_4$, Li^+/H^+ exchange reaction produces oxidation of Mn^{3+} and partial dissolution of the starting spinel [8]. Most of these reactions take place in acidic medium, however some of them can also take place in pure water [9]. For instance the immersion of $Li_{0.30}La_{0.57}TiO_3$ in pure water increased considerably the pH as a consequence of Li^+/H^+ exchange processes. In this case, the titanate seems to dissociate water on the grain surface and then exchange Li^+ for H^+, with the subsequent formation of LiOH at surface particles which reacts with CO_2 to form Li_2CO_3. In these sense the use of organic acids in non-aqueous solutions could prevent the formation of hydroxides and the subsequent carbonation reaction.

On the other hand, the fresh concept of Li-redox flow batteries proposed by Goodenough et al. [10] and Zhou et al. [11], demands additional features to ionic conductors such as good chemical stability in aqueous solutions. In this context, the study of Li^+ for H^+ exchange reaction becomes useful to assess their capacity for future applications as separator (in between cathode and catholyte) in Li-Redox Flow Battery.

NMR spectroscopy is a useful tool to study Li^+/H^+ exchange reactions. In starting solids, location and mobility of Li ions can be analyzed by ^7Li MAS NMR spectroscopy. In proton exchanged materials, formation of OH groups and its interaction with adsorbed water can be investigated by ^1H MAS NMR technique. Li^+/H^+ exchange reactions inform us about stability of starting materials against acidic attack, providing interesting information about the nature of formed hydroxyl groups and the possible application of these compounds as proton electrolytes in fuel-cell devices.

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In this work, the $Li_{0.44}La_{0.52}TiO_3$ perovskite was prepared by solid state reaction and Li/H^+ exchange was studied in pure water, aqueous acidic media, non-aqueous and non-aqueous acidic organic media. The pristine and exchanged materials were characterized by TGA, XRD and high-resolution ^1H and ^7Li MAS NMR spectroscopy. To optimize Li^+/H^+ exchange reactions and reduce limiting kinetic effects, the temperature was increased and the particle size of the pristine sample was decreased by means of mechanical grinding. In resulting compounds the influence of adsorbed water on Li^+ and H^+ mobility was finally investigated.

2. Experimental part

2.1. Materials

The lithium lanthanum titanate $Li_{0.44}La_{0.52}TiO_3$ (named hereafter LLTO) was synthesized by conventional solid state reaction [12] (ceramic route). The reagents used were La_2O_3 (Aldrich 99.99%), Li_2CO_3 (Aldrich 99.99%), and TiO_2 (Aldrich). La_2O_3 powder was heated at 800 °C to eliminate surface carbonates prior to weighing. Stoichiometric amounts of reagents were ground together in an agate mortar and heated at 800 °C for 12 h to decompose Li_2CO_3. Reground products were cold-pressed at 150 MPa and heated at 1150 °C for 24 h. Finally, powders were pressed and heated again at 1350 °C for 6 h. In order to avoid lithium losses, the heating rate was 1 °C/min. Obtained powders were characterized by XRD to assess purity of prepared materials.

In titrations experiments, 0.5 g of prepared powders was neutralized with 1 mL of 0.5 M HCl or 0.5 M HNO_3 solutions, by addition of 0.1 mL every 10 min. The H^+ for Li^+ exchange was performed firstly in aqueous media by treating 0.5 g of the parent sample in 50 mL aliquots of either pure water, 1 M HCl or 1 M HNO_3 solutions. The experiments were carried out under constant stirring at room temperature and 70 °C. The reaction time was varied from 24 to 70 h. After reaction, powders were separated from the solution by paper filtration and finally water washed. The resulting powder was dried during 1 h in an oven at 120 °C to take off residual water. In a second set of experiments, the Li^+ for H^+ exchange was performed in ethanol with and without benzoic acid (10 g of C_6H_5COOH and 100 mL of ethanol). The powder (1 g) was placed into a round-bottom flask containing a magnetic stir bar. The solution was heated at reflux during one week. Finally, the resulting product was washed with ethanol, filtered, and dried at 70 °C.

The pH measurements were performed in a Metrohm 916 Ti-Touch pH-meter. A Metrohm glass electrode, special for organic solvents, was used. The pH values in ethanol were corrected according to the procedure described by Douheret [13].

To analyze the influence of the particle size on exchange reaction, the so-called ceramic powders of LLTO prepared by solid state reaction were mechanically milled in a planetary ball mill Pulverisette 5 (Fritsch) apparatus. The rotation speed of the vessel was 400 rpm, and alternating milling and pause times of 15 min were applied to avoid overheating of samples. Milling was performed at room temperature in agate and zirconia vessels, using 12–14 agate balls of 18–20 mm diameter, keeping a balls/powder mass ratio of 1:20. The powder mixtures were milled from 1 to 20 h. To characterize the so-called milled powders, XRD experiments were used to identify formed phases, and SEM technique to analyze the particles morphology.

2.2. - Characterization techniques

To characterize exchanged powders, XRD, TGA and MAS NMR techniques were used.

XRD patterns were recorded with Cu Kα radiation in a X'Pert Philips diffractometer, with ($\theta/2\theta$) Bragg-Brentano geometry, equipped with a curved graphite monochromator. Data were collected under ambient conditions, with 0.5° divergence, 0.01° receiving and 1° axial divergence soller slits. XRD patterns were recorded over the range $10 \leqslant 2\theta/° \leqslant 70$ (10–115° for Rietveld analyses), with 0.03 (or 0.02°) scan steps and 1 (or 10 s) counting times/step. In a first stage, XRD patterns were indexed with the Dicvol program; afterwards, patterns were analyzed with the Rietveld method, using the Fullprof program [14].

Thermo-gravimetric analysis of proton exchanged samples was performed between 30 and 900 °C, using a TA PerkinElmer Pyris 1 apparatus, with a heating rate of 10 °C/min under flowing nitrogen.

The ^7Li and ^1H NMR spectra were recorded at room temperature, after irradiation of samples with a single pulse (3 μs), in a MSL Bruker AVANCE 400 spectrometer ($B_0 = 9.4T$). The corresponding resonance frequencies of ^7Li and ^1H NMR signals were 155.5 and 400.13 MHz. In MAS experiments, the rotor was of Andrew type and the spinning frequency 10 kHz. The number of scans was 100 for both signals. The analysis of NMR spectra was performed with the Winfit (Bruker) software package. Intensity, position and linewidth of components were determined with a non-linear iterative least-squares method. Chemical shift values of NMR components were referred to those of TMS and 1 M LiCl solution. From fitting of experimental envelopes, relative intensities of resolved components were deduced.

3. Results and discussion

The XRD pattern of the slowly cooled $Li_{0.44}La_{0.52}TiO_3$ pristine sample corresponds to that reported previously for single perovskite phases [12]. In this sample, XRD peaks were indexed with a doubled tetragonal perovskite ($a_p \times a_p \times 2a_p$) with unit-cell parameters, $a = 3.8686(10)$ Å and $c = 7.7354(14)$ Å, (S.G. P4/mmm) [12]. The c-parameter doubling of the perovskite is a consequence of the preference of La for La1 (0, 0, 0) sites, while A-site vacancies are allocated at La2 (0, 0, 1/2) positions [15,16]. The arrangement of vacancies at alternating planes is responsible for distortion of TiO_6 octahedra, with two apical Ti-O distances, one shorter and one larger, 1.85 and 2.05 Å, and four basal ones, 1.95 Å. When Li content increases this preference decreases and octahedra becomes regular with six Ti-O distances ~1.95 Å.

Li^+ ions have smaller size than La^{3+} ions making that Li coordination at A sites was not possible (Li-O = 2.1 Å vs. La-O = 2.56 Å). In these perovskites, as demonstrated by neutron diffraction experiments, Li ions are fourfold coordinated at square windows that connect contiguous A-sites of the perovskite [17]. Depending of the composition, the amount of Li at $z = 1/2$ planes change respect to $z = 0$ planes, being considerably higher for samples with low Li content, favoring a bidimensional conductivity in LLTO perovskites [18]. The resulting distribution of lithium can be considered a consequence of the asymmetric arrangement of La ions.

3.1. Li^+/H^+ exchange in LLTO ceramic powders

Li^+/H^+ exchange reactions in LLTO powders were carried at room temperature and 70 °C by using different exchange media: pure water, acidic 1 M HCl or HNO_3, ethanol and ethanol/benzoic acid solutions.

Fig. 1 (top) shows the time evolution of pH for 50 ml H_2O solutions with different amounts of LLTO at room temperature. In all cases, the pH increases immediately after addition of the LLTO powder in the solution, indicating the formation of a basic solution with a characteristic pH value. This result indicates that Li^+ ions

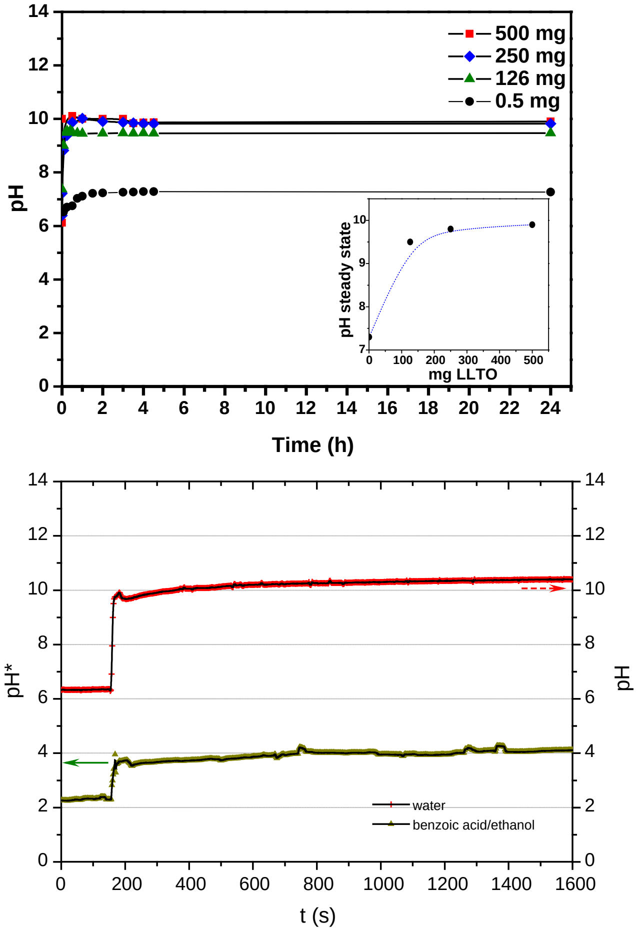

Fig. 1. (Top) pH evolution in pure water after immersion of different quantities of LLTO in 50 ml solution at room temperature. The inset shows the evolution of pH in the steady state (time higher than 2 h) against amounts of LLTO. (Bottom) Evolution of the pH with the immersion time in a benzoic acid/ethanol solution (These pH data have been corrected according Douheret [13]). Data are also compared with those obtained by immersion in water in the same conditions.

have been exchanged by H^+ in the perovskite, increasing the amount of OH^- in the solution [6], according the reaction.

$$Li_{0.44}La_{0.52}TiO_3 + xH_2O \rightarrow H_xLi_{0.44-x}La_{0.52}TiO_3 + x\ Li^+ + x\ OH^- \quad (1)$$

The easy exchange of mobile lithium by protons of water indicates that stabilization of Li in perovskites is rather low and formation of OH^- groups is favored. This observation agrees with those reported in previous works on Li^+/H^+ exchange reactions of Li-perovskites [9] and Li-garnets [19–21]. On the other hand, the increment of LLTO concentration (mg of LLTO/mL of H_2O) was accompanied by the increment of the solution pH from 7 to a maximum value of 10 (inset of Fig. 1, top).

Fig. 2 shows the titration curves, i.e., pH values measured as a function of the volume of acid added into the solution used for the Li^+/H^+ exchange reaction (0.5 g of LLTO in 50 mL of water). The titration experiments were performed with 0.5 M HCl (a) and HNO_3 (b) solutions. All titration curves recorded at room temperature and 70 °C display a similar shape. After addition of LLTO to water the pH increased near 10. The addition of acid aliquots makes to decrease quickly the pH of the solution up to a value near 3.3; then, continues to drop, but more slowly to get values close to 2 for solutions saturated with acid. The inflexion point takes place at pH ~ 3, independently of the acid used. Similar behavior was

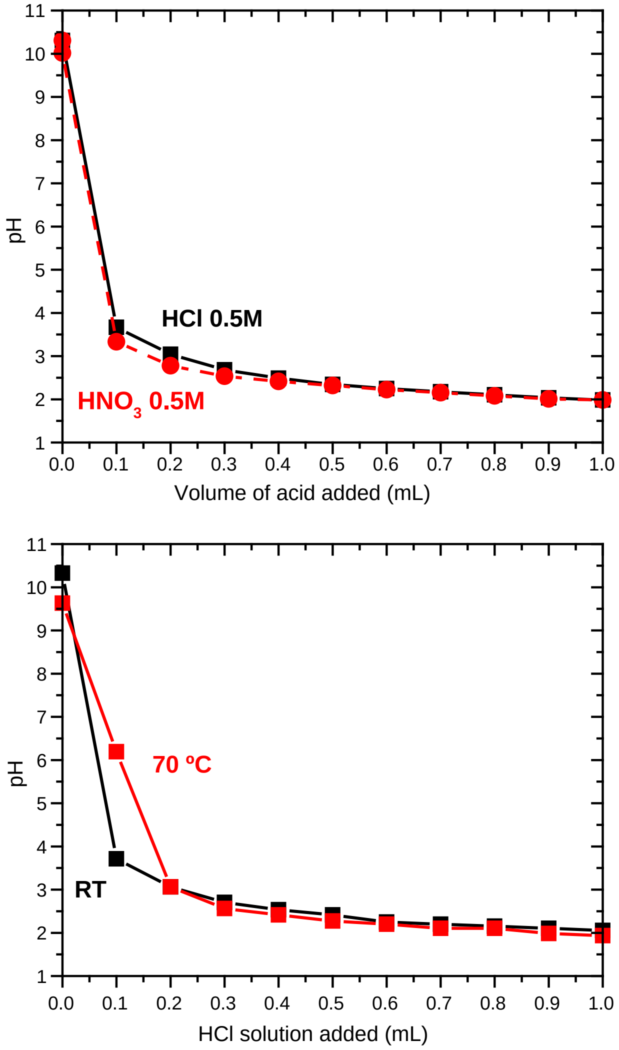

Fig. 2. (Top) Titrations of LLTO powder with 1 ml of HCl and HNO_3 0.5 M. (Bottom) Titrations at room temperature and at 70 °C adding 1 ml of HCl 0.5 M.

found in $Li_4Ti_5O_{12}$ spinel material [5], and in layered Na-magadiite after acid addition [22]. In both cases, the buffer region was achieved at higher pH value; in the case of the silicate magadiite, both regions were separated by an extended plateau. The first stage of titration curves, in which the pH changes quickly from 10 to 3.3, could be related to the neutralization of species LiOH present in solution or adsorbed at the perovskite particles surface. The second one (from 3.3 to 2) could correspond to the real Li^+/H^+ exchange process, with the plateau (amount of added acid) strictly related to the amount of exchanged lithium.

To avoid the participation of water in titration, the Li^+/H^+ exchange was investigated in a benzoic acid/ethanol solution. This study has also been performed in other Li ionic conductors, such as Li-garnets [23], but it has not been yet reported in lanthanum-lithium titanates. In Fig. 1 (bottom) the time evolution of the pH for benzoic acid/ethanol solution is displayed and compared with that of water solutions. A quick increase of pH, around 1 unit was observed when the solid was added to the organic acid solution. Afterwards, no appreciable changes were observed on the pH with time.

Exchanged powders were analyzed by XRD, TGA, titrations, and ^1H and ^7Li NMR techniques. These analyses were carried out, after extraction of powders from solutions, following the procedure described in the experimental section.

In Fig. 3, XRD patterns of the pristine (a), sample treated 70 h at 70 °C with pure water (b), sample treated with 1.5 M $C_6H_6CO_2H$/EtOH (c), 1 M HCl (d) and 1 M HNO_3 (e) solutions are depicted. Two different situations have been found. In the case of samples treated in pure water and benzoic acid/ethanol solution, XRD patterns are similar to those of the parent compound, indicating that exchange reactions proceed through a topotactic reaction, preserving the perovskite structure. The crystallinity of samples, deduced from XRD peaks linewidth, does not change significantly with applied treatments. Unit cell parameters slightly change after exchange reactions (see Fig. 3) displaying a smooth expansion of the unit cell volume; 0.6% and 0.2% for water and benzoic acid treatments respectively. In the case of the sample treated with acid solutions several secondary phases were detected in XRD patterns (lithium titanate Li_2TiO_3 and pyrochlore $La_2Ti_2O_7$), indicating that stability of LLTO perovskites in aqueous acid media is limited. According to this, acid treatment of perovskites produces besides Li^+/H^+ exchanges, La extraction and Ti-O-Ti breaking, favoring the perovskite degradation and the subsequent formation of binary Li_2TiO_3 and $La_2Ti_2O_7$ phases.

Li^+/H^+ exchange was analyzed in non-degraded perovskites. Fig. 4 shows the thermogravimetric curves, recorded in the temperature range 50–900 °C on exchanged LLTO samples prepared in water and benzoic acid. The weight loss detected between RT and 200 °C was related to desorption of water. The same behavior was detected between 200 and 500 °C in two type of samples, indicating that similar species were produced during benzoic acid treatments. The greater weight loss detected above 500 °C in samples prepared in pure water has been attributed to the elimination of carbonates retained by water exchanged samples. The last weight loss, not always detected in TGA curves, was related to the formation of carbonates by exposition of samples to CO_2 [24]. As stated before, the formation of carbonates require high pH values formed during exposition of samples to water [25].

The ability of exchanged samples to carbonation has been previously reported in samples exchanged in water, showing that elimination of surface carbonates by heating at 500 °C favored the reincorporation of Li in perovskites [24,25]. The thermal decomposition of LLTO results from differences on H^+ and Li^+ diffusion: if Li^+/H^+ exchange is favorable, Li reinsertion was produced, if exchange reactions are slower, the perovskite decomposition was produced. If carbonates are segregated, thermal treatment of samples could produce the formation of Li_2O at the particles surface. In this case, the elimination of water from the perovskite will produce its decomposition.

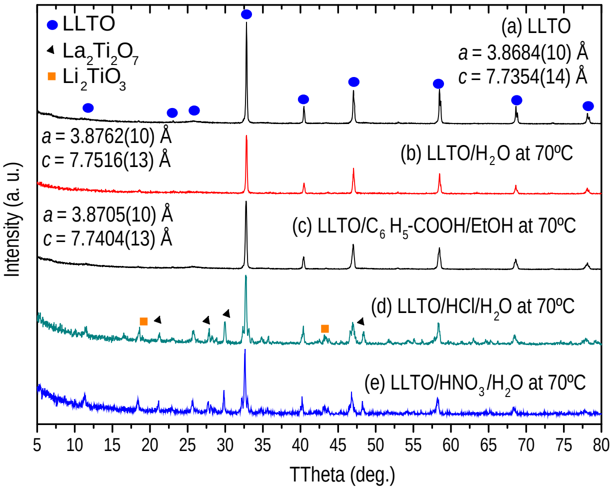

Fig. 3. XRD patterns of pristine samples (a) and after immersion, during 70 h at 70 °C, in pure H_2O (b), $C_6H_6CO_2H$/EtOH (c), HCl (d) and HNO_3 (e).

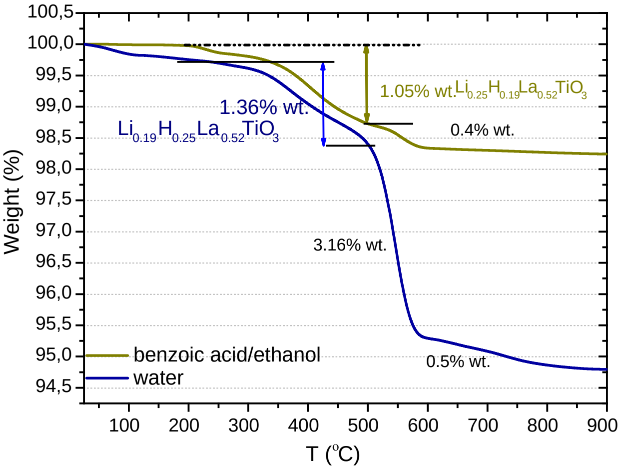

Fig. 4. TGA curves of exchanged samples prepared using pure water and benzoic acid solutions. The weight loss for each sample is also indicated and the stoichiometric formula deduced from the weight loss between 200 and 500 °C. Other weight loss associated to the carbonates decomposition are also indicated (see text).

LiOH species can also be dissolved and removed from the surface of the particles by repeated washing of samples favoring stabilization of acid forms of perovskites. In samples not exposed to CO_2, the amount of exchanged Li^+ can be determined from the weight loss produced between 200 and 500 °C. The weight loss detected in samples exposed to water or treated with benzoic acid/ethanol solutions must be ascribed to elimination of water produced by condensation of OH groups formed during exchange treatments. Taking into account that the oxidation state of La and Ti does not change during thermal treatments, the weight loss produced between 200 and 500 °C, has been used to estimate the hydroxyl content of exchanged samples (see Table 1).

Taking into account that diffusion processes controls exchange reaction, the amount of exchanged Li will depend on temperature, reaction time and immersion media. According to this, the amount of protons increases with immersion time and temperature, being water more effective than EtOH/benzoic acid solutions. The amount of Li exchanged is slightly lower than that reported by Boulant et al. [25], using pure water at 70 °C and samples prepared by sol-gel technique. This observation suggests that Li/H exchange is also controlled by particle surface area. In our case, long periods of time are required to compensate kinetic effects, favoring the extensive carbonation of samples, and decreasing exchange reversibility [9,25].

3.2. Li^+/H^+ exchange in LLTO milled powders

In order to minimize kinetic effects that limit the amount of exchanged lithium, the particle size of LLTO sample was reduced by mechanical milling. When balls and container of agate were used, XRD patterns always showed peaks of silica, even for low milling times. For this reason, the milling was performed in zirconia vessels. During the grinding process, powders are in physical contact with the impacting balls and the container chamber walls. This leads to the contamination of surface particles, which was difficult to detect by XRD. Considering that contamination processes affect mainly crystallites surfaces, the amount of Zr detected by EDS (about 5%wt) should be clearly overestimated. Since no displacements of XRD peaks were detected, the incorporation of Zr atoms to the perovskite structure must be discarded.

Table 1
Chemical composition of exchanged samples under different conditions obtained by TGA experiments. Data of milled samples (milled_w_70) are also included.

Label	Immersion media	Immersion time	% Weight loss (200–500 °C)	Formula
Pristine	–	–	–	$Li_{0.43}La_{0.52}TiO_3$
w_50	H_20 at 50 °C	72 h	1.36%	$H_{0.25}Li_{0.19}La_{0.52}TiO_3$
b_70	EtOH/benzoic acid at 70 °C	168 h	1.05%	$H_{0.19}Li_{0.25}La_{0.52}TiO_3$
w_70	H_20 at 70 °C	24 h	0.7%	$H_{0.13}Li_{0.31}La_{0.52}TiO_3$
milled_w_70	H_20 at 70 °C	24 h	1.0%	$H_{0.18}Li_{0.26}La_{0.52}TiO_3$

The effect of milling treatments (1, 3, 5, 10, 15 and 20 h) was followed by XRD technique (Fig. 5). The milling of samples produces broader and less intense Bragg peaks. This phenomenon was remarkable during the first 5 h of milling: after this treatment, intensity losses become smaller; appearing diffuse halos of amorphous materials below diffraction peaks after 20 h of milling. Another important point is the absence of extra peaks for long milling times, indicating that analyzed materials do not decompose into other oxides.

After milling, the Li^+/H^+ exchange reaction was investigated in the same conditions that in pristine powders (pure water at 70 °C during 70 h). TGA plots of samples milled 20 h, display an additional small weight loss (from RT to 200 °C), associated with superficial water, non detected in pristine samples, where perovskite particles are bigger (Fig. 6). As above mentioned, the second weight loss detected between 200 and 500 °C, was ascribed to elimination of OH^- groups created during Li^+/H^+ exchange. In milled samples, the weight loss was slightly higher than in the pristine one, suggesting that milling treatments favor proton incorporation.

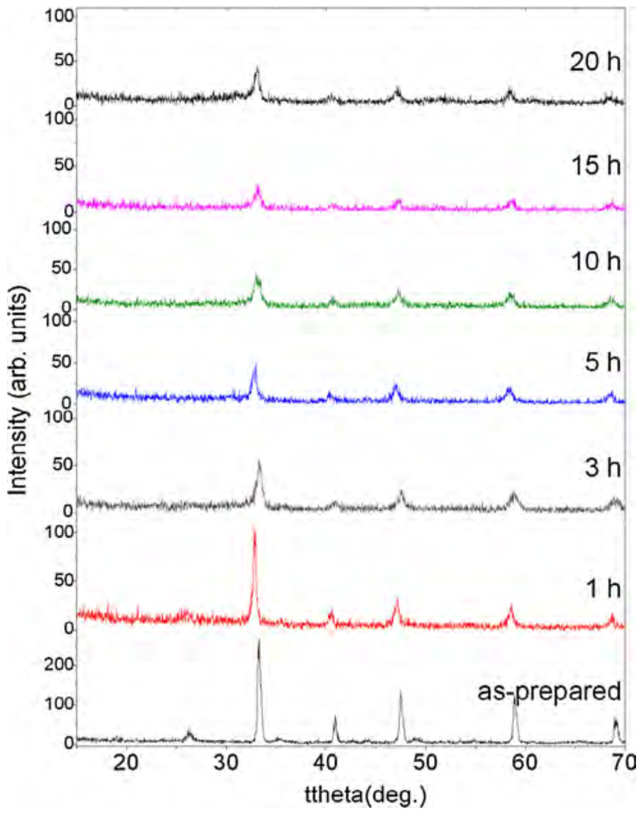

Fig. 5. Evolution of the XRD patterns with the milling times.

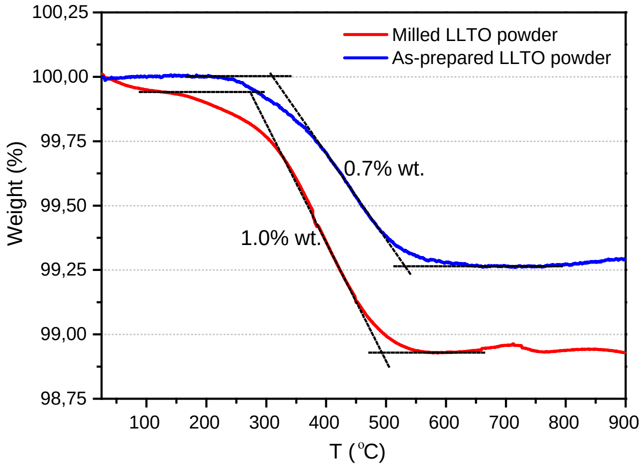

Fig. 6. TGA curves of exchanged samples (pristine and 20 h milled) by immersion in pure water at 70 °C during 24 h.

3.3. MAS NMR characterization

Structural refinements could not be performed on XRD patterns, requiring neutron diffraction techniques to localize protons incorporated in perovskites during exchange processes. The partial exchange produced in water makes this analysis difficult, making spectroscopic ^7Li and ^1H NMR studies more appropriated to determine sites occupied by Li^+ and H^+ ions.

3.3.1. Ceramic powders

Fig. 7 (top) displays ^1H MAS NMR spectra recorded at room temperature on: pristine sample (black), sample exchanged in water at 70 °C for 70 h (green), and sample exchanged in a benzoic acid/ethanol solution during one week (red line). In pristine sample, the presence of OH^- groups was not expected; however, ^1H MAS NMR spectrum reveal~~s~~ a small broad line located at 6.5 ppm, which could be ascribed to OH^- groups formed in surface particles of perovskites. In exchanged samples, three lines were detected at ~8, 6 and 2 ppm. According to the previous work of Boulant et al. [9], three detected signals correspond to different OH^- groups generated in exchanged perovskites. In Li^+/H^+ exchanged samples, the band detected at 0 ppm was ascribed to LiOH species accumulated at the surface particles. According to TGA experiments, the amount of LiOH retained at the particles surface is bigger in samples exchanged in water than in benzoic acid/ethanol solution.

In perovskites, oxygen atoms are surrounded by two Ti and four La cations. The existence of alternating La and vacancy rich planes justify a differentiation of oxygen atoms in Ti octahedra. Structural refinements performed with neutron diffraction showed that Li ions are fourfold coordinated at square windows that connect contiguous A-sites of perovskites. If H^+ ions substituting Li^+ ions, remain in square windows occupied by Li^+ ions, several OH^- groups can be formed. According to structural refinements performed in doubled perovskites, O3 atoms are associated with a higher number of vacant/Li sites than O1 oxygens bonded to a

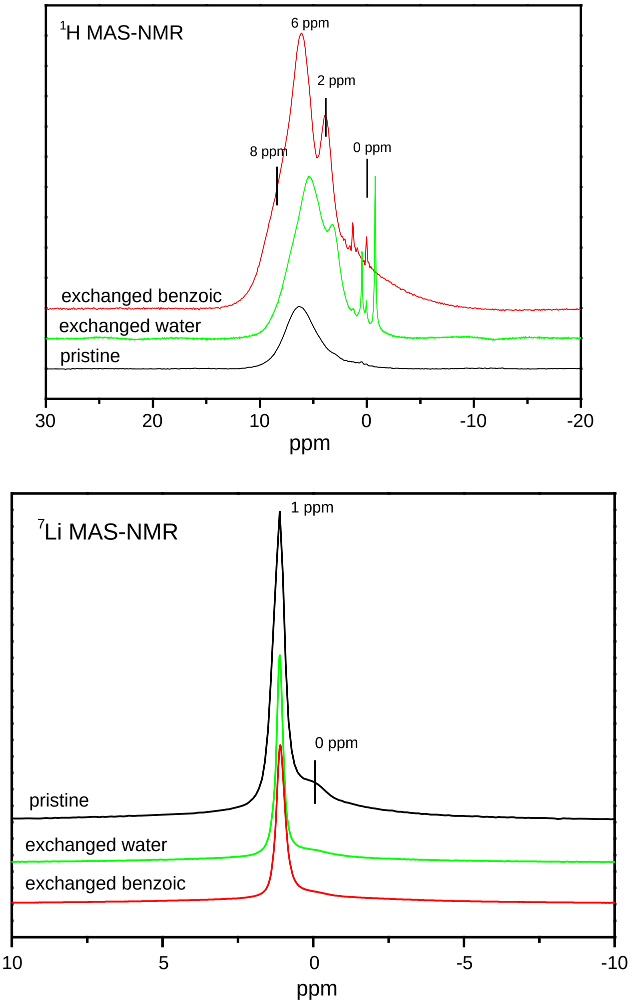

Fig. 7. ^{1}H MAS NMR (top) and ^{7}Li NMR MAS (bottom) spectra of pristine material (black), exchanged in water at 70 °C and 70 h (green) and in benzoic acid/ethanol solution during one week (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

higher amount of La cations [18]. The shift of Ti from the center of octahedra makes Ti-O3 distances shorter (1.85 Å) in vacancy/Li-rich planes that Ti-O1 ones (2.05 Å) in La-rich planes. In Ti octahedra, basal Ti-O distance are near 1.95 Å. Based on these considerations, O3 should be more negatively charged than O2, and O2 more negative than O1 oxygens. Differences on oxygen charge could explain differences on chemical shift values of OH protons; then, detected components at ~8, 6 and 2 ppm have been assigned to protons located at O3, O2 and O1 oxygens. From this fact, the first type of protons should be ascribed to vacancy-rich planes and the last type to La-rich planes. Taking into account different multiplicity of oxygen sites (1:4:1) intensity of the band related to O2 should be higher than those of O1 and O3 oxygens.

In general, more acid OH^- groups are shifted towards 10 ppm and basic ones towards 0 ppm. The location of H^+ ions at square windows will favor hydrogen bonds between contiguous oxygens, stabilizing the acid forms of LLTO perovskites. Taking into account this fact, distribution of OH^- will not be homogeneous and some accumulation of OH^- groups at vacant-rich planers would be produced. Moreover, H^+/Li^+ exchange inside particles is preceded by diffusional processes that make easier proton incorporation at surface particles [24,25]. From this fact, a reversible Li^+/H^+ exchange will be difficult to produce, favoring the OH^- accumulation at the surface particles. This makes sintering of particles difficult, increasing grain boundary chemistry a limiting factor for transport properties in LLTO ceramic samples.

The corresponding ^{7}Li MAS NMR spectra of parent and exchanged samples are given in Fig. 7 (bottom). Spectra of the pristine and exchanged samples display two signals at ~1 and 0 ppm; one with higher intensity, ascribed to Li^+ ions of the perovskite, and other much less intense, ascribed to Li^+ ions of $LiOH/Li_2CO_3$ species formed at particles surface. Two Li sites of perovskite were not resolved, probably because Li exchange motions. The proton mobility is lower making possible the resolution of different environment in ^{1}H MAS NMR spectra. In samples exchanged with benzoic acid in ethanol solution, results are similar to those obtained in water; however, the amount of LiOH species formed at the particles surface is appreciably lower than in water exchanged samples.

3.3.2. Milled powders

Intensity of ^{7}Li and ^{1}H MAS NMR components depend on crystallinity of the sample, particles size and exchange treatments. ^{7}Li MAS NMR spectra of samples, after 20 h of milling, show the progressive decrease and broadening of the signal located at 1 ppm and the detection of a new intense broad line at 0 ppm (bottom of Fig. 8). Both observations indicate the formation of an important

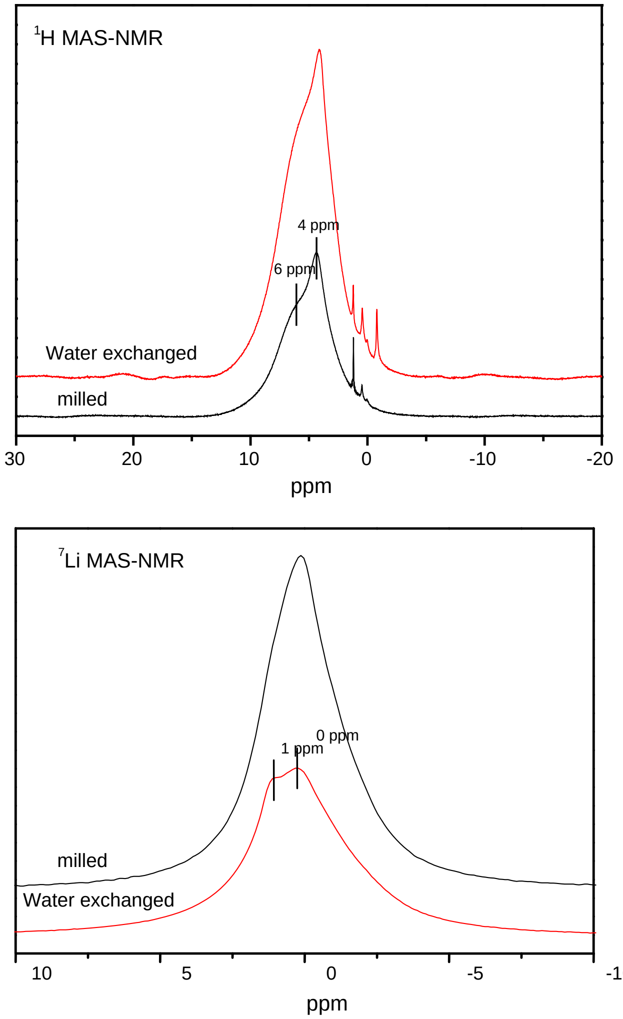

Fig. 8. ^{1}H MAS NMR and ^{7}Li NMR MAS spectra of milled (black) and water exchanged milled samples (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

amount of $LiOH/Li_2CO_3$ species at surface particles. These species do not participate to XRD patterns of milled samples.

After milling, ^1H MAS NMR spectra show the presence of two components at 6 and 4 ppm (top of Fig. 8). Both components have been ascribed to OH^- groups created during milling process. The first component could be ascribed to a highly disordered perovskite and the new component to amorphous generated phases. It is important to remark that neither acidic species at 8 nor basic ones at 3 ppm are detected in milled samples, indicating that structure of the starting perovskite is seriously affected by milling treatments.

4. Concluding remarks

Topotactic Li^+/H^+ exchange reactions produced in different media (benzoic acid/ethanol, water and acidic aqueous solutions) have been investigated in $Li_{0.44}La_{0.52}TiO_3$ perovskite. The products with different Li^+/H^+ exchange levels were analyzed by ^1H and ^7Li MAS NMR, TGA and XRD techniques, concluding:

(1) Exchange reactions produced in water favor the formation of LiOH species at the particles surface that can be subsequently carbonated. In acid treatments, basic species are not formed; but, the partial dissolution of $Li_{0.44}La_{0.52}TiO_3$ perovskite was produced. The precipitation of dissolved species leads to the formation of Li_2TiO_3 and $La_2Ti_2O_7$ phases.

(2) To avoid the perovskite degradation, exchange reactions were produced in benzoic/ethanol solutions (absence of water), concluding that formation of proton exchanged perovskites is preponderant, decreasing considerably the importance of dissolution/recrystallization processes. In these samples, Li^+/H^+ exchange kinetic becomes slower, requiring higher reaction time.

(3) To avoid limiting kinetic effects, the influence of mechanical grinding treatments was investigated. In this case the amount of exchanged species increases; however, the formation of amorphous phases makes difficult the analysis of structural modifications produced in proton exchanged perovskites.

(4) In proton exchanged perovskites, three detected signals at ~8, 6 and 3 ppm were ascribed to different OH^- groups, produced by Ti shift induced by lanthanum ordering. The acid/basic character of formed hydroxyls was investigated by means of ^1H MAS NMR technique. In $Li_{0.44}La_{0.52}TiO_3$ samples exchanged in water, part of formed hydroxyls display acid character that make of exchanged perovskites potential solid-electrolytes for fuel-cells. In this case, materials should be prepared in acidic media to eliminate basic species from the particles surface, what unfortunately reduces stability of perovskites.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apt.2016.10.020.

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