C.K. RHEE◐[1*], Y.B. CHUN◐[1], S.H. KANG◐[1], W.W. KIM◐[1], G. CAO[2]

LITHIUM-ION CONDUCTIVE FILM MEMBRANE OF $Li_{0.3}La_{0.57}TiO_2$ PEROVSKITE STRUCTURE AND ITS APPLICATION IN Li-AIR BATTERIES

Impacts of precursor solution recipe, processing parameters, and pellet thickness on the lithium ionic conductivity of the ceramic materials with perovskite structure of $Li_{0.3}La_{0.57}TiO_3$ were investigated and new method was proposed to synthesize $Li_{0.3}La_{0.57}TiO_3$ solid state electrolyte. The results showed that ionic conductivity of $Li_{0.3}La_{0.57}TiO_3$ membrane which was synthesized by firstly forming colloidal TiO_2 (i.e., TiO_2 sol) and then Li^+ and La^+ were added to the colloidal TiO_2 was on the order of 10^{-5} S/cm. It also showed that the temperatures corresponding to a full decomposition for $Li_{0.3}La_{0.57}TiO_3$ is about 750°C and materials start forming perovskite structure when temperature reaches about 900°C and the lithium ionic conductivity gains about 21% increase when the pellet thickness is reduced to about ¼.

Keywords: Lithium-ion conductive film; membrane; $Li_{0.3}La_{0.57}TiO_2$; perovskite structure; Li-air batteries

1. Introduction

Lithium-air batteries are a type of the most promising energy storage device that has both high energy density and high power density and are therefore potentially suitable for application to electric vehicles [1-3]. A lithium air battery typically consists of an anode made of lithium foil, a cathode comprised of porous carbon adsorbed by for example Pt nanoparticles or metal oxide nanoparticles as catalyst, and a liquid electrolyte filled between the anode and cathode to fulfill ion transport.

From the charge-discharge processes, it can be seen that the electrolyte plays an important role in transporting lithium ions [4,5], However, the use of non-aqueous electrolyte unfortunately brings about a negative impact on the battery performance, since the product at the cathode during the discharge process cannot well dissolve in a non-aqueous electrolyte and thus causes clogging to the cathode [6,7]. To solve the clogging problem, a new design of the lithium air battery structure has been developed by adding a solid state electrolyte membrane between the anode and the cathode so as to use non-aqueous electrolyte on the anode side and however use aqueous electrolyte on the cathode side [8].

Research in this aspect is still at its early stage and commercial product of this type of membrane is very limited at present. The existing membrane materials for lithium conduction mainly include ceramics with Na super-ionic conductor (NASICON) structure which can be described as $LiM_2(PO_4)_3$ (M = Ti, Zr, Ge, Hf), garnet structure with the formulas $Li_5La_3M_2O_{12}$ (M = Nb, Ta) or $Li_6ALa_2M_2O_{12}$ (A = Ca, Sr, Ba; M = Nb, Ta), perovskite structure represented by lithium lanthanum titanate [(Li, La) TiO_3], Li_2S-based glasses, and polymer-based lithium ion conduction materials based on the general consideration of lithium ionic conductivity and chemical stability [9-13].

In this paper, focus has been made on the ceramic materials with perovskite structure of $Li_{0.3}La_{0.57}TiO_3$ in terms of their synthesis, crystal structure characterization, and lithium ionic conductivity.

2. Experimental

The methods for the materials synthesis are based on the preparation of precursor using a solution-based approach. The typical procedures for the synthesis of $Li_{0.3}La_{0.57}TiO_3$ are described as follows: 26.42 g of $LaAc \cdot 1.5H_2O$(Merck, 99.9%) and 4.08 g of $LiAc \cdot 2H_2O$(Merck, 99.0%) were added into 180 mL of DI-water and the solution was fully stirred to get the Li and La solution completely dissolved. In a separate beaker, 160 mL of TiO_2 sol was prepared with a method described elsewhere [14].

[1] KOREA ATOMIC ENERGY RESEARCH INSTITUTE, DAEJEON, 34057, REPUBLIC OF KOREA
[2] UNIVERSITY OF WASHINGTON, SEATTLE, WA 98195, USA

* Corresponding author: ckrhee@kaeri.re.kr

The Li and La solution was then poured into the TiO_2 sol and the mixture was stirred for at least 30 min to form an uniform system comprised of TiO_2 sol and Li and La solution. The mixture solution was then transferred to a furnace and was dried at 125°C, resulting the formation of a dry powder containing Li, La, and TiO_2.

The as-prepared dry powders were then further thermally treated before being used for making pellets, in order to decompose acetate or nitrate salts in the precursor so as to avoid a too much change in the volume of pellets during sintering. The thermal treatment temperature for this purpose was determined by a TGA analysis. Cold press was adopted to make pellets by compressing the powders that have undergone the thermal treatment. The pellets were sintered at a certain temperature, which is required to be as high as enabling the materials to form a liquid phase. The sintered pellets were then deposited with Au or Ag electrode and studied with their lithium ionic conductivity using impedance technique. Ion conductivity of the pellets were performed in air using Li-ion blocking Au-electrodes (Au paste cured at 700°C for 1 h) using an impedance and gain-phase analyzer (HP 4192 A). Prior to each impedance measurement, the samples were equilibrated for 3 h at constant temperature.

3. Results and discussion

3.1. Influence of the method for introducing titanium source on lithium ionic conductivity of $Li_{0.3}La_{0.57}TiO_3$

$Li_{0.3}La_{0.57}TiO_3$ pellets have been prepared and the lithium ionic conductivity of $Li_{0.3}La_{0.57}TiO_3$ was measured. With the total resistance reflected on the impedance spectra, the lithium ionic conductivity, σ, can be calculated according to $\sigma = d/(AR)$, where d is the thickness of the pellet, A is the area of metal electrodes, and R is the total resistance, i.e., the sum of bulk resistance and grain boundary resistance. It can be seen that the lithium ionic conductivity of the $Li_{0.3}La_{0.57}TiO_3$ synthesized at

1200°C is on the order of 10^{-6} S/cm. Such a value is much lower than the reported ones (on the order of $10^{-4} \sim 10^{-3}$ S/cm) mainly due to the relatively low temperature we used for sintering at this stage, which is lower than the melting point of the material and cannot result in the formation a liquid phase.

In order to increase ionic conductivity of the $Li_{0.3}La_{0.57}TiO_3$, three methods which are different in the way to introduce titanium source have been studied to reveal the influence of the method for introducing titanium source on the lithium ionic conductivity of $Li_{0.3}La_{0.57}TiO_3$.

Method 1: The sample was synthesized when Li^+ and La^+ was present during the preparation of a TiO_2 sol through the hydrolysis of titanium isopropoxide in an aqueous solution containing acetic acid. In this method, the formation of Li-La-TiO_3 was thought to start at the molecular level.

Method 2: The sample was synthesized by firstly forming colloidal TiO_2 (i.e., TiO_2 sol) and then Li+ and La+ were added to the colloidal TiO_2. With this method, the Li^+ and La^+ ions take a diffusion way to penetrate into the colloidal TiO_2, and therefore compared to the sample prepared with Method 1, it is expected that more lanthanum vacancy defects can be formed within the $Li_{0.3}La_{0.57}TiO_3$.

Method 3: The sample was prepared with a coagulated solution method mentioned above using commercial P25 TiO_2 nanoparticles.

From the results listed in TABLE 1, we can see that the grain conductivities for samples 2 and 3 are higher than those for sample 1, indicating that the diffusion of La^+ benefits to the formation of lanthanum vacancy defects. The grain conductivities for sample 3 are generally higher than those for sample 2, indicating that more lanthanum vacancy defects can form in the case of P25 nanoparticles compared to the case of colloidal TiO_2. However, the overall conductivity for sample 3 sintered at 1200°C is smaller than that for sample 2. The reason may be from the agglomeration of TiO_2 nanoparticles, resulting in non-ideal packing when a bulk material is formed. All samples

TABLE 1

Impact of method adopted to introduce titanium source on the lithium ionic conductivity of $Li_{0.3}La_{0.57}TiO_3$

Method/Samples	Sintering Temperature (°C)	Grain Conductivity (S/cm)	Overall Conductivity (S/cm)	Condition
Method1/Sample1 (Li^+ and La^+ reacting with TiO_2 at molecular level)	1000	5.22×10^{-5}	1.30×10^{-7}	In Air
	1100	5.76×10^{-5}	2.28×10^{-7}	In Air
	1200	1.82×10^{-4}	1.12×10^{-6}	In Air
	1300	1.44×10^{-4}	1.66×10^{-5}	In Air
Method2/Sample2 (Use Colloidal TiO_2)	1000	1.79×10^{-5}	1.82×10^{-7}	In Air
	1100	7.37×10^{-5}	5.13×10^{-7}	In Air
		7.96×10^{-5}	1.79×10^{-7}	In O_2
	1200	2.66×10^{-4}	1.30×10^{-5}	In Air
		3.93×10^{-4}	1.09×10^{-6}	In O_2
	1300	3.25×10^{-4}	1.33×10^{-5}	In Air
Method3/Sample3 (Use P25)	1000	4.74×10^{-5}	1.06×10^{-7}	In Air
	1100	2.72×10^{-4}	2.30×10^{-6}	In Air
	1200	3.03×10^{-4}	8.34×10^{-6}	In Air
	1300	3.67×10^{-4}	1.38×10^{-5}	In Air

receive an overall conductivity on the order of 10^{-5} S/cm when sintered at 1300°C. This may be attributed to a sufficient fusion of the boundaries between $Li_{0.3}La_{0.57}TiO_3$ grains. Based on these analyses, we can conclude that enabling La^+ to diffuse into TiO_2 is an effective way to generate lanthanum vacancy defects and therefore the grain conductivity of a ceramic material can be improved to some extent. The use of colloidal TiO_2 appears to be an optimal approach which gives rise to both high grain conductivity and high grain boundary conductivity. The overall conductivity obtained with this method for material synthesis at 1200°C is on the order of 10^{-5} S/cm, which is almost same as what is obtained at 1300°C, indicating the advantage of the Method 2 when compared with the other two.

3.2. Effect of annealing temperatures

Shown in Fig. 1 are the X-ray diffraction (XRD) patterns of the $Li_{0.3}La_{0.57}TiO_3$ material annealed at different temperatures. It indicates that the material starts forming **perovskite structure** when temperature reaches about 900°C. Above this temperature threshold, it can be seen that a higher annealing temperature leads to better crystallinity and larger grain size. It suggests that doping should be an effective way that can lower the temperature for sintering the lithium ion conduction materials. This point is important since a decrease of the sintering temperature for the lithium ion conduction material will lead to less loss of lithium from the material due to the diffusion of lithium at high temperature, and therefore remain the material with high lithium ionic conductivity after sintered.
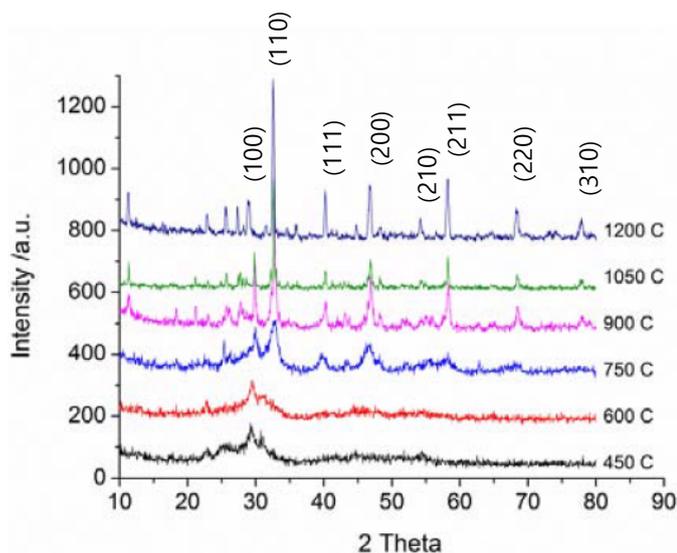

Fig. 1. XRD patterns of $Li_{0.3}La_{0.57}TiO_3$ annealed at different temperatures

Thermal gravimetric analysis (TGA) measurement was carried out in our research to know the decomposition property of the materials in precursor at elevated temperatures, and determine the temperature for pre-treating powder materials before being used for making pellets, with the consideration of avoiding a too big volume change during the pellets are sintered due to the loss of decompositable materials.

Fig. 2 shows the TGA analysis of $Li_{0.3}La_{0.57}TiO_3$ materials produced with the methods mentioned above. It can be seen that the temperatures corresponding to a full decomposition for $Li_{0.3}La_{0.57}TiO_3$ is about 750°C. We accordingly determined the pre-thermal treatment temperature for this materials before they were used for making cold-pressed pellets.
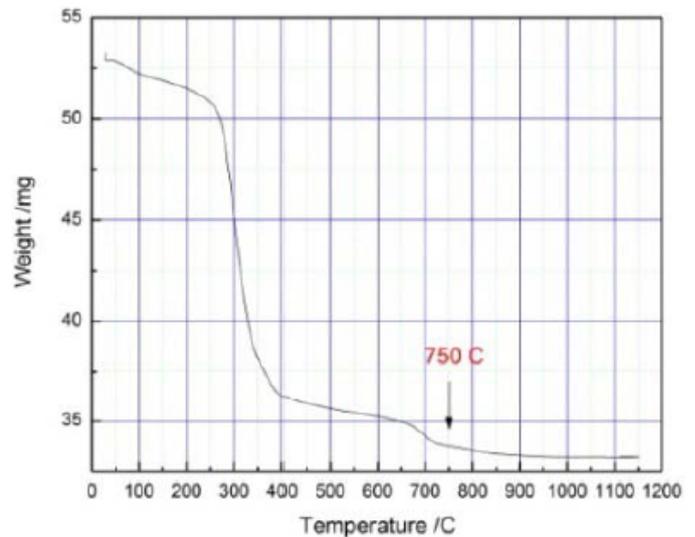

Fig. 2. TGA analysis of $Li_{0.3}La_{0.57}TiO_3$

3.3. Effect of annealing atmospheres

The impact of atmosphere for annealing on the lithium ionic conductivity of $Li_{0.3}La_{0.57}TiO_3$ were studied. Dry air and oxygen (O_2) have been employed for this study. From the results listed in TABLE 1, it can be clearly seen that both the grain conductivity and the overall conductivity of the $Li_{0.3}La_{0.57}TiO_3$ decrease a lot when annealed in O_2 compared to in air. However, it is interesting that the decrease in grain conductivity is much minor, whereas the overall conductivity drops significantly. For the samples annealed at 1100°C, the overall conductivity presents an approximately half of one order drop, while the drop is more than one order for the samples annealed at 1200°C. This indicates that the annealing in O_2 may have an apparent influence on the surface of $Li_{0.3}La_{0.57}TiO_3$ grains in terms of the composition or defects, which result in an increase in the resistance for lithium ion conduction at grain boundaries.

3.4. Thickness effect

To minimize the influence of grain boundaries on the lithium ion conduction, thickness effect on the lithium ionic conductivity of $Li_{0.3}La_{0.57}TiO_3$ were studied. The lithium ionic conductivity of $Li_{0.3}La_{0.57}TiO_3$ pellets with different thicknesses is shown in TABLE 2.

TABLE 2

A comparison of lithium ionic conductivity of $Li_{0.3}La_{0.57}TiO_3$ pellets with different thicknesses

Sample	Thickness	Conductivity (S/cm)	Note
$Li_{0.3}La_{0.57}TiO_3$ (modified with LLTO sol sintered at 1200°C	0.89 mm	1.31×10^{-5}	
	0.19 mm	1.58×10^{-5}	~21% increase

We can see that, for the material which is totally the same, while the pellet thickness is reduced to about ¼, the lithium ionic conductivity gains ~21% increases. The reason that a thinner pellet receives a higher conductivity is owing to reduced number of the grain boundaries through the lithium ions transport. This suggests us to develop technology for making very thin lithium ion conduction membrane to gain possibly high conductivity with the $Li_{0.3}La_{0.57}TiO_3$; the most ideal case is to get the overall conductivity to approach the grain conductivity of the material (– on the order of 10^{-3} S/cm).

4. Conclusions

From the results of the present work, the conclusions are drawn as follows:

1. Solution-based method for the synthesis of lithium ion conduction materials of $Li_{0.3}La_{0.57}TiO_3$. was proposed.
2. Ionic conductivity of $Li_{0.3}La_{0.57}TiO_3$ membrane which is synthesized by firstly forming colloidal TiO_2 (i.e., TiO_2 sol) and then Li^+ and La^+ were added to the colloidal TiO_2 is on the order of 10^{-5} S/cm annealed at 1200°C.
3. Temperatures corresponding to a full decomposition for $Li_{0.3}La_{0.57}TiO_3$ is ~750°C and materials start forming perovskite structure when temperature reaches about 900°C.
4. The lithium ionic conductivity gains ~21% increases when the pellet thickness is reduced to about ¼.

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