Effect of acid treatment of Li$_7$La$_3$Zr$_2$O$_{12}$ on ionic conductivity of composite solid electrolytes

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Abstract. The garnet-type metal oxide Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) is considered to be one of the most promising compounds for solid lithium ion batteries because of its high ionic conductivity at room temperature and excellent chemical stability with the metal Li. LLZO is unstable in humid air and easily forms Li$_2$CO$_3$ on the surface, which leads to the decrease of ion conductivity. In this paper, chemical treatment by oxalic acid is carried out to remove the lithium carbonate on the surface of LLZO. The results show that oxalic acid with a concentration ratio of 5% can completely remove lithium carbonate. Composite polymer electrolyte membranes fabricated by the polyvinylidene fluoride (PVDF) and LLZO before and after the acid treatment are prepared to evaluate the effect on ionic conductivity. The ionic conductivity is $1.4 \times 10^{-4}$ S cm$^{-1}$ and $9.0 \times 10^{-4}$ S cm$^{-1}$ for samples added the LLZO before and after the acid treatment, respectively.

1. Introduction

Lithium-ion batteries are widely used in aerospace, electric vehicles and large-scale energy storage owing to their high energy density, long life and environmental friendliness [1]. However, lithium ion batteries, which currently use liquid electrolytes, have caused a series of safety problems such as spontaneous combustion and even explosion. Therefore, all-solid-state lithium-ion batteries with high safety performance are attracting more and more research [2], and solid electrolytes as the most critical part of all-solid-state batteries are required to have a wide electrochemical window [2], appropriate ionic conductivity and good electrochemical stability [3].

The cubic phase garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) has high ionic conductivity, wide electrochemical window, and good lithium stability [3]. It has been proven to improve the performance of the electrolyte. Therefore, LLZO has favorable application prospects as an inorganic solid electrolyte. Unfortunately, although it has many advantages as a solid electrolyte, it is susceptible to the effects of carbon dioxide and water in the air according to prior reports [3-6]. In the first step, lithium ions of LLZO in water are prone to cation exchange reactions (Li$^+/H^+$) leading to the formation of LiOH, which then reacts with carbon dioxide in the air to form Li$_2$CO$_3$ on its surface. Lithium carbonate affects the transport of lithium ions, which leads to the reduction of ionic conductivity and affects the application in solid composite electrolyte membranes [7-8]. In this work, the X-ray diffraction (XRD) confirmed the formation of Li$_2$CO$_3$ on the surface of LLZO. For the first
time, chemical treatment methods that use different concentrations of acids to react within. The method can effectively avoid the problem that mechanical polishing can't completely remove the impurities, which makes the work simpler. The Fourier Transform Infrared (FTIR) and Raman spectroscopy methods were used to analyze whether the acid treatment can completely remove surface impurities and chemical reaction changes. Subsequently, the LLZO before and after the treatment was used as an inorganic electrolyte filler to prepare CPE, wherein the organic polymer was polyvinylidene fluoride (PVDF). It was found that different LLZO were added, the ionic conductivity of CPE was significantly different. It was found that the ionic conductivity was closely related to the amount of LLZO added. The ionic conductivity of the composite solid electrolytes with the modified LLZO had been improved, and the improvement of the ionic conductivity was attributed to the acid treatment of LLZO.

2. Experiment

2.1 Synthesis of micro-processed LLZO

The LLZO powder was placed in deionized water and stirred well for 8 minutes to completely mix them so that lithium carbonate was formed on the surface of the LLZO. After standing for 5 minutes, the deionized water of the upper layer solution was poured off, and the LLZO was placed in an oven at 80 °C for 5 hours to be completely dried to obtain a hydrated LLZO material. The solid oxalic acid was formulated into a solution having a concentration of 3%, 5%, 7%, and 9% according to mass ratio using alcohol as a solvent. The hydrated LLZO was placed in different concentrations of oxalic acid solution and stirred for 3 minutes, then allowed to stand for 5 minutes and washed twice with alcohol. Placed these samples in a vacuum oven at 150 °C for 12 hours to obtain acid-treated LLZO. The different samples formed are denoted as AL-X (X = 0, 3, 5, 7, 9), where X represents the mass percentage of acid concentration.

2.2 Fabrication of composite polymer electrolytes containing LLZO and PVDF

The composite electrolytes membrane was prepared by solution-casting method. PVDF and LiClO₄ (3:1 weight ratio) were first dissolved in dimethylformamide (DMF). Then, the hydrated LLZO (10% of PVDF quality) treated with 0%, 3%, 5%, 7%, and 9% oxalic acid were added to the above dispersion and stirred until forming highly viscous slurry. Subsequently, the dispersions were cast to Teflon dishes and dried slowly in an argon-filled oven at 60 °C. Finally, the composite polymer electrolytes (~100 μm in thickness) were obtained [8].

2.3 Electrochemical measurements

Using a stainless steel (SS) as an electrode, the composite electrolytes membrane was assembled into an SS/composite electrolytes membrane/SS symmetric blocking battery for AC impedance testing (EIS) to obtain the ionic conductivity of the composite electrolyte membrane. At room temperature, the device uses a CHI604E electrochemical test system with amplitude of 10 mV and a frequency from 10⁻⁶ Hz to 10⁻¹ Hz, and the conductivity of the electrolyte membrane is calculated according to equation (1).

\[ \sigma = \frac{L}{RS} \]  

(1)

Wherein \( R \) is the impedance of the composite electrolyte membrane obtained by the EIS test, \( L \) is the thickness of the composite electrolyte membrane, and \( S \) is the area of the electrode [5]. The electrochemical stability window of the membranes were determined by linear sweep voltammograms (LSV) of the Li/composite electrolytes membrane/SS cell with a working electrode of stainless steel and a counter electrode of lithium metal performed on CHI604E at a scan rate of 1 mV s⁻¹ over the potential range of 2–6 V at 25 °C.
3. Results and Discussion

3.1 The formation of Li₂CO₃ on the surface of Li₇La₃Zr₂O₁₂

Although LLZO has been widely used in composite electrolyte membranes in recent years, the instability in air has led to high requirements on the working condition, which has also restricted its application. The main problem is that lithium carbonate impurities are formed on the surface in a humid environment. Figure 1 demonstrates the formation of Li₂CO₃ on the surface of LLZO. The process of generating lithium carbonate is that LLZO is prone to exchange of Li⁺ and H⁺ in water, LiOH is formed on the surface of LLZO, and then reacts with CO₂ in the air to form lithium carbonate impurities, so that a dense layer of impurity particles forms on the surface of LLZO (Equation 2 and 3).

\[ \text{LiOH} + \text{H}_2\text{O} \rightarrow \text{LiOH} \cdot \text{H}_2\text{O} \]  
\[ 2\text{LiOH} \cdot \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + 3\text{H}_2\text{O} \]

As shown in Figure 3(a) and 2(b), a Li₂CO₃-like layer was observed in the surface of LLZO from SEM image of AL-O, and a new small peak which identify with Li₂CO₃ was found in XRD pattern of AL-0.

3.2 Removal of Li₂CO₃ impurities by acid treatment

Hydrated LLZO was immersed in a solution with a certain acid concentration to remove Li₂CO₃. The specific reaction is with reference to equation 4, and the detailed experimental demonstration is shown in Figure 1. At the beginning of the experiment, oxalic acid, citric acid and acrylic acid were used for acid screening. These three acids were subjected to treat LLZO under same experimental conditions. It is confirmed from the XRD in Figure 2(a) that acrylic acid completely destroyed the crystal structure of LLZO. Obviously, it was excluded first since it damaged LLZO while removing lithium carbonate. The treatment of oxalic acid and citric acid did not cause damage to the crystal structure of the material. As for the acid used in the experiment, oxalic acid is chosen since citric acid is not as soluble as it in alcohol solvent.

\[ \text{Li}_2\text{CO}_3 + 2\text{H}^+ \rightarrow 2\text{Li}^+ + \text{H}_2\text{O} + \text{CO}_2 \]  

The concentration of oxalic acid was analyzed. First, the changes of hydrated LLZO treated with different acid concentrations are observed by a scanning electron microscope. Figure 3(a) shows the surface of hydrated LLZO. What can be clearly seen from the SEM image is that the surface is almost full of impurities. It is assumed that the small particles generated on the surface are lithium carbonate. The subsequent XRD pattern of Figure 2(b) and the Raman spectrum of Figure 2(c) can confirm this speculation. Figure 3(b) shows that the surface of AL-3 is smoother than that of Figure 3(a), but a small portion of impurities still exist, indicating that the lithium carbonate impurities were not completely removed with the acid concentration of X=3. Similarly, Figure 3(c) clearly shows that the surface of the material sample is smooth and no rough interface is visible. In Figure 3(d) and 3(e), although there are no excessive impurities on the surface of the samples, some traces of acid treatment are observed on the surface, which may be caused by an excess of oxalic acid. Therefore, the acid concentration of 5% can more appropriately remove lithium carbonate. After the performance study of the electrolyte membrane, it also showed the highest ionic conductivity.
Figure 2(a) XRD patterns of LLZO powders treated with different acids, and (b) XRD patterns of LLZO powders treated with different acid concentrations. (c) Raman spectroscopy of LLZO powders treated with different acid concentrations. (d) TGA results of acid-treated LLZO and hydrated LLZO.

In order to further investigate the change of hydrated LLZO after acid treatment, XRD and Raman spectroscopy were used respectively. Figure 2(b) shows the XRD patterns of hydrated LLZO with different acid concentration treatments. By comparing the LLZO cubic phase powder diffraction standard card (PDF #45-0109), it is clear that no change in crystal phase structure occurs after a series of treatments. This illustrates that the acid treatment did not damage the crystal structure of LLZO. In Figure 2(b), it is obvious that the hydrated LLZO has a weak impurity peak, and the acid-treated samples do not have it. After comparing with the lithium carbonate standard card, it indicates that this weak peak belongs to lithium carbonate impurity. It is also reasonable to conclude that the chemical treatment not only maintains the crystal phase of LLZO, but also effectively removes impurities on the surface. It is also proved from the Raman spectroscopy of Figure 2(c) that AL-0 shows the peak of lithium carbonate.
Li$_2$CO$_3$ at the wave number 1088 cm$^{-1}$, and the sample of AL-5 does not show this peak, which confirms that this chemical treatment can eliminate the impurity lithium carbonate. As a result, the process of preparing LLZO can be simplified because impurities can be purified by a later chemical treatment. Subsequently, the samples of AL-0 and AL-5 were conducted to thermogravimetric analysis (TGA) the results of which are shown in Figure 2(d). The AL-0 sample lost the weight of 2.5% below 200 °C, which corresponds to a loss of water. Between 200-800 °C, a continuous loss of mass corresponds to the thermal decomposition of LLZO particles. The decomposition temperature of oxalic acid is below 200 °C, and the mass of AL-5 does not change below 400 °C, which shows that chemical treatment of LLZO with oxalic acid concentrations of 5% will not leave excess acid.

3.3 Properties of the composite electrolyte membrane with the acid treated LLZO

In order to illustrate the purpose of chemically treated LLZO more clearly, they were applied as inorganic fillers to the composite electrolyte membranes to analyze the change of properties. Figure 4(a) investigated the conductivity properties by EIS spectra. After calculating with Equation 1, the ionic conductivity of the samples can be clearly seen from Figure 4(b). The sample of AL-0 has the lowest ionic conductivity (1.4×10$^{-4}$ S cm$^{-1}$) and the sample of AL-5 shows the highest ionic conductivity (9.0×10$^{-4}$ S cm$^{-1}$). Figure 4(c) shows the comparison of linear sweep voltammograms (LSV) curves of the AL-0/PVDF and AL-5/PVDF at 1 mV s$^{-1}$ sweep rate. The AL-0/PVDF begins to decompose at ~ 3.95 V (vs. Li$^+$/Li) while AL-5/PVDF decomposes at ~ 4.75 V (vs. Li$^+$/Li) due to acid chemical treatment. As shown in Figure 4(d), the thermal stability of the composite electrolyte membrane was investigated by thermogravimetric analysis (TGA). At around 300 °C, the quality of the electrolyte membrane containing AL-O dropped sharply, while the sample containing AL-5 started to lose quality at higher temperature, showing better stability. This chemical treatment gives LLZO a great advantage in the application of composite solid electrolytes. On the one hand, it solves the interface problem of the composite solid electrolytes due to impurity particles in LLZO. On the other hand, it can increase the ionic conductivity of the composite solid electrolytes.

![Figure 4(a) Impedance spectroscopy, and (b) ionic conductivity of CPE by combination of LLZO powders treated with different acid concentrations and PVDF. (c) Comparison of liner sweep voltammograms of acid-treated LLZO and hydrated LLZO. (d) TGA results of the AL-0/PVDF and AL-5/PVDF composite polymer electrolytes.](image-url)
4. Conclusions
In summary, the LLZO particles were immersed in water for Li\(^+\) and H\(^+\) exchanging to amplify their instability in ambient air. It was confirmed by SEM and XRD analysis that lithium carbonate impurities were formed on the surface. After the lithium carbonate impurity was removed by acid chemical treatment, the ionic conductivity of the prepared composite electrolyte membrane was raised from 1.4\(\times10^{-4}\) S cm\(^{-1}\) to 9.0\(\times10^{-4}\) S cm\(^{-1}\). This change in ionic conductivity is attributed to two reasons: (i) The inorganic filler LLZO in the composite electrolyte does not have lithium carbonate impurities on the surface. (ii) The interaction between LLZO that after acid chemical treatment and PVDF. It has been proved that this method of chemically eliminating uneven impurities on the surface is effective and easy to operate.

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References
[1] Manthiram A, Yu X, Wang S (2017) Lithium battery chemistries enabled by solid-state electrolytes. Nature Reviews Materials 2 (4).
[2] Duan H, Zheng H, Zhou Y, Xu B, Liu H (2018) Stability of garnet-type Li ion conductors: An overview. Solid State Ionics 318:45-53.
[3] Wu JF, Pu BW, Wang D, Shi SQ, Zhao N, Guo X, Guo X (2019) In Situ Formed Shields Enabling Li\(_2\)CO\(_3\)-Free Solid Electrolytes: A New Route to Uncover the Intrinsic Lithiophilicity of Garnet Electrolytes for Dendrite-Free Li-Metal Batteries. ACS Appl Mater Interfaces 11 (1):898-905.
[4] Liu Q, Geng Z, Han C, Fu Y, Li S, He Y-b, Kang F, Li B (2018) Challenges and perspectives of garnet solid electrolytes for all solid-state lithium batteries. Journal of Power Sources 389:120-134.
[5] Xie H, Bao Y, Cheng J, Wang C, Hitz EM, Yang C, Liang Z, Zhou Y, He S, Li T, Hu L (2019) Flexible Garnet Solid-State Electrolyte Membranes Enabled by Tile-and-Grout Design. ACS Energy Letters 4 (11):2668-2674.
[6] Wang S, Gong F, Yang S, Liao J, Wu M, Xu Z, Chen C, Yang X, Zhao F, Wang B, Wang Y, Sun X (2018) Graphene Oxide-Template Controlled Cuboid-Shaped High-Capacity VS4 Nanoparticles as Anode for Sodium-Ion Batteries. Advanced Functional Materials 28 (34):1801806.
[7] Galven C, Dittmer J, Saard E, Le Berre F, Crosnier-Lopez M-P (2012) Instability of Lithium Garnets against Moisture. Structural Characterization and Dynamics of Li\(_{17.9}\)H\(_{2}\)La\(_3\)Sn\(_2\)O\(_{12}\) and Li\(_{15}\)H\(_{2}\)La\(_3\)Nb\(_2\)O\(_{12}\). Chemistry of Materials 24 (17):3335-3345.
[8] Zhang J, Zhao N, Zhang M, Li Y, Chu PK, Guo X, Di Z, Wang X, Li H (2016) Flexible and ion-conducting membrane electrolytes for solid-state lithium batteries: Dispersion of garnet nanoparticles in insulating polyethylene oxide. Nano Energy 28:447-454.