Preparation and Electrochemical Properties of Ba$_{1-x}$La$_x$F$_{2+x}$ Fluoride Electrolyte

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Abstract. A series of Ba$_{1-x}$La$_x$F$_{2+x}$ composition powders with different values of $x$ were prepared by water and ethanol mixed solvent method. The effects of different values of $x$ on the phase composition, crystal structure and electrochemical properties of Ba$_{1-x}$La$_x$F$_{2+x}$ electrolyte were studied. The electrical conductivity of Ba$_{1-x}$La$_x$F$_{2+x}$ at different temperatures was investigated by electrochemical impedance spectroscopy. The results of transmission electron microscopy showed that the prepared Ba$_{1-x}$La$_x$F$_{2+x}$ powders ranged in size from 10 to 25nm and dominated by crystalline phases. XRD results show that the Ba$_{1-x}$La$_x$F$_{2+x}$ electrolyte gradually changes from fluorite structure to tysonite structure with the increase of $x$ value. Electrochemical impedance spectroscopy was used to study the electrical properties at 25, 50, 75, and 100$^\circ$C. It was found that the ionic conductivity of the Ba$_{1-x}$La$_x$F$_{2+x}$ electrolyte at the same temperature increased with the increase of temperature. When $x$ is small, the main carrier of Ba$_{1-x}$La$_x$F$_{2+x}$ electrolyte is F$^-$, while the conductivity of the latter is lower at lower test temperature. The contribution is much larger than the latter, which is also the main reason for the decrease of conductivity of Ba$_{1-x}$La$_x$F$_{2+x}$ electrolyte when $x$ is too large. At the same temperature, Ba$_{0.6}$La$_{0.4}$F$_{2.4}$ is always the maximum conductivity.

1. Introduction
Lithium batteries have long been the most used batteries in daily life, and the electrolytes they use are basically organic electrolytes. This electrolyte is a kind of liquid that can be burned. In addition, lithium batteries are prone to dendrites due to their long use time. With a large expansion rate, there is a great potential safety hazard. For this reason, researchers at the Karlsruhe Institute of Technology in Germany have conducted research on lithium-ion battery replacement systems, and finally developed a new concept of F$^-$ Charge and discharge battery [1]. The basic working principle of this type of battery is that fluoride ions migrate back and forth between the metal fluoride cathode and the metal anode [2]. A key component is the fluoride solid state electrolyte, which provides fast ion conduction for fluoride ion batteries. Unlike conventional batteries using liquid electrolytes, solid electrolytes have a very low expansion ratio, no gassing process, and deposition of metal on the electrode surface.
is suppressed, thereby preventing dendrite, prolonging battery life and increasing energy density. And battery safety and so on.

BaF2 with fluorite structure, because all octahedral voids are not filled, the structure is relatively open, which is conducive to the formation of negative ion interstitials, and also provides conditions for negative ion migration, so it is often studied as an ion conductor. Ivanov-Shits et al. synthesized Ba1-xLaxF2+x by doping rare earth metal fluoride RF3 in BaF2. It was found that the higher the doping concentration, the higher the conductivity, but the presence of a doping threshold[3]. Rongeat and colleagues also prepared nanocrystalline fluorite-type Ba1-xLaxF2+x (0 ≤ x ≤ 0.55) electrolytes and observed similar results [4,5]. Irshad Mohammad et al. synthesized a nano-Ba1-xSbF2+x (x ≤ 0.4) solid electrolyte with fluorite structure by high-energy ball milling, and replaced the divalent Ba2+ with trivalent Sb3+ to increase the interstitial fluoride ion concentration, thereby enhancing Ba1-xSbF2+x. The ionic conductivity of the Ba1-xSbF2+x (0.1 ≤ x ≤ 0.4) system has achieved good results [6]. In this paper, different La3+ doped fluoride Ba1-xLaxF2+x solid electrolytes were prepared by water and ethanol mixed solvent method, and their electrochemical properties and conduction mechanism were studied.

2. Experimental

2.1. Experimental materials
Ba(NO3)2 (99.9%), La(NO3)3 · nH2O (99.9%), NH4F (99.9%) was purchased from International Group Chemical Reagent Co., Ltd.; C2H5OH (99.9%) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd.

2.2. Experimental process
Electrolyte A certain amount of Ba(NO3)2, La(NO3)3, and NH4F are respectively dissolved in a mixed solvent of water and ethanol ratio of 1:1 to prepare three reactant solutions which are just saturated; Then the Ba(NO3)2 solution is slowly added to the La(NO3)3 solution. After mixing, the NH4F solution is slowly added dropwise to the excess under constant stirring; the obtained mixed solution is allowed to stand for 1 h, and the supernatant liquid is sucked up by a pipette; The distilled water is washed with a centrifuge until the supernatant liquid after centrifugation is dropped into the FeSO4 solution and no precipitation occurs; the supernatant liquid is aspirated, and the centrifuge tube is placed in an oven for at least 12 h, and taken out and ground with an agate mortar. A Ba1-xLaxF2+x electrolyte powder is obtained. Ba1-xLaxF2+x electrolyte powders with x values of 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 were prepared by this method.

A Ba1-xLaxF2+x electrolyte powder prepared in an amount of about 0.35 g was placed in a tableting mold having a diameter of Φ10 mm, and pressed into a sheet having a thickness of about 1 mm under a pressure of 15 MPa. The pressed flake samples were plated with metal cerium on both sides by magnetron sputtering, and then the platinum wires were adhered on both sides with silver paste for electrochemical impedance spectroscopy.

2.3. Characterization of samples
The morphology and particle size of the prepared electrolyte were observed by a JMS-2010 transmission electron microscope manufactured by JEOL. The phase composition of the prepared Ba1-xLaxF2+x electrolyte was determined by D8 ADVANCE X-ray diffractometer. The electrochemical impedance spectroscopy of Ba1-xLaxF2+x electrolyte was tested by CHI660D electrochemical workstation.

3. Results and discussion

3.1. Phase composition and structure of prepared Ba1-xLaxF2+x powders
Figure 1 shows the XRD patterns of Ba1-xLaxF2+x powders at different values of x. As can be seen from the figure, the prepared Ba1-xLaxF2+x fluoride powder has a fluorite structure phase and a tysonite structure phase. When the value of x is small, the fluorite structure phase is dominant. With the
increase of x value, the diffraction peak intensity of the fluorite structure phase in the x-ray diffraction pattern is gradually weakened, and the diffraction peak of the tysonite structure phase is gradually enhanced. At the same time, it can be seen from the figure that as the value of x increases, the diffraction peak of the $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ phase of the fluorite structure gradually shifts to a high angle, and the lattice constant changes, which also indicates that La$^{3+}$ has entered Ba$^{2+}$ position.

![XRD patterns of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ powders at different values of x.](image)

Figure 1. The XRD patterns of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ powders at different values of x.

The prepared samples were characterized by transmission electron microscopy. Figure 2 is a TEM photograph of the prepared $\text{Ba}_{0.7}\text{La}_{0.3}\text{F}_{2.3}$ and $\text{Ba}_{0.6}\text{La}_{0.4}\text{F}_{2.4}$ electrolyte powders respectively. It can be seen from the bright field image that the obtained fluoride electrolyte powder has a relatively uniform particle size about 10-25 nm. It can be seen from the diffraction pattern that the diffraction ring has a multi-ring phase set and the stripes are clear, indicating that the prepared sample is a crystal structure.

![TEM picture of powders](image)

Figure 2. TEM picture of powders (a) $\text{Ba}_{0.7}\text{La}_{0.3}\text{F}_{2.3}$; (b) $\text{Ba}_{0.6}\text{La}_{0.4}\text{F}_{2.4}$
3.2. AC Impedance Spectroscopy and Conductivity of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$

Figure 3 shows the AC impedance spectra of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ electrolytes at different temperatures. The AC impedance spectrum generally consists of a semi-circular arc in the high frequency region and a diagonal line in the low frequency region [7]. The high frequency region is a semicircular shape controlled by the interface charge transfer dynamics, and the low frequency region is a straight line of diffusion control. The semicircle represents the parallel connection of resistance and capacitance in the equivalent circuit. It can be seen from the above curve that each curve contains a semicircle and a straight line portion at any temperature, and the linear portion is related to the concentration of doped La, which is high. The frequency semicircle portion is related to the contact resistance between the compound particles. It can be seen from Figure 3, that the semicircular arc diameters of the high frequency regions of the samples $\text{Ba}_{0.6}\text{La}_{0.4}\text{F}_{2.4}$ and $\text{Ba}_{0.7}\text{La}_{0.3}\text{F}_{2.3}$ are always smaller than those of other samples at each test temperature. This indicates that the impedances of the samples $\text{Ba}_{0.6}\text{La}_{0.4}\text{F}_{2.4}$ and $\text{Ba}_{0.7}\text{La}_{0.3}\text{F}_{2.3}$ are relatively small.

In the AC impedance spectrum, the intersection coordinates of the left end point and the real axis of the fitted semicircular arc represent the bulk resistance $R_b$ of the electrolyte $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$, and the intersection coordinates of the right end point and the real axis of the fitted semicircular arc represent the electrolyte. The sum of the bulk resistance $R_b$ of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ and the grain boundary resistance $R_{gb}$ ($R_b+R_{gb}$) represents the actual resistance of the electrolyte $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$, and the conductivity of the fluoride electrolyte $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ can be calculated by the equation (1). Which is as described below:

$$\sigma = \frac{1}{R_b + R_{gb}} \cdot \frac{L}{S}$$

(1)
In the equation (1), $L$ is the thickness of the electrolyte, and $S$ is the contact area between the electrode and electrolyte.

Figure 4 is a plot of conductivity versus temperature for $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ with different values of $x$. It can be seen from Figure 4 that the conductivity of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ electrolyte changes slowly with increasing temperature in the range of 25 to 75 °C, and the conductivity increases sharply with temperature above 75 °C. This is due to an increase in the rate of movement of fluoride ions due to an increase in temperature and an increase in mobility. It can also be seen from the figure that when the $x$ value is 0.3 and 0.4, the conductivity is relatively high, and at 100 °C, the conductivity of $\text{Ba}_{0.6}\text{La}_{0.4}\text{F}_{2.4}$ reaches the extreme value of $1.07 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$.

Figure 4. Conductivity of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ at different temperatures

Conductance measured by AC impedance spectroscopy is a hybrid conductance that includes ionic conductance and electronic conductance. Fluoride electrolytes are fast ion conductors whose ion conductance is much larger than their electron conductance, so the conductance measured by AC impedance spectroscopy can be used as ion conductance.

The relationship between conductivity and temperature generally follows the Arrhenius equation[8].

\[
\sigma_i = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad (2)
\]

\[
\lg(\sigma T) = \lg A - \frac{E_a}{\ln 10 k_B} \frac{1}{T} \quad (3)
\]

In Equations (2) and (3), where $E_a$, $k_B$, and $\sigma_0$ stand for the activation energy, the Boltzmann constant, and the preexponential factor, respectively. It can be seen from the above equation that the conductivity is affected by the conductance activation energy. It can be seen from equation (3) that $\lg(\sigma T)$ is linear with $1/T$, and $\lg(\sigma T)$ of different $x$ values is linearly fitted with $1/T$, and the slope of the fitted straight line is the activation energy $E_a$. The relationship between $\lg(\sigma T)$ and 1000/T of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ electrolytes with different values of $x$ is shown in Figure 5. $\lg(\sigma T)$ has a good linear relationship with 1000/T, which also indicates the temperature range tested. Internally, the conductivity of the $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ electrolyte is primarily affected by a single conductive mechanism. The slope of each fitted straight line is the activation energy $E_a$, and the conductance activation energy
of the $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ electrolyte with different values of $x$ is shown in Table 1. It can be seen from the table that the conductance activation energy of the $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ electrolytes with different values of $x$ is substantially equivalent.

![Figure 5](image)

**Figure 5.** Relationship between $\lg(\sigma T)$ and $1000/T$ of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ electrolytes with different values of $x$

| $x$ value | Activation energy/ev |
|-----------|----------------------|
| 0.2       | 1.898                |
| 0.3       | 2.023                |
| 0.4       | 2.625                |
| 0.5       | 1.940                |
| 0.6       | 2.306                |
| 0.7       | 1.895                |

In the x-ray diffraction analysis, the $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ phase in the presence of a fluorite structure and the $\text{Ba}_y\text{La}_{1-y}\text{F}_{3-y}$ phase in the tysonite structure have been observed. The $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ phase of the fluorite structure is in the fluorite structure of $\text{BaF}_2$, and some of the $\text{Ba}^{2+}$ sites are replaced by $\text{La}^{3+}$, and the reaction equation is shown in equation (4). Since the trivalent ion replaces the divalent ion, one of the $\text{F}^-$ enters the gap position and becomes a conductive carrier. In the $\text{Ba}_y\text{La}_{1-y}\text{F}_{3-y}$ phase of the tysonite structure, $\text{Ba}^{2+}$ enters the $\text{La}^{3+}$ position, and the reaction equation is as shown in equation (5). Since the divalent ion is substituted for the divalent ion, in order to balance the electric price, an $\text{F}^-$ vacancy occurs, and the $\text{F}^-$ vacancy is also a conductive carrier.

Since the binding of the gap $\text{F}^-$ is weak in the fluorite structure, the gap $\text{F}^-$ is easy to achieve migration. In the tysonite structure, the $\text{F}^-$ vacancy is bound by the crystal lattice, and migration can be achieved only at higher temperatures. At lower temperatures, the main contribution of the electrical conductivity comes from the gap position $\text{F}^-$, and the $\text{F}^-$ vacancy has little contribution. Therefore, among the two phases observed, the $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ phase of the fluorite structure is the main conductive
phase at lower test temperature conditions, and the Ba$_{y}$La$_{1-y}$F$_{3-y}$ of the fluorocarbon structure does not contribute to the conductivity.

$$\text{LaF}_3 \xrightarrow{\text{BaF}_2} \text{La}^{2+} + 2\text{F}^{-} + \text{F}^{' -}$$  \hspace{1cm} (4)

$$\text{BaF}_2 \xrightarrow{\text{LaF}_3} \text{Ba}^{2+} + 2\text{F}^{-} + \text{F}^{-}$$  \hspace{1cm} (5)

The Ba$_{1-x}$La$_{x}$F$_{2+x}$ phase forming the fluorite structure or the Ba$_{y}$La$_{1-y}$F$_{3-y}$ phase of the tysonite structure is related to the La$^{3+}$ content. When the content of La$^{3+}$ is low, the Ba$_{1-x}$La$_{x}$F$_{2+x}$ phase which forms the fluorite structure is dominant. With the increase of La$^{3+}$ content, the proportion of Ba$_{y}$La$_{1-y}$F$_{3-y}$ phase of tysonite structure increases gradually. When the Ba$_{y}$La$_{1-y}$F$_{3-y}$ phase which forms the fluorite structure is dominant, the concentration of the gap F$^-$ as the conductive ion increases correspondingly with the increase of the La$^{3+}$ content, thereby facilitating the improvement of the electrical conductivity. With the further increase of La$^{3+}$ content, the Ba$_{y}$La$_{1-y}$F$_{3-y}$ phase of the tysonite structure increases, and the conductive carriers are no longer the gap F$, but the F$^{-}$ vacancy, resulting in the test temperature. The lower conductivity is reduced. Therefore, the La$^{3+}$ content affects the ratio of the fluorite structure phase to the tysonite structure phase in the fluoride Ba$_{1-x}$La$_{x}$F$_{2+x}$, which affects the conductivity of the fluoride Ba$_{1-x}$La$_{x}$F$_{2+x}$.

4. Conclusions

The introduction of La$^{3+}$ ion in BaF$_2$ can effectively improve the conductivity. In the fluoride Ba$_{1-x}$La$_{x}$F$_{2+x}$, the electrical conductivity reaches the extreme value when the $x$ value is 0.3 and 0.4, and the conductivity of Ba$_{0.6}$La$_{0.4}$F$_{2.4}$ is $1.07 \times 10^{-3}$ S·cm$^{-1}$ at 100 °C. In the fluorite structure of Ba$_{1-x}$La$_{x}$F$_{2+x}$, the gap F$^-$ ion is the main conductive ion. The La$^{3+}$ ion content affects the ratio of the fluorite structure phase to the tysonite structure phase in the fluoride Ba$_{1-x}$La$_{x}$F$_{2+x}$.

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