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Wet Mechanical Milling Induced Phase Transition to Cubic Anti-Perovskite Li_2OHCl

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Anti-perovskite solid-state electrolyte Li_2OHCl usually exhibits orthorhombic phase and low ionic conductivity at room temperature. However, its ionic conductivity increases greatly when the temperature is up to 40 ℃, while it goes through an orthorhombic-to-cubic phase transition. The cubic Li_2OHCl with high ionic conductivity is stabilized at room temperature and even lower temperature about 10 ℃ by a simple synthesis method of wet mechanical milling. The cubic Li_2OHCl prepared by this method performs an ionic conductivity of 4.27×10^{-6} S/cm at room temperature, about one order of magnitude higher than that of the orthorhombic Li_2OHCl. The phase-transition temperature is decreased to around 10 ℃. Moreover, it can still remain cubic phase after heat treatment at 210 ℃. This work delivers a huge potential of fabricating high ionic conductivity phase anti-perovskite solid-state electrolyte materials by wet mechanical milling.

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In recent years, lithium-ion conductors have become a new research hotspot and have attracted extensive attention because they can be used as solid-state electrolytes (SSEs), which play key role in all solid-state rechargeable lithium batteries (ASSLBs) that were expected to have higher safety and larger energy-density than conventional lithium-ion batteries.[1–3] With decade years development, several types of SSEs with high ionic conductivities up to 10^{-3} S/cm have been successfully designed and synthesized, including oxide-based SSEs, halogen-based SSEs and sulfur-based SSEs. However, oxide-based SSEs generally are hard and fragile ceramics synthesized by high-temperature sintering, leading to poor interfacial contact and large interfacial resistance with electrodes. Halogen-based and sulfur-based SSEs generally suffer from narrow electrochemical window and poor air stability.[4–6]

The fact that anti-perovskite structural Li_2OHCl possesses relatively high ionic conductivity and soft nature has attracted broad attention.[7–9] Furthermore, in aspect of stability with Li metal for Li/Li_2OHCl/Li symmetric cells, Li_2OHCl is more excellent in contrast to other solid electrolytes.[7] Earlier experimental studies have shown that Li_2OHCl will undergo phase transition from orthorhombic structure to cubic structure at about 40 ℃, and the ionic conductivity of the former is lower than that of the latter.[10] The calculation results also suggest that Li_2OHCl with cubic structure has higher ionic conductivity due to strongly collective movement of the migrated Li ions.[11,12] In this work, we use wet mechanical milling methods to obtain the Li_2OHCl with cubic structure at room temperature, which lets the phase-transition temperature from orthorhombic structure to cubic structure drop down to 10 ℃. Furthermore, the Li_2OHCl treated by 210 ℃ still maintains cubic phase.

Li_2OHCl used in this work was prepared by wet mechanical milling (WWM). First, weighted 0.05 mol of lithium chloride (LiCl, > 99.9%, Aladdin) and 0.055 mol of lithium hydroxide (LiOH, > 99.9%, Aladdin) respectively in the glove box and put them into a 30 mL ball milling jar containing 60 g zirconia balls (8 mm in diameter). Then, added 10 mL n-hexane into it and used a planetary ball-mill for continuous wet ball milling at 400 rpm for 10 h. Finally, the suspension after ball milling was dried under vacuum cabin for 12 h to obtain dried white powders, named as Li_2OHCl-WMM. Moreover, in order to study the effect of annealing on the structure of the samples prepared by this method, the samples were heated up to 210 ℃ at a heating rate of 3 ℃/min and held at 210 ℃ for 5 h, then cooled naturally to room temperature, which is named as Li_2OHCl-WMM-210 ℃.

In contrast, we also prepared Li_2OHCl by solid-

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state sintering (SSS). The same raw materials of LiCl and LiOH as the above-mentioned method were placed in a nickel crucible and heated in box furnace at 360 ℃ for 2 h. After the reaction was completed and naturally cooled to room temperature, took out the solidified Li_2OHCl block and ground it again to obtain the powder, named as Li_2OHCl-SSS.

X-ray diffraction (XRD) with Cu K_α radiation was applied to analyze crystal structure of the prepared samples while the voltage was held at 45 kV and the electric current was held at 200 mA (2θ = 20–90°). The powder should be placed in the groove of the sample table and sealed with Kapton film to isolate moisture in air and prevented the hydrolysis reaction of the sample during transfer and test.

Electrochemical impedance spectroscopy (EIS) was carried out to measure ionic conductivity of the Li_2OHCl. In this study, powders of Li_2OHCl were pressed into a pellet with the diameter of 10 mm under 360 MPa for 6 min in the glove box at room temperature between −10 and 120 ℃ in the frequency range from 1 MHz to 1 Hz with an AC amplitude of 20 mV. The morphology and microstructure of fibers were characterized by scanning electron microscopy (FE-SEM, HITACHI SU8010), with an accelerating voltage of 200 kV.

Figure 1 shows the PXRD pattern of the Li_2OHCl synthesized by three different methods measured at 25 ℃. For Li_2OHCl-SSS, it is clear that the diffraction pattern is fitted with an orthorhombic phase ($Pmc2_1$) of Li_2OHCl whose lattice constants are a = 3.87501 Å, b = 3.82843 Å, c = 8.00396 Å, in agreement with those reported previously.[13,14] For Li_2OHCl-WMM and Li_2OHCl-WMM-210 ℃, it is also clear that the two diffraction patterns are in accord with a cubic phase ($Pm\bar{3}m$) of Li_2OHCl whose lattice constants are $a = b = c$ = 3.90812 Å. More importantly, the structure of Li_2OHCl synthesized by a WWM method has not changed after heat treatment at 210 ℃, which indicates that Li_2OHCl-WWM have good thermal stability.

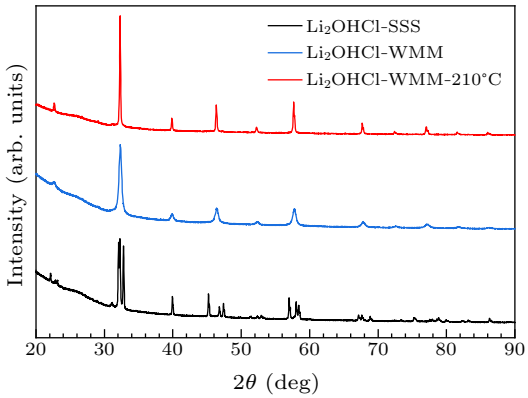

Fig. 1. PXRD patterns plot for Li_2OHCl-SSS, Li_2OHCl-WMM, and Li_2OHCl-WMM-210 ℃.

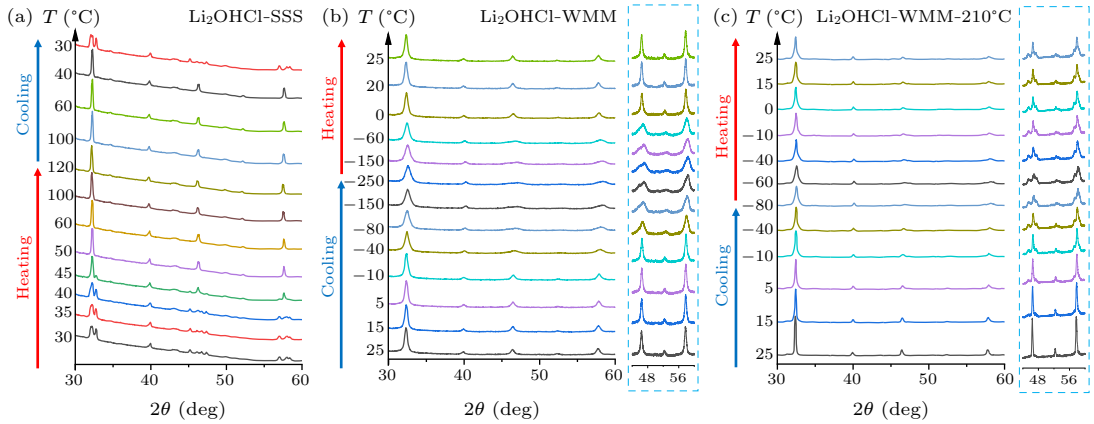

Fig. 2. PXRD patterns at temperatures from 30 to 120 ℃ for (a) Li_2OHCl-SSS, −250 to 25 ℃, (b) Li_2OHCl-WMM, −100 to 25 ℃, and (c) Li_2OHCl-WMM-210 ℃.

Figure 2 shows the temperature-dependent PXRD patterns of the Li_2OHCl synthesized by three different methods. For Li_2OHCl-SSS [Fig. 2(a)], when the temperature changes from 40 ℃ to 50 ℃, a structural phase transition occurs. According to the analysis of the above PXRD pattern, the structure of Li_2OHCl is orthorhombic phase below 40 ℃ and cubic phase above 50 ℃. It is worth noting that when temperature decreases from high temperature to 30 ℃, the transition occurs from cubic phase to orthorhombic phase. In other words, for Li_2OHCl synthesized by solid-state sintering, phase transition caused by temperature is reversible. For Li_2OHCl-WMM [Fig. 2(b)], when the temperature drops from −150℃ to −200℃, peak at 45° broadens and splits, and peak at 60° shifts to the right, which indicates that the cubic-to-orthorhombic phase transition occurs at low temperature. Furthermore, the peaks at 45° and 60° return to the same shape when the solid electrolyte is heated from −250℃ to 25 ℃, which indicates that the phase transition is reversible.

For Li_2OHCl-WMM-210 ℃, it can be observed that the position of diffraction peak at 32° does not change upon cooling, but from −10℃ to −80℃, the peaks at 45° and 60° split and shift to right; while upon heating from −80℃ to 25 ℃, the peaks can-

not return initial shape, proving that the cubic-to-orthorhombic phase transition occurs at low temperature and does not return back with heating.

As mentioned above, both PXRD and temperature-dependent PXRD patterns indicate that cubic Li_2OHCl can be stabilized at room temperature by a WWM method preparation. The PXRD pattern of Li_2OHCl-WMM also index the cubic phase after heating up to 210 ℃. Upon cooling, both Li_2OHCl-WMM and Li_2OHCl-WMM-210 ℃ sample show good thermal stability.

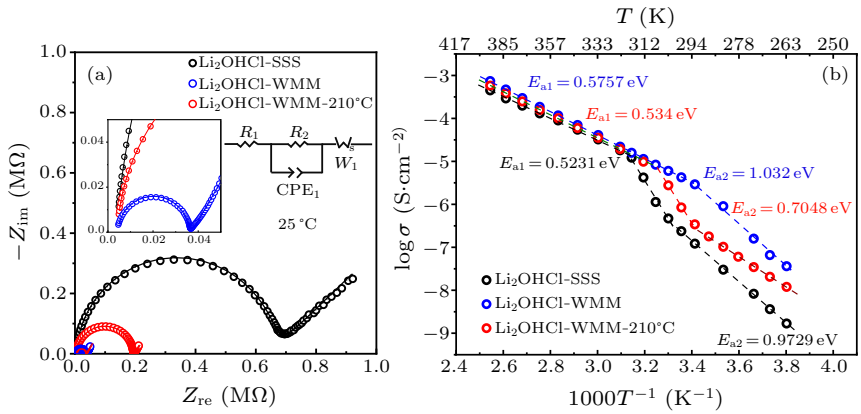

Fig. 3. (a) Typical Nyquist plots of Li_2OHCl-SSS (black), Li_2OHCl-WMM (blue), and Li_2OHCl-WMM-210 ℃ (red). (b) Arrhenius plots of temperature versus ionic conductivity for Li_2OHCl-SSS, Li_2OHCl-WMM and Li_2OHCl-WMM-210 ℃.

Figure 3(a) shows the Nyquist plots of Li_2OHCl measured at 25 ℃. The diameter of semiarch is used to estimate the resistance of Li_2OHCl, and the total ionic conductivity is calculated based on the pellet thickness and diameter. Arrhenius plot of ionic conductivity versus temperature for Li_2OHCl is given in Fig. 3(b). In addition, the activation energy E_a is obtained based on the equation

$$\sigma T = Ae^{(-E_a/k_B T)}, \tag{1}$$

where A is the pre-exponential parameter, σ is conductivity, E_a is activation energy, k_B and T represent the Boltzmann constant and temperature, respectively. The lithium ionic conductivity of Li_2OHCl-SSS is 2.37×10^{-7} S/cm at 25 ℃. The E_a for Li_2OHCl-SSS is 0.5231 eV between 50 ℃ and 120 ℃, which is consistent with the previous studies for Li_2OHCl.[10,15] It is noted that the E_a values for these samples are very close because they have the same cubic structure above 50 ℃. Below 50 ℃, for Li_2OHCl-WMM and Li_2OHCl-WMM-210 ℃, they could remain cubic phase in lower temperature compared to Li_2OHCl-SSS, which results in the ionic conductivity of the Li_2OHCl-SSS to be lower than the values of Li_2OHCl-WMM and Li_2OHCl-WMM-210 ℃. In view of structure, Li^+ could diffuse through the vacancies of the OH^-–Li octahedra. Hence, the cubic phase Li_2OHCl with high symmetry three-dimensional structure could boost ionic diffusion with low activation energy, while the orthorhombic-phase Li_2OHCl with highly anisotropic and two-dimensional structure restricts the transport of lithium ion, resulting in the low conductivity. In previously reports, the molecular dynamics simulation indicated that cubic phase provides larger space for OH^- rotation to boost Li^+ hopping than orthorhombic phase.

For Li_2OHCl-WMM, the lithium ionic conductivity increases to 4.27×10^{-6} S/cm at 25 ℃ compared to Li_2OHCl-SSS (2.37×10^{-7} S/cm). The higher ionic conductivity is attributed to the cubic phase obtained by WWM at room temperature. More importantly, the sudden decrease of ionic conductivity occurs at 10 ℃ for Li_2OHCl-SSS, which is lower than the value of Li_2OHCl-SSS at 50 ℃. These experimental results illustrate that Li_2OHCl-WMM can work in a wider temperature range as solid electrolyte. Due to the fact that Li_2OHCl-WMM-210 ℃ still remains cubic phase after heating to 210 ℃, its ionic conductivity is higher than that of Li_2OHCl-SSS. Upon the temperature 30 ℃, the ion conductivity changes suddenly. On the other hand, at higher temperature, these three samples remain cubic phase, which cause very close E_a and ionic conductivity for them.

In this study, both ac impedance and PXRD measurements reveal that cubic phase Li_2OHCl could be stabilized at room temperature by the wet mechanical milling method, although the Li_2OHCl usually forms orthorhombic phase at room temperature. The cubic phase Li_2OHCl shows higher ionic conductivity than orthorhombic phase at room temperature. This is mainly due to fact that the mechanical ball milling method can effectively synthesize the metastable structure. It has been reported that mechanical milling method could be used as an effective method to synthesize metastable structures, such as metal alloys,[16] metal hydrides,[17] and metal oxides.[18] During mechanical milling, the materials suffer from large stress that lead to generally lower

crystallinity of materials than those materials synthesized by a sintering process at high temperature, therefore the low crystallinity would contribute to stabilized metastable phase at room temperature.

As shown in Fig. 4, among those samples, Li_2OHCl-SSS shows the highest crystallinity, the largest crystal grains and the smoothest surface. On the contrary, Li_2OHCl-WMM shows the worst crystallinity, the smallest crystal grains and the roughest crystal surface. Crystallinity, grain size, and surface roughness of Li_2OHCl-WMM-210 ℃ are at a medium level. Li_2OHCl-WMM with the smallest grain size has the largest surface energy. On the other hand, from the viewpoint of atomic structure, the OH of the orthorhombic Li_2OHCl at room temperature is arranged in an orderly orientation, which leads to the lattice constants $a = b < c$. As the temperature increases, H has more kinetic energy and leads to a disordered arrangement of OH orientation, which leads to the lattice constant $a = b = c$, transforming from the orthorhombic phase to the cubic phase. We think that the larger surface energy of Li_2OHCl-WMM leading to reduction of the OH orientation order and the changing of crystal lattice inhibits transformation from the cubic phase to the orthorhombic at room temperature. However, as the temperature further decreases, the order orientation of OH becomes stronger. When the surface energy is not enough to suppress the lattice change, the transformation from cubic phase to orthorhombic phase would occurs. Therefore, the wet mechanical milling Li_2OHCl compared with the solid-state sintered Li_2OHCl shows a lower phase-transition temperature.

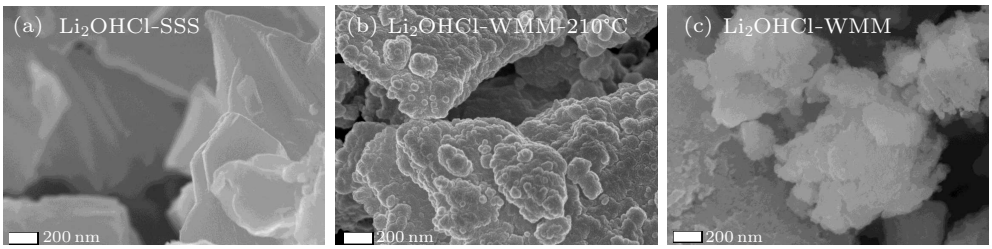

Fig. 4. SEM images for the Li_2OHCl synthesized by (a) solid-state sintering, (b) wet mechanical milling and 210 ℃ heating, and (c) wet mechanical milling.

In summary, we have proposed a novel wet mechanical milling method to synthesize cubic phase Li_2OHCl, of which the ionic conductivity is one order of magnitude higher than that of thermodynamically stable orthorhombic phase at room temperature. Moreover, the phase-transition temperature decreases from 40 ℃ to 10 ℃ by the wet mechanical milling method. This means that the Li_2OHCl can perform higher ionic conductivity at room temperature and work stably in a wider temperature range as solid electrolyte. Furthermore, the wet mechanical milling method with simple preparation process shows a huge potential to fabricate anti-perovskite solid-state electrolyte.

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