Hybrid Polymer/Garnet Electrolyte with a Small Interfacial Resistance for Lithium-Ion Batteries

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Abstract: Li$_3$La$_2$Zr$_2$O$_{12}$-based Li-rich garnets react with water and carbon dioxide in air to form a Li-ion insulating Li$_2$CO$_3$ layer on the surface of the garnet particles, which results in a large interfacial resistance for Li-ion transfer. Here, we introduce LiF to garnet Li$_3$La$_2$Zr$_2$Ta$_2$O$_{12}$ (LLZT) to increase the stability of the garnet electrolyte against moist air; the garnet LLZT-2 wt% LiF (LLZT-2LiF) has less Li$_2$CO$_3$ on the surface and shows a small interfacial resistance with Li metal, a solid polymer electrolyte, and organic-liquid electrolytes. An all-solid-state Li/polymer/LLZT-2LiF/LiFePO$_4$ battery has a high Coulombic efficiency and long cycle life; a Li-S cell with the LLZT-2LiF electrolyte as a separator, which blocks the polysulfide transport towards the Li-metal, also has high Coulombic efficiency and kept 93% of its capacity after 100 cycles.

Interest in all-solid-state Li-ion batteries with better safety and in Li-redox-flow batteries has stimulated research on solid Li-ion electrolytes. Inorganic oxide electrolytes with garnet (e.g., Li$_3$La$_2$Zr$_2$O$_{12}$), perovskite (e.g., Li$_3$La$_2$Ta$_2$O$_{12}$), anti-perovskite (e.g., Li$_3$OHCl) and NASICON (e.g., Li$_3$Al$_2$Ti$_5$(PO$_4$)$_3$) structures have suitable Li-ion transport channels and show acceptable Li-ion conductivities at room temperature. Li$_3$La$_2$Zr$_2$O$_{12}$ (LLZO)-derived garnet electrolytes, which have a Li-ion conductivity of 10$^{-3}$ S cm$^{-1}$ at 25 °C and better stability versus Li metal than the other ceramic electrolytes, face two great challenges: 1) a large interfacial resistance for Li-ion transfer and 2) lithium-dendrite penetration along grain boundaries.

The origin of the large interfacial resistance is related to the cubic garnet instability at room temperature. The Li$^+$ of the garnet electrolyte reacts with moisture and carbon dioxide in air to form LiOH and Li$_2$CO$_3$ on the surface of LLZO grains; this reaction also occurs inside the pellets through the grain boundaries. Both LiOH and Li$_2$CO$_3$ are Li-ion insulators, which leads to a large interfacial resistance of the garnet electrolyte against lithium metal and other materials. The garnet materials are also unstable in an aprotic solvent and show a large, increasing interfacial resistance with a commercial organic liquid electrolyte.

Here, we used LiF to increase the stability of the garnet electrolyte Li$_3$La$_2$Zr$_2$Ta$_2$O$_{12}$ (LLZT) against moisture and carbon dioxide in air (Figure S1 in the Supporting Information); the interfacial resistances between LLZT and lithium metal or a solid polymer electrolyte were reduced significantly, which makes LLZT a possible electrolyte in all-solid-state Li-ion rechargeable batteries and in Li-S batteries. In an all-solid-state Li/polymer/LLZT-2LiF/LiFePO$_4$ battery, the Li-ion conducting, cross-linked polyethylene oxide (CPEO)-LiTFSI polymer with a melting point of 240 °C works as a buffer layer that is wet by Li metal and suppresses the Li-dendrite growth. The LiFePO$_4$ cathode was mixed with the CPEO-LiTFSI polymer to reduce the interfacial resistance between garnet electrolyte and LiFePO$_4$.

The XRD patterns of the as-prepared Li$_3$La$_2$Zr$_2$Ta$_2$O$_{12}$ (LLZT) with different amounts of LiF are shown in Figure 1a and Figure S2; all the pellets crystallize in a cubic garnet structure with high purity and the lattice parameters of all the LLZT pellets calculated by the refinement with the Fullprof software were $a = 12.9340$ Å. LiF does not enter into the LLZT grains. The constant cubic lattice parameter shows that the LiF has little influence on the incorporation of any adventitious Al$^{3+}$ and little substitution of F$^-$ for bulk O$^{2-}$; LiF melts at 845 °C and covers the surfaces of the LLZT particles (Figure S1), which is confirmed by the EDS mapping in Figure S3; it reduces the reaction between LLZT grains and moist air. Moreover, the Li–Al–O glass phase in the LLZT grain boundaries is also unstable with moist air. The LiF on the grain surface of LLZT helps to stabilize the grain boundaries of LLZT by reducing the reaction of the Li–Al–O grain-boundary phase with moist air. A 2 wt% LiF was the best concentration to optimize the stability of LLZT against moist air and to keep the high total conductivity of LLZT. The densities of LLZT and LLZT fired with 2 wt % LiF (LLZT-2LiF) pellets are 93.2 and 92.2%, respectively; a good connection between the grains (Figure S3) reduced the grain-boundary resistance.

The ionic conductivities of LLZT with and without LiF were measured with Li-ion blocking electrodes; the impedance plots with typical semicircles are shown in Figure 1b.
and Figure S4a. The LLZT pellets with and without LiF have the same bulk conductivities of $10^{-3}$ S cm$^{-1}$ at 25°C. The grain-boundary resistance of LLZT-2LiF pellet is a little larger than that of the pellet without LiF; the total conductivities of the LLZT pellets and LLZT-2LiF are 5.5 and 5.2 \times 10^{-4} \text{S cm}^{-1} at 25°C, respectively. The Arrhenius plots of LLZT and LLZT-2LiF in Figure S4b over the range 298–450 K gives the activation energies of 0.35 and 0.30 eV, respectively. The impedance plots of the Li/garnet/Li symmetrical cells at 25°C are shown in Figure 1d; the interfacial resistance of the Li/LLZT-2LiF/Li was 345 \Omega cm$^{-1}$, which is far smaller than that of Li/LLZT/Li (1260 \Omega cm$^{-2}$). The density of the LLZT pellets had little influence on the interfacial resistance between Li metal and LLZT pellets with different amounts of LiF are shown in Figure S6; the LLZT pellet with 2 wt% LiF had the smallest interfacial resistance against Li metal.

The LiF has a strong ionic bond and is insoluble in water; in a grain boundary of the garnet, it prevents diffusion of moisture and carbon dioxide into the pellet. The XPS data of the fresh LLZT sample is shown in Figure 1c; the two peaks in the Cls spectrum located at 285.0 and 290.0 eV correspond to adventitious carbon and carbonate, respectively; and the ratio of Li$_2$CO$_3$ to the C peak of LLZT and LLZT-2LiF was 79.8 and 20.7%, respectively. The Li$_2$CO$_3$ in the starting material decomposes above 900°C and reforms on the surface of the LLZT particles during cooling. The LLZT pellets with and without LiF were aged in air for two weeks and their thermal stabilities were studied with TGA (Figure 2a); the weight losses before 100 and 400°C can be assigned to the dehydration of superficial water molecules on the particle surfaces and the decomposition of Al-OH and the Zr-OH hydroxides, respectively. The weight loss of LLZT-2LiF pellets (0.6 wt%) is far smaller than that of the LLZT pellet (2.2 wt%), which confirms the surface LiF suppresses the build-up of surface adsorbents.

The Raman spectra and mapping results of LLZT and LLZT-2LiF pellets, which had been aged in air for two weeks, are shown in Figure 2b; the introduction of LiF changed the surface composition significantly. Three extra peaks located at 154, 192 and 1090 cm$^{-1}$ in LLZT without LiF, which correspond to the vibration of CO$_2^{2-}$- [10] disappeared in the LLZT-2LiF. The low number Raman peaks are characteristic of cubic LLZT. The change of relative intensity of peaks at 98, 121, 247 and 363 cm$^{-1}$ is the result of different Li–O bonding in LLZT and LLZT-2LiF. The reduction of the Raman peak width and the symmetry change of LLZT may be related to the Li loss. [11] Typical signals of CO$_2^{2-}$ are observed in fixed spots of the mapping spectra in Figure 2c,d. 400 different positions (spot size $3 \times 3 \mu m^2$) in one $50 \times 50 \mu m^2$ area were selected for the Raman mapping. The color in Figure 2c and d corresponds to the integral area, which was calculated from the characteristic peak of Li$_2$CO$_3$ at 1090 cm$^{-1}$. The LLZT pellet displayed much stronger signals of CO$_2^{2-}$ than the LLZT-2LiF pellet, which confirmed the smaller Li$_2$CO$_3$ formation on the surface and grain boundaries of LLZT with LiF. The LiF on the surface and grain boundaries of the pellet reduced the contact of the LLZT with moisture and CO$_2$ in air and stabilized the LLZT pellet. However, with more than 3 Li per formula unit Li$_{2}$La$_{2}$Zr$_2$Ta$_2$O$_{12}$ may result in an instability of a Li-rich garnet in moist air. The reaction of LLZT with carbon dioxide in the surface reaction 2Li$^+$ + O$^{2-}$ + CO$_2$ = Li$_2$CO$_3$ would reduce the strong coulombic repulsion between Li ions in the face-shared tetrahedra.
and octahedra of Li-rich LLZT; the resulting layer of Li$_2$CO$_3$ on the surface of the pellets blocks the Li-ion transport across the interface. Li$_2$CO$_3$ was distributed on the surface of the particles inside the LLZT pellets, which was confirmed by the Raman mapping of the polished samples (Figure S7); polishing of LLZT surface is not able to eliminate the Li$_2$CO$_3$ on the surfaces of the particles inside the pellets.

The LLZT pellets are chemically stable with Li metal, but lithium dendrites penetrate the LLZT pellets in a very short time. A thin gold layer sputtered on the surface of garnet electrolytes has been reported to form one Li-alloy layer and to reduce the interfacial resistance with Li metal,[12] the obtained interfacial resistance was from Li-alloy/garnet, and Li metal worked as a current collector. This method cannot suppress Li-dendrite formation; the Li/Au/LLZT/Au/Li cell short circuited in 10 min at 100 $\mu$A cm$^{-2}$.[13] In addition to the interfacial resistance of Li/garnet, the reduction of the interfacial resistance between garnet and the cathode and any organic catholyte are more important where garnet electrolytes are used in an all-solid-state Li-ion battery or a Li-redox-flow battery. To prepare an all-solid-state Li battery, a Li-metal anode and garnet pellets were separated by a solid-state Li-ion-conducting polymer membrane that is not reduced by Li metal and is wet by Li metal, which suppresses any formation of either dendrites or solid-electrolyte interphase at the Li-metal/polymer interface at 65°C.[19] The LiFePO$_4$ cathode, in a loading of 5 mg cm$^{-2}$, was prepared by mixing LiFePO$_4$ powder with the solid-state polymer and carbon black, which provide LiFePO$_4$ access to a Li-ion conductor and an electronic conductor at the three-phase boundary. In Figure S5a, the total resistance of an all-solid-state Li/polymer/LLZT-2LiF/LiFePO$_4$ battery is almost half that of the all-solid-state battery with garnet LLZT without LiF. LLZT-2LiF shows a lower interfacial resistance of 385 $\Omega$ cm$^{-2}$ with the solid polymer than that of LLZT (about 900 $\Omega$ cm$^{-2}$). The charge/discharge voltage profiles of LLZT and LLZT-2LiF at current densities of 80 and 160 $\mu$A cm$^{-2}$ at 65°C are shown in Figure 3. The all-solid-state Li/polymer/LLZT-2LiF pellet/LiFePO$_4$ battery had a lower overpotential of 0.2 V at 80 $\mu$A cm$^{-2}$ because of the smaller interfacial resistance; the initial discharge capacities were 142 and 128 mAh g$^{-1}$ at 80 and 160 $\mu$A cm$^{-2}$, respectively. The capacity is retained at 120 mAh g$^{-1}$ during 100 cycles at 80 $\mu$A cm$^{-2}$ with a high coulombic efficiency of 99.8–100%; the lack of an SEI layer on both the anode and the cathode increases the coulombic efficiency of the cell. The LLZT-2LiF shows a smaller interfacial resistances with the solid CPEO polymer and LiFePO$_4$ cathode than the antiperovskite Li$_x$(OH)$_y$F$_z$Cl electrolyte. The total resistance of the all-solid-state Li/CPEO-LiTFSI/LLZT-2LiF/LiFePO$_4$ battery is one third of the all-solid-state Li/CPEO-LiTFSI/Li$_x$(OH)$_y$F$_z$Cl/LiFePO$_4$ battery; moreover, the all-solid-state battery with LLZT-2LiF electrolyte showed higher capacities and much longer cycling life than the all-solid-state battery with Li$_x$(OH)$_y$F$_z$Cl electrolyte.[16] The solid polymer layer has a stable interface with Li metal and garnet, which helps to improve the cycling of the all-solid-state battery. The all-solid-state ceramic batteries with garnet electrolyte usually have larger internal resistances and only work at small current densities; for example, one interface-engineered all-solid-state ceramic battery based on garnet electrolyte has a large resistance of 10000 $\Omega$ and has a capacity of 20 Ah kg$^{-1}$ at a current of 2 A kg$^{-1}$ at 95°C.[14]

To demonstrate further the advantages of the LiF modification that decreases the interfacial resistance, Li-S cells with a LLZT and a LLZT-2LiF solid electrolyte were assembled. The solid electrolyte can efficiently block the polysulfide shuttle, which is a severe problem in Li-S batteries.[15] The total resistance of the cells with LLZT and LLZT-2LiF in Figure 4a were 1000 and 2620 $\Omega$ cm$^{-2}$, respectively. The cells with LLZT and LLZT-LiF display well-defined discharge/charge plateaus and low overpotentials, suggesting full electrolyte wetting. The cell with LLZT-2LiF exhibited a much lower voltage gap (0.34 V) than that with LLZT (0.59 V) at the current density of 200 $\mu$A cm$^{-2}$. The much reduced interfacial resistance allows the cells to be cycled at high current densities. As shown in Figure 4c, discharge capacities of 1137, 1074, and 1042 mAh g$^{-1}$ can be obtained at the rates of 100, 200 and 300 $\mu$A cm$^{-2}$, respectively. Notably, since the polysulfide shuttle can be completely blocked by the solid electrolyte, the hybrid cells assembled also exhibit a stable cyclability at 200 $\mu$A cm$^{-2}$. The reversible capacity stabilized at 988 mAh g$^{-1}$ after 100 cycles with the retention of 93% of the stabilized capacity in the second cycle (Figure 4d). Furthermore, the coulombic efficiency maintains almost 100% over the subsequent 100 cycles, which is much higher than the Li-S cell without garnet in Figure S8, indicating that the solid electrolyte can successfully block the polysulfide shuttle during the whole cycling process.

In summary, a garnet LLZT with a clean surface and a good stability against moist air was easily prepared by adding 2 wt.% LiF. The small interfacial resistance between garnet LLZT-2LiF and Li metal, solid-state-polymer electrolyte and organic electrolyte makes it more promising as a solid

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**Figure 3.** a) The impedance plots of Li/LLZT/LiFePO$_4$ battery, b) charge and discharge voltage profiles of Li/LLZT/LiFePO$_4$ at 80 $\mu$A cm$^{-2}$ and c) 160 $\mu$A cm$^{-2}$, d) capacity retention and cycling efficiency of the LiFePO$_4$/Li cells at 80 and 160 $\mu$A cm$^{-2}$.

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**Figure 4.** a) The impedance plots of Li/LLZT/LiFePO$_4$ battery, b) charge and discharge voltage profiles of Li/LLZT/LiFePO$_4$ at 80 $\mu$A cm$^{-2}$ and c) 160 $\mu$A cm$^{-2}$, d) capacity retention and cycling efficiency of the LiFePO$_4$/Li cells at 80 and 160 $\mu$A cm$^{-2}$.
electrolyte in Li-S batteries and all-solid-state rechargeable lithium batteries.

Acknowledgements

The polymer development work was supported by the National Science Foundation Grant No.CBET-1438007, and the LLZT solid electrolyte work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award No. DESC0005397. Research has been partly supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy through the Advanced Battery Materials Research (BMR) Program.

Conflict of interest

The authors declare no conflict of interest.

Keywords: all-solid-state battery · interfacial resistance · Li-rich garnet · Li-S battery · lithium fluoride

How to cite: Angew. Chem. Int. Ed. 2017, 56, 753–756
Angew. Chem. 2017, 129, 771–774


Manuscript received: September 12, 2016
Revised: November 14, 2016
Final Article published: December 9, 2016