

NASICON $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ Solid Electrolyte for an All-Solid-State Li-Metal Battery

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A thin solid electrolyte with a high Li^+ conductivity is used to separate the metallic lithium anode and the cathode in an all-solid-state Li-metal battery. However, most solid Li-ion electrolytes have a small electrochemical stability window, large interfacial resistance, and cannot block lithium-dendrite growth when lithium is plated on charging of the cell. Mg^{2+} stabilizes a rhombohedral NASICON-structured solid electrolyte of the formula $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ (LMZP). This solid electrolyte has Li-ion conductivity two orders of magnitude higher at 25 °C than that of the triclinic $\text{LiZr}_2(\text{PO}_4)_3$. ^7Li and ^6Li NMR confirm the Li-ions in two different crystallographic sites of the NASICON framework with 85% of the Li-ions having a relatively higher mobility than the other 15%. The anode–electrolyte interface is further investigated with symmetric Li/LMZP/Li cell testing, while the cathode–electrolyte interface is explored with an all-solid-state Li/LMZP/LiFePO₄ cell. The enhanced performance of these cells enabled by the $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ solid electrolyte is stable upon repeated charge/discharge cycling.

1. Introduction

The need to develop a safe all-solid-state Li-metal battery with performance comparable to or better than commercial rechargeable Li-ion batteries with a toxic and flammable organic liquid electrolyte has stimulated intense research efforts into Li^+ solid electrolytes.^[1–5] Moreover, a solid electrolyte serves as a critical component in enabling Li–S and Li–air batteries as it prevents the diffusion of dissolved species (e.g., sulfide polyanions) toward the Li-metal anode.^[6–8] For these applications, the fast Li^+ conducting solid electrolyte should have a large electrochemical window, fast Li^+ transfer across the electrolyte/electrode interface, and an overall thickness of less than 20 μm . Oxide-based Li^+ conductors are good candidates for these batteries owing to their

stability in air and larger electrochemical windows compared to sulfide and halide electrolytes. In framework crystal structures such as LISICON ($\text{Li}_{11-x}\text{Me}_{2-x}\text{P}_{1+x}\text{S}_{12}$ with $\text{Me} = \text{Ge}, \text{Sn}$),^[9,10] garnet (e.g., $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12}$),^[11] NASICON (e.g., $\text{Li}_{1+x}\text{Al}_x(\text{Ti}/\text{Ge})_{2-x}(\text{PO}_4)_3$),^[12–15] perovskite (e.g., $\text{Li}_{0.33}\text{La}_{0.55}\text{TiO}_3$),^[16] and antiperovskite electrolytes (e.g., $\text{Li}_{3-x}\text{OH}_x\text{Cl}$),^[17] the Li^+ sites and Li^+ vacancies form a 3D and size-matched channel for Li^+ movement. However, most oxide electrolytes show a large resistance at the solid-electrolyte/electrode interfaces because of the mechanically rigid physical contact intrinsic to a solid–solid interface as well as a weak chemical interaction between the solid electrolyte and the electrode. Additionally, solid electrolytes with strong $\text{Li}^+ - \text{O}^{2-}$ ionic bonds are usually unstable in air, resulting in the formation of a surface layer largely consisting of Li^+ -insulating compounds (e.g., Li_2CO_3 and LiOH).^[18,19] This surface layer has several attributes detrimental to the material's capability to serve as a viable solid electrolyte; 1) Li^+ movement across grain boundaries and at the electrolyte/electrode interface is severely slowed, and 2) the wettability of the solid electrolyte by a Li-metal anode is drastically reduced, causing poor interfacial compatibility. Exploring new materials for a solid electrolyte that is stable in air with a high Li^+ conductivity and a small resistance at the solid-electrolyte/electrode interface remains a great challenge in establishing a commercially viable all-solid-state battery.

Several compounds have provided hope for a competitive solid electrolyte. The NASICON-structured $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ shows a maximum bulk Li^+ conductivity of $10^{-3} \text{ S cm}^{-1}$ at

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25 °C and is water-stable, providing a small interfacial resistance in aqueous Li-air batteries. Unfortunately, the Ti^{4+} present in $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ is easily reduced at low voltages (<2 V versus Li^+/Li), making it chemically unstable against Li metal.^[20–23] NASICON-structured $LiZr_2(PO_4)_3$ provides a more electrochemically stable option than $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ because the energy of the Zr^{4+}/Zr^0 redox couple in $LiZr_2(PO_4)_3$ is above the Fermi level of Li metal. The crystal structure of $LiZr_2(PO_4)_3$ is highly dependent on the sintering temperature and has four different crystalline phases. The rhombohedral $LiZr_2(PO_4)_3$ prepared at high temperatures shows the best Li^+ conductivity but is only stable at temperatures above 50 °C,^[24,25] and does not show ionic conductivity to the levels required for full cell battery operation at room temperature. This lack of sufficient conductivity compared to the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ material stems from the small Li^+ population in $LiZr_2(PO_4)_3$ relative to the available Li-sites in the NASICON framework. We recently reported the preparation of the rhombohedral $LiZr_2(PO_4)_3$ phase with acetate precursor materials.^[26] The resulting material showed excellent Li^+ transfer across the $Li/LiZr_2(PO_4)_3$ interface.

We have introduced Ca^{2+}/Y^{3+} doping to stabilize the rhombohedral $LiZr_2(PO_4)_3$ phase at room temperature;^[27,25] however, the Li-ion local environment and the performance of the doped $LiZr_2(PO_4)_3$ in an all-solid-state Li-metal battery are not characterized. In this work, we set out to improve the Li-ion population in the NASICON framework starting from $LiZr_2(PO_4)_3$ with Mg^{2+} -

doping. This doping strategy improves the Li^+ conductivity of $LiZr_2(PO_4)_3$ by increasing the Li^+ concentration in the material as well as by stabilizing the rhombohedral phase of the material at 25 °C by introducing Mg^{2+} into the structure. 6Li NMR was performed to examine the local Li^+ environments and the mobilities of Li^+ -ions in different sites of $Li_{1.2}Mg_{0.1}Zr_{1.9}(PO_4)_3$ (LMZP). The $Li_{1.2}Mg_{0.1}Zr_{1.9}(PO_4)_3$ solid electrolyte was tested in symmetric $Li/LMZP/Li$ cells and all-solid-state Li-metal batteries with an $LiFePO_4$ cathode. Ex situ time-of-flight secondary ion mass spectrometry (TOF-SIMS) on a LMZP pellet cycled in a symmetric $Li/LMZP/Li$ cell confirmed the chemical formation of a Li_3P layer that allows fast Li^+ -transfer across the $Li/LMZP$ interface and suppresses dendrite formation during lithium plating.

2. Results and Discussion

The samples of $Li_{1+2x}Mg_xZr_{2-x}(PO_4)_3$ ($0.05 \leq x \leq 0.15$) for diffraction and ionic conductivity measurements were prepared with two different sintering methods. A set of samples for each composition of $x = 0.05$, $x = 0.1$, and $x = 0.15$ were sintered by conventional sintering (CS) in a box furnace, and a separate set of samples for each of the aforementioned compositions were sintered via spark plasma sintering (SPS). The X-ray diffraction (XRD) patterns of these samples are shown in Figure 1a and Figure S1 in the Supporting Information. Two

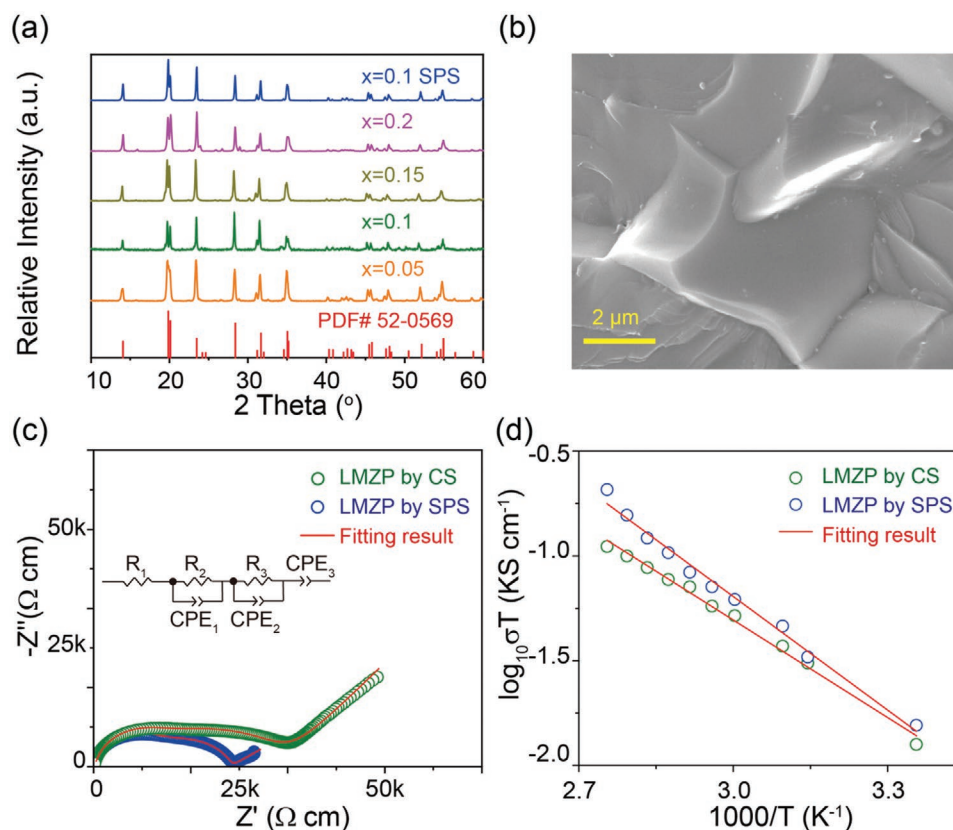


Figure 1. a) XRD patterns of $Li_{1+2x}Mg_xZr_{2-x}(PO_4)_3$ samples ($0.05 \leq x \leq 0.15$) sintered by CS and SPS, b) cross-sectional SEM image of $Li_{1.2}Mg_{0.1}Zr_{1.9}(PO_4)_3$ (LMZP) pellet sintered by SPS at 1050 °C for 10 min, c) room-temperature electrochemical impedance spectra (inset: equivalent circuit), and d) Arrhenius plots of LMZP pellet sintered by CS and SPS in the temperature range of 298–370 K.

complementary factors dictate the phase composition of the final $\text{Li}_{1+2x}\text{Mg}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ samples at 25 °C, the sintering temperature and Mg^{2+} doping concentration. The $\text{Li}_{1+2x}\text{Mg}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ samples ($x = 0.05, 0.1, \text{ and } 0.15$) fired at 1150 °C for 16 h by CS have a pure rhombohedral phase (space group: $R\bar{3}c$); impurity phases began to show in the sample with $x = 0.2$. Refinement of the XRD patterns of $\text{Li}_{1+2x}\text{Mg}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ ($x = 0.05, 0.1, \text{ and } 0.15$) showed a slight reduction of lattice parameter a and a slight increase of lattice parameter c (Figure S1c, Supporting Information) compared to those reported for the rhombohedral $\text{LiZr}_2(\text{PO}_4)_3$ phase at 150 °C.^[28] The minute change in the a and c lattice parameters in the doped samples can be attributed to Mg^{2+} and Zr^{4+} having the same ionic radius of 0.72 Å. Pure rhombohedral phase LMZP pellets were also obtained at 1050 °C for 10 min with SPS. The molar ratio of Li^+ , Mg^{2+} , and Zr^{4+} in LMZP, confirmed by ICP, was 1.28:0.11:1.86; the higher Li^+ concentration is attributed to the excess lithium precursor added during preparation. The LMZP ($x = 0.1$) pellet prepared by SPS has a much higher density (2.95 g cm⁻³) than that of the CS pellet (2.66 g cm⁻³), which is confirmed with scanning electron microscopy (SEM) images (Figure 1b; Figure S2, Supporting Information). The porous LMZP pellet prepared by CS at 1150 °C for 16 h shows relatively poor grain contact, while the LMZP pellet prepared by SPS shows good contact between particle grains. The powders sintered at 1150 °C by CS were used to prepare the dense SPS pellet. Therefore, LMZP prepared by SPS has a larger grain size than the sample prepared by CS, which also helps to reduce the grain boundary resistance. The improved contact between the grains of the SPS pellet could drastically reduce the Li^+ grain boundary resistance.

The electrochemical impedance spectra of $\text{Li}_{1+2x}\text{Mg}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ pellets prepared by CS and SPS shown in Figure 1c and Figure S3 in the Supporting Information have two semicircles at the high and moderate frequencies, which correspond respectively to the Li^+ movement in the bulk and across grain boundaries of $\text{Li}_{1+2x}\text{Mg}_x\text{Zr}_{2-x}(\text{PO}_4)_3$. $\text{Li}_{1+2x}\text{Mg}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ with $x = 0.1$ ($\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$; LMZP) has the highest bulk and total Li^+ conductivities of 1.2×10^{-4} and 2.8×10^{-5} S cm⁻¹ at 25 °C, respectively. These conductivity values are much higher

than those of $\text{LiZr}_2(\text{PO}_4)_3$ (10^{-6} S cm⁻¹ at 25 °C). The total Li^+ conductivity of $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ is further increased to 4.2×10^{-5} S cm⁻¹ at 25 °C with SPS (Figure 1c) by increasing the density of the pellet, which reduces grain boundary resistance. The cyclic voltammogram of a Li/LMZP/Au cell verified that the LMZP is stable up to 5.5 V versus Li^+/Li (Figure S3d, Supporting Information). The activation energies for Li^+ transport of the $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ sintered by CS and SPS are 0.40 and 0.36 eV (Figure 1d), respectively. Activation energies on this scale are similar to those of other solid electrolytes with fast Li^+ conductivity, such as the garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$.^[29] Doping NASICON electrolytes can stabilize the fast Li-ion conducting rhombohedral phase. Further aliovalent doping for P^{5+} or Zr^{4+} ions in this material could provide an additional pathway to increase the concentration of mobile Li^+ -ions, potentially improving its bulk Li-ion conductivity.

The chemical stability of $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ in air was investigated with thermogravimetric analysis (TGA). The TGA results of LMZP pellets aged in air ($\approx 15\%$ relative humidity) for 30 days (Figure S4a, Supporting Information) show no weight loss at temperatures from 25 to 600 °C, indicating that the material did not absorb any species from ambient atmosphere, such as H_2O . The fresh and aged LMZP samples had similar XRD results (Figure S4b, Supporting Information), confirming that LMZP is stable in air. The air-stability of LMZP, which can be related to the strong covalent bonding between $\text{P}^{5+}\text{-O}^{2-}$ in the phosphate anion, could help increase the lithium metal wettability of the pellet by negating the formation of a Li^+ -insulating surface layer such as Li_2CO_3 and/or LiOH .

^6Li solid-state NMR was employed to study the local Li^+ environments and mobilities in $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$. Figure 2 summarizes the high-resolution ^7Li and ^6Li MAS (25 kHz) NMR spectra, and ^7Li T_1 relaxation time measurement of LMZP. Three individual peaks are necessary to simulate the whole ^7Li lineshape in the spectrum of Figure 2a. Of these three peaks, two sharp resonances (-0.93 ppm, blue; -0.67 ppm, brown) are superimposed on a broad component at -0.9 ppm (green dotted line). The two narrower peaks are ascribed to the $+1/2 \leftrightarrow -1/2$ central transition, while the broad component underneath originates

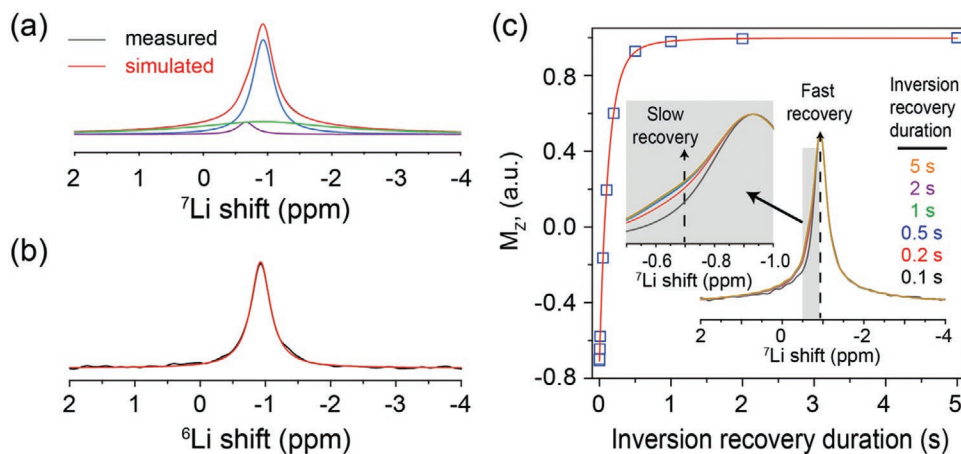


Figure 2. a) ^7Li and b) ^6Li MAS NMR spectra, and c) ^7Li NMR spectra of $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ extracted from ^7Li T_1 relaxation time measurement. Central transitions are filled with colors for the sake of clarity. The blue and purple lines in (a) represent two Li-ion local environments, and the green line is originated from the satellite transition.

from satellite transitions ($3/2 \leftrightarrow 1/2$ and $-1/2 \leftrightarrow -2/3$).^[30] This characteristic of ^7Li NMR lineshape is commonly observed in polymer, glass-ceramic, and glass electrolytes as well as crystalline solid electrolytes.^[31–33] Simulation of the LMZP ^7Li spectrum results in a 9:1 integral ratio (blue peak:brown peak) when taking into account the contribution only from central transitions. This result confirms that most of the lithium resides in one crystallographic site in LMZP, which corroborates reported neutron powder diffraction data where 90% of Li^+ sits in the sixfold disordered 36f tetrahedral site, and the remaining 10% Li^+ ions occupy the threefold disordered 18e tetrahedral site.^[30]

Simulation of the ^6Li spectrum in Figure 2b shows one symmetric peak with a Lorentzian lineshape. The small missing component expected to appear at -0.67 ppm, as in the ^7Li spectrum, is likely attributed to the limited amount of Li sitting in the disordered 18e tetrahedral site as well as low sensitivity of ^6Li NMR, rendering the -0.67 ppm unresolved from the major resonance at -0.93 ppm.^[34] To rule out the possibility that the -0.67 ppm resonance has a slow T_1 relaxation resulting in its invisibility, ^6Li spectra with varied recycle delays from 5 to 500 s were acquired (Figure S5, Supporting Information). The nearly identical lineshape in these ^6Li spectra rules out this possibility. A relatively rapid relaxation of ^6Li magnetization, which is induced by fast ion dynamics, is implied from the Lorentzian lineshape identified in the ^6Li spectrum of LMZP; otherwise, a Gaussian-type lineshape due to orientation-dependent shifts should be observed in ^6Li spectra with longer recycle delays.

We probed the Li-ion mobility in LMZP at room temperature with ^7Li T_1 relaxation time measurements using an inversion-recovery approach. The recovery process of the magnetization is illustrated in the inset of Figure 2c. As the time duration after inversion increases, which shows that the -0.93 ppm resonance recovers much faster than the -0.67 ppm resonance. To more quantitatively analyze the difference, the recovery curve in Figure 2c shows the kinetics for the inverted magnetization returning to its equilibrium. This curve was fitted with a biexponential function, giving rise to two ^7Li T_1 relaxation times with different fractions. 85% of ^7Li spins of the -0.93 ppm resonance have a short relaxation time of 0.12 s, whereas those of the 0.67 ppm resonance LMZP have a much longer T_1 of up to 0.45 s. Different T_1 relaxation times suggest the difference in Li-ion mobility. The T_1 relaxation time (0.12 s) for the majority of the Li^+ -ions is as short as the reported value for the garnet fast Li^+ -ion conductor $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, which implies the potential of LMZP to serve as a solid electrolyte for all-solid-state Li-ion batteries.

A symmetric Li/LMZP/Li cell was assembled to study the stability and Li^+ -transfer at the Li/LMZP interface at 60°C and elucidate any interphase formation. The electrochemical impedance plot of the symmetric cell is shown in Figure 3a. The area-specific resistance of the Li/LMZP interface is about $460 \Omega \text{ cm}^2$, which is significantly lower than that of Li/untreated-garnet interface.^[6] The Li/LMZP interfacial resistance rather than the bulk ionic resistance of the solid electrolyte dominates the total resistance of the cell. Cycling the symmetric Li/LMZP/Li cell at

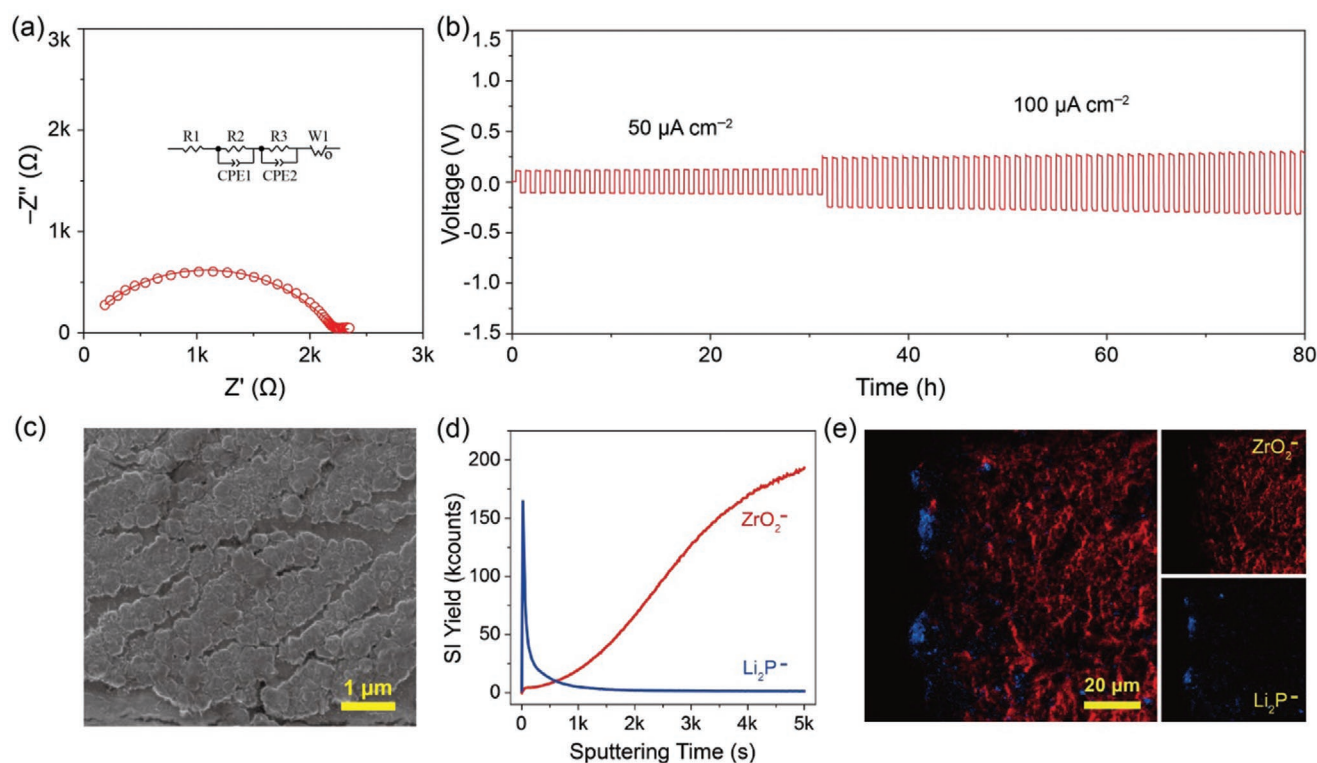


Figure 3. Symmetric Li/LMZP/Li cell at 60°C . a) Electrochemical impedance spectra with the fitting of the symmetric Li/LMZP/Li cell. b) Li/LMZP/Li symmetric cell cycling at different current densities at 60°C . Ex situ characterization of the LMZP pellet after symmetric Li/LMZP/Li cell cycling: c) SEM of lithium metal surface after cycling in a Li/LMZP/Li cell. d) TOF-SIMS depth profiles of Li_2P^- and ZrO_2^- , representing the Li_3P and LMZP, respectively. e) High-resolution cross-sectional chemical map of the LMZP pellet; the interfacial Li_3P layer is partially attached to the lithium foil during battery disassembly.

50 and 100 $\mu\text{A cm}^{-2}$ (Figure 3b) showed an overpotential of 0.12 and 0.25 V, respectively, with no clear additional overpotential increase within 80 h. This symmetric cell data with LMZP is promising as it does not require any other surface treatments or modifications to achieve stable cycling at room temperature. Other solid electrolyte materials, e.g., the garnet family, usually require a Li-alloy buffering layer or a polymer layer to avoid a short-circuit and stabilize the solid electrolyte/lithium metal interface. These modifications are even necessary at low current densities. SEM images of lithium metal cycled in a Li/LMZP/Li symmetric cell show no evidence of dendrite nucleation (Figure 3c), indicating uniform plating/stripping of the lithium-metal anode during cycling and good wettability of the LMZP electrolyte by the Li-metal anode.

The surface of the LMZP pellet changed color, becoming black, when contacted with lithium metal or was cycled in the symmetric Li/LMZP/Li cell. This color change indicates a chemical reaction between the Li metal and the LMZP electrolyte. TOF-SIMS depth profiling and high-resolution cross-sectional chemical mapping on the Li/LMZP interface were performed to elucidate the Li/LMZP interfacial reaction. From the observation of the obtained depth profiles, representative species were chosen to represent each component: 1) the interfacial layer, and 2) the bulk LMZP electrolyte. Li_2P^- was selected to represent the interfacial Li_3P layer that forms at the solid electrolyte/Li-metal interface while ZrO_2^- was selected to represent the bulk LMZP

electrolyte. The superimposed depth profiles of these species are shown in Figure 3d. Li_3P from the reaction between the metallic lithium anode and LMZP has a high concentration after low sputtering times, representing a high species concentration at the surface of the pellet that was in contact with lithium metal.^[26,35] This result is confirmed with the high-resolution cross-sectional mapping of the Li/LMZP interface in Figure 3e, showing the surface of LMZP was covered by Li_3P with a thickness of about 3 μm . Although the LMZP electrolyte is not itself stable against lithium metal, the in situ formed Li_3P layer has been shown to be a good Li^+ -ion conductor. Thus, this in situ formed Li_3P layer that forms at the Li/LMZP interface 1) provides a high Li^+ conductivity across the Li/LMZP interface, 2) maintains a good contact between the metallic lithium anode and LMZP during cycling, and 3) suppresses the lithium-dendrite nucleation and growth by homogenizing the current density on the plating/stripping Li-metal surface. Tailoring the composition of a solid electrolyte to introduce a self-limiting Li-ion conducting and electronically insulating passivation layer at the Li/electrolyte interface is a useful strategy to suppress lithium dendrite growth and achieve stable lithium plating/stripping.

Once the anode/electrolyte interface was clarified, the cathode interface and all-solid-state battery performance of the LMZP electrolyte was studied with a Li/LMZP/LiFePO₄ cell. The electrochemical impedance spectra of the cell is provided in Figure 4a. The cathode composite/electrolyte interfacial

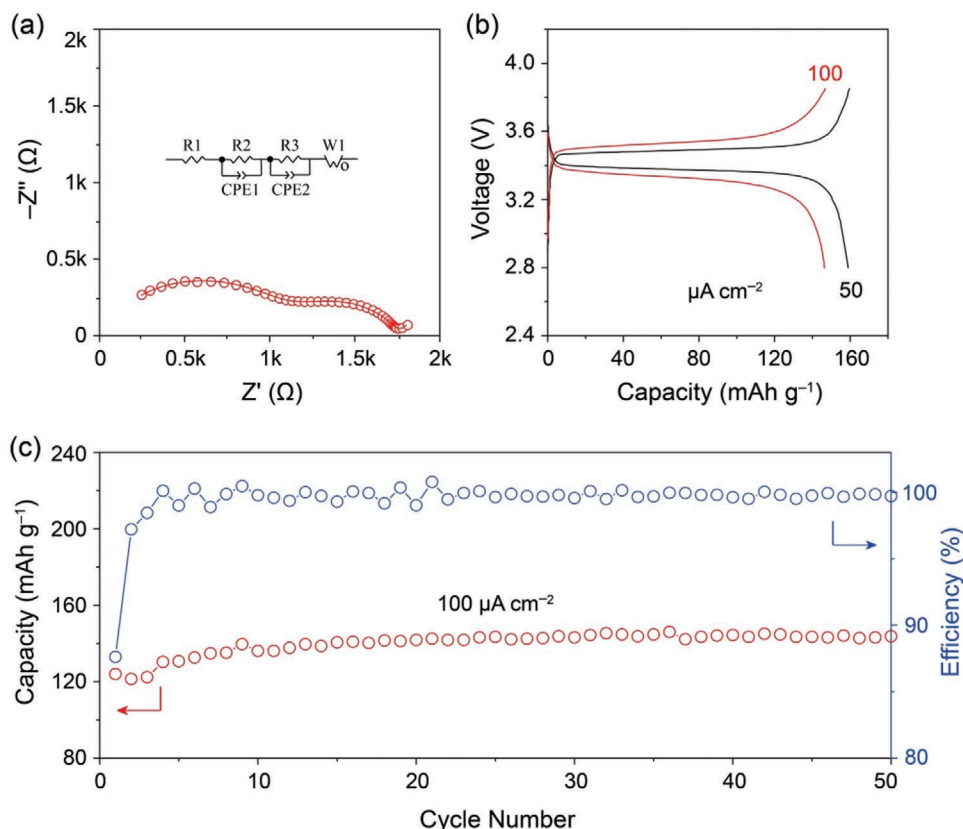


Figure 4. All-solid-state Li/LMZP/LiFePO₄ cell at 60 °C. a) The electrochemical impedance plots of the Li/LMZP/LiFePO₄ cell. b) Galvanostatic charge/discharge voltage profiles. c) Capacity retention and cycling efficiency of the Li/LMZP/LiFePO₄ cell. The active material loading of LiFePO₄ is 3–5 mg cm⁻², and the thickness of the lithium foil is about 0.1 mm.

resistance is $330 \Omega \text{ cm}^2$, which is much lower than those found for the fast Li^+ conducting garnet electrolyte.^[36,37] Galvanostatic cycling of the Li/LMZP/LiFePO₄ cell at a current density of 0.1 mA cm^{-2} was performed in the voltage window of 3.85 to 2.8 V (Figure 4b); the cell has a discharge capacity of 155 and 140 mAh g⁻¹ at 0.05 and 0.1 mA cm^{-2} , respectively, with a high Coulombic efficiency of about 99.5%. This stable cycling shows the stability of the LMZP/LiFePO₄ interface. The cell showed 90% capacity retention after 50 charge/discharge cycles (Figure 4c).

3. Conclusion

The introduction of Mg^{2+} into $\text{LiZr}_2(\text{PO}_4)_3$ stabilizes the fast-ion conducting rhombohedral NASICON-structure at room temperature and increases the Li^+ concentration in the framework structure. Particularly, the rhombohedral $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ phase showed two orders of magnitude higher Li^+ conductivity than the triclinic $\text{LiZr}_2(\text{PO}_4)_3$ phase at 25 °C. The strong Li^+ - Li^+ Coulombic repulsion in the NASICON framework distributes the Li^+ into two different crystallographic sites and reduces the activation energy for Li^+ movement. The surface reduction of $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ by a metallic Li-anode generates the in situ formation of an Li_3P interphase that improves the wettability of $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ by the Li-metal anode and suppresses the nucleation and growth of lithium dendrites. Symmetric Li/LMZP/Li cells and an all-solid-state Li/LMZP/LiFePO₄ battery demonstrate the interfacial stability of the $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ solid electrolyte at the anode/electrolyte interface and the cathode/electrolyte interface, respectively. The good cycling of these cells is enabled by the stability of the electrode/electrolyte interfaces that manifest small interfacial resistances, allowing for greater Coulombic efficiency and capacity retention.

4. Experimental Section

Preparation of Mg^{2+} -Doped $\text{LiZr}_2(\text{PO}_4)_3$: $\text{Li}_{1+2x}\text{Mg}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ ($0.05 \leq x \leq 0.15$) materials were prepared with a traditional solid-state reaction. A stoichiometric amount of LiNO_3 , $\text{Mg}(\text{NO}_3)_2$, ZrO_2 , and $(\text{NH}_4)_2\text{HPO}_4$ were ball-milled for 6 h with a 20 wt% excess of LiNO_3 to compensate for Li_2O loss at elevated temperatures generated during milling. The powders were then sintered at 950 °C for 10 h to decompose the residual nitrates, and the obtained product was ball-milled again for 12 h. The $\text{Li}_{1+2x}\text{Mg}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ powders were then pressed into pellets and fired at 900–1150 °C for 16 h in a box furnace. The powders sintered at 1150 °C were used to prepare dense $\text{Li}_{1.2}\text{Mg}_{0.1}\text{Zr}_{1.9}(\text{PO}_4)_3$ pellets via SPS at different temperatures (900–1150 °C) for 10 min with an applied pressure of 50 MPa.

Material Characterization: The phase composition of the $\text{Li}_{1+2x}\text{Mg}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ ($0.05 \leq x \leq 0.15$) solid electrolytes was determined with powder X-ray diffraction. The fracture surface morphology of the pellets was observed with a field-emission scanning electron microscope. The composition of the $\text{Li}_{1+2x}\text{Mg}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ sample with $x = 0.1$ was measured with the inductively coupled plasma-optical emission spectroscopy (ICP-OES). Electrochemical impedance spectroscopy was performed with a perturbation amplitude of 10 mV in the frequency range of 1 MHz to 1 Hz at varying temperatures between 298 and 370 K on an Autolab potentiostat to measure the A.C. impedance of these materials; Au was sputtered on both sides of the pellet to serve as Li^+ -blocking electrode for this measurement. An Arrhenius model was used to fit the conductivity data and extract the

activation energy for the materials shown in Figure 1d. More than three pellets of each $\text{Li}_{1+2x}\text{Mg}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ composition were tested to confirm the Li^+ conductivity; the error range of the resistance was less than 6%. Cyclic voltammetry (CV) was performed on an Auto-Lab workstation with a Li/LMZP/Au cell to check the electrochemical stability of LMZP.

^{6,7}Li solid-state magic-angle spinning (MAS) NMR experiments were performed on a Bruker 500 spectrometer (11.75 T) equipped with a 2.5 mm HXY Bruker probe. MAS rate was set to 25 kHz, and the operating Larmor frequencies of ⁶Li and ⁷Li were 73.6 and 194.4 MHz, respectively. ⁶Li NMR spectra were collected using a single-pulse sequence with a solid 90° pulse length of 4.75 μs with a variety of recycle delay from 5 to 500 s. ⁷Li NMR spectra were collected using a rotor-synchronized spin-echo pulse sequence. A solid 90° pulse length of 3.35 μs and a recycle delay of 2 s was used. The ^{6,7}Li NMR shift was referenced to $\text{LiCl}_{(s)}$ at -1.1 ppm. Rotor-synchronized (MAS = 25 kHz) spin-echo pulse sequence and single-pulse sequence were employed to acquire ⁷Li spectra with a 90° pulse length of 3.35 μs (R.F. field ≈ 74 kHz) and a recycle delay of 2 s. ⁶Li spectra were obtained via a single pulse with a solid 90° pulse length of 4.75 μs (R.F. field ≈ 52 kHz) and varied recycle delay from 5 to 500 s. ⁷Li T₁ relaxation time was measured using an inversion-recovery sequence. ^{6,7}Li chemical shift was referenced to $\text{LiCl}_{(s)}$ at -1.1 ppm.

An LMZP pellet of 350 μm thickness and a metallic lithium anode with a surface area of 0.5 cm² were used in all battery testing, symmetric cells, and full cells. The symmetric Li/LMZP/Li cell was cycled at 60 °C at different current densities. The area-specific resistance (ASR) was calculated with the equation: $R_{ASR} = ((R_{Total} - R_{LMZP})/2) \times S$; R_{Total} , R_{LMZP} , and S are the total resistance of the symmetric cell, the resistance of the pellet, and the Li/LMZP contact surface area (0.5 cm²), respectively. The symmetric cell after cycling was disassembled in the glovebox for the SEM characterization and ex situ TOF-SIMS characterization. The TOF-SIMS analysis was performed on a ION-TOF GmbH (2010) TOF-SIMS 5 instrument equipped with a Bi⁺ analysis ion gun and a dual sputtering (Cs⁺ and O₂⁺) ion gun. The depth profiles were acquired with the analysis ion gun setup in high current (H.C.) mode (Bi⁺ at 30 keV ion energy, ≈3.7 pA measured sample current) and raster scanned over 100 × 100 μm² areas, while the sputtering gun, using the Cs⁺ source (2 keV ion energy and ≈70 nA measured sample current), was raster scanned over 300 × 300 μm² areas, centered around the analyzed areas.

An all-solid-state Li/LMZP/LiFePO₄ cell was assembled with a Li anode, a LMZP pellet as the solid electrolyte, and a LiFePO₄ composite cathode. The LiFePO₄ cathode was prepared by mixing LiFePO₄, carbon black, polyethylene oxide, and LiTFSI with a weight ratio of 60:12:20:8. Ten cells were assembled and tested to verify the cycling performance of the Li/LMZP/LiFePO₄ all-solid-state batteries; these cells were cycled between 2.8 and 3.85 V versus Li⁺/Li with a LAND battery tester.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

all-solid-state Li-metal batteries, interfacial stability, Li-ion environments, lithium dendrites, NASICON electrolytes

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- [1] Q. Zhao, S. Stalin, C.-Z. Zhao, L. A. Archer, *Nat. Rev. Mater.* **2020**, 5, 229.
- [2] T. Nakamura, K. Amezawa, J. Kulisch, W. G. Zeier, J. Janek, *ACS Appl. Mater. Interfaces* **2019**, 11, 19968.
- [3] A. Manthiram, X. Yu, S. Wang, *Nat. Rev. Mater.* **2017**, 2, 16103.
- [4] M. Weiss, F. J. Simon, M. R. Busche, T. Nakamura, D. Schröder, F. H. Richter, J. Janek, *Electrochem. Energy Rev.* **2020**, 3, 221.
- [5] J. Janek, W. G. Zeier, *Nat. Energy* **2016**, 1, 16141.
- [6] Y. Li, B. Xu, H. Xu, H. Duan, X. Lu, S. Xin, W. Zhou, L. Xue, G. Fu, A. Manthiram, J. B. Goodenough, *Angew. Chem., Int. Ed. Engl.* **2017**, 56, 753.
- [7] J. Liang, Q. Sun, Y. Zhao, Y. Sun, C. Wang, W. Li, M. Li, D. Wang, X. Li, Y. Liu, K. Adair, R. Li, L. Zhang, R. Yang, S. Lu, H. Huang, X. Sun, *J. Mater. Chem. A* **2018**, 6, 23712.
- [8] H. Zhou, Y. Wang, H. Li, P. He, *ChemSusChem* **2010**, 3, 1009.
- [9] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, *Nat. Mater.* **2011**, 10, 682.
- [10] A. Kuhn, O. Gerbig, C. Zhu, F. Falkenberg, J. Maier, B. V. Lotsch, *Phys. Chem. Chem. Phys.* **2014**, 16, 14669.
- [11] Y. Li, C.-A. Wang, H. Xie, J. Cheng, J. B. Goodenough, *Electrochem. Commun.* **2011**, 13, 1289.
- [12] B. Lang, B. Ziebarth, C. Elsässer, *Chem. Mater.* **2015**, 27, 5040.
- [13] P. Zhang, M. Matsui, A. Hirano, Y. Takeda, O. Yamamoto, N. Imanishi, *Solid State Ionics* **2013**, 253, 175.
- [14] M. Kotobuki, M. Koishi, Y. Kato, *Ionics* **2013**, 19, 1945.
- [15] F. Ma, E. Zhao, S. Zhu, W. Yan, D. Sun, Y. Jin, C. Nan, *Solid State Ionics* **2016**, 295, 7.
- [16] V. Thangadurai, W. Weppner, *Ionics* **2000**, 6, 70.
- [17] Y. Li, W. Zhou, S. Xin, S. Li, J. Zhu, X. Lu, Z. Cui, Q. Jia, J. Zhou, Y. Zhao, J. B. Goodenough, *Angew. Chem., Int. Ed. Engl.* **2016**, 55, 9965.
- [18] L. Cheng, E. Crumlin, W. Chen, R. Qiao, H. Hou, S. Lux, V. Zorba, R. Russo, R. Kostecki, Z. Liu, K. Persson, W. Yang, J. Cabana, T. Richardson, G. Chen, M. Doeff, *Phys. Chem. Chem. Phys.* **2014**, 16, 18294.
- [19] W. Xia, B. Xu, H. Duan, Y. Guo, H. Kang, H. Li, H. Liu, *ACS Appl. Mater. Interfaces* **2016**, 8, 5335.
- [20] P. Hartmann, T. Leichtweiss, M. R. Busche, M. Schneider, M. Reich, J. Sann, P. Adelhelm, J. Janek, *J. Phys. Chem. C* **2013**, 117, 21064.
- [21] Y. Liu, Q. Sun, Y. Zhao, B. Wang, P. Kaghazchi, K. R. Adair, R. Li, C. Zhang, J. Liu, L. Y. Kuo, Y. Hu, T. K. Sham, L. Zhang, R. Yang, S. Lu, X. Song, X. Sun, *ACS Appl. Mater. Interfaces* **2018**, 10, 31240.
- [22] B. Wu, S. Wang, J. Lochala, D. Desrochers, B. Liu, W. Zhang, J. Yang, J. Xiao, *Energy Environ. Sci.* **2018**, 11, 1803.
- [23] Y. Zhu, X. He, Y. Mo, *J. Mater. Chem. A* **2016**, 4, 3253.
- [24] K. Arbi, M. A. Paris, J. Sanz, *J. Phys. Chem. B* **2006**, 110, 6454.
- [25] H. Xie, J. B. Goodenough, Y. Li, *J. Power Sources* **2011**, 196, 7760.
- [26] Y. Li, W. Zhou, X. Chen, X. Lu, Z. Cui, S. Xin, L. Xue, Q. Jia, J. B. Goodenough, *Proc. Natl. Acad. Sci. USA* **2016**, 113, 13313.
- [27] Y. Li, M. Liu, K. Liu, C.-A. Wang, *J. Power Sources* **2013**, 240, 50.
- [28] M. Catti, A. Comotti, S. Di Blas, *Chem. Mater.* **2003**, 15, 1628.
- [29] Z. Zhang, Y. Shao, B. Lotsch, Y.-S. Hu, H. Li, J. Janek, L. F. Nazar, C.-W. Nan, J. Maier, M. Armand, L. Chen, *Energy Environ. Sci.* **2018**, 11, 1945.
- [30] M. C. Paulus, M. F. Graf, P. Harks, A. Paulus, P. P. M. Schleker, P. H. L. Notten, R. A. Eichel, J. Granwehr, *J. Magn. Reson.* **2018**, 294, 133.
- [31] K. Hayamizu, Y. Terada, K. Kataoka, J. Akimoto, *J. Chem. Phys.* **2019**, 150, 194502.
- [32] P. Heitjans, M. Wilkening, *MRS Bull.* **2009**, 34, 915.
- [33] Y. Xiang, X. Li, Y. Cheng, X. Sun, Y. Yang, *Mater. Today* **2020**, 36, 139.
- [34] Z. Jian, Y. S. Hu, X. Ji, W. Chen, *Adv. Mater.* **2017**, 29, 1601925.
- [35] H. El-Shinawi, A. Regoutz, D. J. Payne, E. J. Cussen, S. A. Corr, *J. Mater. Chem. A* **2018**, 6, 5296.
- [36] X. Han, Y. Gong, K. K. Fu, X. He, G. T. Hitz, J. Dai, A. Pearce, B. Liu, H. Wang, G. Rubloff, Y. Mo, V. Thangadurai, E. D. Wachsman, L. Hu, *Nat. Mater.* **2017**, 16, 572.
- [37] K. Fu, Y. Gong, B. Liu, Y. Zhu, S. Xu, Y. Yao, W. Luo, C. Wang, S. D. Lacey, J. Dai, Y. Chen, Y. Mo, E. Wachsman, L. Hu, *Sci. Adv.* **2017**, 3, e1601659.