ABSTRACT

Title of Dissertation:	REVISITING THE ELECTROCHEMICAL STABILITY WINDOW OF SOLID ELECTROLYTES FOR THE DEVELOPMENT OF BULK-TYPE ALL-SOLID-STATE LITHIUM BATTERIES		
	Fudong Han, Doctor of Philosophy, 2018		
Dissertation directed by:	Professor Chunsheng Wang, Department of Chemical and Biomolecular Engineering		

Bulk-type all-solid-state lithium-ion batteries (ASSLIBs) are being considered as the ultimate solution for safe lithium-ion batteries due to the replacement of volatile and flammable liquid electrolytes by nonflammable inorganic solid electrolytes (SEs). Significant advances have been made in achieving superionic SEs with a wide electrochemical stability window (ESW) from 0 to 5 V. The ESW of solid electrolytes was usually measured from the Li/SE/inert metal semi-blocking electrode. Because of the wide ESW, solid electrolytes hold great promise for high energy density batteries with high columbic efficiency and long cycle life.

In this dissertation, we challenge the claimed ESW of solid electrolytes. The conventional method to measure ESW provides an overestimated value because the kinetics of the electrochemical decomposition reaction is limited in the semi-blocking electrode. A novel experimental method using Li/SE/SE+carbon cell is proposed to

approach the intrinsic stability window of solid electrolytes. The ESWs of $Li_{10}GeP_2S_{12}$ (LGPS) and $Li_7La_3Zr_2O_{12}$ (LLZO), the most promising SE for sulfide and oxide electrolytes respectively, are examined using the novel experimental method. The results suggest that both SEs have much narrower electrochemical stability window than what was previously claimed. The cathodic and anodic decomposition products for both electrolytes are also characterized. The measured stability window and the decomposition products agree well with the calculated results from first principles. The reversible decompositions of LGPS at both high and low voltages enable the realization of a battery made from a single material.

The electrochemical decompositions of the SEs in ASSLIBs can lead to large interfacial resistances between electrode and electrolyte. The interfacial resistances arising from the decomposition of SEs have been ignored in previous research efforts because the batteries are cycled within the "claimed" stable window of SEs. Suppressing the (electro)chemical reactions between LiCoO₂ cathode and LLZO electrolyte by engineering their interphase enables a high performance all-ceramic lithium battery. By taking advantage of the electrochemical decomposition of SEs, an effective approach to suppress Li dendrite formation in sulfide electrolyte is also demonstrated.

REVISITING THE ELECTROCHEMICAL STABILITY WINDOW OF SOLID ELECTROLYTES FOR THE DEVELOPMENT OF BULK-TYPE ALL-SOLID-STATE LITHIUM BATTERIES

by

Fudong Han

Dissertation submitted to the Faculty of the Graduate School of the University of Maryland, College Park, in partial fulfillment of the requirements for the degree of Doctoral of Philosophy 2018

Advisory Committee: Professor Chunsheng Wang, Chair, Advisor Professor Michael R. Zachariah Professor Dongxia Liu Professor Yifei Mo Professor Sang Bok Lee, Dean's representative © Copyright by Fudong Han 2018

Dedication

To my family

Acknowledgements

I would like to thank my PhD advisor, Professor Chunsheng Wang, for his insightful supervision and great support through the duration of my Ph.D. research. I have always considered myself very lucky to be a student of Professor Wang. The most important thing I learned from Professor Wang is how to think differently with others, which I believe is the most important character for an excellent researcher. I appreciate the freedom and independence Professor Wang provided in pursuing my research interests. I was also deeply impressed by his dedication to research and mentoring. I will try my best to achieve the standard of dedication that I have seen him over the years in my future endeavors.

I would like to thank our collaborators, Dr. Kang Xu from Army Research Lab, Professor Yifei Mo from Department of Materials Science and Engineering, Dr. Karen Gaskell from Department of Chemical and Biochemistry, Dr. Xiangxin Guo from Shanghai Institute of Ceramics. In addition, I would also like to thank my committee members, Professor Sang Bok Lee, Professor Michael R. Zachariah, Professor Dongxia Liu and Professor Yifei Mo. I feel honored to have you on my dissertation committee.

I would like to thank our group members, Dr. Yunhua Xu, Dr. Shiyou Zheng, Dr. Yujie Zhu, Dr. Xiulin Fan, Dr. Tao Gao, Dr. Chao Luo, Dr. Yang Wen, Dr. Liumin Suo, Dr. Zhaohui Ma, Dr. Xiwen Wang, Dr. Fei Wang, Dr. Ji Chen, Dr. Long Chen, Dr. Chongyin Yang, Dr. Xiaogang Li, Dr. Mohammad Kaiser, Mr. Xiangyang Zhu, Mr. Xiao Ji for their help on my research. Finally and most importantly, this work is dedicated to my family. I appreciate their constant encouragement and support. I always feel lucky to have such a lovely family, and I also feel guilty for not having too much time with them. My deepest gratitude goes to my wife, Jie Yue, for her unconditional faith in me and the sacrifice she made to support my dream.

This work is supported by National Science Foundation (Award No. 1235719), Army Research Office (Award No. W911NF1510187), and NEES-EFRC (Award No. DESC0001160). I also thank the financial support from Harry K. Wells Fellowship and All-S.T.A.R. Fellowship from University of Maryland.

Table of Contents

Dedication	ii
Acknowledgements	iii
Table of Contents	v
List of Abbreviations	. vii
Chapter 1: Introduction	1
1.1 All-Solid-State Lithium Ion Batteries	1
1.2 Solid Electrolytes	3
1.3 Interfacial Challenges in All-Solid-State Lithium Ion Batteries	6
1.4 Electrochemical Stability Window of Solid Electrolytes	8
1.4.1 Conventional understandings	9
1.4.2 Inconsistent results in the published literature	. 10
1.5 Motivation and Research Objective	. 11
1.6 Dissertation Overview	. 14
Chapter 2: Electrochemical Stability of Li ₁₀ GeP ₂ S ₁₂ and Li ₇ La ₃ Zr ₂ O ₁₂	. 16
2.1 Introduction	. 16
2.2 Experimental	. 16
2.2.1 Material synthesis	. 16
2.2.2 Material characterization	. 17
2.2.3 Electrochemistry	. 18
2.2.4 First principles computation methods	. 19
2.3 Results and Discussion	. 20
2.3.1 Electrochemical stability of $Li_{10}GeP_2S_{12}$. 20
2.3.2 Electrochemical stability of Li7La3Zr2O12	. 26
2.3.3 Discussion	. 40
2.4 Conclusion	. 46
Chapter 3: A Battery Made from a Single Material	. 47
3.1 Introduction	. 47
3.2 Experimental	. 51
3.2.1 Material synthesis	. 51
3.2.2 Material characterization	. 51
3.2.3 Electrochemistry	. 52
3.3 Results and Discussion	. 54
3.3.1 Feasibility of a single-mateiral battery	. 54
3.3.2 Electrochemical performances of $Li_{10}GeP_2S_{12}$ as a cathode and an anode	e 60
3.3.3 Reaction mechanisms of $Li_{10}GeP_2S_{12}$ cathode and anode	. 63
3.3.4 Single-Li ₁₀ GeP ₂ S ₁₂ all-solid-state lithium-ion battery	. 68
3.3.5 Interfacial behavior of the single- $Li_{10}GeP_2S_{12}$ battery	. 73
3.3.6 Discussion	. 76
3.4 Conclusion	. 79
Chapter 4: Interphase Engineering Enabled All-Ceramic Lithium Battery	. 81
4.1 Introduction	. 81
4.2 Experimental	. 86

4.2.1 Material synthesis	86
4.2.2 Material characterization	87
4.2.3 Preparation of the all-solid-state cell	88
4.2.4 Electrochemistry	88
4.3 Results and Discussion	89
4.3.1 Characterizations of Li ₂ CO ₃ coatings on Li ₇ La ₃ Zr ₂ O ₁₂ and LiCoO ₂	89
4.3.2 All-ceramic LiCoO ₂ /Li ₇ La ₃ Zr ₂ O ₁₂ cathode/electrolyte	92
4.3.3 Electrochemical performances of Li/Li ₇ La ₃ Zr ₂ O ₁₂ /LiCoO ₂ cells	98
4.3.4 Discussion	. 106
4.4 Conclusion	. 108
Chapter 5: Li Dendrite Suppression in Li ₂ S-P ₂ S ₅ by LiI Incorporation	. 110
5.1 Introduction	. 110
5.2 Experimental	. 112
5.2.1 Material synthesis	. 112
5.2.2 Material characterization	. 113
5.2.3 Electrochemistry	. 113
5.3 Results and Discussion	. 114
5.3.1 Stuctrural analysis of (100-x)(0.75Li ₂ S-0.25P ₂ S ₅)-xLiI	. 114
5.3.2 Critical current density of (100-x)(0.75Li ₂ S-0.25P ₂ S ₅)-xLiI	. 116
5.3.3 Cycle stability of 0.75Li ₂ S-0.25P ₂ S ₅ and 70(0.75Li ₂ S-0.25P ₂ S ₅)-30LiI	. 121
5.3.4 Discussion	. 124
5.4 Conclusion	. 127
Chapter 6: Conclusions and Future Work	. 128
6.1 Conclusions	. 128
6.2 Major Contributions	. 128
6.3 Future Work	. 129
6.4 Resulting Publications, Patents, Awards and Conference Presentations	. 132
Bibliography	. 135

List of Abbreviations

- ESW electrochemical stability window
- ASSLIB all solid state lithium ion battery
- LIB lithium ion battery
- EIS electrochemical impedance spectroscopy
- XPS X-ray photoelectron spectroscopy
- XRD X-ray diffraction
- ICP-MS inductively coupled plasma mass spectrometry
- TGA thermogravimetric analysis
- DSC differential scanning calorimetry
- SEM scanning electron microscopy
- EDS energy-dispersive X-ray spectroscopy
- TEM transmission electron microscopy
- OCP open circuit potential
- SEI solid electrolyte interphase
- CV cyclic voltammetry
- EIS electrical impedance spectroscopy
- GITT galvanostatic intermittent titration technique
- ASR area specific resistance
- EC ethylene carbonate
- LiTFSI lithium bis(trifluoromethanesulfonyl)imide
- DME dimethoxyethane

DMC — dimethyl carbonate

- PTFE polytetrafluoroethylene
- PVDF polyvinylidene fluoride

NMP — n-Methyl-2-pyrrolidone

LiPON — lithium phosphorous oxynitride

LISICON — lithium super ionic conductor

NASICON — sodium super ionic conductor

 $LCBO - Li_{2.3-x}C_{0.7+x}B_{0.3-x}O_3$

 $LCO - LiCoO_2$

- $LLZO Li_7La_3Zr_2O_{12}$
- LLTO $Li_{0.33}La_{0.55}TiO_3$
- LNMO LiNi_{0.5}Mn_{1.5}O₄
- $LGPS Li_{10}GeP_2S_{12}$

Chapter 1: Introduction

1.1 All-Solid-State Lithium Ion Batteries

Lithium ion batteries (LIBs) with their high energy density have conquered the market for the portable electronics and are being considered as the most promising energy storage technology for electric vehicles and smart grids. However, packing a lot of energy into a small volume could also cause the safety concerns especially with the ever-increasing demands for the energy density of LIBs. Commercialized LIBs are generally constructed using a graphite anode and a cathode based on transition metal oxide, separated by a membrane soaked with an organic liquid electrolyte (e.g. 1M LiPF₆ in EC/DMC), as shown in **Figure 1.1.**¹ The safety issues are mainly related to the volatile and flammable liquid electrolyte which will cause fires or explosions if the battery is working under abuse conditions such as over-charge and over-heating. All-solid-state lithium-ion batteries (ASSLIBs) are being considered as the ultimate solution for the safety issues because the replacement of the volatile and flammable liquid electrolyte with nonflammable inorganic solid electrolyte could essentially improve the safety of the battery. In addition to that, ASSLIBs also have great potentials to use lithium metal anode (Figure 1.1) because the dense, rigid solid electrolyte could help to suppress the lithium dendrite formation. The utilization of lithium metal anode can largely improve the energy density of battery, and a recent report also show that the energy density of all-solid-state batteries can be higher than that of the conventional liquid-electrolyte batteries when Li metal is used as anode.²



Figure 1.1 Schematic illustration of the conventional liquid-electrolyte lithium battery and bulk-type all-solid-state lithium battery.¹

All-solid-state lithium ion batteries can be generally divided into two categories: thin-film battery and bulk-type battery. **Figure 1.2** shows the cross-section SEM of these two types of all-solid-state batteries.^{3,4} The thin-film micro-battery (total thickness ~15 μ m) prepared by vaccum deposition (pulsed laser deposition, magnetron sputtering, or chemical vapor deposition) techniques have been welldeveloped in the past decade. Despite the excellent cycle stability, the limited stored energy (<100 μ Ah/cm²) restricts its application only in the microelectronic devices. Bulk-type solid-state batteries are more desired for large-scale energy storage such as in electric vehicles and smart grids. A three-phase composite (solid electrolyte, active material, and electro-conductive additives) is usually required for the thick electrode in a bulk-type all-solid-state lithium ion battery.



Figure 1.2 Cross-section SEM images of the thin-film type (a) and bulk-type (b) all-solid-state lithium-ion batteries. ^{3,4}

1.2 Solid Electrolytes

As one of the most important components in all-solid-state lithium ion batteries, solid electrolytes have attracted significant research interest. Similar to an organic liquid electrolyte, a solid electrolyte has also to satisfy several critical requirements: (1) high Li ionic conductivity of $>10^{-4}$ S/cm; (2) low electronic conductivity; (3) electrochemical and chemical compatibility with the anode and cathode and so on. A detailed description about the requirements for an ideal solid electrolyte regarding its application in an all-solid-state battery is shown in **Figure 1.3**.⁵ A variety of materials with either crystalline or amorphous structure have been reported as solid electrolytes for lithium ion batteries.



Fgiure 1.3 Radar Diagram showing the requirements for an ideal solid electrolyte and the qualitative attributes of three inorganic solid electrolytes (LiPON, LGPS and Ligarnet).⁵

Table 1.1 summarizes the room temperature ionic conductivity and activation energy of the common inorganic solid electrolytes which are generally classified to oxides and sulfides depending on their anion species. Sulfide based solid electrolytes can show high reactivity in humid air, forming toxic H₂S gas, and therefore the fabrication and processing have to be done under inert atmosphere. Although most of oxide-based electrolytes seem to be stable in air, the reaction between LLZO and H₂O/CO₂ in humid air leads to the formation of Li₂CO₃.⁶ The formation of Li₂CO₃ can decrease the ionic conductivity of LLZO and increase the interfacial resistance between LLZO and Li metal anode.⁷ Sulfide based solid electrolytes are compliant particles with a low Young's modulus, which allows to form a good contact with electrode by a simple cold press,⁸ but shows a low fracture toughness compared to oxide electrolytes.⁹ Oxide-based solid electrolytes are generally hard particles, and therefore high-temperature sintering is usually required to ensure sufficient contact area and to achieve dense layers. Sulfide electrolytes can have higher ionic conductivities than oxide electrolytes, but Li-garnet oxide is more electrochemically stable than sulfides.¹⁰ Because of the distinct differences between sulfide and oxide electrolytes, different approaches should be used when designing all-solid-state lithium ion batteries with these solid electrolytes.

Table 1.1 Summary of inorganic solid electrolytes for all-solid-state lithium ion

 batteries.

Classes	Solid electrolytes	σ _{RT} (mS/cm)	E _a (eV)	Reference
Oxides	LiI-Al ₂ O ₃	0.26	0.42	11
	LiPON-Li ₂ PO ₂ N	0.003	0.57	12
	Perovskite-Li _{0.33} La _{0.55} TiO ₃	1	0.4	13
	LISICON-Li ₁₄ ZnGe ₄ O ₁₆	0.001	0.4-0.6	14
	NASICON-Li _{1.3} Al _{0.3} Ti _{1.7} (PO ₄) ₃	3	0.35	15
	Garnet-Li ₇ La ₃ Zr ₂ O ₁₂	1	0.35	16
	Antiperovskite-Li ₃ OCl	0.2	0.35	17
Sulfides	β -Li ₃ PS ₄	0.16	0.36	18
	$Li_2S-P_2S_5$ glass-ceramic	2.1	0.15	19
	Argyrodite-Li ₆ PS ₅ Cl	0.2-0.7	0.3-0.4	20
	$Li_{3.25}Ge_{0.25}P_{0.25}S_4$	2.2	0.21	21
	$Li_{10}GeP_2S_{12}$	12	0.27	22
	$Li_{9.64}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$	25	0.24	23

As summarized in the table, major advances have been achieved in increasing the Li ionic conductivity of solid electrolytes. The state-of-the-art solid electrolyte materials, such as Li-garnet Li₇La₃Zr₂O₁₂ (LLZO) for oxides and Li₁₀GeP₂S₁₂ (LGPS) for sulfides have achieved an ionic conductivity of 10^{-3} to 10^{-2} S/cm, which is

comparable to commercial organic liquid electrolyte. After achieving adequate Li ionic conductivity in the solid electrolyte materials, current research efforts turned to enhancing the electrochemical stability of the solid electrolytes and chemical compatibility between the solid electrolyte and electrodes; so that Li metal anode and high-voltage cathodes can be enabled in all-solid-state Li-ion batteries.

1.3 Interfacial Challenges in All-Solid-State Lithium Ion Batteries



Mechanical strain/stress generated at the interface

Figure 1.4 Different sources of interfacial resistance between solid electrolyte and solid electrode in all-solid-state lithium ion batteries.²⁴⁻²⁶

The highly resistive interface was mainly resulted from the insufficient contact between solid electrodes and solid electrolyte because the solid electrolytes are not wettable and infiltrative like liquids, as can be seen in **Figure 1.4**. The poor interfacial contact restricts the fast transport of lithium ions and also decreases the number of active sites for charge transfer reaction. Various attempts have been made to improve the interfacial contact by reducing the electrode particle-size,²⁷ uniaxial or dynamic pressing,^{28,29} molten-salt,^{30,31} screen-printing,²⁴ lattice-matching,³² and onestep spark plasma sintering methods.^{4,33} However, only limited success in enhancing the power density has been achieved because a new interfacial phase layer with a high resistance might also be generated from the unwanted chemical reactions³⁴⁻³⁶ and elemental inter-diffusions³⁷ between the different electrode and electrolyte materials during either synthesis or the charge/discharge cycles. Even worse, the intimate initial contact achieved in the fabrication and/or sintering process may even accelerate the unwanted chemical reactions and elemental inter-diffusions.^{34,38} In addition, the space-charge layers formed at the hetero-interface between the electrode and electrolyte due to their electrochemical potential difference might also increase the interfacial resistance.^{39,40} To minimize these unwanted interfacial interactions (chemical reactions, elemental inter-diffusions and space-charge layer formations), intentional surface coatings with various materials, including ionically conductive,^{39,41} electronically conductive,⁴² or even insulating layers,⁴³ on the electrodes were also reported. Despite apparent improvements using the abovementioned methods, the interfacial resistance still remains too high and may even continuously increase with charge/discharge cycles.⁴⁴ The continuous increase of the interfacial resistance with charge/discharge cycles could be mainly related to the high strain/stress generated at the interface because the large volume changes of the electrodes (especially for the high-capacity electrodes) during lithiation/delithiation are highly constrained by the solid electrolyte.^{26,45} Unfortunately, this problem gets even worse for a thicker electrode that is desired for a high energy-density battery.

Therefore, the exact mechanisms for the high interfacial resistance between solid electrolyte and solid electrolyte are still poorly understood.



1.4 Electrochemical Stability Window of Solid Electrolytes

Figure 1.5 The electrochemical stability window of PP₁₄PF₆.⁴⁶

Electrochemical stability window (ESW) is the voltage range between which the susbstance does not get oxidized or reduced, i.e. inert within this range. Experimentally, it is tested by a linear sweep or cyclic voltammetry (CV). The oxidation and reduction of the substance can be represented by the current above and below 0 A, respectively. The electrochemical stability window can be determined by the voltage difference between the anodic limit (E_{AL}) and cathodic limit (E_{CL}). For example, **Figure 1.5** shows the CV curve of PP₁₄PF₆, and the green region indicates the electrochemical stability window of this material.⁴⁶ 1.4.1 Conventional understandings



Figure 1.6 (a) The conventional cell to test the electrochemical stability window of solid electrolytes. The electrochemical stability window of LGPS (b) and LLZO (c) were determined to be wider than 5 V.^{22,47}

To enable the highest voltage output of the solid-state battery by coupling a lithium metal anode with a high voltage cathode material, a very wide electrochemical stability window (0.0-5.0 V) is desired for an ideal solid electrolyte. The electrochemical stability window of solid electrolytes was commonly tested by a linear sweep or cyclic voltammetry on the Li/solid electrolyte/inert metal electrode, with the voltage starting from negative values to high voltage up to 10 V. Tested by this method, very wide electrochemical stability windows of 0.0 to 5.0 V were reported for many solid electrolytes including LGPS and LLZO,^{22,47} as shown in **Figure 1.6.** Despite this wide stability window, high performance 5 V-class all-solid-state batteries based on LGPS and LLZO electrolytes have not been reported. As a matter of fact, the performances of all-solid-state lithium ion batteries with a voltage < 5V based on these solid electrolytes are far worse than that based on the liquid-electrolyte, even though these solid electrolytes have a comparable ionic conductivity

with the liquid electrolyte. Therefore, high resistance persists at the electrode/electrolyte interface, limiting the performance improvement of all-solid-state batteries.



1.4.2 Inconsistent results in the published literature

Figure 1.7 Phase evolution of the Li-Ge-P-S system as a function of voltage at 0 V (a), 1.8 V (b), and 2.5 V (c).⁴⁸

Recent studies have challenged the claimed stability of the solid electrolyte materials. For example, first principles computational study (**Figure 1.7**)⁴⁸ demonstrated LGPS will be reduced into Li_2S , Li_3P , and $\text{Li}_{15}\text{Ge}_4$ at 0 V, and will be oxidized to S, P₂S₅, and GeS₂ at 2.5 V. These results indicated a true electrochemical window of the LGPS is significantly narrower than the 0.0–5.0 V window obtained using the semi-blocking electrode.

It is also shown that the color of the LLZO pellet will turn from white to black after it was immersed into molten Li,^{49,50} or cycled with Li metal anode. **Figure 1.8** shows the photos of the Nb-doped LLZO pellet after cycling with Li.⁵¹ The color change of LLZO implies that LLZO is not stable with Li metal, and therefore the

electrochemical stability window of LLZO is not as wide as claimed from previous experimental test.



Figure 1.8 Photos of the Nb-doped LLZO pellet after cycling with Li metal anode.⁵¹

1.5 Motivation and Research Objective

The inconsistent results above suggest that the electrochemical window measurements based on the semi-blocking electrodes significantly overestimated the true electrochemical window governed by the intrinsic thermodynamics of the material. The overestimated electrochemical stability of solid electrolytes is caused by the slow kinetics of the decomposition reactions due to the small contact area between LGPS and current collectors. Because of the slow reaction kinetics, the decomposition current is too small to be observed in the CV scan, especially with the presence of the huge Li deposition/dissolution peaks. However, a large amount of carbon and solid electrolyte are mixed together with the active material to form the electrode composite in the bulk-type all-solid-state battery, as shown in **Figure 1.9**.⁵²



Figure 1.9 Schematic showing the electrode composites of bulk-type all-solid-state lithium ion batteries.⁵²

As a result, the reduction or oxidation kinetics of the solid electrolyte in the composite electrode is significantly accelerated because of the significantly-increased contact area between the solid electrolyte and electronic conductive additives. The electrochemical stability window of the electrolyte in the carbon-electrolyte-active material electrode composite cannot be properly captured by the semi-blocking electrodes, which may be only more suitable for the cell configurations in thin-film solid-state batteries. Therefore, a proper cell design is needed to evaluate the electrochemical window of the solid electrolyte in the bulk-type all-solid-state batteries.

More importantly, the limited stability of the solid electrolyte materials, though still neglected by battery community, has significantly restricted the performance of all-solid-state Li-ion batteries. At the cycling voltages beyond the stability window of the solid electrolyte, the decomposition products of the solid electrolyte would form

as an interphase at the interfaces between solid electrolyte and electronic conductive additives. Depending on the properties of the decomposition products, the interphase may lead to an increase in interfacial resistances and a decrease in the performance of the bulk-type solid-state battery. Unfortunately, the interfacial resistance arising from the decomposition of solid electrolytes has been ignored so far due to the overestimated stability window from the semi-blocking electrode measurements. The intrinsic (true) electrochemical stability window of solid electrolytes is critical in understanding the origins of high interfacial resistance in the bulk-type solid-state Liion batteries. However, only few theoretical studies have examined the electrochemical stability of solid electrolytes, and no existing experimental technique can measure the true stability window of the solid electrolytes.

The objective of this proposal is to test the hypothesis that the electrochemical decomposition of solid electrolytes occurs and causes a high interfacial resistance within bulk-type all-solid-state lithium ion batteries. The high interfacial resistance is expected to significantly restrict the performance improvement of all-solid-state lithium batteries. The objective will be realized through combined computational and experimental efforts: (1) first principles calculation of the thermodynamic electrochemical stability window of solid electrolytes, (2) measurement of the intrinsic electrochemical stability window of solid electrolytes with a new experimental method, (3) characterization of the decomposition product by X-ray photoelectron spectroscopy, (4) evaluation of the interfacial resistances due to the decomposition of solid electrolytes by electrochemical impedance spectroscopy, (5) fabrication of a single-material battery, (6) interphase engineering towards a high-

voltage all-ceramic lithium battery. The combined computational and experimental approach offer unprecedented fundamental information of the electrochemical stability of solid electrolytes for the development of high-performance all-solid-state lithium batteries.

1.6 Dissertation Overview

This dissertation consists of six chapters.

Chapter 1 gives an introduction about all-solid-state lithium-ion batteries and an overview about the overestimated electrochemical stability window of solid electrolytes.

Chapter 2 presents the intrinsic electrochemical stability windows of LGPS and LLZO, which are the most promising solid electrolytes for sulfide and oxide, respectively. The thermodynamic electrochemical stability windows of LGPS and LLZO are determined by first-principles calculation. A novel experimental approach using Li/SE/SE+C cell is also proposed to measure the intrinsic stability window of solid electrolytes. The compositions of the decomposition products are also determined by XPS. The relation between the limited electrochemical stability of solid electrolytes and the interfacial resistance is also discussed. The content in this chapter has been published in *Advanced Energy Materials*.¹⁰

Chapter 3 presents a proof of concept for a single-material battery by taking advantage of the reversible electrochemical decompositions of LGPS at both high and low voltages. The electrochemical performances of LGPS as a cathode and an anode are tested with liquid electrolyte and LGPS electrolyte. The remarkable improvement on the interfacial behavior by using a single material as cathode, electrolyte and

anode is also discussed. The content in this chapter has been published in *Advanced Materials*.⁵³

Chapter 4 presents an effective approach to suppress unwanted (electro)chemical reaction between LLZO electrolyte and LCO cathode by interphase engineering. An all-ceramic cathode-electrolyte with an extremely low interfacial resistance is realized by thermally soldering LCO and LLZO together with the $Li_{2.3-x}C_{0.7+x}B_{0.3-x}O_3$ solid electrolyte interphase through the reaction between the $Li_{2.3}C_{0.7}B_{0.3}O_3$ solder and the Li_2CO_3 layers that can be conformally coated on both LLZO and LCO. The all-solid-state Li/LLZO/LCO battery with such an all-ceramic cathode/electrolyte exhibits great cycling stability and high rate performance. The content in this chapter has been published on *Joule*.⁵⁴

Chapter 5 presents a viable approach to suppress lithium dendrite formation in sulfide electrolytes by tuning the composition of the interphase between Li metal and solid electrolyte. We demonstrate that the incorporation of LiI into the Li₂S-P₂S₅ glass electrolytes can effectively improve the dendrite suppression capability, and the $70(0.75Li_2S-0.25P_2S_5)$ -30LiI (LPS30I) electrolyte exhibits the highest capability for dendrite suppression. The mechanisms for the enhanced dendrite suppression capability are also discussed. The content in this chapter has been published on *Advanced Energy Materials*.⁵⁵

Finally, we conclude in Chapter 6 with the main contributions of this dissertation and potential topics for future studies of this dissertation.

Chapter 2: Electrochemical Stability of $Li_{10}GeP_2S_{12}$ and $Li_7La_3Zr_2O_{12}$

2.1 Introduction

In this study, we challenge the claimed stability of the solid electrolyte materials and the use of semi-block electrode design for evaluating the electrochemical window for solid electrolyte materials. The most promising solid electrolytes, Li₁₀GeP₂S₁₂ and cubic Li-garnet Li₇La₃Zr₂O₁₂, were chosen as the model materials for sulfide and oxide solid electrolytes, respectively. First principles calculations were performed to obtain the intrinsic thermodynamic electrochemical stability windows. A new Li/electrolyte/electrolyte-carbon cell was proposed to replace current Li/electrolyte/Pt semi-blacking electrode for the measurement of the true electrochemical stability window of solid electrolytes. The first principles computation and experimental results are in good agreement, indicating that both of these solid electrolyte materials have narrower electrochemical window than what was previously claimed. The understanding of the intrinsic thermodynamics about the solid electrolyte materials at different voltages during the battery cycling provides invaluable guidance for the development of the bulk-type all-solid-state battery.

2.2 Experimental

2.2.1 Material synthesis

Polycrystalline $Li_{10}GeP_2S_{12}$ powder was prepared with the same method reported elsewhere.²² A Ta-doped cubic garnet compound with the composition of

Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂ was prepared through solid state reaction. Starting materials of LiOH·H₂O (99.995%, Sigma Aldrich), La(OH)₃ (99.9%, Sigma Aldrich), ZrO₂ (99.99%, Sigma Aldrich), Ta₂O₅ (99.99%, Sigma Aldrich), were weighed and mixed based on the stoichiometric ratio. 10% excess LiOH·H₂O was used to compensate the Li loss during high-temperature calcinations and sintering. The mixture was ballmilled (PM 100, Retsch) in 2-propanol for 24 hours with zirconia balls in a zirconia vial, and then dried, heated in air at 950 °C for 12 hours. The ball-milling and heating were repeated once to enhance purity. The collected powder samples were pressed into pellets under isostatic pressure (120 MPa). The pellet was fully covered with powder with the same composition and sintered in air at 1230 °C for 12 hours in a MgO crucible. The residual powder samples were transferred to the Ar-filled glovebox to protect its slow reaction with the H_2O/CO_2 in air. For the preparation of the carbon-coated LLZO particles, the as-prepared LLZO powder was grinded using a high-energy vibrating mill (SPEX SamplePrep* 8000M Mixer/Mill) for 1 hour (to reduce its particle size), dispersed into a solution of polyvinylpyrrlidone (10 wt. % in ethanol), and then vigorously stirred for 30 minutes. The product was then dried and sintered at 700 °C for 1 hour in argon flow to enable carbon coating.

2.2.2 Material characterization

Powder X-ray diffraction patterns were obtained with a D8 Advance with LynxEye and SolX (Bruker AXS, WI, USA) using Cu Kα radiation. The morphologies of the sample were examined using a Hitachi a SU-70 field-emission scanning electron microscope and JEOL 2100F field emission transmission electron microscope (TEM). The surface chemistry of the samples was examined by X-ray

photoelectron spectroscopy (XPS) using a Kratos Axis 165 spectrometer. To prepare the sample for XPS test, LLZO electrodes were charged or discharged to a certain voltage in a liquid electrolyte using a Swagelok cell, and held at that voltage for 24 hours. The electrodes were then taken out from the cell, and rinsed by dimethyl carbonate (DMC) inside the glove box for three times. All samples were dried under vacuum overnight, placed in a sealed bag, and then transferred into the XPS chamber under inert conditions in a nitrogen-filled glove bag. Ar⁺ sputtering was performed for 2 hours (0.5 hour per step) until the carbon and/or SEI layer on the surface of the LLZO electrodes are removed. XPS data were collected using a monochromated Al K α X-ray source (1486.7 eV). The working pressure of the chamber was lower than 6.6×10^{-9} Pa. All reported binding energy values are calibrated to the C 1s peak at 284.8 eV.

2.2.3 Electrochemistry

120 mg LGPS powder was pressed into a pellet (diameter 13 mm; thickness 2 mm) under isostatic pressure (120 MPa) in an Ar atmosphere. It was then sputtered with Pt on one side and attached with Li metal on the other side to make the Li/LGPS/Pt cell. To make the Li/LGPS/LGPS-C cell, 10 mg LGPS-C powder (LGPS: graphite is 75:25 in weight) was put on the top of 120 LGPS powder and then cold-pressed together under 360 MPa, while Li metal was attached on the other side of LGPS pellet. The cyclic voltammograms of the Li/LGPS/Pt and Li/LGPS/LGPS-C cells were measured with a scan rate of 0.1 mV s⁻¹. The LLZO electrodes were prepared by mixing the carbon-coated LLZO and carbon black (weight ratio of carbon-coated LLZO to carbon is 40:60) by hand-grinding in the mortar, and mixing

with 10 wt.% polyvinylidene fluoride (PVDF) and n-methylpyrrolidinone (NMP) to make the electrode slurry. The electrodes were prepared by casting the electrode slurry onto copper or aluminum foils and dried at 120 °C overnight. The loading of the active material on each electrode is about 1 mg. The charge/discharge tests of the LLZO electrodes were carried out in Swagelok cells using Li metal as the counter electrode and 1M LiPF₆ in a mixed solvent of FEC, HFE, and FEMC (volume ratio is 2:6:2) as the liquid electrolyte. To make the Li/LLZO/LLZO-C cell for the electrochemical stability window test, the LLZO electrode slurry was coated on the top surface of LLZO pellet, dried at 120 °C overnight, and then sputtered with Pt to improve the electrical contact. After that, Li metal was attached on the other side of the pellet and cured at 200 °C to enhance the interfacial contact between Li and LLZO. The cyclic voltammogram of the Li/LLZO/LLZO-C cell was tested with a scan rate of 0.01 mV s⁻¹. The charge/discharge behavior was tested using an Arbin BT2000 workstation at room temperature. The cyclic voltammetry measurements were carried on an electrochemistry workstation (Solartron 1287/1260).

2.2.4 First principles computation methods

All density functional theory (DFT) calculations in the work were performed using the Vienna *Ab initio* Simulation Package (VASP) within the projector augmented-wave approach, and the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) functional was used. The DFT parameters were consistent with the parameters used in *Materials Project* (MP)⁵⁶. The crystal structures of LGPS and LLZO were obtained from the ICSD database and ordered using *pymatgen* if the material has disordering sites. The electrochemical stability of

the solid electrolyte materials was studied using the grand potential phase diagrams, constructed using *pymatgen*⁴⁸, which identify the phase equilibria of the material in equilibrium with an opening Li reservoir of Li chemical potential μ_{Li} . As in the previous studies,^{48,57} the applied potential ϕ was considered in the Li chemical potential μ_{Li} as

$$\mu_{\rm Li}(\phi) = \mu_{\rm Li}^0 - e\phi,$$

where μ_{Li}^0 is the chemical potential of Li metal, and the potential ϕ is referenced to Li metal.

2.3 Results and Discussion

2.3.1 Electrochemical stability of Li10GeP2S12

Lithium sulfide-based solid electrolytes exhibit high ionic conductivity, low grain boundary resistance, and the excellent mechanical property, which allows forming a good interfacial contact with the electrode by cold-pressing without high temperature sintering.^{28,58} In this study, $Li_{10}GeP_2S_{12}$ (LGPS) is chosen as a typical example of sulfide electrolytes. LGPS was reported to have the highest room-temperature ionic conductivity (~10⁻² S cm⁻¹)²² among all solid electrolyte materials and a wide "apparent" electrochemical stability window of 0.0 - 5.0 V determined by cyclic voltammetry of a Li/LGPS/Pt semi-block electrode.²²



Figure 2.1 The first principles calculation results for the voltage profile and phase equilibria of LGPS solid electrolyte upon lithiation and delithiation.

However, the first principles computation using Li grand potential phase diagram demonstrated that the intrinsic stability window is much narrower than 0.0 - 5.0 V.⁴⁸ The Li grand potential phase diagram identifies the phase equilibria at different potentials and the most thermodynamically favorable reactions at the given potential, assuming the full thermodynamic equilibrium and no kinetic limitation in the reaction and transportation. The same computation scheme has been used in the calculations of voltages and reaction energies in the lithiation/delithiation of battery materials. **Figure 2.1** shows the calculated voltage profile and phase equilibria of LGPS upon lithiation and delithiation, confirming that LGPS has a much narrower electrochemical window than 5.0 V.²² The reduction of the LGPS starts at 1.71 V, where LGPS is lithiated and turns into Li₄GeS₄, P, and Li₂S. With further decrease of the potential, there are multiple thermodynamic voltage plateaus corresponding to the

Li-P and Li-Ge alloying processes upon lithiation. Our calculations predicted the reduction products of LGPS to be Li_2S , $Li_{15}Ge_4$, Li_3P at 0 V, which have been confirmed by the experimental results.⁵³ On the other hand, the oxidization of the LGPS to Li_3PS_4 , S, and GeS₂ starts at only 2.14 V, and the formed Li_3PS_4 is further oxidized into S and P₂S₅ at 2.31 V. In summary, our calculation results have shown that the LGPS has a limited electrochemical stability window from 1.7 to 2.1 V.



Figure 2.2 Potential sweep of the Li/LGPS/Pt semi-blocking electrode at a scan rate of 0.1 mV/s in the voltage range of 0.0-2.5 V (a) and 2.5-4.0 V (b).

The cyclic voltammetry (CV) was used to experimentally evaluate the electrochemical stability of LGPS. Using the conventional Li/LGPS/Pt semi-blocking electrode (voltage range: -0.6 to 5.0 V), the decomposition current within the voltage window of 0.0 to 5.0 V cannot be observed from the CV of LGPS.^{22,53} The "wide" electrochemical stability window of 0.0 - 5.0 V is because the decomposition current is very small and is underestimated by the huge Li deposition/dissolution peaks.⁵⁹ To avoid the huge Li deposition/dissolution peaks, the conventional Li/LGPS/Pt semi-blocking electrode was scanned within restricted voltage windows (0.0 - 2.5 V and

2.5 - 4.0 V). As shown in Figure 2.2, apparent current due to the decomposition of LGPS could be clearly observed in the linear scan of the Li/LGPS/Pt although the reaction current is still very low due to the limited interfacial contact between LGPS and Pt in the Li/LGPS/Pt cell. In this regard, we propose a novel experimental method to measure the electrochemical stability window of LGPS using a Li/LGPS/LGPS-C/Pt cell. A large amount of carbon (graphite, KS-4) was mixed into LGPS (weight ratio of LGPS to carbon is 75:25) to form the electrode. The increased contact between LGPS and carbon would significantly improve the kinetics of the decomposition reaction due to the facile electron transport as well as the significantly increased active area for charge-transfer reaction. Thus, the intrinsic stability window of LGPS is expected to be obtained from the CV scan of the Li/LGPS/LGPS-C/Pt cell. Since the electrochemical decomposition and the lithiation/delithiation of the LGPS are essentially the same process but described from two different perspectives, the reversible decomposition of LGPS electrolyte had been demonstrated using the same Li/LGPS/LGPS-C/Pt cell in the supporting information in Figure 2.3.



Figure 2.3 Electrochemical stability windows of LGPS measured from the Li/LGPS/Pt cell (a) and the Li/LGPS/LGPS+C cell (b and c).

The result indicates that the reduction of LGPS starts at 1.7 V while the oxidation of LGPS starts at 2.1 V. This electrochemical behavior agrees very well with the computational results, and both computational and experimental results indicate the true electrochemical stability window of 1.7 to 2.1 V for LGPS. Additionally, the oxidation of S at high potentials and the formation of Li-Ge and Li-P alloys at the low potentials were also confirmed by the X-ray photoelectron spectrum results.⁵³ The main function of carbon in the LGPS-C composite is to increase the electronic conductivity of LGPS so that the decomposition kinetics could be improved. In this regard, carbon is not the only option for the electronic-conductive additive.



Figure 2.4 Cyclic voltammetry of Li/LGPS/LGPS-Pt/Pt semi-blocking electrode at a scan rate of 0.1 mV/s in the voltage range of 0-2.0 V (a) and 1.0-3.5 V (b).

To exclude the potential interactions between carbon and LGPS, we replaced carbon with the inert metal powder (Pt black), i.e. 25 wt. % Pt black and mixed Pt with LGPS to form the LGPS-Pt composite electrode. The CV curves of the Li/LGPS/LGPS-Pt/Pt cell are shown in **Figure 2.4**. Both the oxidation and reduction peaks could be observed at similar voltages in the CV curves of the Li/LGPS/LGPS-C/Pt cell. The result implies that the redox peaks in Li/LGPS/LGPS-C/Pt cell is not induced by the reaction between carbon and LGPS but the decomposition of LGPS itself. These results demonstrated that the thermodynamic electrochemical stability window of LGPS can be accurately calculated using our computation scheme, and that Li/LGPS/LGPS-C/Pt cell can be used to measure the true electrochemical stability of LGPS.

Therefore, our proposed method of measuring the electrochemical stability of the electrolyte in Li/electrolyte/electrolyte-C cell is demonstrated to obtain the "true" electrochemical stability window based on the intrinsic thermodynamics of the solid electrolyte calculated using the first principles computation. The Li/electrolyte/electrolyte-C cell provides improved kinetics from large and continuous physical contacts between solid electrolyte and carbon to facilitate the thermodynamically favorable decomposition reactions of the solid electrolyte The kinetics of these reactions is limited in the semi-blocking electrode, which yields overestimated electrochemical stability. Moreover, the use of the Li/electrolyte/electrolyte-C cell mimics the cell configuration in the bulk-type solid-state battery and represents the real microstructural architectures in the solid-state electrode composite, where carbon and solid electrolyte are mixed with the active material.

In addition, we calculated the electrochemical stability of other sulfide electrolytes, such as $Li_{3.25}Ge_{0.25}P_{0.75}S_4$, Li_3PS_4 , Li_4GeS_4 , Li_6PS_5Cl , and $Li_7P_2S_8I$, using the same computation scheme.⁶⁰ The thermodynamically intrinsic
electrochemical stability windows and the decomposition phase equilibria beyond their stability window are very similar to those of LGPS. The cathodic limit is around 1.6 - 1.7 V for the reduction of Ge or P contained in the sulfide electrolytes, and the anodic limit is usually around 2.1 - 2.3 V corresponding to the oxidization of S. Doping halogen elements, such as Cl and I, into the materials increases the anodic limit.⁶¹⁻⁶³ The results indicate that the narrow electrochemical stability window is originated from the reduction of P/Ge and the oxidization of S.

2.3.2 Electrochemical stability of Li₇La₃Zr₂O₁₂

Despite the high ionic conductivity, most of the sulfide electrolytes are sensitive to moisture and/or oxygen in the ambient environment. The oxide-based solid electrolytes, which have better stability in air, therefore attract a lot of interests. In particular, cubic Li-stuffed garnet (i.e. $Li_7La_3Zr_2O_{12}$) reported with a wide electrochemical stability window of 0.0 - 6.0 V^{47,64} and a high ionic conductivity of $10^{-4} - 10^{-3}$ S cm⁻¹,⁶⁵ is considered as one of the most promising oxide solid electrolytes. In this section, the same research methodology was applied to study the electrochemical stability window of lithium oxide-based solid electrolyte, especially LLZO.



Figure 2.5 The first principles calculation results for the voltage profile of LLZO solid electrolyte upon lithiation and delithiation.

The voltage profile of LLZO upon lithiation/delithiation and the detailed phase equilibria of LLZO at different voltages were calculated using the first principles method (**Figure 2.5**). The results show that the thermodynamic electrochemical stability window of LLZO is also smaller than the reported value of 0.0 - 6.0 V.⁴⁷ The oxidation decomposition of LLZO occurs at as low as 2.91 V to form Li₂O₂, Li₆Zr₂O₇, and La₂O₃. As the voltage increases above 3.3 V, O₂ is generated from the oxidation of Li₂O₂ (Figure 2.5). LLZO is lithiated and reduced into Li₂O, Zr₃O, and La₂O₃ at below 0.05 V, and Zr₃O may be further reduced into Zr metal at below 0.004 V (Figure 2.5). The thermodynamic results based on the energetics of DFT calculations indicate LLZO is not thermodynamically stable against Li metal. However, the reduction potential of LLZO (0.05 V) is very close to Li metal deposition potential (0 V), the thermodynamic driving force for the reduction is very small. Since these values of energy and voltage (0.004 V) for the further reduction of Zr_3O are as small as the potential errors of typical DFT calculations and the approximations in our calculation scheme, the exact potential to reduce Zr_3O into Zr may be below or above 0 V. However, if the potential is significantly lower than 0 V, the formation of Zr would be thermodynamically favorable.

In addition, we also evaluated the electrochemical stability of the garnet phases doped by the cation dopants, such as Ta, Nb, and Al (Table 2.1-2.3), which are commonly applied to stabilize the cubic phase of LLZO and to increase the Li ionic conductivity. The calculations indicate that a small amount of dopants, such as Ta, Al, Nb, which may have be reduced at a slightly higher reduction potential, does not have a large effect on the reduction/oxidation of the host elements in LLZO (Table 2.1-2.3). At 0.0 V, the doped cations Ta and Nb are reduced into metallic states, and Al is reduced into Zr-Al alloys. Considering the low amount of dopants in LLZO, the effects of dopants on the stability window are small. Given the low reduction potentials for the garnet reduction, the good stability of the garnet LLZO may be explained by the formation of surface passivation after decomposition, such as Li_2O , La_2O_3 , and other oxides. In addition, the formation of Li_2CO_3 surface layers due to reaction of LLZO with the H_2O/CO_2 in the air may also help passivating the LLZO.^{6,66} These results may explain why LLZO was widely observed to be stable with Li at room temperature in many studies.^{64,67}

Potential ϕ ref. to Li/Li ⁺ [V]	$\mu_{\rm Li}$ ref. to Li metal [eV]	$\Delta n_{\rm Li}$ per formula	Phase equilibria	
0.004	-0.004	8.25	Li ₂ O, La ₂ O ₃ , Zr, Ta	
0.05	-0.05	7.083	Li ₂ O, Zr ₃ O, La ₂ O ₃ , Ta	
0.35	-0.35	1.25	Li ₂ O, Li ₆ Zr ₂ O ₇ , La ₂ O ₃ , Ta	
		0	$Li_{6.75}La_{3}Zr_{1.75}Ta_{0.25}O_{12}$	
2.91	-2.91	-0.125	Li ₂ O ₂ , Li ₆ Zr ₂ O ₇ , Li ₅ TaO ₅ , La ₂ O ₃	
3.11	-3.11	-0.375	Li ₂ O ₂ , La ₆ Zr ₂ O ₇ , Li ₃ TaO ₄ , La ₂ O ₃	
3.17	-3.17	-3	Li ₂ O ₂ , La ₂ Zr ₂ O ₇ , Li ₃ TaO ₄ , La ₂ O ₃	
3.24	-3.24	-3.375	Li ₂ O ₂ , La ₂ Zr ₂ O ₇ , La ₂ O ₃ , La ₃ TaO ₇	
3.3	-3.3	-6.75	O ₂ , La ₃ TaO ₇ , La ₂ Zr ₂ O ₇ , La ₂ O ₃	

 $\textbf{Table 2.1} \ \text{Phase equilibria of Ta-doped LLZO} \ (Li_{6.75}La_{3}Zr_{1.75}Ta_{0.25}O_{12}) \ \text{upon}$

lithiation/delithiation at different voltages

Table 2.2 Phase equilibria of Nb-doped LLZO $(Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12})$ upon

Potential ϕ ref. to Li/Li ⁺ [V]	$\mu_{\rm Li}$ ref. to Li metal [eV]	$\Delta n_{\rm Li}$ per formula	Phase equilibria	
0.004	-0.004	8.25	Li ₂ O, La ₂ O ₃ , Zr, Nb	
0.05	-0.05	7.083	Li ₂ O, Zr ₃ O, La ₂ O ₃ , Nb	
0.55	-0.55	1.25	Li ₂ O, Li ₆ Zr ₂ O ₇ , La ₂ O ₃ , Nb	
0.62	-0.62	0.5	LiNbO ₂ , Li ₆ Zr ₂ O ₇ , La ₂ O ₃ , Li ₂ O	
		0	$Li_{6.75}La_{3}Zr_{1.75}Nb_{0.25}O_{12}$	
2.91	-2.91	-0.25	Li ₂ O ₂ , Li ₈ Nb ₂ O ₉ , Li ₆ Zr ₂ O ₇ , La ₂ O ₃	
3.16	-3.16	-0.375	Li_2O_2 , Li_3NbO_4 , $La_6Zr_2O_7$, La_2O_3	
3.17	-3.17	-3	Li ₂ O ₂ , Li ₃ NbO ₄ , La ₂ Zr ₂ O ₇ , La ₂ O ₃	
3.29	-3.29	-3.375	Li ₂ O ₂ , La ₃ NbO ₇ , La ₂ Zr ₂ O ₇ , La ₂ O ₃	
3.3	-3.3	-6.75	O ₂ , La ₃ NbO ₇ , La ₂ Zr ₂ O ₇ , La ₂ O ₃	

lithiation/delithiation at different voltages

Potential ϕ ref. to Li/Li ⁺ [V]	μ_{Li} ref. to Li metal [eV]	$\Delta n_{\rm Li}$ per formula	Phase equilibria
0.004	-0.004	8.72	Li ₂ O, La ₂ O ₃ , Zr, Zr ₃ Al
0.05	-0.05	7.87	Li ₂ O, Zr ₃ O, La ₂ O ₃ , Zr ₃ Al
0.06	-0.06	3.6	Li ₂ O, Li ₆ Zr ₂ O ₇ , La ₂ O ₃ , Zr ₃ Al
0.12	-0.12	2	Li ₂ O, Li ₆ Zr ₂ O ₇ , La ₂ O ₃ , Zr ₄ Al ₃
0.125	-0.125	1.36	Li ₂ O, Li ₆ Zr ₂ O ₇ , La ₂ O ₃ , Zr ₂ Al ₃
0.133	-0.135	1.2	Li ₂ O, Li ₆ Zr ₂ O ₇ , La ₂ O ₃ , ZrAl ₂
0.28	-0.28	0.4	Li ₅ AlO ₄ , Li ₆ Zr ₂ O ₇ , La ₂ O ₃ , ZrAl ₂
		0	$Li_{6.28}La_{3}Zr_{2}Al_{0.24}O_{12}$
3.04	-3.04	-0.02	Li ₂ O ₂ , LiAlO ₂ , Li ₆ Zr ₂ O ₇ , La ₂ O ₃
3.17	-3.17	-3.02	Li ₂ O ₂ , LiAlO ₂ , La ₂ Zr ₂ O ₇ , La ₂ O ₃
3.27	-3.27	-3.14	Li ₂ O ₂ , La ₄ Al ₂ O ₉ , La ₂ Zr ₂ O ₇ , La ₂ O ₃
3.30	-3.30	-6.28	O ₂ , La ₄ Al ₂ O ₉ , La ₂ Zr ₂ O ₇ , La ₂ O ₃

Table 2.3 Phase equilibria of Al-doped LLZO (Li_{6.28}La₃Zr₂Al_{0.24}O₁₂) upon

lithiation/delithiation at different voltages

The CV of the Li/LLZO/LLZO-C/Pt cell was used to measure the electrochemical stability window of LLZO, which was doped with a small amount of Ta to stabilize the cubic phase of LLZO.⁶⁸ To increase the contact area between the LLZO and carbon, the as-obtained LLZO powder was grinded using a high-energy ball mill to reduce its particle size below 1 μ m, and then a thin-layer of carbon was coated on LLZO, as shown in **Figure 2.6**.



Figure 2.6 SEM images of the as-prepared LLZO (a), ball-milled LLZO (b), and carbon-coated LLZO after ball-milling (c). HRTEM image of the carbon coated LLZO after ball-milling.

The carbon-coated LLZO was then mixed with carbon black (weight ratio is 40:60) to make the LLZO-C composite electrode. All these processes were done in an Ar atmosphere to protect the LLZO from the slow reaction with the H_2O/CO_2 in air.^{6,66} The XRD test (**Figure 2.7**) confirmed that the LLZO structure remained after grinding and carbon-coating processing.



Figure 2.7 XRD of the as-prepared LLZO, ball-milled LLZO, and carbon-coated LLZO after ball-milling.

The same Zr 3*d* spectra of LLZO before and after carbon coating (**Figure 2.8**) indicates that LLZO is stable upon high-temperature carbonization process and no apparent carbothermal reduction of Zr could be observed.



Figure 2.8 High resolution Zr 3d core XPS spectra of LLZO before and after carbonization process.



Figure 2.9 Cyclic voltammetry of Li/LLZO/LLZO-C/Pt cell within the voltage range of 2.6 - 10.0 V.

The thermodynamic oxidation stability of the LLZO was examined by the CV scan of the Li/LLZO/LLZO-C cell within the voltage range of 2.6 - 10.0 V. As can be observed from **Figure 2.9**, the apparent oxidation of LLZO starts at about 4.0 V, which is much lower than the reported value of 6.0 V. The subsequent cathodic scan indicates the oxidation reaction is not reversible, and no oxidation peak can be observed in the second cycle. The maximum current of ~5 μ A in Figure 2.9 indicates that only a small amount of LLZO was oxidized. It should also be noted that the small oxidation current could also come from the insufficient ionic conduction in the LLZO-C composite because of the large amount of carbon additives as well as the large grain boundary resistance between LLZO particles. A larger current would be expected if a continuous ionic pathway through LLZO was formed in the LLZO-C composite (e.g. from co-sintering of LLZO solid electrolyte and LLZO-C electrode⁴). The higher voltage (4.0 V) compared with the calculation result (2.91 V) can be

explained by the large over-potential for the oxidation of LLZO. It should be noted that the CV scan of Li/LLZO/LLZO-C/Pt cell was tested in an Ar-filled glovebox and similar results were obtained when graphite was used as the electronic conductive additive, excluding the oxidation of carbon additives if LLZO is stable. Since the reduction potential of the LLZO at 0.05 V is very close to the voltage of Li metal, it is difficult to distinguish the reduction of LLZO from the Li deposition in the CV scan and to quantify the reduction potential of LLZO.



Figure 2.10 (a) Charge curve of carbon-coated LLZO to 4.5 V using Li metal as counter and reference electrode in liquid electrolyte. (b) Discharge curve of carbon-coated LLZO to 0 V using Li metal as counter and reference electrode.

X-ray photoelectron spectroscopy (XPS) was used to identify the reduction and oxidation products of LLZO beyond its stability window. In order to increase the yields of decomposition products for characterization, the LLZO-C composite electrode was cycled against Li metal in a liquid electrolyte, which provided faster reaction kinetics. A 5-V class liquid electrolyte, 1 M LiPF₆ in a mixed solvent of FEC, FEMC, and HFE (volume ratio is 2:6:2), was used to minimize the oxidation

from the liquid electrolyte. The Li/LLZO half-cells were charged to 4.5 V or discharged to 0 V at a current density of 10 mA g^{-1} and were then maintained at the voltages for 72 hours. The charge and discharge curves of the LLZO-C composite electrodes are provided in the Supporting Information (**Figure 2.10**). However, it is impossible to conclude the decomposition of the LLZO simply from the charge/discharge curve of the LLZO-C electrode in Figure 2.10 because carbon in the LLZO-C electrode will also reacts with lithium and SEI is also formed on carbon.



Figure 2.11 (a) The XPS survey spectrum of the fresh and charged LLZO. The atomic percentage of O and Zr in the sample is obtained from the area of O 1*s* and Zr 3*d* peak, respectively. (b) High resolution Zr 3*d* core XPS spectra of fresh and discharged LLZO. The curve fits were obtained using fixed spin splits $(3d_{3/2} - 3d_{5/2} = 2.43 \text{ eV})$.

Samples	O content [at. %]	Zr content [at. %]	O/Zr Ratio
Fresh	6.64	0.87	7.6:1
Charged to 4.5 V	2.12	0.43	4.9:1

Table 2.4 XPS analysis-derived O and Zr elements atomic concerntrations.

Therefore, XPS was used to characterize the decomposition of LLZO. Figure 2.11(a) shows the XPS survey of the fresh and charged LLZO electrodes. The atomic percentages of the O and Zr derived from the survey (Table 2.4) indicates the atomic ratio of O to Zr decreases from 7.6:1 to 4.9:1 after LLZO was charged to 4.5 V. It should be noted that 2h Ar⁺ sputtering was performed on the surface of the charged LLZO before collecting the atomic concentrations of O and Zr in order to completely remove the surface layers caused by the decomposition of the liquid electrolyte at a high potential. The complete removal of SEI after sputtering is confirmed by the XPS spectra of C 1s of the LLZO-C samples upon different sputtering times (Figure 2.12). Multiple peaks above 284.6 eV (carbon black) could be observed for the charged LLZO before sputtering, indicating that several carbon-containing species are present at the surface. These carbon-containing species are most likely attributed to the decomposition products of the liquid electrolyte. However, after 1h sputtering, only one peak at 284.6 eV corresponding to the carbon black in the LLZO-C electrode could be observed in the sample, which means that all the SEI species were removed. One more hour sputtering was performed in order to completely remove the surface layer.



Figure 2.12 High resolution C 1*s* core XPS spectra of the charged LLZO after different sputtering times.

This result confirms that O_2 was released from the charged LLZO, which is consistent with our computation result. No obvious binding energy shift can be observed for Li, La, Zr, O elements after the LLZO was charged. On the other hand, Figure 2.11(b) compares the high-resolution spectra of Zr 3*d* of LLZO electrodes at the fresh and discharged states. All Zr 3*d* spectra exhibit a doublet with a fixed difference of 2.43 eV because of the spin-split coupling between $3d_{5/2}$ and $3d_{3/2}$. For the fresh LLZO electrode, two different chemical environments of the Zr can be observed. The main peak of Zr $3d_{5/2}$ located at the 181.8 eV corresponds to the Zr in the cubic garnet,⁶⁶ while the side peak of the Zr $3d_{5/2}$ at the 179.7 eV may be ascribed

to the oxide impurities (e.g. $La_2Zr_2O_7$) at the surface of the sample though the amount of the impurities is too small to be detected in the XRD test.^{69,70} Both Zr peaks remained with the increased relative intensity of the side peak at 179.7 eV, after the LLZO was discharged to 0 V. In addition, another peak at a lower binding energy of 178.2 eV also appears for the discharged LLZO. It is known that various Zr suboxides exist and their binding energy will shift to a lower value as the oxidation state of Zr decreases.⁷¹ The increase of the relative intensity of side peak at 179.7 eV as well as the appearance of a new peak at a lower binding energy (178.2 eV, ascribed to Zr₃O herein) confirmed the reduction of Zr in the discharged LLZO, which agrees with the calculation result. It should be noted that the main peak at 181.8 eV of Zr still remained after the LLZO was discharged to 0 V, indicating that only the surface of the LLZO was being reduced and most of LLZO was still stable. Nevertheless, our results demonstrated that the electrochemical stability window of garnet is not as wide as previously reported, and the reduction of Zr and the oxidation of O contained in LLZO occur beyond the stability window of LLZO.

Our computation and experimental results provide a new mechanism for the short-circuiting across the Li/LLZO/Li cell during Li striping/plating test at a high overpotential.⁷²⁻⁷⁴ It was reported that the Li dendrite growth across the LLZO electrolyte layer is responsible for the short circuiting of Li/LLZO/Li electrolyte cell. However, the growth of soft, ductile Li dendrite through the hard, dense layer of the LLZO is not understood. Here, we propose an alternative mechanism on the basis of the reduction of LLZO at very large overpotentials. As a result of the cation reduction, the formation of metallic states at the interfaces of the Li-LLZO and of the

LLZO grain boundaries facilitates the electronic conduction at these interfaces. The electronic conduction would facilitate the deposition of Li in the materials from the Li electrode or the Li ions in the garnet materials. In addition, the coloration of the LLZO surface from tan white to gray black was observed after LLZO was immersed in molten Li (300 °C) for 168 hours.⁴⁹ We believe the coloration is related to the reduction of Zr and/or the dopant (Al) in LLZO. The undetected oxidation change of Zr in their XPS result⁴⁹ may be caused by the re-oxidation of the top-surface of the sample stored in dry room, since the surface of Zr is very sensitive to oxygen and will be gradually oxidized to ZrO_2 after long time explosion of air.⁷¹

The thermodynamic electrochemical stability windows and the decomposition phase equilibria at different voltages of other common oxide solid electrolytes were also calculated.⁶⁰ The oxide solid electrolytes generally have a wider stability window than sulfides. The stability window of oxide solid electrolyte varies significantly from one material to another. Li-garnet LLZO has the lowest cathodic limit of 0.05 V, suggesting the best resistance to reduction. The NASICON-type materials, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) and $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP), have the highest reduction potential of 1.7 and 2.2 V, respectively, and also have the highest oxidization potential of ~4.2 V. We found that the anodic limit of the electrolyte is related with the oxidation of the O in the compounds except for LiPON. The reduction of Ge, Ti, P, Zn and Al elements contained in the solid electrolytes is generally responsible for the cathodic limit.

2.3.3 Discussion

Our first principle computation and experimental results indicate all the solid electrolytes, especially sulfides, have an intrinsically narrower electrochemical stability window than the "apparent" window obtained from the linear scan of semiblocking electrode. No solid electrolyte is thermodynamically stable over the wide range from 0.0 to 5.0 V. Therefore, most electrolytes are not stable within the cycling voltage range of typical Li-ion battery cells based on the lithium anode and $LiCoO_2$ cathode. The main problem for operating the solid electrolyte beyond the limited thermodynamic stability window is the formation of new interphases due to the decomposition at the active material-electrolyte and carbon-electrolyte interfaces. The decomposition interphases, which likely have poorer Li ion conductivity than the solid electrolyte, would impede the Li transport between the solid electrolyte and the active materials and increase the interfacial resistance. Therefore, the performance of the bulk-type solid-state battery is greatly affected depending on the properties of the decomposition interphases, such as ionic conductivity, electronic conductivity, and electrochemical reversibility.

The most desired properties of the interphases are electrochemically irreversible, highly ionic conducting but electronic insulating. The interphase with such properties is essentially the solid-electrolyte-interphases (SEI), which kinetically inhibit further decompositions of solid electrolyte and extend the electrochemical window. The formation of the SEI layer is similar to that on the graphite electrode in the commercialized lithium ion battery, which enabled the liquid electrolyte to be used beyond its stability window. ⁷⁵For example, the decomposition products of Li₂O,

Li₃N, and Li₃P formed at the reduction and lithiation of LiPON serve as an excellent SEI,⁷⁶ enabling its stability with Li metal for extremely long charge/discharge cycles.³ In addition, Li₃N and Li₃P are good Li ionic conductor materials, which lower the interfacial resistance.^{77,78} However, it is more likely to have the interphase with lower Li ionic conductivity than the original electrolyte, causing high interfacial resistance at the interface. Even worse, the interphase would be highly detrimental if the decomposition products have sufficient electronic conductivity. In this case, the decomposition of the solid electrolyte would continue into the bulk of the solid electrolyte, eventually causing short circuiting of the battery. For example, the wellknown reduction of the LLTO is due to the high electronic conductivity of LLTO after the reduction of Ti at low potentials.⁷⁹ The formation of metals at reduction, which is typical for the solid electrolytes containing cations, such as Ge, Ti, Zn and Al, prevents the formation of SEI layers. For such solid electrolyte materials, an artificial SEI layer is required to be interpolated at the electrode/electrolyte interface to passivate the solid electrolyte and to suppress the decomposition of the solid electrolyte beyond its stability window.



Figure 2.13 EIS plots of the Li/LGPS/LGPS-C/Pt cell at different voltages corresponding to the decompositions of LGPS. (b, d) are enlarged versions of (a, c) at high frequencies. The content of carbon in LGPS-C electrode is only 5 wt. % so that the electrochemical behavior of LGPS in this cell will be similar as that in a real solid state battery.

In addition, it is highly undesired to have reversible or partially reversible decomposition reactions during lithiation/delithiation, which makes the electrolyte essentially an active electrode.^{79,80} The decomposition of the electrolyte at the interfaces would reduce the electrolyte content in the electrode composite, and the

repeated volume changes during the cycling may lead to the poor physical contacts at the interfaces of the electrolyte. For example, the oxidation products of sulfide electrolytes at high voltages contain S, which is a well-known cathode material in Li-S batteries. The lithiation/delithiation of S at the interfaces of LGPS-cathode and LGPS-carbon interfaces generates a large volume change of up to 180 % at the interface.⁸¹ In addition, the changes of electronic and ionic conductivities in the interphase upon lithiation/delithiation would also affect the interfacial resistances and performance of the solid state batteries during cycling. The EIS test of the Li/LGPS/LGPS-C cells at different voltages (**Figure 2.13**) confirmed that oxidation and reduction decomposition of LGPS will increase the interfacial resistance of the cells.

To avoid the undesirable decompositions of the solid electrolyte, one strategy is to limit the voltage of the battery to suppress the formation of detrimental decomposition products. For example, the decomposition of LLZO will be intrinsically avoided if we use Li-In alloy as an anode (0.6 V) and S as a cathode (2.1 V). In addition, Li-In anode is widely used for the sulfide solid electrolytes, because the Li-In alloying potential higher than the reduction of Ge suppresses the Li-Ge alloying and further decompositions in the sulfide solid electrolytes. However, the use of Li-In anode significantly decreases the capacity and voltage of the battery. Another strategy to extend the stability of the solid electrolyte is to apply the coating layers at the electrolyte-electrode interfaces, since the choice of the materials is very limited to simultaneously satisfy all battery criteria (e.g. voltage, capacity, and chemical compatibility).⁶⁰ For example, the artificial coating layer, such as Li₄Ti₅O₁₂ and

LiNbO₃, has been applied at the interface between the sulfide solid electrolyte and cathode materials.^{39,82} These coating layers are found to suppress the interfacial mutual diffusion and to reduce the interfacial resistance. In addition, the formation of Li₂CO₃ on the surface of LLZO after exposing to air^{6,66} can be considered as a SEI, which protects the reduction of LLZO against Li. At the anode side, Polyplus has applied the coating layers to stabilize the LATP materials against Li metal anode.⁸³ The above examples suggest the formation and coating of the SEI-like layers is an effective strategy to extend the stability window of the solid electrolyte and to improve the performance of the all-solid-state batteries.

On the basis of our new understanding, we provide specific recommendations for the engineering of sulfides and oxides solid electrolyte materials in the all-solid-state batteries. Since LGPS has a limited electrochemical stability window with a reduction potential of 1.7 V and an oxidization potential of 2.1 V, the anode materials, such as In, with the lithiation potential higher than Li-Ge alloying is recommended for LGPS electrolyte to avoid the formation of highly electronic conductive Li-Ge alloys. The problems of the LGPS solid electrolyte at the cathode side is that the oxidation products, P₂S₅, S, and GeS₂ are neither electronic nor ionic conductive, and that the oxidation product S is electrochemically reversible if mixed with carbon. Therefore, applying an artificial SEI layer is recommended at the interface between the high voltage cathode and LGPS to provide good battery performance. LLZO has a wider electrochemical window than LGPS. In particular, LLZO holds great promises for the application with lithium metal anode, because the stability of LLZO against Li metal can be easily circumvented by kinetic protections, given the very small

thermodynamic driving force for the reduction of LLZO at 0 V. Such kinetic protections should be able to sustain large current densities and high temperatures, which would facilitate the Li reduction of LLZO, during the operation of the LLZObased batteries. At the cathode side, the stability of the LLZO may not be an issue as the oxidation products consisting electronic insulating La₂Zr₂O₇ and La₂O₃ can provide good passivation. However, these decomposition phases are poor ionic conductors, which give rise to high interfacial resistance. Therefore, the application of coating layers is also recommended between LLZO and the cathode to reduce interfacial resistance. The introduction of Nb oxides at cathode interfaces is recently demonstrated to effectively reduce the interfacial resistance. ^{82,84}

In addition to decomposition of the solid electrolyte at the interface with electronic conductive materials (such as carbon), the interphase layer at the interface between solid electrolytes and active materials may also be formed due to the chemical reaction in high-temperature annealing process and the electrochemical reaction in lithiation/delithiation process at room temperature in a real solid state cells. Therefore, the thermodynamic electrochemical stability and thermodynamic thermal stability (if annealing process is required) of the solid electrolyte reacting with active materials should also be considered in the real cells. Moreover, the reaction kinetics and passivation also affect the interface resistance in the real cells. The particle size of solid electrolyte, the amount of carbon in the electrolyte-carbon composite, the electronic conductivity of decomposition products, and the applied current (or CV scan rate) for the test will all affect the degree of the decomposition of

solid electrolyte. However, even a slight decomposition of the solid electrolyte may cause a huge interfacial resistance in the real cell.

2.4 Conclusion

In summary, the thermodynamic stability windows and decomposition phase equilibria of LGPS and LLZO were calculated using the first principles computation method. A Li/electrolyte/electrolyte-carbon cell was proposed to replace current Li/electrolyte/Pt semi-blocking electrode to obtain the intrinsic stability window of the solid electrolytes. The reduction and oxidation of both LGPS and LLZO are confirmed by the new CV scans and the XPS results. The results indicate that both of these two solid electrolytes have significantly narrower electrochemical window than previously reported apparent window based on the semi-blocking electrode. Therefore, the high interfacial resistances arising from the decomposition of solid electrolyte should be addressed by stabilizing the solid electrolyte. Extending the stability window of the solid electrolytes through the spontaneous formation or artificial application of SEI layers is the key to good performance of the bulk-type allsolid-state lithium ion batteries.

Chapter 3: A Battery Made from a Single Material

3.1 Introduction

All-solid-state lithium-ion batteries (ASSLIBs) are receiving intense interest for energy storage systems because the replacement of the volatile and flammable liquid electrolyte⁸⁵ with nonflammable inorganic solid electrolyte could essentially improve the safety and reliability of the battery.⁸⁶ The conventional ASSLIBs consist of three distinct components: an anode, an electrolyte, and a cathode. In addition, current collectors should also be used to ensure the electron transport through the electrodes and the external circuit. The anode, cathode, and electrolyte normally use three different materials due to the stringent different requirements for each component. The electrodes are expected to be reversibly lithiated/delithiated at a low potential (anode) or a high potential (cathode) with good mixed electronic/ionic conductivities, whereas the electrolyte should have a wide electrochemical stability window with a very high ionic conductivity but negligible electronic conductivity. To develop a highly-performed ASSLIB, two critical challenges have to be overcome; one is the high ionic resistance of the solid electrolyte and the other is the large interfacial resistance between the solid electrodes and solid electrolyte. Because of the great success in minimizing the solid electrolyte thickness based on a series of advanced deposition techniques, thin-film ASSLIBs (total thickness ~15 µm) using lowconductivity solid electrolyte (LIPON with $\sigma_{Li} \sim 10^{-6}$ S/cm) have received extensive research.^{3,87} Despite excellent cycle stability, the limited stored energy and the

expensive, multistep fabrication process of this thin-film battery are still the main obstacles towards their wide applications.



Figure 3.1 Schematic diagrams of (a) a typical bulk-type all-solid-state lithium-ion battery and (b) a single- $Li_{10}GeP_2S_{12}$ all-solid-state lithium-ion battery.

Increasing the thickness of the electrodes and electrolyte to make the so-called bulk-type ASSLIBs (**Figure 3.1**a) is highly desired for their widespread use in the large-scale energy storage systems.⁸⁸ However, the performances of this type of battery, especially in terms of power density and cycle life, are too low for their practical applications. This is because the increase in the thickness of the battery would require a high ionic conductivity of the solid electrolyte and a very low interfacial resistance between the electrodes and electrolyte. Considerable efforts have been focused on developing highly conductive materials as solid electrolytes.^{22,89-91} Even though the solid electrolyte with a comparable or a higher ionic conductivity than the liquid electrolyte was used, and more solid electrolyte (~50 wt.% compared with ~30 vol.% for liquid-electrolyte LIBs) and a large amount of electronically-conductive additive (25 wt.% carbon for Li₂S) were added in the

composite electrodes, the rate and cycling performances of the bulk-type ASSLIBs are still much lower than those of the liquid-electrolyte LIBs with similar loading of the electrodes.⁹² Bulk-type ASSLIBs using ductile sulfide electrolytes (σ_{Li} >10⁻³ S/cm) are only operated at very low current densities,^{28,93,94} and the ones using rigid oxide electrolytes (e.g. garnet-type Li₇La₃Zr₂O₁₂ with σ_{Li} >10⁻⁴ S/cm) can hardly even be cycled because of the huge overpotentials during the charge/discharge process.⁹² These results indicate that the interfacial resistance between the solid electrodes and solid electrolyte is becoming the dominant kinetic limitation, given the significantlydecreased resistance of the electrolyte layer by using highly conductive solid electrolyte.⁹⁵

To overcome the intrinsic limitations of those aforementioned methods, a new concept of growing an electrode from an electrolyte^{96,97} or growing an electrolyte from an electrode⁹⁸ has been reported to achieve intimate and stabilized interfacial contact in the ASSLIBs. For instance, a lithium metal anode could be in-situ formed in the "Li-free" thin-film ASSLIBs by electrochemical plating during the initial charge,⁹⁶ and a MnO₂ cathode could also be in-situ formed at the interface through the reaction between the Li_{1+x+y}Al_yTi_{2-y}Si_xP_{3-x}O₁₂ electrolyte (OHARA sheet) and Mn current collector under an external high driving force (16 V D.C. voltage).⁹⁷ Additionally, a solid electrolyte of LiI could also be in-situ formed at the negative electrode/positive electrode interface through the chemical reaction of Li anode and I₂ cathode.⁹⁸ All of these in-situ formed materials could facilitate the formation of a good electrode/electrolyte interface with a low resistance. However, the in-situ formed electrolyte (or electrolyte) material is still a different from the parent electrolyte

(or electrode) material, thus the interface between electrode and electrolyte still exist and the stain/stress at the interface will be generated during lithiation/delithaition cycles. Ideally, the electrode and electrolyte should use the same material, in which case the interface between electrolyte and electrode will be eliminated or at least minimized to the level of internal electrode resistance (such as the internal interface resistance of a conversion electrode where the metal nano-particles are uniformly distributed in the Li-ion conducting matrix). Although the well-known solid electrolytes, OHARA sheet and Li_{3x}La_{2/3-x}TiO₃ (LLTO), can also serve as anodes at a low potential due to the existence of Ti^{4+,97,99-101} providing an ideal interface between the anode and electrolyte. Both OHARA and LLTO cannot serve as cathodes and therefore a different cathode material is still required for a battery, which would lead to a high resistive cathode/electrolyte interface. The Fe doped LLTO (LLFTO) electrolyte has two lithiation/delithiation potential plateaus at 2.1 and 1.7 V, but the high electronic conductivity of LLFTO and low voltage between two plateaus (<0.4 V) limit its application only for an electrochromic device that has to be operated under a constant voltage due to high self-discharge rate.^{101,102} To the best of our knowledge there is no any single material which could be used for all the electrolyte, anode and cathode for high energy Li-ion batteries.

Herein, we reported a novel high energy single-material ASSLIB (Figure 3.1b) to address the interfacial problem, wherein the cathode, electrolyte, and anode were made from a single material. The feasibility of using the highly-conductive $Li_{10}GeP_2S_{12}$ (LGPS) electrolyte as both a cathode and an anode after mixing with electronically-conductive carbon allows us to use it as a model material for the single-

material ASSLIB. It would be expected that a perfect physical contact between the electrodes and electrolyte could be intrinsically achieved, the unwanted interfacial interactions could be avoided, and the strain/stress at the interface could be alleviated. As a result, a superior electrode/electrolyte interface with an extremely low resistance could be achieved in the single-LGPS ASSLIB, beneficial to a high-power, high-energy, and long-cycling all-solid-state battery with a low cost.

3.2 Experimental

3.2.1 Material synthesis

Li₁₀GeP₂S₁₂ was prepared following the previous report.²² Li₂S (Sigma-Aldrich, 99.98%), P₂S₅ (Sigma-Aldrich, 99%) and GeS₂ (MP Biomedicals LLC, 99.99%) were used as starting materials. These materials were weighed in the molar ratio of Li₂S/P₂S₂/GeS₂ = 5/1/1 in an argon (Ar)-filled glove box, subjected to a zirconia ceramic vial and mixed for 30 minutes using a high energy vibrating mill (SPEX SamplePrep* 8000M Mixer/Mill). The powder obtained was then pressed into pellets, sealed in an evacuated quartz tube at 30 Pa and heated at 550 °C for 8 h in a furnace placed inside the glove box. The sample was then naturally cooled down to the ambient temperature.

3.2.2 Material characterization

Powder X-ray diffraction patterns were obtained with a D8 Advance with LynxEye and SolX (Bruker AXS, WI, USA) using CuKα radiation. The P/Ge ratio was determined by inductively coupled plasma spectroscopy (Perkin-Elmer ICP-OES). The morphology of the sample was examined using a Hitachi a SU-70 fieldemission scanning electron microscope. The surface chemistry of the samples was examined by X-ray photoelectron spectroscopy using a Kratos Axis 165 spectrometer. To prepare the sample for XPS test, LGPS electrodes were charged or discharged to a certain voltage in a liquid electrolyte using a Swagelok cell, and held at that voltage for 24 h. The electrodes were then taken out from the cell, and rinsed by dimethoxyethane (DME) inside the glove box. All samples were dried under vacuum overnight, placed in a sealed bag, and then transferred into the XPS chamber under inert conditions in a nitrogen-filled glove bag. Ar⁺ sputtering was performed for 180 s on the surface of the discharged and charged LGPS anodes to remove the SEI layer. XPS data was collected using a monochromated Al K α X-ray source (1486.7 eV). The working pressure of the chamber was lower than 6.6 x 10⁻⁹ Pa. All reported binding energy values are calibrated to the C 1*s* peak at 284.8 eV.

3.2.3 Electrochemistry

The LGPS powder was pressed into a pellet (diameter 13 mm; thickness ~2 mm) in an Ar atmosphere. It was then sputtered with Au to form an electrode for the ionic conductivity measurement. The electrochemical impedance spectrums of the Au/LGPS/Au cell were measured between 23 and 132 °C by applying a 100 mV amplitude AC potential in a frequency range of 10 MHz to 0.1 Hz. The cyclic voltammogram of the Li/LGPS/Pt cell was measured between -0.6 and 5.0 V with a scan rate of 0.05 mV/s. The electrochemical performances of LGPS electrodes were firstly tested using a liquid electrolyte with Celgard 3501 as the separator in either two- or three- electrode Swagelok cells. 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixture of 1:1 volume ratio of

tetraethylene glycol dimethyl ether (TEGDME) and *n*-methyl-(*n*-butyl) pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₃TFSI) was used as the liquid electrolyte. Composite electrodes consisting of LGPS and carbon black with a weight ratio of 75:25 were prepared by hand-grinding in the mortar, which were then mixed with 10 wt.% polyvinylidene fluoride (PVDF) and n-methylpyrrolidinone (NMP) to make the electrode slurries. The electrodes were prepared by casting these slurries onto stainless steel, copper or aluminum foils and drying at 110 °C overnight inside the glove box. The loading of active material on each electrode is about 0.75 mg. Halfcells were assembled using a lithium metal foil as the counter electrode, and full cells in the liquid electrolyte were assembled with an electrode mass ratio of ~ 1 between the cathode and the anode sides. For the assembly of the all-solid-state LGPS-C/LGPS/Li half-cell, the LGPS-C powder (10 mg) was put on the top of the LGPS powder (120 mg) and cold-pressed together under 360 Mpa in a PTFE tank with a diameter of 13 mm. After that, a 100 μ m thick lithium metal was then attached on the other side of the LGPS electrolyte layer as a counter and reference electrode. The formed three-layered pellet was then cold-pressed under 120 Mpa between two stainless-steel rods which serve as current collectors. The single LGPS all-solid-state full cell was simply prepared by direct cold-pressing 10 mg LGPS-C powder as anode, 120 mg LGPS powder as solid electrolyte and 30 mg LGPS-C powder as cathode under 360 Mpa. Both the electrode preparation and cell assembly were performed in the Ar-filled glove box. The charge/discharge behavior was tested using an ArbinBT2000 workstation (Arbin Instruments, TX, USA) at room temperature. The

electrochemical impedance spectrum and cyclic voltammetry measurements were carried on an electrochemistry workstation (Solartron 1287/1260).

3.3 Results and Discussion

3.3.1 Feasibility of a single-mateiral battery

The realization of a single-material all-solid-state lithium-ion battery is based on the fact that some highly ionic conductive solid electrolytes could store Li ions at both a high and a low potential after incorporating electronic conductive materials. With the above considerations, $Li_{10}GeP_2S_{12}$ was used as a model material to demonstrate the single-material battery concept. LGPS has the highest ionic conductivity ($\sigma_{Li} \sim 10^{-2}$ S/cm) in all solid electrolytes.²² The electrochemical window of LGPS was reported as high as ~5.0 V.²² Several >4.0 V ASSLIBs using LGPS as the solid electrolyte have also been fabricated.^{103,104} However, the measured wide stability window of 5.0 V benefits from the poor kinetics of the oxidation and reduction reactions of LGPS due to its low electronic conductivity $(\sigma_e \sim 10^{-9} \text{ S/cm})^{22}$, since the intrinsic thermodynamic stability window of LGPS is calculated to be only less than 2.5 V.⁴⁸ The theoretical calculation from first principle modeling also indicates that LGPS will be oxidized to P₂S₅, S, and GeS₂ at high potentials and be reduced to Li₂S, Li₃P and Li₁₅Ge₄ at a low potential.⁴⁸ The S in the oxidation product of LGPS and the Li₁₅Ge₄ in the reduction product of LGPS are well-known cathode and anode materials, respectively, for a lithium-ion battery in a charged state if electronic conductive materials are introduced into two electrodes. Therefore both the oxidative and reductive reactions could reversibly occur beyond the stability window of LGPS, and LGPS-carbon composite may be used as both a cathode and anode due

to the enhanced reaction kinetics. Actually, the Li-S component in LGPS has the same local structure as Li₂S, which is a well-accepted cathode with a theoretical capacity of 1166 mAh/g at ~2.2 V,^{27,105} indicating that LGPS may probably function as a cathode after mixing with carbon. In addition, it is known that the Sn-O component contained in Sn1.0B0.56P0.40Al0.42O3.6 (TCO glass) is still electro-active for lithiation/delithiation as an anode even after a new phase formation.¹⁰⁶ Given the similarity between Sn-O in TCO and Ge-S in LGPS, LGPS may also function as an anode after mixing with carbon, since GeS₂ is a well-accepted anode with a theoretical capacity of 863 mAh/g at ~0.5 V.^{107,108} Thus, after mixing with carbon, LGPS could likely be able to serve as both a cathode and an anode. At a low potential the Ge-S component will be active for lithiation/delithiation but the Li-S component will remain inactive, and at a high potential only the Li-S component will be active. Therefore, pure LGPS could be used as the solid electrolyte while LGPS-carbon composites (LGPS/C) could serve as both a cathode and an anode. A single-LGPS ASSLIB could be fabricated by simply sandwiching LGPS/C cathode, LGPS solid electrolyte, and LGPS/C anode (Figure 3.1b), wherein carbon is considered as the extension of current collectors.



Figure 3.2 Characterizations of as-obtained Li₁₀GeP₂S₁₂. (a) XRD pattern and Rietveld refinement of the as-obtained LGPS powder. The black, red and green lines represent the experimental, calculated and difference patterns, respectively. The blue markers correspond to the position of diffraction lines. The insert shows the background XRD pattern of the tape used for testing. (b) SEM image of the asprepared LGPS powder. (c) Arrhenius conductivity plots of LGPS. The insert was electrochemical impedance spectroscopy measured with Au/LGPS/Au cell at different temperatures. (d) Cyclic voltammetry curve of Li/LGPS/Pt cell within the voltage range of -0.6-5.0 V at a scan rate of 0.05 mV/s.

The feasibility of the single-LGPS ASSLIB has also been experimentally demonstrated. LGPS was synthesized following the previous report.²² The Rietveld refinement of its X-ray powder diffraction pattern (**Figure 3.2**a) indicates that the asobtained LGPS has a typical space group of $P4_2$ /nmc with the cell parameters of a = 8.6995(3) Å, c = 12.669(6) Å, and V = 954.1 Å³, which is in good agreement with the previous report.²² The green line in Figure 3.2a means the difference between experimental and calculated patterns. The fluctuation at low angles is due to experimental errors including the systematic errors and the structural deviations or minor impurities in the sample. The atomic ratio of P to Ge in the sample was determined to be 2.06 by inductively coupled plasma (ICP) spectroscopy (**Figure 3.3**), consistent with the stoichiometric ratio of P/Ge = 2 in Li₁₀GeP₂S₁₂.



Figure 3.3 Individual ICP-OES Ge (**a**) and P (**b**) quantification results. Black lines represent a simple, linear regression through data obtained. The atomic ratio of P to Ge was measured to be 2.06.

The SEM image (Figure 3.2b) reveals that the particle size of the sample is about 2-5 μ m. Figure 3.2c shows the Arrhenius plot of LGPS calculated from the

impedance spectroscopy shown in the inset. Both the grain boundary and bulk conductivities are included. At 27 °C, the ionic conductivity of the cold-pressed LGPS is 7.4 mS/cm, which is lower than that of the previous annealed LGPS²². The reduced ionic conductivity may be due to the lower density of cold-pressed LGPS pellet. Additionally, the presence of minor impurities, as can be observed from the XRD pattern, may also contribute to the decrease of the ionic conductivity. The activation energy for the ionic transport was calculated to be 0.26 eV.



Figure 3.4 Cyclic voltammograms of Li/LGPS/LGPS-C/Pt cell within 1.0 - 3.5 V (a), and 0 - 2 V (b) at a scan rate of 0.05 mV/s.

Figure 3.2d shows the electrochemical window of the LGPS obtained from cyclic voltammetry (CV) of a Li/LGPS/Pt cell at a scan rate of 0.05 mV/s. The LGPS is observed to be stable at a high potential up to 5.0 V, which agrees well with the previous report.^{22,104} However, when the Pt is replaced by an LGPS-C layer (LGPS:carbon is 75:25 in weight) to form a Li/LGPS/LGPS-C half cell, a reversible redox peak at a low potential between 0.0-0.5 V can be observed if the LGPS-C is scanned between 0.0 and 2.0 V, and another reversible redox peak located at the high

potential of 1.6-2.7 V can also be observed if the LGPS-C is scanned between 1.0 and 3.5 V (**Figure 3.4**). This result demonstrates that an LGPS-C composite can serve as both a cathode at 1.6-2.7 V and an anode at 0.0-0.5 V. The lack of these peaks in the CV of the Li/LGPS/Pt cell (Figure 3.2d) is because the contact area between LGPS and electronically-conductive Pt is very small, thus the reaction currents are too small to be observed in the CV scan.



Figure 3.5 Impedance profiles of the Au/LGPS/Au cell (0.1 Hz to 1MHz) at its initial state and after it was charged to 2.7 V at a scan rate of 0.005 mV/s.

In fact, the electrochemical oxidation and reduction reactions of LGPS at the interface between the LGPS and Au in the Au/LGPS/Au blocking electrode beyond the stability window have been detected using the sensitive electrochemical impedance spectrum (EIS) (**Figure 3.5**). The EIS of the fresh Au/LGPS/Au electrode shows a typical Nyquist plot of a solid electrolyte with a nearly vertical capacitive line for blocking electrodes. However, after a linear potential scan of the Au/LGPS/Au cell at a very low scan rate of 0.005 mV/s from 0.0 to 2.7 V, the Nyquist plot turns into a typical battery-like behavior with charge-transfer semi-

circles in the medium frequency and a near 45° slope diffusion line in the low frequency. This result demonstrates that even the Au/LGPS/Au blocking electrode may turn into a single-LGPS micro-battery because the LGPS electrolyte would be oxidized and reduced as electrodes when it contacts with the electronicallyconductive Au.⁹⁷ These results indicate that it is feasible to fabricate an ASSLIB based on the single material LGPS.

а С 1200 Voltage (V) GPS Cathode in Coin Cell Capacity (mAh/g) 007 001 001 001 3 LGPS Anode in Coin Cell GPS/LGPS in Flooded Full Cell 50 100 150 200 b 0 Voltage (V) 1st Cycle 2nd Cycle 3rd Cycle 0 0

0

200 400 600 800 1000 Capacity (mAh/g) Ò

50

100

Cycle number

150

200

3.3.2 Electrochemical performances of $Li_{10}GeP_2S_{12}$ as a cathode and an anode

Figure 3.6 Electrochemical performance of $Li_{10}GeP_2S_{12}$ cathode and anode with liquid electrolyte. 1 M LiTFSI in TEGDME and PYR₁₃TFSI with a volume ratio of 1:1 was used as electrolyte for testing. Charge/discharge curves of Li/LGPS half-cell at a current density of 100 mA/g_(LGPS) in the voltage range of 1.0-3.5 V (a), and 0.0-2.0 V (b). (c) Cycling performance of the LGPS cathode, LGPS anode and LGPS/LGPS flood full cell. All the specific capacities are reported based on the weight of LGPS.

The electrochemical performances of LGPS-C electrodes (LGPS:carbon is 75:25

in weight) were firstly tested in a coin cell using the liquid electrolyte (1 M LiTFSI in TEGDME and PYR₁₃TFSI). The cathode performance of LGPS was evaluated in the potential range between 1.0 to 3.5 V (vs. Li/Li⁺) and the anode performance was measured between 0.0 and 2.0 V. **Figure 3.6**a shows the initial three charge/discharge curves of the LGPS cathode between 1.0 to 3.5 V. A small voltage bump followed by a plateau at ~2.8 V could be observed during the first charging while the subsequent discharge curve exhibits two plateaus at 2.5 V and 2.1 V, giving a specific charge capacity of 186 mAh/g_(LGPS) and a discharge capacity of 151 mAh/g_(LGPS). The galvanostatic charge/discharge curves and CV scans (**Figure 3.7**) are very similar to the behavior of a Li₂S cathode in a liquid electrolyte.¹⁰⁵



Figure 3.7 Cyclic voltammograms of LGPS cathode (**a**) and LGPS anode (**b**) in liquid electrolyte with lithium metal as counter and reference electrode at a scan rate of 0.05 mV/s.

The bump observed at only the first charge process represents the kinetic activation process, and two plateaus showing up at the discharge process could possibly be attributed to the reduction process from solid sulfur to liquid high-order
polysulfides, and from liquid high-order polysulfides to solid Li_2S_2 or Li_2S , respectively.¹⁰⁹ This result indicates that the Li-S component in LGPS could be electro-active for the cathode performance, and the irreversible capacity of the LGPS cathode is probably due to the expected "shuttle" reaction of high-order lithium polysulfides as in Li-S batteries.¹¹⁰

Figure 3.6b displays the charge/discharge behavior of the LGPS anode in the first three cycles between 0.0 to 2.0 V (vs. Li/Li⁺). An irreversible sloped plateau at 0.9~0.5 V and a reversible plateau at ~0.5 V could be observed in the first cycle, consistent with the CV scans (Figure 3.7b). It should be noted that this behavior is very similar to the GeS₂ anode. ^{107,108} The irreversible plateau at 0.9-0.5 V is attributed to the irreversible conversion reaction from GeS₂ to Ge and Li₂S, giving a large irreversible capacity during the first cycle. The reversible plateau could mainly correspond to the alloying/de-alloying of Li and Ge,¹⁰⁷ which contributes a lot to the reversible capacity of 205 mAh/ $g_{(LGPS)}$ for the first cycle. This result demonstrates that the Ge-S component in LGPS could still act as the active center for lithiation/delithiation as an anode, although the carbon and the phosphorus in LGPS-C electrode may also slightly contribute to the capacity. Figure 3.6c shows the cycling stability of the LGPS cathode and anode in the liquid electrolyte coin cell. Despite that capacity decays could be observed for both LGPS cathode and anode in the long term charge/discharge cycles, the LGPS cathode and anode could still deliver 89 and 79 mAh/ $g_{(LGPS)}$ after 200 cycles, repectively.

The cycling performance of the LGPS/liquid electrolyte/LGPS full cell was tentatively examined in a three-electrode liquid-electrolyte flooded cell using Li metal

as a reference electrode (Figure 3.6c). The initial irreversible capacity of the LGPS anode was compensated by pre-cycling the LGPS anode against Li reference electrode between 1.5 and 0 V. After the LGPS anode was recharged to 1.5 V, it was coupled with the fresh LGPS cathode to form an LGPS/liquid electrolyte/LGPS full cell. As shown in Figure 3.6c, the LGPS/LGPS full cell shows similar cycling stability as the individual LGPS anode and LGPS cathode thus demonstrating a high Coulombic efficiency of both the pre-cycled LGPS anode and LGPS cathode during long-term charge/discharge cycles.





Figure 3.8 Deconvoluted S 2p and Ge 3d core XPS spectra of LGPS electrodes. a,

S 2p spectrum of the LGPS cathode at the fresh state, charged to 3.5 V, and then redischarged to 1.0 V; **b**, Ge 3d spectrum of LGPS anode at the fresh state, discharged to 0.0 V, and then re-charged to 2.0 V.

Table 3.1 XPS binding energies of low B.E. peak (E_{low}) and high B.E. peak (E_{high}) of S 2*p* spectra in LGPS cathodes.

Samples	$E_{\rm low}{\rm S2}p_{3/2}({\rm eV})$	$E_{\mathrm{high}}\mathrm{S2}p_{1/2}(\mathrm{eV})$	Area Ratio
Fresh	162.1	163.7	4.9:1
Charged	161.9	164.3	1.8:1
Discharged	161.4	163.0	4.2:1

Note: The curve fits were obtained using fixed spin splits $(2p_{2/3} - 2p_{1/2} = 1.18 \text{ eV})$ and fixed area ratio $(2p_{3/2}/2p_{1/2} = 2)$.

X-ray photoelectron spectroscopy (XPS) was used to understand the electrochemical reaction mechanisms of the LGPS cathode and anode in the liquid electrolyte. Figure 3.8a compares the XPS spectra of S 2p obtained from the LGPS cathodes at the fresh, fully-charged (to 3.5 V) and fully-discharged (to 1.0 V) states. The result indicates that all these cathodes exhibit a main peak around ~ 163 eV, while the LGPS cathodes at fully-charged and fully-discharged states show another peak at ~169 eV attributed to -SO₂CF₃ from the LiTFSI in the electrolyte.¹¹¹ The detailed fitting for the main peak of interest results in two peaks at ~163.5 eV and ~161.8 eV. Unfortunately, it is very difficult to designate either of them because of the complicated chemical environment of S in the samples (Ge-S, P-S, Li-S in LGPS, elemental sulfur and a series of lithium sulfides), and therefore they were simply denoted as a high B.E. binding energy peak (at ~163.5 eV) and a low B.E. peak (at ~161.8 eV). Nevertheless, the electronegativity difference of cations that are bonded with S could tell a general trend of their binding energy positions (S-S > P-S > Ge-S> Li-S). Additionally, the peak for the bonding with each cation will shift to a higher binding energy as the oxidation state of S increases, meaning that lithium sulfide with a sulfur oxidation state of -2 is always located in the low B.E. peak. These results

allow us to use the area ratio of the low B.E. peak to the high B.E. peak to infer the reaction mechanism of the LGPS cathode (Table 3.1). The area ratio decreased from 4.9:1 for the fresh LGPS cathode to 1.8:1 after it was charged to 3.5 V indicating that the oxidation of sulfur (Li-S) to S-S occurred during the charge process. After the LGPS was discharged to 1.0 V, the ratio increased back to 4.2:1, which means the reduction of S. In addition, the area ratio after the 1st cycle (4.2:1) is very close to the original ratio for the fresh LGPS cathode (4.9:1), thus demonstrating the high reversibility of the reaction. This result confirmed that the cathode performance of LGPS could be attributed to the oxidation and reduction of the Li-S component contained within LGPS.



Figure 3.9 Deconvoluted P 2p core XPS spectra of LGPS electrodes at different charge/discharge states. P 2p spectrum of LGPS anode at the fresh state (**a**), after discharged to 0 V without Ar⁺ sputtering (**b**), after discharged to 0 V with Ar⁺ sputtering for 180 s (**c**), and then re-charged to 2.0 V without Ar⁺ sputtering (**d**), re-charged to 2.0 V with Ar⁺ sputtering for 180 s (**e**).

Samples	Ge (%)	P (%)
Fresh	3.1	3.8
Charged without Sputtering	0	2.7
Discharged without Sputtering	0	2.6
Charged with Sputtering	1.1	4.6
Discharged with Sputtering	1.1	3.6

Table 3.2 Relative atomic composition of Ge and P in the LGPS anodes from XPS

Figure 3.8b demonstrates the high resolution Ge 3d spectra of the LGPS anodes at the fresh, fully-discharged (to 0.0 V) and fully-charged (to 2.0 V) states. For the fresh LGPS anode, the main peak positioned at 30.3 eV could be attributed to the GeS_4 tetrahedra in the LGPS, while the other two small peaks at 31.3 eV and 33.3 eV stand for the Ge-S¹¹² and Ge-O¹¹³ from the impurities or contaminants on the surface, respectively. However, for the fully-discharged and fully-charged LGPS anodes, the main Ge 3d peak at 30.3 eV shifted to a high binding energy at 31.3 eV, while a new peak at 29.7 eV appeared. The new peak at 29.7 eV could be ascribed to the Ge metal.¹¹⁴ Given the minimal difference of the binding energy between Ge-metal alloy¹¹² and Ge metal itself¹¹⁴ due to the similar metallic bonding, the peak at 29.7 eV can also be ascribed to the Li-Ge alloy. The appearance of this peak confirms that the Ge-S component in LGPS is electro-active and would be reduced to a Li-Ge alloy after the first discharge to 0.0 V and oxidized back to the Ge metal after the LGPS anode was re-charged to 2.0 V. The peak at 31.3 eV may be attributed to the Ge-S bonding in the residue intermediate product (Li-Ge-S compound) from an incomplete reaction of the LGPS anode. In addition, the high-resolution P 2p spectra of the LGPS anodes at the fresh, fully-discharged, and fully-charged states (Figure 3.9) indicates

that P contained in the LGPS has only a slight contribution to the reversible Li storage of the LGPS anode. Therefore, the anode performance of LGPS could mainly be attributed to the Ge-S component in LGPS, and it exhibits a similar reaction mechanism as the GeS_2 anode with an irreversible conversion reaction followed by a reversible alloying reaction.

Together with the charge/discharge behaviors of the LGPS cathode and anode discussed above, the XPS results confirm that the LGPS cathode and anode performance could be mainly attributed to the Li-S and Ge-S components in LGPS following the similar reaction mechanism as the Li₂S cathode and GeS₂ anode, respectively. Based on their stoichiometric ratio in LGPS, the theoretical capacities could be roughly calculated as 456 mAh/g_(LGPS) for the LGPS cathode and 250 mAh/g_(LGPS) for the LGPS anode (including the contribution from carbon black). This means that 41% and 80% of the theoretical capacity of the LGPS cathode and LGPS anode were achieved in the liquid electrolyte respectively. The incomplete reactions are probably caused by the large particle size (2-5 μ m) of LGPS electrodes and the non-uniform mixing of carbon through hand-grinding.

3.3.4 Single-Li₁₀GeP₂S₁₂ all-solid-state lithium-ion battery

The electrochemical performances of all-solid-state batteries were tested in a specially-designed Swagelok cell (**Figure 3.10**a), wherein the solid electrolyte and electrodes are cold-pressed sequentially between two stainless steel rods inside an insulating PTFE tank.



Figure 3.10 Electrochemical performance of $Li_{10}GeP_2S_{12}$ cathode and anode with $Li_{10}GeP_2S_{12}$ solid electrolyte. (a) Schematic representation of the cell configuration for all-solid-state battery test. Charge/discharge curves of the Li/LGPS/LGPS-C all-solid-state cell at a current density of 10 mA/g in the voltage range of 1.5-3.5 V (b), 0.0-2.0 V (c). (d) Charge/discharge curve of the Li/LGPS/LGPS-C all-solid-state cell at different current densities in the voltage range of 1.5-3.5 V (d), 0.0-2.0 V (e).

The LGPS and carbon was ball-milled for 20h to achieve a uniform distribution of the carbon in the composite electrode (**Figure 3.11**).



Figure 3.11 SEM image and the elemental mapping of carbon (red) and sulfur (blue) of the LGPS-carbon composite after ball-milling for 20h.

The half-cell tests (Li/LGPS/LGPS-C) within different voltage ranges were first conducted to evaluate the performances of the LGPS as a cathode and an anode in the all-solid-state configuration using LGPS as the solid electrolyte. Figure 5b shows that

the LGPS cathode in the LGPS solid electrolyte exhibits a significantly different behavior from that measured in the liquid electrolyte. No voltage bump corresponding to the activation process in the liquid electrolyte could be observed at the first charge process, and the subsequent discharge curve shows only one plateau at ~ 2.2 V. The galvanostatic charge/discharge curves (Figure 3.10b) shows one plateau in the charge/discharge curve. The one-plateau behavior of LGPS cathode in the solid state battery may be attributed to the only binary solid-solid phase transition,¹¹⁵ which is similar to the Li₂S electrodes in solid electrolyte.²⁷ The one redox couple in CV scans of LGPS cathode also further confirms that the Li-S component contained in LGPS is mainly responsible for its cathode performance. The LGPS anode in the all-solid-state cell (Figure 3.10c) exhibits a very similar behavior as that in the liquid electrolyte with a large irreversible plateau at 0.9~0.5 V and a reversible plateau at ~0.5 V in the first cycle, which is also consistent with the CV scans. An interesting phenomenon should be noted that a higher reversible capacity at the first cycle could be observed for both the LGPS cathode (275 mAh/ $g_{(LGPS)}$) and anode (253 mAh/ $g_{(LGPS)}$) in the allsolid-state half-cell than that in the liquid electrolyte cell. This is probably because of the activation of the LGPS solid electrolyte²⁷ and the much lower current density used in the all-state-battery test. In addition, the rate performances of the LGPS cathode and LGPS anode in the LGPS solid electrolyte at different current densities were also tested. As shown in Figure 5d, the LGPS cathode exhibits reversible capacities of 267, 140, 80 mAh/ $g_{(LGPS)}$ at the current densities of 10, 50, 100 mA/g respectively. Reversible capacities of 130, 60, and 36 mAh/ $g_{(LGPS)}$ could be achieved for the LGPS anodes at the current densities of 10, 50, and 100 mA/g respectively (Figure 3.10e).



Figure 3.12 Electrochemical performance of the single-Li₁₀GeP₂S₁₂ battery. (a) Cross-section SEM images of the single-LGPS battery. (b) Elemental mappings of C (red) and S (blue) of the single-LGPS battery. (c) High-magnification SEM image displaying the interface between LGPS electrode and LGPS electrolyte. (d) Charge/discharge curves of the single-LGPS battery in the voltage range of 0.0-2.5 V from the 2nd cycle at a current density of 10 mA/g. (e) Charge/discharge curves of the single-LGPS battery in the voltage range of 0.0-2.5 V from the 2nd cycle at different current densities. (f) Charge/discharge curves of the single-LGPS battery in the voltage range of 0.0-2.5 V from the 2nd cycle at 50 °C at a current density of 50 mA/g. The weight ratio of LGPS cathode to LGPS anode was tentatively set as 3 for the capacity balance. The specific capacity and the current density of the all-solidstate full cell were calculated based on the weight of LGPS anode. All the electrochemical perfomances of the batteires were tested at room temperature unless specified.

The feasibility of using the Li superionic conductor LGPS electrolyte as both the cathode and anode allows us to build up a single-LGPS ASSLIB. To construct the single-LGPS all-solid-state full cell (LGPS-C/LGPS/LGPS-C), the weight ratio of the LGPS cathode to the LGPS anode was tentatively set as 3 to compensate the large irreversible capacity of the LGPS anode during the first discharge. Figure 3.12a shows the cross-section SEM image of the single-LGPS battery. No apparent delamination could be observed across the cell, indicating its great mechanical integrity. The layered composition of the cell identified from the elemental mapping was demonstrated in Figure 3.12b, from which we can see that the LGPS was continuously distributed across the entire thickness of the cell while the top and bottom layers of the LGPS were surrounded by carbon. The two different regions of the LGPS with and without carbon correspond to the LGPS electrodes and LGPS electrolyte respectively, and the thickness of the cathode and anode are defined by the depth of carbon penetration. The thicknesses of the LGPS/C cathode, LGPS electrolyte, LGPS/C anode layers in the single-LGPS battery are 222, 330, 148 µm, respectively. The high-magnification image of the interface was also provided in Figure 3.12c. There is no clear distinction between the electrode and electrolyte except that some small carbon black particles could be observed within the top layer of the LGPS. Figure 3.12d reveals the electrochemical behavior of the single-LGPS battery at a current density of 10 mA/g between 0.0 and 2.5 V, and it shows that the single-LGPS ASSLIB is able to deliver a reversible capacity of 104 mAh/ $g_{(LGPS)}$. Moreover, similar charge/discharge curves could be observed from the 2nd to the 6th cycle with no apparent capacity decay. The rate performance of the single-LGPS

battery was also evaluated by cycling the battery at the current of 10, 50, and 100 mA/g, respectively. The result shown in Figure 6e indicates that the reversible capacity of the single-LGPS battery decreases from 104 to 37 mAh/g_(LGPS) as the current increases from 10 to 100 mA/g. In addition, the electrochemical performance of the single-LGPS battery was also evaluated at an elevated temperature of 50 °C. As demonstrated in Figure 3.12f, at the current density of 50 mA/g, the reversible capacity of the single-LGPS battery increases from 70 to 96 mAh/g_(LGPS) as the temperature increases from room temperature to 50 °C because of the decrease of the electrode, electrolyte and interfacial resistances.

3.3.5 Interfacial behavior of the single- $Li_{10}GeP_2S_{12}$ battery



Figure 3.13 Impedance profiles of (a) LGPS-C/80Li₂S·20P₂S₅/LGPS-C and (b) LGPS-C/LGPS/LGPS-C all-solid-state LIBs after charging to 2.5 V in the 1 - 10^{6} Hz frequency range at room temperature.

The interfacial behavior of the single-LGPS ASSLIB (LGPS-C/LGPS/LGPS-C) was evaluated by electrochemical impedance spectroscopy, and compared with a control battery (LGPS-C/80Li₂S \cdot 20P₂S₅/LGPS-C) which has exactly the same

configuration, except with the replacement of LGPS with 80Li₂S·20P₂S₅ glass as the solid electrolyte. Both batteries were galvanostatically charged to 2.5 V, held at 2.5 V for 20 h, and rested at open-circuit potential for 2 h prior to EIS testing. Figure 3.13 shows the EIS plots of these batteries at room temperature. Each EIS plot consists of a small semicircle in the high frequency region (> 100 kHz) and a large semicircle in the medium frequency region, followed by a straight line corresponding to the Warburg impedance in the low frequency region. The small semi-circle at high frequency could be assigned to the lithium ionic conduction in the solid electrolyte (R_{SE}) while the large semi-circle corresponds to the interfacial resistance (R_{int}) between LGPS-C electrodes and solid electrolyte.¹¹⁶ The resistance values were obtained by the least-square fittings of the impedance data using the equivalent circuit of two R//CPE (constant phase element) in series. As expected, the small difference in R_{SE} (192 Ω cm² for the LGPS/80Li₂S·20P₂S₅/LGPS cell and 45 Ω cm² for the LGPS/LGPS cell) consists with the ionic conductivity difference of the solid electrolytes used. However, the interfacial resistance of the LGPS-

C/80Li₂S·20P₂S₅/LGPS-C cell (1053 Ω cm²) is about 10 times higher than that of the single-LGPS battery (103 Ω cm²), which might be the reason for the fast capacity decay of the LGPS-C/80Li₂S·20P₂S₅/LGPS-C cell (**Figure 3.14**).



Figure 3.14 Charge/discharge curves of the LGPS-C/80Li₂S·20P₂S₅/LGPS-C allsolid-state full-cell in the voltage range of 0.0-2.5 V from the 2^{nd} cycle at the current density of 10 mA/g.

Moreover, the area-specific interfacial resistance of the single-LGPS battery (103 Ω cm²) is only 1.5 time of the electrodes in the liquid-electrolyte battery (~63 Ω cm²)¹¹⁷, although the single-LGPS battery has a 8-20 times higher loading of active material and ~10 times larger thickness than that in the liquid-electrolyte battery.¹¹⁷ Despite the sensitivity of the EIS test to the processing of the battery (pressure used, relative content of the component in the composite electrode), the interfacial resistance of the single-LGPS battery is significantly lower than most of the bulk-type ASSLIBs.^{4,43,92,118} Although the composition and fabrication process of single-LGPS battery have not been optimized, its interfacial resistance is still comparable to that of optimized ASSLIBs reported.^{35,41} Since the ionic conductivity of solid electrolyte does not have significant influence on the interfacial resistance, ¹¹⁹ this result confirmed that the interfacial behavior could be remarkably improved in the single-material ASSLIB using the LGPS as both electrodes and electrolyte.

3.3.6 Discussion

A single element arrangement (SEA) concept has been proposed by Weppner to prepare a fuel/electrolysis cell and an electro-chromic cell using a single material.¹²⁰ Both of these devices exhibit low interfacial resistance by avoiding interfacial chemical reactions and mechanical disrupture. However, there is no report about using a single-material for a rechargeable battery, wherein a severer compositional and structural change occurs at the electrode/electrolyte interface during charge/discharge. Herein, we reported the first single-material battery based on LGPS, which shows a remarkably improved interfacial performance as expected. The significant improvement of the interfacial behavior of the single-LGPS ASSLIB could be ascribed to the following reasons. (1) Using a single LGPS as both the electrodes (cathode and anode) and the electrolyte would allow an intimate physical contact between the electrodes and electrolyte at an atomic scale since the electrodes are essentially evolved from the electrolyte. For a conventional bulk-type ASSLIB with poor electronically-conductive electrodes, the charge transfer reaction usually occurs at the "triple phase contact" region where the active material should contact with both the lithium ionic conductive solid electrolyte and the electronicallyconductive carbon.¹²¹ However, in the proposed single-LGPS ASSLIB, only a twophase contact between carbon and solid electrolyte is required, which would effectively increase the active sites for electrochemical reaction. Since there is no carbon in the pure electrolyte layer and the electronic conductivity of LGPS cathode is very low, the progressive decomposition of the solid electrolyte would also be prevented. (2) The chemical reactions and elemental inter-diffusion between

electrodes and electrolyte could be eliminated because the electrodes are essentially gradually evolved from the electrolyte. More importantly, a transition region with a smooth chemical-composition and potential gradient distribution could be formed across the electrodes and electrolyte.¹²² The smooth electrochemical potential distribution will restrict the formation of space-charge layers between the electrodes and electrolyte. (3) The stress/strain generated at the interface would also be relieved because of the existence of the transition region across the electrodes and electrolyte. Consequently, a very low interfacial resistance could be achieved in the single-LGPS ASSLIB during long-term charge/discharge cycles.



Figure 3.15 The cross-section SEM image and elemental mappings of carbon (red) and sulfur (blue) of the single-LGPS battery with a thinner LGPS electrolyte (205 μ m).



Figure 3.16 Charge/discharge curves of the single-LGPS battery with a thinner solid electrolyte in the voltage range of 0.0-2.5 V from the 2^{nd} cycle at a current density of 10 mA/g.

Despite the remarkable improvement of interface behavior, the electrochemical performance of the single-LGPS battery is still not as good as that in the liquidelectrolyte battery at the same current density of 100 mA g⁻¹. This is because in the single-LGPS solid state battery the loading of LGPS in anode and cathode are 6 and 18 mg/cm² respectively, which is about 8-20 times higher than the LGPS loading in the liquid-electrolyte cell (0.75 mg cm⁻²). It is well known that the electrochemical performance of the electrode quickly decreases with the increase of the active material loading even in the liquid electrolyte battery. Moreover, the thickness of LGPS electrolyte layer (330 μ m) used in the single-LGPS battery is about 10 times larger than that of the separator (25-40 μ m) used in the liquid-electrolyte cell, which will also contribute to the high resistance of the battery. This could be supported by the fact that additional capacity of ~20 mAh/g_(LGPS) could be achieved at the current density of 10 mA/g by reducing the thickness of the LGPS electrolyte layer from 330 to 205 μ m (**Figure 3.15** and **3.16**).

A series of engineering efforts are still required to further improve the performance of the proposed battery, such as the optimization of the content of carbon black in the composite electrodes, the design of porous, nanostructured electrodes, and the application of a constant pressure during testing. In particular, infiltration of electronic conductive materials into the porous layer of the porous-LGPS/dense-LGPS/porous-LGPS sandwich structure using a mature technology in solid oxide fuel cell (SOFC) is more suitable for the single-material battery concept.¹²³ The key point of this work is to demonstrate a new single-material battery concept to address the interfacial problem for the bulk-type all-solid-state batteries. Moreover, the addition of large amounts of solid electrolyte (~50 wt.%) in the composite electrodes, which is usually required in a conventional bulk-type all-solid-state batteries (Figure. 1a) to ensure efficient transport of lithium ions and electrons in the electrode volume, would be unnecessary for the single-material battery due to the high ionic conductivity of the electrode itself.

3.4 Conclusion

In summary, we demonstrated a proof of concept of a single-material battery using LGPS as the electrolyte, anode and cathode, with the aim to eliminate the highly-resistive interfacial resistance of ASSLIB. After mixing LGPS with carbon, the Li-S and Ge-S components in LGPS could act as active centers for its cathode and anode performance in a way similar to the Li₂S cathode and GeS₂ anode, respectively. The single-LGPS ASSLIB exhibited a remarkably low interfacial resistance due to

(1) the improvement of interfacial contact, (2) the modification of the interfacial interactions, and (3) the suppression of the strain/stress at the interface. The single-material battery concept provides a promising direction to address the most challenging interfacial problem in all-solid-state lithium-ion battery. This concept is not limited to the use of LGPS, and it can also be broadly applied to other solid-state battery systems, beneficial to a high-power, high-energy, long-cycling all-solid-state battery. Additional implications of this concept include the fabrication of a nanobattery by introducing electronically-conductive material on the both surfaces of the LGPS nanomaterials.

Chapter 4: Interphase Engineering Enabled All-Ceramic Lithium Battery

4.1 Introduction

Achieving a high-performance solid-state battery (SSB) with nonflammable, inorganic solid electrolyte has been considered as the ultimate solution for the safety issue of lithium ion batteries.^{2,117} Sulfide-based solid electrolytes such as $Li_{10}GeP_2S_{12}^{22,23,124}$ and garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO)⁸⁹ are being considered as the most promising solid electrolytes for SSBs because of their high ionic conductivities. Significant advance has been made to achieve both high-voltage and high-power SSBs based on sulfide-based electrolytes owing to their excellent mechanical properties.^{22,23} However, the challenges of the formation of toxic H₂S from the hygroscopic sulfides and the poor electrochemical stability of the sulfide-based electrolytes^{10,125,126} still remain. Garnet-type LLZO has therefore attracted increasing attentions due to its higher air stability and electrochemical stability,^{10,89} although slight reactions between LLZO and H₂O/CO₂ in the air also occur.^{6,127} Moreover, LLZO also holds great promise of using high-capacity lithium metal as an anode. The stable cycling of Li metal with LLZO with a low interfacial resistance has been reported by several groups,^{25,128-130} although the lithium dendrite formation along the grain boundaries at high currents is still a challenge.¹²⁹⁻¹³³ Despite these great promises, the performance of the LLZO-based all-solid-state lithium battery is far worse than that of the sulfide-based SSBs because of the huge interfacial resistances between the cathode and the rigid LLZO electrolyte.^{2,25,134}

The high cathode/electrolyte interfacial resistance in all-solid-state lithium batteries is mainly attributed to (i) the poor contact between the solid active material and solid electrolyte in the cathode composite, and between the cathode composite layer and the rigid electrolyte layer;^{4,33} (ii) the (electro)chemical instability between active material and solid electrolyte during charge/discharge^{53,125} and/or hightemperature sintering^{25,84} processes; (iii) the strain/stress at the interface generated from the large volume change of the electrode materials during charge/discharge¹³⁵ and/or from the different coefficients of thermal expansion between electrode and electrolyte during high-temperature sintering; and (iv) the formation of space-chargelayer at the interface.^{39,134}

Several attempts have been made to lower the cathode/electrolyte interfacial resistance in LLZO-based SSBs. LiCoO₂ (LCO) was mainly used as the cathode in these work presumably because the high electronic conductivity of both LCO and the delithiated LCO allows fast lithiation/delithiation of LCO cathode without any electronically conductive additives.^{136,137} Vacuum deposition of thin-film LCO cathode on LLZO electrolyte pellet could improve the interfacial contact,¹³⁸ but the vacuum deposition method is undesired to prepare high-loading electrode (usually tens of microns thick) for a high-energy bulk-type lithium battery. The direct coating of active material on a LLZO pellet at room temperature using the mature slurry-casting technology would not work because of the insufficient interfacial contact.²⁵ High-temperature sintering can improve the interfacial contact, but may also lead to the formation of a highly resistive interphase because of the chemical instability between cathode and LLZO.^{25,67} For example, the LCO cathode prepared by sintering

LCO on a LLZO pellet at 700°C could only deliver a low capacity of 35 mAh/g, which is only 25% of theoretical capacity of LCO (140 mAh/g), due to the elemental cross-diffusions and the formation of tetragonal LLZO phase at the LCO/LLZO interface.²⁵ To address the chemical instability between LCO and LLZO at high temperature, Li₃BO₃ with a low melting point (700°C) was added in the cathode composite to lower the sintering temperature.^{24,25,139-141} However, the improvement on the battery performance was still limited because simply adding a sintering additive in the cathode cannot guarantee a complete separation between the LCO particles and LLZO electrolyte, especially if the sintering additive has poor wetting capabilities with LCO and LLZO. As a result, LLZO and LCO will still be in partial contact with each other, causing severe reactions between them during sintering and charge/discharge processes. Up to date, for the bulk-type LLZO-based all-solid-state batteries, the highest reported capacity is 101 mAh/g that was achieved at a low current density of 0.025 C with no cycling data,¹⁴⁰ while the longest cycle number of 10 was achieved at 0.2 C with a low capacity of 67 mAh/g.²⁵ As a compromise, flammable polymer^{142,143} or liquid^{128,144} electrolyte was usually added at the cathode/LLZO interface to reduce the interfacial resistance, which will clearly sacrifice the intrinsic safety of SSBs.

The critical challenge to achieve a high-performance all-solid-state Li/LLZO/LCO battery with an all-ceramic cathode and electrolyte lies into the complete separation of LCO and LLZO by an interphase that has high ionic conductivity, is (electro)chemically stable, and wets with both LCO and LLZO. Unfortunately, the complete separation between LCO and LLZO could not be achieved by simply adding a sintering additive such as Li_3BO_3 .²⁵ By taking advantages of the spontaneous formation of the conformal coatings of Li_2CO_3 on the surfaces of both $LLZO^{6,66}$ and LCO^{145} when exposed to air, here we present an innovative approach to lower the LCO/LLZO interfacial resistance by thermally soldering LCO and LLZO together through the reaction between the $Li_{2.3}C_{0.7}B_{0.3}O_3$ solder and the Li_2CO_3 coatings to form the $Li_{2.3-x}C_{0.7+x}B_{0.3-x}O_3$ (LCBO) interphase. The basic configuration of the interphase-engineered cathode/electrolyte is shown in





Figure 4.1 Schematic diagrams of the interphase-engineered all-ceramic

cathode-electrolyte. A thin layer of Li₂CO₃ (3 nm) was artificially coated on LCO because the spontaneously-formed Li₂CO₃ on LCO is too thin. The Li₂CO₃-coated LCO (LCO@Li₂CO₃) was then mixed with a spontaneously Li₂CO₃-coated LLZO (LLZO@Li₂CO₃), and Li_{2.3}C_{0.7}B_{0.3}O₃ solder to make a cathode composite. The cathode composite was then coated on a LLZO ceramic pellet which was also spontaneously coated by Li₂CO₃. After sintering at 700°C, Li_{2.3}C_{0.7}B_{0.3}O₃ will melt, and react with the Li₂CO₃ coatings on both LLZO and LCO to form Li_{2.3-x}C_{0.7+x}B_{0.3-x}O₃ (LCBO) interphase.

Different from the conventional approach of using Li₃BO₃ as a sintering additive to lower the sintering temperature, $Li_{2,3}C_{0,7}B_{0,3}O_3$ added in the cathode composite will react with the Li₂CO₃ layers that were conformally coated on both LCO and LLZO, ensuring a complete separation between LCO and LLZO. Li_{2.3}C_{0.7}B_{0.3}O₃ was selected as the solder because $Li_{2+y}C_{1-y}B_yO_3$ (y = 0~0.3) is isostructural as $Li_2CO_3^{146}$ and can further form solid solution with $Li_2CO_3^{147}$. Another unique advantage of this approach is that the LCBO interphase has a high ionic conductivity (much higher than Li₃BO₃).¹⁴⁶ The high ionic conductivity of LCBO has enabled it to be solid electrolyte for the all-solid-state lithium ion battery¹³⁵. It is well known that the inevitable formation of Li₂CO₃ on LLZO and some layered transition-metal oxide cathodes when exposed to air was always considered as an inherent drawback for these materials because of the low ionic conductivity of Li₂CO₃.^{66,145,148} However, this problem was uniquely addressed in our approach by reacting Li₂CO₃ with Li_{2.3}C_{0.7}B_{0.3}O₃ to form LCBO electrolyte interphase that has the Li-ion conductivity several orders of magnitude higher than Li₂CO₃.¹⁴⁷ The great wetting properties of $Li_{2.3}C_{0.7}B_{0.3}O_3$ with both LLZO@Li₂CO₃ and LCO@Li₂CO₃ could enable excellent interfacial contact within the cathode composite, and between the composite cathode and LLZO pellet. The complete separation between LCO and LLZO by LCBO could effectively suppress the elemental diffusions and chemical reactions between LCO and LLZO and suppress the formation of space-charge-layer at the LLZO/LCO interface. The LLZO particles contained in the cathode could not only improve the ionic conductivity of the cathode, but also function as a mechanical reinforcing phase to improve the mechanical property of the SSB,¹⁴⁹ which will help to accommodate

the strain/stress generated during lithiation/delithiation. It should be noted that the thin interfacial layer (~6 nm) between LCO particles will deform during sintering, and this will help ensure the interconnectivity between LCO particles that determines the electronic conductivity of electrode. A thicker coating of electronic insulating layer (e.g. $Li_4Ti_5O_{12}$, ³⁹ Li_2S -P₂S₅, ⁴¹ Li_6PS_5Cl , ¹⁵⁰ or LiI- Li_4SnS_4 , ¹⁵¹) on LCO has been reported for a high performance all-solid-state battery. The simultaneous improved the interfacial contact, (electro)chemical stability, ionic conductivity, and mechanical property of the all-ceramic cathode and electrolyte enabled an all-solid-state Li/LLZO/LCO battery to provide an extremely high electrochemical performance.

4.2 Experimental

4.2.1 Material synthesis

Polycrystalline LLZO powder was prepared by solid state reaction method. Ta was doped into LLZO (with the composition of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$) to stabilize the cubic phase at room temperature. Starting materials of LiOH·H₂O (99.995%, Sigma Aldrich), La(OH)₃ (99.9%, Sigma Aldrich), ZrO₂ (99.99%, Sigma Aldrich), Ta₂O₅ (99.99%, Sigma Aldrich), were weighed and mixed based on the stoichiometric ratio. 10% excess LiOH·H₂O was used to compensate the Li loss during high-temperature calcinations and sintering. The mixture was mechanically milled (PM 100, Retsch) with 2-propanol and zirconia balls in a zirconia vial for 24 hours, and then dried, heated in air at 950°C for 12 hours. The ball-milling and heating were repeated to enhance purity. The as-prepared LLZO powder was grinded using a high-energy vibrating mill (SPEX SamplePrep* 8000M Mixer/Mill) for 1 hour to reduce its particle size, and then stored in air. Detailed description of LLZO pellets can be found in our previous reports^{142,152} and in Figure S4. $Li_{2,3}C_{0,7}B_{0,3}O_3$ powder was prepared by heating a mixture of Li_2CO_3 and Li_3BO_3 in air at 650°C for 10 hours.¹⁴⁷ LiCoO₂ cathode was prepared by heating a mixture of Li_2CO_3 and Co_3O_4 in air at 850°C for 12 hours. To coat a thin-layer of Li_2CO_3 on LiCoO₂, the as-prepared LiCoO₂ was soaked in a mixed aqueous solution of 1M LiOH and 0.25M LiNO₃ for 30 mins, filtered out, then dried up in a vacuum oven, and finally heated at 250°C in CO₂ for 5 hours.¹⁵³

4.2.2 Material characterization

X-ray diffraction (XRD) patterns of the materials were measured with a D8 Advance with LynxEye and SolX (Bruker AXS, WI, USA) using Cu K α radiation. The morphologies of the sample were examined using a Hitachi a SU-70 fieldemission scanning electron microscope and JEOL 2100F field emission transmission electron microscope (TEM). Raman spectra were collected on a Horiba Jobin Yvon Labram Aramis using a 532 nm diode-pumped solid-state laser. The surface chemistry of the samples was examined by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis 165 spectrometer. XPS data were collected using a monochromated Al K α X-ray source (1486.7 eV). The working pressure of the chamber was lower than 6.6×10^{-9} Pa. All reported binding energy values are calibrated to the C 1s peak at 284.8 eV.

4.2.3 Preparation of the all-solid-state cell

LLZO powder and LLZO pellets were stored in air to ensure the spontaneous coating of Li_2CO_3 on the surfaces. LiCoO₂ and LLZO powders with or without Li_2CO_3 coating, and $Li_{2,3}C_{0,7}B_{0,3}O_3$ powders were mixed in a weight ratio of 58:30:12 (the corresponding volume ratio is 45:30:25). The cathode composite was mixed with ethyl cellulose as a binder, and α -terpineol as the solvent to prepare the electrode slurry. The slurry was then coated on the top surface of the LLZO solid electrolyte pellet, and the solvent was removed by drying at 100°C under vacuum. The LLZOsupported cathode composite was then heated at 700°C for 1 hour in air. A thin layer of gold (~200 nm) was sputtered on top of the cathode using a sputter coater (Cressington 108auto) to improve the electrical contact between cathode and current collector. Li metal anode was attached on the other side of LLZO pellets in an Arfilled glovebox to make the solid-state battery. The anode-side of the LLZO pellet was thoroughly polished in glovebox before attaching Li metal anode in order to remove the Li₂CO₃ coated on the surface. The as-assembled solid-state battery was sealed in a Swagelok cell with stainless steel rods as current collectors. For the performance test at 25°C, the as-assembly cell was put in a 100°C oven for 5 hours to ensure a good contact between lithium and LLZO.

4.2.4 Electrochemistry

Galvanostatic charge and discharge of the all-solid-state lithium batteries were conducted between 3.0 and 4.05 V (or 4.2 V) at different temperatures. The charge/discharge behavior was tested using an Arbin BT2000 workstation at different temperatures. The current density is determined based on 1 C corresponding to 115

mA/g. The current density and the specific capacity were calculated based on the weight of $LiCoO_2$ in the cathode. The electrochemical impedance spectroscopy (EIS) tests were carried on an electrochemistry workstation (Solartron 1287/1260). All-solid-state cells were fully charged to 4.05 V, held at 4.05 V for 20 hours and rest at open-circuit potential for 2 hours prior to EIS test.

4.3 Results and Discussion

4.3.1 Characterizations of Li₂CO₃ coatings on Li₇La₃Zr₂O₁₂ and LiCoO₂

It is known that the lithium in the Li-stuffed garnet (LLZO) is unstable when LLZO is exposed to air and could be extracted to react with the CO₂, forming Li₂CO₃.^{6,66}A recent work shows that Li₂CO₃ can be spontaneously formed on LLZO surface even during the synthesis process when the sample is cooling down in air.⁶ **Figure 4.2**A shows the SEM image of the LLZO particles after exposed to air for several days. The particle size is less than 1 μ m. The TEM image (Figure 4.2B) demonstrates a coating layer on the LLZO surface with a thickness around 30 nm. The elemental mapping (Figure 4.2C) demonstrates that the coating layer contains uniformly distributed carbon. Although no additional peaks other than cubic LLZO can be observed from the XRD pattern of the air-exposed LLZO (Figure 4.2H), Raman (Figure 4.2I) and XPS (Figure 4.2J) results confirmed that the coating layer on the surface of LLZO is Li₂CO₃, consistent with the previous report.⁶⁶



Figure 4.2 Characterizations of Li₂**CO**₃ **coatings on LLZO and LCO.** (A-I) SEM (A) and TEM (B) images of the LLZO@Li₂CO₃. SEM image and elemental mappings of C and Zr (C) of the LLZO@Li₂CO₃. SEM (D) and TEM (E) images of the as-synthesized LCO. SEM (F) and TEM (G) images of the LCO@Li₂CO₃. XRD (H), Raman (I), and XPS (J) of the as-synthesized LCO, LCO@Li₂CO₃ and LLZO@Li₂CO₃, respectively. The Raman spectrum of Li₂CO₃ was also included in (I).

The LLZO without Li_2CO_3 coating was also prepared by heating the air-exposed LLZO at 750°C under Ar atmosphere for 2 hours, and the TEM image and Raman

spectra (**Figure 4.3**) confirm that Li_2CO_3 was successfully removed. Figure 4.2D and 4.2E show the SEM and TEM images of the as-prepared LCO, respectively.



Figure 4.3 (A and B) TEM image (A) and Raman spectra (B) of the LLZO@Li₂CO₃ after heat treatment at 750 $^{\circ}$ C for 2 hours in Ar atmosphere. The results indicate that Li₂CO₃ was successfully removed from the surface of LLZO particles.

The particle size of LCO is around 2 μ m (Figure 4.2D) with a bare surface (Figure 4.2E). The absence of the Li₂CO₃ coating on the as-prepared LCO implies the spontaneously formed Li₂CO₃ on LCO is too thin, which is probably due to slower growth kinetics of Li₂CO₃ on LCO than that on LLZO. Therefore, an artificial Li₂CO₃ layer was coated on LCO (see Experimental Procedures). The morphology of LCO did not change after coating with Li₂CO₃ (Figure 4.2F). However, the TEM image (Figure 4.2G) shows that the thickness of the coated Li₂CO₃ is 3 nm. Raman (Figure 4.2I) and XPS (Figure 4.2J) confirmed that the coating layer is Li₂CO₃, although the intensity of the peak corresponding to Li₂CO₃ in the Raman spectrum of LCO@Li₂CO₃ is lower than that in LLZO@Li₂CO₃ because of the thinner coating.

The exact amount of Li_2CO_3 can be determined by thermal gravimetric analysis (TGA) as Li_2CO_3 will gradually decompose into Li_2O and CO_2 above $680^{\circ}C$,¹⁵⁴ and the results (**Figure 4.4**) show that the contents of Li_2CO_3 coated on LLZO and LCO are 2.9 and 4.4 wt. %, respectively.



Figure 4.4 (A and B) TGA-DSC results of LLZO@Li₂CO₃ (A) and LCO@Li₂CO₃ (B) particles under Ar atmosphere. The endothermic peak at around 680 °C is attributed to the decomposition of Li₂CO₃ and therefore the corresponding weight loss is ascribed to the released CO₂ gas from Li₂CO₃. The contents of Li₂CO₃ in the LLZO@Li₂CO₃ and LCO@Li₂CO₃ particles are then determined to be 2.9 and 4.4 wt. %, respectively.

4.3.2 All-ceramic LiCoO₂/Li₇La₃Zr₂O₁₂ cathode/electrolyte

 $Li_{2.3}C_{0.7}B_{0.3}O_3$ was synthesized by the solid-state reaction between Li_2CO_3 and Li_3BO_3 .¹³⁵ All the diffraction peaks of $Li_{2.3}C_{0.7}B_{0.3}O_3$ (**Figure 4.5**A) could be attributed to a monoclinic phase with a space group C2/*c*, isostructural with Li_2CO_3 . The peak shifts from Li_2CO_3 are caused by slight changes of the lattice parameter after introducing additional Li in the compound.^{135,146} Detailed characterizations

(Figure 4.5) indicate that $Li_{2.3}C_{0.7}B_{0.3}O_3$ has a high ionic conductivity of ~10⁻⁵ S/cm at 100°C and has a melting point of 690°C.



Figure 4.5 Characterizations of $Li_{2.3}C_{0.7}B_{0.3}O_3$. (A) XRD pattern of the assynthesized $Li_{2.3}C_{0.7}B_{0.3}O_3$ and Li_2CO_3 showed that they have the same structure. (B) SEM image of the as-synthesized $Li_{2.3}C_{0.7}B_{0.3}O_3$. The particle size of the as-obtained $Li_{2.3}C_{0.7}B_{0.3}O_3$ is around 5 µm. (C) TGA-DSC of the as-synthesized $Li_{2.3}C_{0.7}B_{0.3}O_3$ under Ar atmosphere. The melting point of $Li_{2.3}C_{0.7}B_{0.3}O_3$ was determined to be 690 °C. (D) The EIS plot of an Au/ $Li_{2.3}C_{0.7}B_{0.3}O_3/Au$ blocking electrode at 100 °C. The ionic conductivity of $Li_{2.3}C_{0.7}B_{0.3}O_3$ was determined to be 1.1 x 10⁻⁵ S/cm at 100 °C.

In order to test the chemical stability of $Li_{2.3}C_{0.7}B_{0.3}O_3$ to $LCO@Li_2CO_3$ and $LLZO@Li_2CO_3$ during high-temperature sintering process, $Li_{2.3}C_{0.7}B_{0.3}O_3$ was sintered with $LCO@Li_2CO_3$, with $LLZO@Li_2CO_3$, and with both $LCO@Li_2CO_3$ and $LLZO@Li_2CO_3$ at 700°C for 1 hour, respectively.



Figure 4.6 Characterizations of the interphase-engineered all-ceramic cathodeelectrolyte. (A) XRD of the composites of $Li_{2.3}C_{0.7}B_{0.3}O_3 + LCO@Li_2CO_3$ (12:58 in weight), $Li_{2.3}C_{0.7}B_{0.3}O_3 + LLZO@Li_2CO_3$ (12:30 in weight), and $Li_{2.3}C_{0.7}B_{0.3}O_3 +$ $LLZO@Li_2CO_3 + LCO@Li_2CO_3$ (12:30:58 in weight) after sintering at 700°C for 1 hour in air. These composites were ball-milled with the corresponding weight ratio and pressed into pellets before sintering. (B and C) SEM images of cross-section (B)

and top surface (C) of the cathode composite ($Li_{2.3}C_{0.7}B_{0.3}O_3 + LLZO@Li_2CO_3 + LCO@Li_2CO_3$) coated on a LLZO pellet before sintering. (D and E) SEM images of cross-section (D) and top surface (E) of the cathode composite coated on a LLZO pellet after sintering at 700°C for 1 hour in air. (F-I), High-magnification cross-section SEM image (F) and elemental mappings of Zr (G), Co (H) and B (I) of the cathode composite after sintering at 700°C for 1 hour in air.

Figure 4.6A shows the XRD patterns of the composites after sintering. No impurities could be observed from the XRD patterns of all the sintered composites. Although more careful characterizations at the LCO/LLZO interface are still required to confirm if there are any other products with a tiny amount or with an amorphous structure, the absence of the tetragonal LLZO²⁵ in the sintered three-phase composites $(Li_{2.3}C_{0.7}B_{0.3}O_3 + LCO@Li_2CO_3 + LLZO@Li_2CO_3)$ implies that the LCBO electrolyte interphase could effectively suppress the chemical reaction and elemental diffusions between LCO and LLZO at 700°C. Note that a slight shift of the peaks of LCBO at around 32 degree in the XRD of the sintered composite is attributed to the lower content of Li₃BO₃ in the LCBO solid-solution.¹⁴⁶ Therefore, 700°C was used as the temperature to sinter the cathode composite $(LLZO@Li_2CO_3 + LCO@Li_2CO_3 + LCO@Li_3CO_3 + LCO@Li_3CO_3 + LCO@Li_3CO_3 +$ $Li_{2,3}C_{0,7}B_{0,3}O_3$) on a LLZO electrolyte pellet to prepare the all-ceramic cathode/electrolyte. The LLZO electrolyte pellet has a thickness of roughly 1 mm and a diameter of about 1 cm. Detailed characterizations (Figure 4.7) show that the LLZO electrolyte pellet has a cubic garnet structure with a high ionic conductivity of

 1.4×10^{-3} S/cm at 25°C and 8.2 x 10^{-3} S/cm at 100°C, and a thin layer of Li₂CO₃ was also spontaneously formed on the LLZO ceramic pellet.



Figure 4.7 Characterizations of the LLZO solid electrolyte pellets. (A) Picture of the LLZO pellets. The diameter of the pellet is around 11 mm and the thickness of the pellet is around 1 mm. (B) Cross-section SEM image of the LLZO pellet. A highly dense ceramic pellet was obtained, and the relative density was determined to be 99.6 %. (C) XRD of the LLZO pellet confirms its cubic garnet structure. (D) Raman spectra of the LLZO pellet stored in air confirms the presence of Li₂CO₃ on the surface. (E) Arrhenius plot of the LLZO solid electrolyte pellet. The activation energy was determined to be 0.26 eV. The ionic conductivity of the LLZO pellet was measured to be 1.4 x 10^{-3} and 8.2 x 10^{-3} S/cm at 25 and 100 °C, respectively.

Figure 4.6B and 4.6C show the SEM images of the cross-section and top-surface of the cathode composites coated on a LLZO electrolyte pellet before sintering. The thickness of the cathode composite is around 20 μ m. The elemental mappings (**Figure 4.8**) show the three phases are uniformly distributed in the cathode.



Figure 4.8 Cross-section SEM image and elemental mappings of Co, Zr and C in the $LCO@Li_2CO_3 + Li_{2.3}C_{0.7}B_{0.3}O_3 + LLZO@Li_2CO_3$ cathode composite before sintering. A uniform distribution of $LCO@Li_2CO_3$, $Li_{2.3}C_{0.7}B_{0.3}O_3$, $LLZO@Li_2CO_3$ was achieved in the cathode composite.

Figure 4.6D and 4.6E shows the SEM images of cross-section and top-surface of the cathode composites after sintering at 700°C. The results indicate that after sintering, the cathode composite turns into a dense cathode with LLZO and LCO particles embedded in a LCBO matrix. High magnification cross-section SEM image
and elemental mappings of Co, Zr, B (Figure 4.6F-4.6I) demonstrated that both LLZO and LCO are tightly surrounded by the LCBO matrix. The intimate interfacial contact between the cathode composite and LLZO pellet (Figure 4.6D) and within the cathode composite (Figure 4.6F) confirmed the great wetting properties of LCBO with both LCO and LLZO.



4.3.3 Electrochemical performances of Li/Li₇La₃Zr₂O₁₂/LiCoO₂ cells

Figure 4.9 Electrochemical performances of all-ceramic Li/LLZO/LCO cells. (A) Charge/discharge profiles of the interphase-engineered all-ceramic Li/LLZO/LCO cell for the first three cycles at 0.05 C at 100°C. (B) Charge/discharge profiles of the interphase-engineered all-ceramic Li/LLZO/LCO cell at different rates from 0.05 C to

1 C at 100°C. Note that the profiles at five different C rates were obtained from five fresh cells after one activation cycle at 0.05 C. (C) Rate performance of the interphase-engineered all-ceramic Li/LLZO/LCO cell at 100°C. Note that the capacities at five different C rates were obtained from five fresh cells with each cell represented by one color. (D) Cycling performance of the interphase-engineered allceramic Li/LLZO/LCO cell at 0.05 C at 100°C. The cycling performances of allceramic Li/LLZO/LCO cells with the cathode composites consisting of uncoated LCO (LCO + Li_{2.3}C_{0.7}B_{0.3}O₃ + LLZO@Li₂CO₃) and uncoated LLZO (LCO@Li₂CO₃ + Li_{2.3}C_{0.7}B_{0.3}O₃ + LLZO) were also included. (E) Charge/discharge profiles of the interphase-engineered all-ceramic Li/LLZO/LCO cell for the first three cycles at 0.05 C at 25°C. (F) Cycling performance of the interphase-engineered all-ceramic Li/LLZO/LCO cell at 0.05 C at 25°C. The specific capacity was calculated based on the weight of LCO in the cathode composite.

We then tested the electrochemical performance of the interphase-engineered allceramic Li/LLZO/LCO cell. The thickness of the cathode layer is around 20 μ m and the loading of LCO in the cell is about 1.0 mg/cm². **Figure 4.9**A shows the first three charge/discharge curves of the interphase-engineered all-ceramic Li/LLZO/LCO cell at the current density of 0.05 C at 100°C. The charging cutoff voltage of 4.05 V was used in the previous reports^{24,135} to limit the volume change of the electrode during lithiation/delithiation. The theoretical capacity of LiCoO₂ within the voltage range of 3.0-4.05 V is 115 mAh/g, corresponding to 0.42 Li per CoO₂. The first charge and discharge capacities are 142 and 106 mAh/g, respectively. The irreversible capacity at 3.75 V in the first charge process is attributed to the decomposition of organolithium compounds that were produced during the sintering process.²⁴ Highly reversible lithiation/delithiation processes were observed in the following cycles. Figure 4.9B and 4.9C show the rate performances of the interphase-engineered all-ceramic Li/LLZO/LCO cell at different current densities at 100°C. The all-solid-state cell can still deliver a high capacity of 70 mAh/g even at 1 C. Moreover, the reversible capacity could increase to 90 mAh/g at 0.05 C after cycling at 1 C, indicating the great stability of the battery during high-rate charge/discharge processes. It should be noted that the rate performances of the cathode composite were measured using different fresh cells. This procedure allows us to determine the real capacity that can be delivered by the cathode composite at different C rates without the effect of capacity degradation over long-term cycling.¹⁵⁵ The critical role of the Li₂CO₃ coatings on LCO and LLZO in the cycling stability is demonstrated in Figure 4D, which compares the cycling performances of the three different cathode composites: (1) uncoated LLZO (LCO@Li₂CO₃ + Li_{2.3}C_{0.7}B_{0.3}O₃ + LLZO), (2) uncoated LCO $(LCO + Li_{2,3}C_{0,7}B_{0,3}O_3 + LLZO@Li_2CO_3)$, and (3) coated LCO with coated LLZO $(LCO@Li_2CO_3 + Li_{2.3}C_{0.7}B_{0.3}O_3 + LLZO@Li_2CO_3)$. The result shows that the cathode composite with Li₂CO₃ coating on both LCO and LLZO exhibits the best performance, with a high capacity of 67 mAh/g after 40 cycles at 0.05 C at 100°C.



Figure 4.10 (A) Nyquist plot of the Pt/LLZO/Pt cell. The insert shows the enlarged spectra for the high-frequency region. (B) Nyquist plot of the Li/LLZO/Li cell. The insert shows the equivalent circuit used for fitting. (C) Galvanostatic cycling of the Li/LLZO/Li symmetrical cell at a current density of 0.2 mA/cm². (D) Equivalent circuit used for fitting the Nyquist plots of all-solid-state full cells. (E-G) Nyquist plots of all-solid-state full cells. (E-G) Nyquist plots of all-solid-state full cells with different cathode composites. LCO@Li₂CO₃ + Li_{2.3}C_{0.7}B_{0.3}O₃ + LLZO (E), LCO + Li_{2.3}C_{0.7}B_{0.3}O₃ + LLZO@Li₂CO₃ (G) cathode composites were denoted by coated LCO + uncoated LLZO, uncoated LCO + coated LLZO, and coated LCO + coated LLZO, respectively. Open symbols indicate experimental data,

while the lines represent fitted data. The values obtained by fitting the impedance data are listed in Table R1. Note that all the results shown in this figure were tested at 100 °C. All EIS results were tested within the frequency range of 1 MHz to 0.01 Hz.

Table 4.1 Summary of Fitted Data for Full cells with Different Cathode Composites

Cathode Composition	R0 (Ω cm ²)	R1 (Ω cm ²)	R2 (Ω cm ²)
$LCO@Li_2CO_3 + Li_{2.3}C_{0.7}B_{0.3}O_3 + LLZO$	63	32	282
$LCO + Li_{2.3}C_{0.7}B_{0.3}O_3 + LLZO@Li_2CO_3$	44	28	203
$LCO@Li_{2}CO_{3} + Li_{2.3}C_{0.7}B_{0.3}O_{3} + LLZO@Li_{2}CO_{3}$	31	30	101

R0, R1, and R2 represent the area specific resistances of the solid electrolyte, anode/electrolyte interface, and cathode/electrolyte interface, respectively.

The result is consistent with detailed impedance analysis (**Figure 4.10** and Table **4.1**), wherein the cell with Li₂CO₃ coated on both LCO and LLZO cathode shows the smallest area specific resistance (ASR) for the cathode/electrolyte interface. It should also be noted that the ASR of the Li/LLZO interface is much smaller than that of the cathode/electrolyte interface, indicating that the interfacial resistance of the cell is mainly controlled by the cathode/electrolyte interface. In addition, we also tested the electrochemical performance of the LCO@Li₂CO₃ + LLZO@Li₂CO₃ cathode composite without Li_{2.3}C_{0.7}B_{0.3}O₃ sintering additive. The cell could only deliver a low reversible capacity of 35 mAh/g for the first cycle with a fast capacity (**Figure 4.11**), demonstrating the important role of Li_{2.3}C_{0.7}B_{0.3}O₃ in the interfacial properties of the cathode composite.



Figure 4.11 (A) Charge/discharge profiles of the LCO@Li₂CO₃ + LLZO@Li₂CO₃ (without Li_{2.3}C_{0.7}B_{0.3}O₃ sintering additive) cathode composite for the first three cycles at a rate of 0.05 C. (B) Cycling performance of the LCO@Li₂CO₃ + LLZO@Li₂CO₃ cathode composite at 0.05 C. The cell was tested at 100 °C, and the specific capacity was calculated based on the weight of LCO.

The performances of the interphase-engineered Li/LLZO/LCO cell at 25°C were also tested. Although a large overpotential could be observed from the charge/discharge curve (Figure 4.9E) when compared with that tested at 100°C (Figure 4.9A), the cell delivered excellent cycle stability at 25°C. The reversible capacity could be stabilized at around 83 mAh/g for 100 cycles (Figure 4.9F), representing the best cycle life for all-ceramic lithium batteries.



Figure 4.12 (A and B) Charge/discharge profiles (A) and cycling performance (B) of the interphase-engineered all-ceramic lithium battery with a LiCoO₂ loading of 3 mg/cm² cycled within 3 – 4.05 V at 1/20 C at 100 °C. (C and D) Charge/discharge profiles (C) and cycling performance (D) of the interphase-engineered all-ceramic lithium battery with a LiCoO₂ loading of 1 mg/cm² cycled within 3 – 4.2 V at 1/20 C at 100 °C. (E and F) Charge/discharge profiles (E) and cycling performance (F) of the interphase-engineered all-ceramic lithium battery with a LiCoO₂ loading of 1 mg/cm² cycled within 3 – 4.2 V at 1/20 C at 100 °C. (E and F) Charge/discharge profiles (E) and cycling performance (F) of the interphase-engineered all-ceramic lithium battery with a high LiCoO₂ loading of 1 mg/cm² cycled within 3 – 4.2 V at 1/40 C at 25 °C.

In addition, we also tested the performances of the interphase-engineered cell with increased LCO loading and within a wider voltage range. The results were summarized in **Figure 4.12**. The cell with an increased LCO loading (3 mg/cm^2) delivered similar capacity as the one with 1 mg/cm² loading at 100°C. Increasing the cutoff voltage to 4.2 V could largely increase the reversible capacity to 124 mAh/g for the first cycle at 100°C, but fast capacity decay could be also observed for the first few cycles. Interestingly, the cell worked well within the cut-off voltage range of 3.0-4.2 V at 25°C (Figure 4.12D), and an initial capacity of 104 mAh/g was achieved at 0.025 C.

Study	Cathode Composition	Temp.	Current	Capacity** (mAh/g)	No. of Cycles	Rate (Max.)
Kotobuki et al.67	LCO	RT*	$2 \ \mu A/cm^2$	0.274	3	$2 \ \mu A/cm^2$
Park et al.25	LCO	50°C	0.2 C	35	10	0.2 C
Shoji et al. ¹⁴¹	$LCO + Li_3BO_3$	60°C	$14 \ \mu A/cm^2$	0.6 - 7	5	$14 \ \mu A/cm^2$
Ohta et al. ²⁴	$LCO + Li_3BO_3$	25°C	0.05 C	85	5	0.05 C
Park et al.25	$LCO + Li_3BO_3$	50°C	0.2 C	67	10	0.2 C
Ohta et al. ¹³⁹	$LCO + Li_3BO_3 + LLZO$	RT*	0.01 C	78	1	0.01 C
Liu et al. ¹⁴⁰	$LCO + Li_3BO_3 + In_2O_5Sn$	RT*	0.025 C	101	1	0.025 C
Current work	$ \begin{array}{l} LCO@Li_{2}CO_{3}+Li_{2.3}C_{0.7}B_{0.3}O_{3}+\\ LLZO@Li_{2}CO_{3} \end{array} $	100°C	0.05 C	106	40	1 C
		25°C	0.05 C	94	100	0.05 C

Table 4.1 Electrochemical Performances of LLZO-Based Bulk-Type All-Ceramic

 Lithium Batteries

*RT (Room Temperature) is assumed if the test temperature was not specified. **The reversible capacity for the 1^{st} cycle is listed.

Table 4.1 summarizes the performances of all reported LLZO-based bulk-type allceramic lithium batteries. The results indicate our interphase-engineered Li/LLZO/LCO cell significantly-improved electrochemical performances in terms of the capacity, cycle life and rate capability.

4.3.4 Discussion



Figure 4.13 Cross-section SEM image of the cathode composite after 40 cycles at 100 °C

Despite the exceptional electrochemical performance for the interphaseengineered all-ceramic lithium cell, the capacity decay could still be observed, especially when tested at 100°C. The capacity decay is most likely related with the mechanical degradation of the cathode/electrolyte interface due to the volume change of LCO, because a large amount of micro-fractures with some flakes could be observed in the cycled cathode (**Figure 4.13**). Cycling the battery at 100°C helped to largely improve the specific capacity when compared with cycling at 25°C, but could also cause a larger strain/stress within the cathode composite because of larger volume change of the electrode. The capacity decay due to the mechanical degradation of the interface is consistent with the previous report¹³⁵ and could also be supported by the electrochemical performances of the cathode composites with a higher content of LLZO and without LLZO (**Figure 4.14**).

106



Figure 4.14 Electrochemical performance of the cathode composite with a higher content of LLZO and without LLZO. (A and B) Charge/discharge curves (A) and cycling performance (B) of the LCO@Li₂CO₃ + Li_{2.3}C_{0.7}B_{0.3}O₃ + LLZO@Li₂CO₃ cathode composite with a weight ratio of 44:12:44 at 0.1 C. (C and D) Charge/discharge curves (C) and cycling performance (D) of the LCO@Li₂CO₃ + Li_{2.3}C_{0.7}B_{0.3}O₃ cathode composite at 0.05 C. The cells were tested at 100 °C, and the specific capacity was calculated based on the weight of LiCoO₂.

The cycling performance of cathode composite with a higher content of LLZO (and a lower content of LCO) could be largely improved, while the cathode

composite without LLZO particles shows a really poor cycling performance. The reason for such a huge difference is that (i) increasing the content of LLZO as a reinforcing phase could help improve the mechanical strength of the cathode composite, ¹⁴⁹ and (ii) lowering the content of LCO in the cathode composite could help reduce the strain/stress during cycling. We believe further improving the cycling performance is highly likely by improving the mechanical strength of the cathode composite, for example, by using LLZO nanowires as the reinforcing phase. In addition, the rate performance of the interphase-engineered all-ceramic lithium battery at room temperature still needs to be improved. This could be achieved by optimizing the composition of $Li_{2+y}C_{1-y}B_yO_3$ (y = 0~0.3) interphase to achieve a high ionic conductivity or introducing electronically conductive additives into the cathode composite by spark plasma sintering method.¹⁵⁶

4.4 Conclusion

In conclusion, we demonstrated an innovative approach to address the huge interfacial resistance between LCO cathode and LLZO electrolyte by thermal soldering LCO and LLZO together with the Li_{2.3-x}C_{0.7+x}B_{0.3-x}O₃ solid electrolyte interphase through the reaction between Li_{2.3}C_{0.7}B_{0.3}O₃ solder and Li₂CO₃ coatings on both LLZO and LCO, by taking advantages of the spontaneous formation of Li₂CO₃ on the surfaces of both LLZO and LCO. A superior LCO/LLZO interface was achieved with the simultaneous improvements on the interfacial contact, electrochemical and chemical stability, ionic conductivity and mechanical strength, leading to a significantly-improved all-ceramic Li/LLZO/LCO cell. The interphase-engineered all-ceramic Li/LLZO/LCO cell delivered a large initial capacity with great

cycling (100 cycles at 25°C) and high-rate performances, representing the best performance of the all-ceramic Li batteries, and therefore is a significant breakthrough towards the development of intrinsically safe, high-performance allsolid-state lithium batteries. Moreover, this approach is not limited to LCO cathode but can also be applied to other layered transition-metal oxide cathodes,¹⁴⁸ promoting the practical application of all-solid-state lithium batteries.

Chapter 5: Li Dendrite Suppression in Li₂S-P₂S₅ by LiI Incorporation

5.1 Introduction

Lithium metal is believed to be the most promising anode due to its extremely high capacity, low density and the lowest electrode potential.^{157,158} However, the utilization of lithium metal anodes with the conventional liquid or polymer electrolytes has not been successful because of the unavoidable lithium dendrite growth which can cause internal short circuit and life-threaten accidents.¹⁵⁹ Solid electrolytes have been considered to be the ideal solution to prevent dendrite growth because of their high shear modulus^{160,161} and high Li transference number¹⁶². In addition, the utilization of nonflammable, inorganic solid electrolytes can also dramatically improve battery safety.^{2,117,163} While various lithium ion conducting materials have been developed, sulfide-based compounds (Li₂S-P₂S₅ and its derivatives) are being considered as one of the most promising solid electrolytes due to their excellent mechanical property (can be densified simply by cold pressing) and high ionic conductivity.^{8,23,164} Unexpectedly, recent reports indicate that the Li dendrites also form in 70Li₂S-30P₂S₅ glass, 75Li₂S-25P₂S₅ glass, 80Li₂S-20P₂S₅ glass-ceramic, and polycrystalline β -Li₃PS₄.¹⁶⁵⁻¹⁶⁷ The formation of Li dendrites leads to rapid short circuit of the Li/electrolyte/Li (Li-Li) cells at current densities larger than 1 mA/cm².^{165,167} It should be noted that even in the conventional liquid electrolyte (1M LiPF₆ in EC/DMC), the lithium metal anode is still able to cycle hundreds of hours at 2 mA/cm² without shorting.¹⁶⁸ This indicates that sulfide

electrolytes tend to promote, rather than suppress, dendrite formation when compared with liquid electrolytes. However, until now, there is still no effective approach to suppress the Li dendrite growth in sulfide electrolytes because the mechanism for the "unexpected" dendrite formation is unclear. To the best of our knowledge, there is only one report on the suppression of the lithium dendrite formation in sulfide electrolyte by optimizing the processing conditions.¹⁶⁷ It was shown that hot pressing $75Li_2S-25P_2S_5$ solid electrolyte can help to increase the critical current density (at which current the cell will be short circuited by dendrite formation) because of the formation of a highly conductive thio-LISICON phase and the improvement of adhesion between particles. However, the critical current density for the hot-pressed $75Li_2S-25P_2S_5$ solid electrolyte is still limited to 1 mA/cm², much lower than that in the liquid electrolyte Li batteries. It is fair to conclude that, similar as in the liquidelectrolyte lithium-metal batteries, the main challenge to utilize lithium anode with sulfide solid electrolytes is how to effectively suppress the dendrite formation at a large current.

It has been known that the sulfide solid electrolytes have a limited thermodynamic electrochemical stability window around 1.7 V to 2.1 V.^{10,53,60} Therefore, the interfacial stability between Li metal and sulfide electrolytes is achieved by forming solid electrolyte interphase (SEI) as a passivating layer. The composition of the SEI mainly includes Li_3P , Li_2S and other Li-containing compounds depending on the composition of the electrolyte.^{10,60,126,169,170} Since the Li dendrites have to grow through the SEI, the composition of the SEI should play an important role in the

111

dendrite formation. It is therefore hypothesized that the dendrite formation in sulfide electrolytes can be suppressed by tuning the composition of the electrolyte.

In this work, we demonstrated that the formation of Li dendrites in $Li_2S-P_2S_5$ glass can be suppressed by incorporating LiI into the electrolyte. Our interest in glasstype electrolyte originates from its two fundamental attributes: the absence of highly resistive grain boundaries and the high flexibility to tune its composition. LiI was chosen as the additive because both the ionic conductivity^{62,171-173} and the electrochemical stability of sulfide electrolytes can be improved after LiI incorporation ^{60,61,174-176}. In addition, incorporating LiI into Li₂S-P₂S₅ glass can also introduce highly ionic conductive but electronic insulating LiI in the SEI,^{60,170} and more importantly, improve the surface mobility of Li at the Li/electrolyte interface, ^{177,178} suppressing the dendrite growth. Our results show that the critical current density was improved significantly after introducing LiI into Li₂S-P₂S₅ glass electrolyte, reaching 3.90 mA/cm² at 100 °C after adding 30 mol% LiI. Stable cycling of the Li-Li symmetrical cells for 200 hours was also achieved at 1.50 mA/cm² with a charge/discharge capacity of 1.5 mAh/cm² at 100 °C.

5.2 Experimental

5.2.1 Material synthesis

 $(100-x)(0.75Li_2S-0.25P_2S_5)$ -xLiI (x= 0, 10, 20, 30 and 40) solid electrolytes were synthesized using high-energy mechanical milling.^{62,172} Li₂S (Sigma-Aldrich, 99.98%), P₂S₅ (Sigma-Aldrich, 99%) and LiI (Sigma-Aldrich, 99.99%) were used as starting materials. These materials were weighed based on the molar ratios of

112

Li₂S/P₂S₅/LiI in an argon-filled glovebox, subjected to a zirconia ceramic vial, and ball-milled (PM 100, Retsch) at 500 rpm for 10 hours.

5.2.2 Material characterization

Powder X-ray diffraction patterns were obtained with a D8 Advance with LynxEye and SolX (Bruker AXS, WI, USA) using Cu Kα radiation. The morphologies of the sample were examined using a Hitachi a SU-70 field-emission scanning electron microscope. Raman spectra were measured on a Horiba Jobin Yvon Labram Aramis using a 532 nm diode-pumped solid-state laser.

5.2.3 Electrochemistry

To assemble the Li/electrolyte/Li cell, 180 mg solid electrolyte powder was pressed into a pellet under 360 MPa in a PTFE tank with a diameter of 10 mm. After that, two 45 µm-thick Li discs with a diameter of 10 mm were attached on both sides of the solid electrolyte. The formed Li/electrolyte/Li cell was then sandwiched between two stainless steel rods which function as current collectors. For the assembly of the all-solid-state full cells, LiNbO₃ coated LiCoO₂ (LiCoO₂@LiNbO₃) was mixed with LPS30I glass electrolyte with a weight ratio of 70:30 to prepare the cathode composite. The cathode composite (10 mg) was put on the top of the LPS30I glass electrolyte (150 mg) and cold pressed together under 360 MPa in a PTFE tank with a diameter of 10 mm. After that, a 45-µm thick Li metal was attached on the other side of the LPS30I layer as a counter and reference electrode. The formed threelayered pellet was then cold-pressed under 120 MPa between two stainless steel rods which function as current collectors. The Li/electrolyte/Li and Li/LPS30I/LiCoO₂@LiNbO₃ cells were rested for 6 hours prior to test to stabilize the interface between Li and electrolyte. No formation cycles at small currents were used in this work.^[35] The ionic conductivity of the solid electrolytes was measured from the EIS test of the Pt/electrolyte/Pt cell at room temperature. All the electrode preparation and cell assembly processes were performed in the glovebox. The galvanostatic cycling charge/discharge behavior was tested at different temperatures using an Arbin BT2000 workstation (Arbin Instruments, TX, USA). The time for each charge (and discharge) is 1 hour. The electrochemical impedance spectrum was measured on an electrochemistry workstation (Solartron 1287/1260).

5.3 Results and Discussion



5.3.1 Stuctrural analysis of (100-x)(0.75Li₂S-0.25P₂S₅)-xLiI

Figure 5.1 XRD patterns (a), Raman spectra (b), and deconvoluted Raman spectra (c) of $(100-x)(0.75\text{Li}_2\text{S}-0.25\text{P}_2\text{S}_5)$ -xLiI, where x = 0, 10, 20, 30 and 40. The XRD pattern and Raman spectrum of LiI are also included as a reference.

Sample	Species	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Area ratio (%)
x = 0	PS_4^{3-}	421	15	89.2
	$P_2S_7^{4-}$	404	20	4.5
	$P_2 S_6^{4-}$	386	19	6.3
x = 10	PS_4^{3-}	421	14	90.1
	$P_2S_7^{4-}$	404	16	3.6
	$P_2S_6^{4-}$	385	17	6.3
x = 20	PS_4^{3-}	421	15	87.7
	$P_2S_7^{4-}$	404	16	4.8
	$P_2 S_6^{4-}$	386	19	7.5
x = 30	PS_4^{3-}	421	15	89.9
	$P_2S_7^{4-}$	405	16	3.4
	$P_2S_6^{4-}$	386	19	6.7
x = 40	PS_4^{3-}	421	15	89.6
	$P_2S_7^{4-}$	405	16	3.0
	$P_2 S_6^{4-}$	386	17	7.4

Table 5.1 The detailed results from the deconvolution of Raman spectra of (100-x)(0.75Li₂S-0.25P₂S₅)-xLiI glass electrolytes, where x = 0, 10, 20, 30, and 40.

Different amount of LiI was introduced into $Li_2S-P_2S_5$ glass electrolytes by highenergy ball-milling of Li_2S , P_2S_5 and LiI at the compositions of $(100-x)(0.75Li_2S-0.25P_2S_5)-xLiI$ (mol %), where x = 0, 10, 20, 30 and 40. Figure 5.1a shows the XRD patterns of as-prepared $(100-x)(0.75Li_2S-0.25P_2S_5)-xLiI$ glass electrolytes. All the solid electrolytes have amorphous structure except the sample with 40 mol % LiI addition wherein some unknown crystalline phases were formed after ball-milling. No apparent change could be observed from the Raman spectra (Figure 5.1b) after introducing different amounts of LiI into the $Li_2S-P_2S_5$ electrolytes. More importantly, no LiI can be detected from XRD and Raman spectra, indicating that LiI has been successfully dissolved into the electrolytes. Figure 5.1c shows the deconvoluted Raman spectra in a specified region. The peaks at around 421, 404 and 386 cm^{-1} can be attributed to PS_4^{3-} , $P_2S_7^{4-}$, $P_2S_6^{4-}$ in the glass electrolytes, respectively.¹⁷⁹ The relative ratio of these peaks does not change much after introducing different amounts of LiI in Li₂S-P₂S₅ (**Table 5.1**), indicating that the local structure around phosphorus of these glasses does not change by LiI incorporation, consistent with the previous reports.^{62,171,180}



5.3.2 Critical current density of (100-x)(0.75Li₂S-0.25P₂S₅)-xLiI

Figure 5.2 Galvanostatic cycling of the Li-Li cells at step-increased current densities at 25 °C with $(100-x)(0.75\text{Li}_2\text{S}-0.25\text{P}_2\text{S}_5)$ -xLiI electrolytes, where x = 0 (a), 10 (b), 20 (c), 30 (d) and 40 (e). The time for each charge and discharge is 1 hour. The step size for the current increase is 0.04 mA/cm². The critical current densities versus the composition of the sulfide electrolytes (f).

We evaluated the dendrite suppression capability of $(100-x)(0.75Li_2S-0.25P_2S_5)$ xLiI (x=0, 10, 20, 30, and 40) glass electrolytes by galvanostatic cycling of Li-Li cells at step-increased current densities at 25 °C. **Figure 5.2**a-e shows the voltage-time profiles for solid electrolytes with different amounts of LiI incorporation. Initially, the voltages increased with currents for all solid electrolytes, and the magnitudes of the voltage at the same current follow the trend: x=0 > x=10 > x=20 > x=40 > x=30, consistent with the ionic conductivity of the solid electrolytes (**Figure 5.3**).



Figure 5.3 The ionic conductivity vs the composition of the solid electrolytes. The ionic conductivity of the solid electrolyte was obtained from the EIS test of the Pt/electrolyte/Pt cell at room temperature.

After cycling for a certain amount of time, all of the Li-Li cells experienced a voltage drop. The voltage drop is considered as a result of lithium dendrite formation in the solid electrolytes, as can be observed from the backscattering electron images and the elemental mappings of the cross-section of electrolyte after cycling (**Figure 5.4** and **5.5**).



Figure 5.4 Backscattering electron image and elemental mappings of the crosssection of LPS glass electrolyte after cycling at stepped current densities. Dark precipitates indicates the presence of light elements and are considered to be dendrites because they don't contain P and S, but are rich in O due to the contamination of the lithium from air.



Figure 5.5 Backscattering electron image and elemental mappings of the crosssection of the LPS30I electrolyte after cycling at stepped current densities. Dark precipitates are considered to be dendrites because they don't contain P, S and I, but are rich in O.

The current density at which voltage dropped is considered as the critical current density for the Li dendrite formation in electrolyte, and the magnitude of the critical current density is used to evaluate the capability of dendrite suppression.^{74,129,130} Figure 5.2f compares the critical current densities for the electrolytes with different LiI contents. The critical current density for the $0.75Li_2S-0.25P_2S_5$ (LPS) glass electrolyte without LiI addition is determined to be 0.40 mA/cm^2 . The critical current density increases with increasing the content of LiI, reaching the maximum value of 1.00 mA/cm^2 (corresponding to a 150% increase) at x= 30 (LPS30I), and then decreases to 0.35 mA/cm^2 at x= 40. The reason for the decreased critical current density at x = 40 is still not clear, but it may be related to the unknown impurities in the electrolyte as demonstrated in Figure 5.1a. The critical current density of LPS30I

is much higher than the reported critical current densities of garnet-type $Li_7La_3Zr_2O_{12}$ solid electrolytes.^{74,130,181,182}



Figure 5.6 Galvanostatic cycling of the Li/LPS/Li and Li/LPS30I/Li cells at stepincreased current densities at 60 $^{\circ}$ C (a, b) and 100 $^{\circ}$ C (c, d). The time for each charge and discharge is 1 hour. The step sizes for the current increase are 0.08 mA/cm² at 60 $^{\circ}$ C and 0.15 mA/cm² at 100 $^{\circ}$ C.

As high temperature operation is one important advantage for all-solid-state lithium batteries, the effects of temperature on the critical current densities of LPS and LPS30I were also investigated. **Figure 5.6** shows the galvanostatic cycling of the Li/LPS/Li and Li/LPS30I/Li cells at 60 °C and 100 °C. The critical current density for LPS is 0.88 mA/cm² at 60 °C and 2.40 mA/cm² at 100 °C, while the critical current density for LPS30I is 2.16 mA/cm² at 60 °C and 3.90 mA/cm² at 100 °C. The critical current densities of both LPS and LPS30I increase with increasing temperature, a trend consistent with the previous report on the dendrite formation in $Li_7La_3Zr_2O_{12}$.^{129,130} However, the increase in critical current density of LPS30I is much more significant than that of LPS, and 3.9 mA/cm² is the highest critical current density that has been reported so far for Li cycling with sulfide electrolytes.

It should be noted that the exact value for the critical current density depends on the step size for the increase of current and the capacity for each charge and discharge. Ideally, the step size should be as small as possible to get the most accurate critical current density. This explains why the critical current density of $75Li_2S$ - $25P_2S_5$ glass electrolyte measured in this work (step size: 0.04 mA/cm^2) is much smaller than that in the previous work (step size: 0.5 mA/cm^2).¹⁶⁷ Nevertheless, the critical current density of different electrolytes tested under the same condition can be used to compare their capabilities for dendrite suppression.^{74,129,130,167,182,183} The obtained values for the critical current densities in this work are reproducible from another set of experiment, and we estimate the error from different measurements is less than 10 %.

5.3.3 Cycle stability of 0.75Li₂S-0.25P₂S₅ and 70(0.75Li₂S-0.25P₂S₅)-30LiI

We then compared the cycling performances of the Li/LPS/Li and Li/LPS30I/Li cells at different temperatures. **Figure 5.7**a shows the voltage profile of the Li/LPS/Li cell cycled at 0.3 mA/cm^2 at 25 °C. The voltage of the cell seems to be stable for 9 cycles, and then suddenly drops at the 10^{th} cycle (around 20 hour).



Figure 5.7 Galvanostatic cycling of the Li/LPS/Li and Li/LPS30I/Li cells at constant current densities at 25 $^{\circ}$ C (a, b), 60 $^{\circ}$ C (c, d), and 100 $^{\circ}$ C (e, f). The time for each charge and discharge is 1 hour.

The voltage drop is considered to be a result of the soft-shorting by foramiton of dendrites in the electrolyte,¹⁵⁷ as supported by the EIS result of the cell after cycling for 64 hours (**Figure 5.8**). The voltage was then stablized at around 0.006 V in the following cycles. The non-zero voltage after short-circult implies the non-zero resistance of the dendrites.¹⁸⁴ The short-circult of the Li/LPS/Li cells can also be observed, within 60 hours, when it was cycled at 0.6 mA/cm² at 60 °C and 1.5 mA/cm² at 100 °C. However, all the three Li/LPS30I/Li cells were able to stably cycle for more than 200 hours at the same currents and at the same temperatures as the Li/LPS/Li cells.



Figure 5.8 Impedance plots of the Li-Li cell with the $0.75Li_2S-0.25P_2S_5$ (LPS) glass electrolyte before cycling (a) and after cycling 64 hours at 0.3 mA/cm² at 25 °C (b).

In addition, the feasibility of using LPS30I electrolyte with Li metal is demonstrated in a full cell with a LiNbO₃ coated LiCoO₂ (LiCoO₂@LiNbO₃) cathode. Such a Li/LPS30I/LiCoO₂@LiNbO₃ full cell can be charged/discharged for more than 40 cycles with a capacity around 102 mAh/g (corresponding to 0.91 mAh/cm²) at 0.2 C (corresponding to 0.25 mA/cm²) at 25 °C (**Figure 5.9**). The stable cycling of the Li/LPS30I/LiCoO₂@LiNbO₃ full cell also implies the great anodic stability of the LPS30I electroyte.



Figure 5.9 Charge/discharge curves (a) and cycling performance (b) of the Li/LPS30I/LiCoO₂@LiNbO₃ full cell at 0.2 C at 25 $^{\circ}$ C. The voltage range is 3.0 – 4.2 V.

5.3.4 Discussion

All of the above results indicate the dendrite suppression capability of $Li_2S-P_2S_5$ electrolytes could be significantly enhanced by LiI incorporation, and LPS30I glass can be used as a promising electrolyte with Li metal anode. The exact mechnisam about such a significant improvement is not fully understood but could be related with the introduction of LiI in the SEI at the Li/electrolyte interface. Both theoretical and experimental works have demonstrated that LPS will be decomposed into Li_2S and Li_3P (with a molar ratio of 1/4), while LPS30I will be decomposed into Li_2S , Li_3P and LiI (with a molar ratio of 7/28/6) when contacting with Li.^{10,60,169,170} The formation of LiI was also confirmed from the Raman spectra of the Li disc detached from the Li/LPS30I/Li after cycling (**Figure 5.10**).



Figure 5.10 Raman spectra of the lithium metal discs detached from the Li/LPS/Li and Li/LPS30I/Li cells after cycling at 25 °C.

The formation of LiI at the Li/electrolyte interface can improve the ionic conductivity of SEI, and more importnatly improve the surface mobility of Li,^{177,178} promoting the Li depositon at the interface and thus suppressing the dendrite growth. In addition, introducing LiI in the SEI also helps to lower the electronic conductivity of SEI based on the larger bandgap of LiI (6.4 eV)¹⁸⁵ than that of Li₃P (0.7 eV)¹⁸⁶, although the formation of non-stoichiometric LiI may also slightly increase the electronic conductivity.^{187,188}



Figure 5.11 XRD patterns of the sulfide electrolytes after the incorporation of LiF (a), LiCl (c), LiBr (e). The stoichiometric ratios and the preparation method are the same as those of the LiI-incorporated $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ electrolyte. Galvanostatic cycling of the Li-Li cells with LPS10F (b), LPS10Cl (d), and LPS10Br (f) electrolytes at step-increased current densities at 25 °C. The time for each charge and discharge is 1 hour. The step size for the current increase is 0.04 mA/cm².

Although all lithium halides have been reported to be able to improve the surface mobility of Li atoms¹⁷⁷ and reduce the electronic conductivity, the critical current densities of the Li₂S-P₂S₅ electrolytes after the incorporations of LiF, LiCl, LiBr are much smaller than that of LPS30I (**Figure 5.11**), possibly due to the limited solubilities of LiF, LiCl and LiBr in Li₂S-P₂S₅ glass. Nevertheless, it should be noted that the dendrite suppression capability may also be influenced by other factors, such as the microstructure of electrolyte,^{74,181} defects,¹⁶⁶ mechanical and electrical properties of the solid electrolyte especially around the particle boundaries.¹⁸⁹ Further work is needed to elucidate the effect of LiI incorporation on these variables to gain a better understanding of the mechanism.

5.4 Conclusion

In summary, we demonstrate that the incorporation of LiI into the Li₂S-P₂S₅ glass electrolytes can effectively improve the dendrite suppression capability, and the $70(0.75Li_2S-0.25P_2S_5)$ -30LiI (LPS30I) electrolyte exhibits the highest capability for dendrite suppression. The critical current density of LPS30I reaches 3.90 mA/cm² at 100 °C, and the Li/LPS30I/Li cell could cycle 200 hours at 1.50 mA/cm² at 100 °C, representing the best performance for Li cycling with sulfide electrolyte reported to date. This work provides a viable strategy to suppress the dendrite formation in inorganic solid electrolyte by tuning the composition of SEI at the Li/electrolyte interface.

127

Chapter 6: Conclusions and Future Work

6.1 Conclusions

The detailed conclusions of this dissertation are summarized below:

(1) The electrochemical stability windows of solid electrolytes were overestimated from the conventional approach.

(2) A novel experimental method using Li/electrolyte/electrolyte+carbon cell is proposed to approach the intrinsic electrochemical stability window.

(3) The electrochemical stability windows of LGPS and LLZO measured with the novel method are much narrower than 5 V. The measured stability windows and the decomposition products agree well with first-principles calculations.

(4) The reversible decomposition of LGPS at both high and low voltages enabled a single-material battery.

(5) Suppressing the (electro)chemical reactions between LCO cathode and LLZO electrolyte by the LCBO interphase leads to a high-performance all-ceramic battery.

(6 Li dendrite formation in $Li_2S-P_2S_5$ electrolyte can be suppressed by introducing LiI in the interphase between Li and solid electrolyte.

6.2 Major Contributions

This dissertation demonstrates that the electrochemical stability window of solid electrolytes is overestimated from the conventional measurement. The electrochemical decomposition of solid electrolytes occurs, and can cause large interfacial resistance in all-solid-state lithium ion batteries. Interphase engineering is demonstrated an effective approach to suppress the electrochemical decomposition of solid electrolytes in all-solid-state lithium ion batteries. By taking advantages of the electrochemical decomposition of solid electrolytes, one may come up with new strategies to address critical challenges in all-solid-state lithium ion batteries such as lithium dendrite suppression.

6.3 Future Work

This dissertation demonstrates that the electrochemical decomposition of solid electrolytes occurs and can cause large interfacial resistance between electrode and electrolyte. However, the electrode/electrolyte interface is very complex and its resistance is determined by many factors including poor contact, (electro)chemical instability of electrolyte/carbon interface, (electro)chemical instability of electrolyte/carbon interface, (electro)chemical instability of electrolyte/electrode interface, and mechanical strain/stress. However, there is still no any information about the relative contribution of interfacial resistance from each factor. The future work could be to develop and use state of the art experimental and computational techniques with standard electrochemical methods to identify the main reason for the interfacial resistance between a 5-V class LiNi_{0.5}Mn_{1.5}O₄ (LNMO) cathode and LGPS electrolyte, and to develop strategies leading to a minimized and stabilized interfacial resistance for high-voltage all-solid-state lithium batteries.



Figure 6.1 Schematic showing the research overview for future work

The objective can be achieved by developing and using state of the art experimental techniques, such as soft/tender X-ray absorption spectroscopy (sXAS/tXAS), X-ray nanotomography, focused ion beam/scanning electron microscope (FIB/SEM), in-situ pressure measurement, with first-principles computation and standard electrochemical methods (**Figure 6.2**) to

(i) establish the correlation between interfacial resistance with each factor (poor contact, (electro)chemical instability of LGPS/C, (electro)chemical instability of LGPS/LNMO, and mechanical strain/stress);

(ii) identify the main reason for the interfacial resistance between LGPS and LNMO.



Figure 6.2 Integration of the research approaches for future work

Novel experimental strategies to optimize the interface between LNMO and LGPS will also be developed. Depending on the new understandings, the strategies may include but are not limited to:

(i) development of novel methods for cathode composite preparation (such as infiltrating LGPS solution into a porous matrix of LNMO and C) to improve the interfacial contact,

(ii) development of surface coatings as a buffer layer on LGPS, or on both LNMO and carbon, and

(iii) development of reinforced binders for a mechanical robust cathode composite.

6.4 Resulting Publications, Patents, Awards and Conference Presentations

Selected Publications

- <u>F. Han</u>⁺, J. Yue⁺, X. Zhu, C. Wang, Suppressing Li Dendrite Formation in Li₂S-P₂S₅ Solid Electrolyte by LiI Incorporation. *Adv. Energy Mater.*, DOI: 10.1002/aenm.201703644.
- <u>F. Han</u>[†], J. Yue[†], C. Chen, N. Zhao, X. Fan, Z. Ma, T. Gao, F. Wang, X. Guo, C. Wang, Interphase Engineering Enabled-All-Ceramic Lithium Battery. *Joule*, 2 (2018) 497. *Feature Article*.
- <u>F. Han</u>, J. Yue, X. Fan, T. Gao, C. Luo, Z. Ma, L. Suo, C. Wang, High-Performance All-Solid-State Lithium–Sulfur Battery Enabled by a Mixed-Conductive Li₂S Nanocomposite. *Nano Lett.*, 16 (2016) 4521.
- <u>F. Han</u>[†], Y. Zhu[†], X. He, Y. Mo, C. Wang, Electrochemical Stability of Li₁₀GeP₂S₁₂ and Li₇La₃Zr₂O₁₂ Solid Electrolytes, *Adv. Energy Mater.*, 6 (2016) 1501590.
- <u>F. Han</u>, T. Gao, Y. Zhu, K. J. Gaskell, C. Wang, A Battery Made from a Single Material, *Adv. Mater.*, 27 (2015) 3473. *VIP Paper*.
- J. Yue[†], <u>F. Han[†]</u>, X. Fan, X. Zhu, Z. Ma, J. Yang, C. Wang, High-Performance All-Inorganic Solid-State Sodium-Sulfur Battery, *ACS Nano*, 11 (2017) 4885.

Patents

 C. Wang, <u>F. Han</u>, A Battery Made from a Single Material, Application No.: US 15/583,479.

- C. Wang, Y. Mo, Y. Zhu, <u>F. Han</u>, X. Zhu, J. Yue, Novel Strategies to Stabilize Li Metal Anode, Application No.: US 62/637,584.
- C. Wang, <u>F. Han</u>, J. Yue, Garnet-Type Li₇La₃Zr₂O₁₂-Based All Solid State Battery with a Full Ceramic Cathode, University of Maryland Invention Disclosure PS-2017-016.

Honors and Recognition

Materials Research Society (MRS) Graduate Student Gold Award, 2017 Chinese Government Award for Outstanding Self-Financed Student Abroad, 2016 All-S.T.A.R. Fellowship, University of Maryland, College Park, 2016 Harry K. Wells Fellowship, University of Maryland, College Park, 2016 Future Faculty Fellow, University of Maryland, College Park, 2016 TA of the Year, Department of Chemical and Biomolecular Engineering, 2014

Conference Proceedings

- <u>F. Han</u>, J. Yue, X. Zhu, C. Wang, Lithium Dendrite Suppression in Solid Electrolytes, 2017 MRS Fall Meeting & Exhibit, Oral Presentation, Boston, MA, Nov.26–Dec. 1, 2017.
- <u>F. Han,</u> J. Yue, C. Wang, Improved Cathode/Electrolyte Interfaces in All-Solid-State Batteries, 2017 MRS Fall Meeting & Exhibit, Poster Presentation, Boston, MA, Nov.26–Dec. 1, 2017.
- <u>F. Han</u>, J. Yue, X. Fan, Z. Ma, T. Gao, C. Wang, Cathode/Electrolyte Interface: Revisiting the Electrochemical Stability of Solid Electrolytes, 2017 MRS Spring Meeting & Exhibit, Oral Presentation, Phoenix, AZ, Apr.17-21, 2017.
- <u>F. Han</u>, T. Gao, Y. Zhu, J. Yue, Y. Zhu, Y. Mo and C. Wang, Electrochemical Stability of Li₁₀GeP₂S₁₂ and Li₇La₃Zr₂O₁₂ Solid Electrolytes, 18th International Meeting on Lithium Batteries, Poster Session, Chicago, IL, Jun.19-24, 2016.
- <u>F. Han</u>, T. Gao, Y. Zhu, K. J. Gaskell, and C. Wang, A Battery Made from a Single Material, 20th International Conference on Solid State Ionics, Poster Session, Keystone, CO, Jun.14-19, 2015.

Bibliography

(1) Yao, X. Y.; Huang, B. X.; Yin, J. Y.; Peng, G.; Huang, Z.; Gao, C.; Liu, D.; Xu, X. X. *Chin. Phys. B* **2016**, *25*, 018802.

(2) Janek, J.; Zeier, W. G. Nat. Energy 2016, 1, 16141.

(3) Bates, J. B.; Dudney, N. J.; Neudecker, B.; Ueda, A.; Evans, C. D. Solid State *Ionics* **2000**, *135*, 33.

(4) Aboulaich, A.; Bouchet, R.; Delaizir, G.; Seznec, V.; Tortet, L.; Morcrette, M.; Rozier, P.; Tarascon, J. M.; Viallet, V.; Dolle, M. Adv. Energy Mater. **2011**, *1*, 179.

(5) Albertus, P.: Integration and Optimization of Novel Ion-Conducting Solids (IONICS) Funding Opportunity Announcement No. DE-FOA-0001478. **2016**.

(6) Wang, Y.; Lai, W. J. Power Sources 2015, 275, 612.

(7) Sharafi, A.; Kazyak, E.; Davis, A. L.; Yu, S.; Thompson, T.; Siegel, D. J.; Dasgupta, N. P.; Sakamoto, J. *Chem. Mater.* **2017**, *29*, 7961.

(8) Sakuda, A.; Hayashi, A.; Tatsumisago, M. Sci. Rep. 2013, 3, 2261.

(9) McGrogan, F. P.; Swamy, T.; Bishop, S. R.; Eggleton, E.; Porz, L.; Chen, X. W.; Chiang, Y. M.; Van Vliet, K. J. *Adv. Energy Mater.* **2017**, *7*, 1602011.

(10) Han, F. D.; Zhu, Y. Z.; He, X. F.; Mo, Y. F.; Wang, C. S. *Adv. Energy Mater.* **2016**, *6*, 1501590.

(11) Maekawa, H.; Tanaka, R.; Sato, T.; Fujimaki, Y.; Yamamura, T. *Solid State Ionics* **2004**, *175*, 281.

(12) Bates, J. B.; Dudney, N. J.; Gruzalski, G. R.; Zuhr, R. A.; Choudhury, A.; Luck, C. F.; Robertson, J. D. *Solid State Ionics* **1992**, *53*, 647.

(13) Stramare, S.; Thangadurai, V.; Weppner, W. Chem. Mater. 2003, 15, 3974.

(14) Bruce, P. G.; West, A. J. Electrochem. Soc. 1983, 130, 662.

(15) Maldonado-Manso, P.; Losilla, E. R.; Martinez-Lara, M.; Aranda, M. A. G.; Bruque, S.; Mouahid, F. E.; Zahir, M. *Chem. Mater.* **2003**, *15*, 1879.

(16) Li, Y.; Han, J.-T.; Wang, C.-A.; Xie, H.; Goodenough, J. B. J. Mater. Chem. **2012**, *22*, 15357.

(17) Lu, X.; Howard, J. W.; Chen, A.; Zhu, J.; Li, S.; Wu, G.; Dowden, P.; Xu, H.; Zhao, Y.; Jia, Q. *Adv. Sci.* **2016**, *3*, 1500359.

(18) Liu, Z.; Fu, W.; Payzant, E. A.; Yu, X.; Wu, Z.; Dudney, N. J.; Kiggans, J.; Hong, K.; Rondinone, A. J.; Liang, C. *J. Am. Chem. Soc.* **2013**, *135*, 975.

(19) Minami, K.; Mizuno, F.; Hayashi, A.; Tatsumisago, M. Solid State Ionics 2007, 178, 837.

(20) Boulineau, S.; Courty, M.; Tarascon, J. M.; Viallet, V. Solid State Ionics 2012, 221, 1.

(21) Kanno, R.; Maruyama, M. J. Electrochem. Soc. 2001, 148, A742.

(22) Kamaya, N.; Homma, K.; Yamakawa, Y.; Hirayama, M.; Kanno, R.; Yonemura, M.; Kamiyama, T.; Kato, Y.; Hama, S.; Kawamoto, K.; Mitsui, A. *Nat. Mater.* **2011**, *10*, 682.

(23) Kato, Y.; Hori, S.; Saito, T.; Suzuki, K.; Hirayama, M.; Mitsui, A.; Yonemura, M.; Iba, H.; Kanno, R. *Nat. Energy* **2016**, *1*, 16030.

(24) Ohta, S.; Komagata, S.; Seki, J.; Saeki, T.; Morishita, S.; Asaoka, T. J. Power Sources **2013**, 238, 53.

(25) Park, K.; Yu, B. C.; Jung, J. W.; Li, Y. T.; Zhou, W. D.; Gao, H. C.; Son, S.; Goodenough, J. B. *Chem. Mater.* **2016**, *28*, 8051.

(26) Liu, T.; Zhang, Y. B.; Chen, R. J.; Zhao, S. X.; Lin, Y. H.; Nan, C. W.; Shen, Y. *Electrochem. Commun.* **2017**, *79*, 1.

(27) Nagao, M.; Hayashi, A.; Tatsumisago, M. J. Mater. Chem. 2012, 22, 10015.

(28) Tatsumisago, M.; Mizuno, F.; Hayashi, A. J. Power Sources 2006, 159, 193.

(29) Jak, M. J. G.; Pontfoort, M. S.; Van Landschoot, N.; Best, A. S.; Kelder, E. M.; MacFarlane, D. R.; Forsyth, M.; Schoonman, J. *Solid State Ionics* **2001**, *143*, 57.

(30) Birke, P.; Salam, F.; Doring, S.; Weppner, W. Solid State Ionics 1999, 118, 149.

(31) Chen, K.; Shen, Y.; Zhang, Y. B.; Lin, Y. H.; Nan, C. W. J. Power Sources **2014**, 249, 306.

(32) Rosciano, F.; Pescarmona, P. P.; Houthoofd, K.; Persoons, A.; Bottke, P.; Wilkening, M. *Phys. Chem. Chem. Phys.* **2013**, *15*, 6107.

(33) Delaizir, G.; Viallet, V.; Aboulaich, A.; Bouchet, R.; Tortet, L.; Seznec, V.; Morcrette, M.; Tarascon, J. M.; Rozier, P.; Dolle, M. *Adv. Funct. Mater.* **2012**, *22*, 2140.

(34) Kim, K. H.; Iriyama, Y.; Yamamoto, K.; Kumazaki, S.; Asaka, T.; Tanabe, K.; Fisher, C. A. J.; Hirayama, T.; Murugan, R.; Ogumi, Z. *J. Power Sources* **2011**, *196*, 764.

(35) Kobayashi, T.; Yamada, A.; Kanno, R. Electrochim. Acta 2008, 53, 5045.

(36) Jeong, E.; Chan, H. A.; Tak, Y.; Nam, S. C.; Cho, S. J. Power Sources 2006, 159, 223.

(37) Sakuda, A.; Hayashi, A.; Tatsumisago, M. Chem. Mater. 2010, 22, 949.

(38) Kanno, R.; Murayama, M.; Inada, T.; Kobayashi, T.; Sakamoto, K.; Sonoyama, N.; Yamada, A.; Kondo, S. *Electrochem. Solid State Lett.* **2004**, *7*, A455.

(39) Ohta, N.; Takada, K.; Zhang, L. Q.; Ma, R. Z.; Osada, M.; Sasaki, T. Adv. Mater. **2006**, *18*, 2226.

(40) Haruyama, J.; Sodeyama, K.; Han, L.; Takada, K.; Tateyama, Y. *Chem. Mater.* **2014**, *26*, 4248.

(41) Sakuda, A.; Hayashi, A.; Ohtomo, T.; Hama, S.; Tatsumisago, M. J. Power Sources 2011, 196, 6735.

(42) Cervera, R. B.; Suzuki, N.; Ohnishi, T.; Osada, M.; Mitsuishi, K.; Kambara, T.; Takada, K. *Energy Environ. Sci.* **2014**, *7*, 662.

(43) Woo, J. H.; Trevey, J. E.; Cavanagh, A. S.; Choi, Y. S.; Kim, S. C.; George, S. M.; Oh, K. H.; Lee, S. H. *J. Electrochem. Soc.* **2012**, *159*, A1120.

(44) Boulineau, S.; Tarascon, J. M.; Leriche, J. B.; Viallet, V. Solid State Ionics 2013, 242, 45.

(45) Okumura, T.; Nakatsutsumi, T.; Ina, T.; Orikasa, Y.; Arai, H.; Fukutsuka, T.; Iriyama, Y.; Uruga, T.; Tanida, H.; Uchimoto, Y.; Ogumi, Z. *J. Mater. Chem.* **2011**, *21*, 10051.

(46) Murugesan, S.; Quintero, O. A.; Chou, B. P.; Xiao, P. H.; Park, K.; Hall, J. W.; Jones, R. A.; Henkelman, G.; Goodenough, J. B.; Stevenson, K. J. *J. Mater. Chem. A* **2014**, *2*, 2194.

(47) Ohta, S.; Kobayashi, T.; Asaoka, T. J. Power Sources 2011, 196, 3342.

(48) Mo, Y. F.; Ong, S. P.; Ceder, G. Chem. Mater. 2012, 24, 15.

(49) Wolfenstine, J.; Allen, J. L.; Read, J.; Sakamoto, J. J. Mater. Sci. 2013, 48, 5846.

(50) Thangadurai, V.; Weppner, W. Adv. Funct. Mater. 2005, 15, 107.

(51) Kim, Y.; Yoo, A.; Schmidt, R.; Sharafi, A.; Lee, H.; Wolfenstine, J.; Sakamoto, J. *Front. Energy Res.* **2016**, *4*, 20.

(52) Jung, Y. S.; Oh, D. Y.; Nam, Y. J.; Park, K. H. Isr. J. Chem. 2015, 55, 472.

(53) Han, F. D.; Gao, T.; Zhu, Y. J.; Gaskell, K. J.; Wang, C. S. Adv. Mater. **2015**, 27, 3473.

(54) Han, F. D.; Yue, J.; Chen, C.; Zhao, N.; Fan, X. L.; Ma, Z. H.; Gao, T.; Wang, F.; Guo, X. X.; Wang, C. S. *Joule* **2018**, *2*, 497.

(55) Han, F. D.; Yue, J.; Zhu, X. Y.; Wang, C. S. Adv. Energy Mater. 2018, 1703644.

(56) Ong, S. P.; Wang, L.; Kang, B.; Ceder, G. Chem. Mater. 2008, 20, 1798.

(57) Ong, S. P.; Mo, Y.; Richards, W. D.; Miara, L.; Lee, H. S.; Ceder, G. *Energy Environ. Sci.* **2013**, *6*, 148.

(58) Tatsumisago, M.; Hayashi, A. Solid State Ionics 2012, 225, 342.

(59) Shin, B. R.; Nam, Y. J.; Oh, D. Y.; Kim, D. H.; Kim, J. W.; Jung, Y. S. *Electrochim. Acta* **2014**, *146*, 395.

(60) Zhu, Y. Z.; He, X. F.; Mo, Y. F. ACS Appl. Mater. Interfaces 2015, 7, 23685.

(61) Rangasamy, E.; Liu, Z. C.; Gobet, M.; Pilar, K.; Sahu, G.; Zhou, W.; Wu, H.; Greenbaum, S.; Liang, C. D. J. Am. Chem. Soc. **2015**, *137*, 1384.

(62) Ujiie, S.; Hayashi, A.; Tatsumisago, M. Solid State Ionics 2012, 211, 42.

(63) Chen, H. M.; Maohua, C.; Adams, S. Phys. Chem. Chem. Phys. 2015, 17, 16494.

(64) Thangadurai, V.; Pinzaru, D.; Narayanan, S.; Baral, A. K. J. Phys. Chem. Lett. **2015**, *6*, 292.

(65) Thangadurai, V.; Narayanan, S.; Pinzaru, D. Chem. Soc. Rev. 2014, 43, 4714.

(66) Cheng, L.; Crumlin, E. J.; Chen, W.; Qiao, R.; Hou, H.; Franz Lux, S.; Zorba, V.; Russo, R.; Kostecki, R.; Liu, Z.; Persson, K.; Yang, W.; Cabana, J.; Richardson, T.; Chen, G.; Doeff, M. *Phys. Chem. Chem. Phys.* **2014**, *16*, 18294.

(67) Kotobuki, M.; Munakata, H.; Kanamura, K.; Sato, Y.; Yoshida, T. *J. Electrochem. Soc.* **2010**, *157*, A1076.

(68) Wang, Y.; Huq, A.; Lai, W. Solid State Ionics 2014, 255, 39.

(69) Toda, S.; Ishiguro, K.; Shimonishi, Y.; Hirano, A.; Takeda, Y.; Yamamoto, O.; Imanishi, N. *Solid State Ionics* **2013**, *233*, 102.

(70) Tietz, F.; Wegener, T.; Gerhards, M. T.; Giarola, M.; Mariotto, G. Solid State Ionics 2013, 230, 77.

(71) Bespalov, I.; Datler, M.; Buhr, S.; Drachsel, W.; Rupprechter, G.; Suchorski, Y. *Ultramicroscopy* **2015**, *159*, 147.

(72) Ishiguro, K.; Nakata, Y.; Matsui, M.; Uechi, I.; Takeda, Y.; Yamamoto, O.; Imanishi, N. *J. Electrochem. Soc.* **2013**, *160*, A1690.

(73) Sudo, R.; Nakata, Y.; Ishiguro, K.; Matsui, M.; Hirano, A.; Takeda, Y.; Yamamoto, O.; Imanishi, N. *Solid State Ionics* **2014**, *262*, 151.

(74) Cheng, L.; Chen, W.; Kunz, M.; Persson, K.; Tamura, N.; Chen, G.; Doeff, M. ACS Appl. Mater. Interfaces **2015**, *7*, 2073.

(75) Goodenough, J. B.; Kim, Y. Chem. Mater. 2010, 22, 587.

(76) Schwobel, A.; Hausbrand, R.; Jaegermann, W. Solid State Ionics 2015, 273, 51.

(77) Alpen, U. v.; Rabenau, A.; Talat, G. Appl. Phys. Lett. 1977, 30, 621.

(78) Nazri, G. Solid State Ionics 1989, 34, 97.

(79) Wenzel, S.; Leichtweiss, T.; Krüger, D.; Sann, J.; Janek, J. Solid State Ionics **2015**, 278, 98.

(80) Hartmann, P.; Leichtweiss, T.; Busche, M. R.; Schneider, M.; Reich, M.; Sann, J.; Adelhelm, P.; Janek, J. J. Phys. Chem. C 2013, 117, 21064.

(81) Yang, Y.; Zheng, G.; Cui, Y. Chem. Soc. Rev. 2013, 42, 3018.

(82) Ohta, N.; Takada, K.; Sakaguchi, I.; Zhang, L.; Ma, R.; Fukuda, K.; Osada, M.; Sasaki, T. *Electrochem. Commun.* **2007**, *9*, 1486.

(83) Visco, S. WO Patent 2,013,074,772, 2013.

(84) Kato, T.; Hamanaka, T.; Yamamoto, K.; Hirayama, T.; Sagane, F.; Motoyama, M.; Iriyama, Y. *J. Power Sources* **2014**, *260*, 292.

(85) Xu, K. Chem. Rev. 2004, 104, 4303.

(86) Kim, T. H.; Park, J. S.; Chang, S. K.; Choi, S.; Ryu, J. H.; Song, H. K. *Adv. Energy Mater.* **2012**, *2*, 860.

(87) Phan, V. P.; Pecquenard, B.; Le Cras, F. Adv. Funct. Mater. 2012, 22, 2580.

(88) Notten, P. H. L.; Roozeboom, F.; Niessen, R. A. H.; Baggetto, L. Adv. Mater. **2007**, *19*, 4564.

(89) Murugan, R.; Thangadurai, V.; Weppner, W. Angew. Chem. Int. Ed. 2007, 46, 7778.

(90) Seino, Y.; Ota, T.; Takada, K.; Hayashi, A.; Tatsumisago, M. *Energy Environ. Sci.* **2014**, *7*, 627.

(91) Mizuno, F.; Hayashi, A.; Tadanaga, K.; Tatsumisago, M. Adv. Mater. 2005, 17, 918.

(92) Jin, Y.; McGinn, P. J. J. Power Sources 2013, 239, 326.

(93) Takada, K.; Inada, T.; Kajiyama, A.; Kouguchi, M.; Sasaki, H.; Kondo, S.; Michiue, Y.; Nakano, S.; Tabuchi, M.; Watanabe, M. *Solid State Ionics* **2004**, *172*, 25.

(94) Yersak, T. A.; Stoldt, C.; Lee, S. H. J. Electrochem. Soc. 2013, 160, A1009.

(95) Takada, K. Langmuir 2013, 29, 7538.

(96) Neudecker, B. J.; Dudney, N. J.; Bates, J. B. J. Electrochem. Soc. **2000**, 147, 517.

(97) Yada, C.; Iriyama, Y.; Abe, T.; Kikuchi, K.; Ogumi, Z. *Electrochem. Commun.* **2009**, *11*, 413.

(98) Greatbatch, W.; Lee, J. H.; Mathias, W.; Eldridge, M.; Moser, J. R.; Schneider, A. A. *IEEE Trans. Biomed. Eng.* **1971**, *18*, 317.

(99) Iriyama, Y.; Yada, C.; Abe, T.; Ogumi, Z.; Kikuchi, K. *Electrochem. Commun.* **2006**, *8*, 1287.

(100) Birke, P.; Scharner, S.; Huggins, R. A.; Weppner, W. J. Electrochem. Soc. **1997**, *144*, L167.

(101) Klingler, M.; Chu, W. F.; Weppner, W. Ionics 1997, 3, 289.

(102) Weppner, W. Ionics 2001, 7, 404.

(103) Kato, Y.; Kawamoto, K.; Kanno, R.; Hirayama, M. *Electrochemistry* **2012**, *80*, 749.

(104) Hassoun, J.; Verrelli, R.; Reale, P.; Panero, S.; Mariotto, G.; Greenbaum, S.; Scrosati, B. *J. Power Sources* **2013**, *229*, 117.

(105) Yang, Y.; Zheng, G. Y.; Misra, S.; Nelson, J.; Toney, M. F.; Gui, Y. J. Am. Chem. Soc. **2012**, 134, 15387.

(106) Idota, Y.; Kubota, T.; Matsufuji, A.; Maekawa, Y.; Miyasaka, T. *Science* **1997**, 276, 1395.

(107) Kim, Y.; Hwang, H.; Lawler, K.; Martin, S. W.; Cho, J. *Electrochim. Acta* **2008**, *53*, 5058.

(108) Cho, Y. J.; Im, H. S.; Myung, Y.; Kim, C. H.; Kim, H. S.; Back, S. H.; Lim, Y. R.; Jung, C. S.; Jang, D. M.; Park, J.; Cha, E. H.; Choo, S. H.; Song, M. S.; Cho, W. I. *Chem.Commun.* **2013**, *49*, 4661.

(109) Zhang, S. S. J. Power Sources 2013, 231, 153.

(110) Mikhaylik, Y. V.; Akridge, J. R. J. Electrochem. Soc. 2004, 151, A1969.

(111) Su, Y. S.; Fu, Y.; Cochell, T.; Manthiram, A. Nat. Commun. 2013, 4, 2985.

(112) Saffarini, G.; Saiter, J. Mater. Lett. 2000, 46, 327.

(113) Timbrell, P.; Puchert, M.; Lamb, R. Surf. Interface Anal. 1994, 21, 731.

(114) Prabhakaran, K.; Ogino, T. Surf. Sci. 1995, 325, 263.

(115) Takeuchi, T.; Kageyama, H.; Nakanishi, K.; Tabuchi, M.; Sakaebe, H.; Ohta, T.; Senoh, H.; Sakai, T.; Tatsumi, K. J. Electrochem. Soc. **2010**, *157*, A1196.

(116) Noguchi, Y.; Kobayashi, E.; Plashnitsa, L. S.; Okada, S.; Yamaki, J. *Electrochim. Acta* **2013**, *101*, 59.

(117) Li, J. C.; Ma, C.; Chi, M. F.; Liang, C. D.; Dudney, N. J. Adv. Energy Mater. **2015**, *5*, 1401408.

(118) Takada, K.; Ohta, N.; Zhang, L. Q.; Xu, X. X.; Hang, B. T.; Ohnishi, T.; Osada, M.; Sasaki, T. *Solid State Ionics* **2012**, *225*, 594.

(119) Ohtomo, T.; Hayashi, A.; Tatsumisago, M.; Tsuchida, Y.; Hama, S.; Kawamoto, K. *J. Power Sources* **2013**, *233*, 231.

(120) Weppner, W. Ionics 2003, 9, 444.

(121) Machida, N.; Maeda, H.; Peng, H.; Shigematsu, T. J. Electrochem. Soc. 2002, 149, A688.

(122) Yamamoto, K.; Iriyama, Y.; Asaka, T.; Hirayama, T.; Fujita, H.; Nonaka, K.; Miyahara, K.; Sugita, Y.; Ogumi, Z. *Electrochem. Commun.* **2012**, *20*, 113.

(123) Vohs, J. M.; Gorte, R. J. Adv. Mater. 2009, 21, 943.

(124) Hu, Y.-S. Nat. Energy **2016**, 1, 16042.

(125) Zhu, Y. Z.; He, X. F.; Mo, Y. F. J. Mater. Chem. A 2016, 4, 3253.

(126) Wenzel, S.; Randau, S.; Leichtweiss, T.; Weber, D. A.; Sann, J.; Zeier, W. G.; Janek, J. *Chem. Mater.* **2016**, *28*, 2400.

(127) Sharafi, A.; Yu, S. H.; Naguib, M.; Lee, M.; Ma, C.; Meyer, H. M.; Nanda, J.; Chi, M. F.; Siegel, D. J.; Sakamoto, J. J. Mater. Chem. A **2017**, *5*, 13475.

(128) Han, X. G.; Gong, Y. H.; Fu, K. K.; He, X. F.; Hitz, G. T.; Dai, J. Q.; Pearse, A.; Liu, B. Y.; Wang, H.; Rubloff, G.; Mo, Y. F.; Thangadurai, V.; Wachsman, E. D.; Hu, L. B. *Nat. Mater.* **2017**, *16*, 572.

(129) Sharafi, A.; Meyer, H. M.; Nanda, J.; Wolfenstine, J.; Sakamoto, J. J. Power Sources 2016, 302, 135.

(130) Tsai, C. L.; Roddatis, V.; Chandran, C. V.; Ma, Q.; Uhlenbruck, S.; Bram, M.; Heitjans, P.; Guillon, O. *ACS Appl. Mater. Interfaces* **2016**, *8*, 10617.

(131) Ren, Y. Y.; Shen, Y.; Lin, Y. H.; Nan, C. W. *Electrochem. Commun.* **2015**, *57*, 27.

(132) Cheng, E. J.; Sharafi, A.; Sakamoto, J. Electrochim. Acta 2017, 223, 85.

(133) Zhou, W. D.; Wang, S. F.; Li, Y. T.; Xin, S.; Manthiram, A.; Goodenough, J. B. *J. Am. Chem. Soc.* **2016**, *138*, 9385.

(134) Luntz, A. C.; Voss, J.; Reuter, K. J. Phys. Chem. Lett. 2015, 6, 4599.

(135) Okumura, T.; Takeuchi, T.; Kobayashi, H. Solid State Ionics 2016, 288, 248.

(136) Ménétrier, M.; Saadoune, I.; Levasseur, S.; Delmas, C. J. Mater. Chem. 1999, 9, 1135.

(137) Sander, J. S.; Erb, R. M.; Li, L.; Gurijala, A.; Chiang, Y. M. Nat. Energy 2016, 1, 16099.

(138) Ohta, S.; Kobayashi, T.; Seki, J.; Asaoka, T. J. Power Sources 2012, 202, 332.

(139) Ohta, S.; Seki, J.; Yagi, Y.; Kihira, Y.; Tani, T.; Asaoka, T. J. Power Sources **2014**, 265, 40.

(140) Liu, T.; Ren, Y. Y.; Shen, Y.; Zhao, S. X.; Lin, Y. H.; Nan, C. W. J. Power Sources **2016**, *324*, 349.

(141) Shoji, M.; Munakata, H.; Kanamura, K. Front. Energy Res. 2016, 4, 32.

(142) Du, F. M.; Zhao, N.; Li, Y. Q.; Chen, C.; Liu, Z. W.; Guo, X. X. J. Power Sources 2015, 300, 24.

(143) Li, Y.; Xu, B.; Xu, H.; Duan, H.; Lu, X.; Xin, S.; Zhou, W.; Xue, L.; Fu, G.; Manthiram, A.; Goodenough, J. B. *Angew. Chem. Int. Ed.* **2017**, *56*, 753.

(144) Wang, Y. X.; Lai, W. Electrochem. Solid State Lett. 2012, 15, A68.

(145) Mijung, N.; Lee, Y.; Cho, J. J. Electrochem. Soc. 2006, 153, A935.

(146) Shannon, R. D.; Taylor, B. E.; English, A. D.; Berzins, T. *Electrochim. Acta* **1977**, *22*, 783.

(147) Zelyutin, G. V.; Menzorova, L. M.; Obrosov, V. P.; Batalov, N. N. *Inorg. Mater.* **1990**, *26*, 1074.

(148) Haik, O.; Leifer, N.; Samuk-Fromovich, Z.; Zinigrad, E.; Markovsky, B.; Larush, L.; Goffer, Y.; Goobes, G.; Aurbach, D. J. Electrochem. Soc. **2010**, *157*, A1099.

(149) Tjong, S. C. Adv. Eng. Mater. 2007, 9, 639.

(150) Yubuchi, S.; Teragawa, S.; Aso, K.; Tadanaga, K.; Hayashi, A.; Tatsumisago, M. J. Power Sources **2015**, 293, 941.

(151) Park, K. H.; Oh, D. Y.; Choi, Y. E.; Nam, Y. J.; Han, L. L.; Kim, J. Y.; Xin, H. L.; Lin, F.; Oh, S. M.; Jung, Y. S. *Adv. Mater.* **2016**, *28*, 1874.

(152) Li, Y. Q.; Wang, Z.; Li, C. L.; Cao, Y.; Guo, X. X. J. Power Sources **2014**, 248, 642.

(153) Zhang, J.; Xiang, Y. J.; Yu, Y.; Xie, S.; Jiang, G. S.; Chen, C. H. J. Power Sources **2004**, *132*, 187.

(154) Beyer, H.; Meini, S.; Tsiouvaras, N.; Piana, M.; Gasteiger, H. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11025.

(155) Cheon, S.-E.; Ko, K.-S.; Cho, J.-H.; Kim, S.-W.; Chin, E.-Y.; Kim, H.-T. J. *Electrochem. Soc.* **2003**, *150*, A800.

(156) Woo, S. P.; Shin, S. Y.; Lee, S. H.; Yoon, Y. S. Compos. B Eng. 2017, 124, 242.

(157) Albertus, P.; Babinec, S.; Litzelman, S.; Newman, A. Nat. Energy 2018, 3, 16.

(158) Zhang, K.; Lee, G. H.; Park, M.; Li, W.; Kang, Y. M. Adv. Energy Mater. 2016, 6, 1600811.

(159) Zheng, J. M.; Yan, P. F.; Mei, D. H.; Engelhard, M. H.; Cartmell, S. S.; Polzin, B. J.; Wang, C. M.; Zhang, J. G.; Xu, W. *Adv. Energy Mater.* **2016**, *6*, 1502151.

(160) Monroe, C.; Newman, J. J. Electrochem. Soc. 2005, 152, A396.

(161) Zhou, D.; Liu, R. L.; He, Y. B.; Li, F. Y.; Liu, M.; Li, B. H.; Yang, Q. H.; Cai, Q.; Kang, F. Y. *Adv. Energy Mater.* **2016**, *6*, 1502214.

(162) Brissot, C.; Rosso, M.; Chazalviel, J. N.; Lascaud, S. J. Power Sources **1999**, *81*, 925.

(163) van den Broek, J.; Afyon, S.; Rupp, J. L. M. Adv. Energy Mater. **2016**, *6*, 1600736.

(164) Oh, D. Y.; Nam, Y. J.; Park, K. H.; Jung, S. H.; Cho, S. J.; Kim, Y. K.; Lee, Y. G.; Lee, S. Y.; Jung, Y. S. *Adv. Energy Mater.* **2015**, *5*, 1500865.

(165) Nagao, M.; Hayashi, A.; Tatsumisago, M.; Kanetsuku, T.; Tsuda, T.; Kuwabata, S. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18600.

(166) Porz, L.; Swamy, T.; Sheldon, B. W.; Rettenwander, D.; Frömling, T.; Thaman, H. L.; Berendts, S.; Uecker, R.; Carter, W. C.; Chiang, Y. M. *Adv. Energy Mater.* **2017**, *7*, 1701003.

(167) Garcia-Mendez, R.; Mizuno, F.; Zhang, R. G.; Arthur, T. S.; Sakamoto, J. *Electrochim. Acta* **2017**, *237*, 144.

(168) Markevich, E.; Salitra, G.; Chesneau, F.; Schmidt, M.; Aurbach, D. ACS *Energy Lett.* **2017**, *2*, 1321.

(169) Wenzel, S.; Weber, D. A.; Leichtweiss, T.; Busche, M. R.; Sann, J.; Janek, J. Solid State Ionics **2016**, 286, 24.

(170) Wenzel, S.; Sedlmaier, S. J.; Dietrich, C.; Zeier, W. G.; Janek, J. *Solid State Ionics* **2018**, *318*, 102.

(171) Mercier, R.; Malugani, J. P.; Fahys, B.; Robert, G. Solid State Ionics **1981**, *5*, 663.

(172) Ujiie, S.; Hayashi, A.; Tatsumisago, M. J. Solid State Electrochem. 2013, 17, 675.

(173) Takada, K.; Inada, T.; Kajiyama, A.; Sasaki, H.; Kondo, S.; Watanabe, M.; Murayama, M.; Kanno, R. *Solid State Ionics* **2003**, *158*, 269.

(174) Sedlmaier, S. J.; Indris, S.; Dietrich, C.; Yavuz, M.; Draeger, C.; von Seggern, F.; Sommer, H.; Janek, J. *Chem. Mater.* **2017**, *29*, 1830.

(175) Aihara, Y.; Ito, S.; Omoda, R.; Yamada, T.; Fujiki, S.; Watanabe, T.; Park, Y.; Doo, S. *Front. Energy Res.* **2016**, *4*, 18.

(176) Bron, P.; Roling, B.; Dehnen, S. J. Power Sources 2017, 352, 127.

(177) Lu, Y.; Tu, Z.; Archer, L. A. Nat. Mater. 2014, 13, 961.

(178) Ma, L.; Kim, M. S.; Archer, L. A. Chem. Mater. 2017, 29, 4181.

(179) Dietrich, C.; Weber, D. A.; Sedlmaier, S. J.; Indris, S.; Culver, S. P.; Walter, D.; Janek, J.; Zeier, W. G. *J. Mater. Chem. A* **2017**, *5*, 18111.

(180) Phuc, N. H. H.; Hirahara, E.; Morikawa, K.; Muto, H.; Matsuda, A. J. Power Sources 2017, 365, 7.

(181) Sharafi, A.; Haslam, C. G.; Kerns, R. D.; Wolfenstine, J.; Sakamoto, J. J. *Mater. Chem. A* **2017**, *5*, 21491.

(182) Basappa, R. H.; Ito, T.; Morimura, T.; Bekarevich, R.; Mitsuishi, K.; Yamada, H. J. Power Sources **2017**, *363*, 145.

(183) Wakasugi, J.; Munakata, H.; Kanamura, K. J. Electrochem. Soc. **2017**, *164*, A1022.

(184) Rosso, M.; Gobron, T.; Brissot, C.; Chazalviel, J. N.; Lascaud, S. J. Power Sources 2001, 97, 804.

(185) Gao, Y. M.; Jiang, Y. F.; Wang, N. P. Phys. B 2014, 447, 47.

(186) S. N. Wu, S. S. Neo, Z. L. Dong, F. Boey, P. Wu, J. Phys. Chem. C 2010, 114, 16706.

(187) Liang, C. C.; Epstein, J.; Boyle, G. H. J. Electrochem. Soc. 1969, 116, 1452.

(188) Jones, S. D.; Akridge, J. R.; Shokoohi, F. K. Solid State Ionics 1994, 69, 357.

(189) Yu, S.; Schmidt, R. D.; Garcia-Mendez, R.; Herbert, E.; Dudney, N. J.; Wolfenstine, J. B.; Sakamoto, J.; Siegel, D. J. *Chem. Mater.* **2016**, *28*, 197.