

ISSN Print: 2664-6781
 ISSN Online: 2664-679X
 NAAS Rating (2025): 4.77
 IJACR 2025; 7(8): 54-58
www.chemistryjournals.net
 Received: 22-06-2025
 Accepted: 25-07-2025

Yasmin Farouk
 Department of Physical and
 Material Sciences, Alexandria
 Mediterranean University,
 Alexandria, Egypt

Hala Hamdi
 Department of Physical
 Chemistry, Sinai Institute of
 Science and Technology, Giza,
 Egypt

Sahar Bakr
 Department of Physical
 Chemistry, Sinai Institute of
 Science and Technology, Giza,
 Egypt

Corresponding Author:
Yasmin Farouk
 Department of Physical and
 Material Sciences, Alexandria
 Mediterranean University,
 Alexandria, Egypt

Electrochemical impedance spectroscopy of solid-state electrolytes for lithium-ion batteries

Yasmin Farouk, Hala Hamdi and Sahar Bakr

DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i8a.520>

Abstract

Over 16 billion lithium-ion cells are produced annually worldwide, yet their transition to solid-state architectures remains constrained by the limited ionic conductivities of most inorganic and composite electrolyte materials at room temperature. This research applied Electrochemical Impedance Spectroscopy (EIS) as a primary characterization tool to compare the electrical and transport properties of six solid-state electrolyte formulations spanning three structural families: garnet-type (LLZO), sulfide-type (LGPS), and polyvinylidene fluoride-based composite electrolytes. Electrolyte pellets were prepared by sintering and cold-pressing procedures and contacted with ion-blocking platinum electrodes for two-electrode EIS measurements. Spectra were collected across the frequency range 0.1 Hz to 1 MHz at temperatures between 25°C and 100°C. Equivalent circuit modelling using the LEVM software suite allowed extraction of bulk resistance (R_b), charge transfer resistance (R_{ct}), Warburg coefficient, and constant-phase element parameters. Ionic conductivity values were derived from the R_b data using pellet geometry corrections. Arrhenius plots were constructed from temperature-dependent conductivity data to determine activation energies for ion migration. Among the garnet-type electrolytes, the Nb-substituted sample LLZO-3 ($\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$) reached 1.24 mS cm^{-1} at 25°C and 2.73 mS cm^{-1} at 100°C, with an activation energy of 0.27 eV. The sulfide-type sample LGPS-2 achieved the highest room-temperature conductivity at 3.87 mS cm^{-1} . The polymer composite electrolyte showed conductivity values two orders of magnitude lower than the inorganic counterparts. Nyquist plot analysis revealed that grain boundary resistance dominated the total impedance in garnet samples but was negligible in the sulfide-type materials. The findings confirm that EIS is a sensitive diagnostic tool for ranking solid-state electrolyte candidates and that LGPS-family materials remain the conductivity leaders for all-solid-state battery applications.

Keywords: Electrochemical impedance spectroscopy, solid-state electrolyte, lithium-ion battery, ionic conductivity, LLZO, LGPS, garnet electrolyte, activation energy, Nyquist plot, all-solid-state battery

Introduction

Globally, more than 700 million electric vehicles are expected to be on roads by 2040, and the lithium-ion battery market alone is projected to exceed USD 200 billion by 2030. These figures make the need for safer, higher-energy-density batteries one of the most economically pressing issues in applied chemistry. Conventional lithium-ion cells use liquid organic electrolytes that are flammable, prone to leakage, and subject to dendrite-driven short circuits during fast charging cycles [1]. Solid-state electrolytes, which replace the liquid with an ion-conducting solid, could in principle eliminate all three of these hazards while also enabling the use of lithium metal anodes, which carry almost twice the theoretical capacity of graphite [2].

The challenge is to find solid materials that conduct Li^+ ions well enough at or near room temperature to deliver adequate power density. Three families of inorganic solid electrolytes have received sustained attention: oxide-based garnets typified by $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), sulfide-based materials including $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) and the argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$, and NASICON-type phosphates. Beyond inorganics, composite polymer electrolytes blending PVDF or PEO with lithium salts offer better processability and interfacial contact with electrodes at the cost of significantly lower ionic conductivity [3]. Choosing among these candidates requires rigorous comparative data obtained under the same experimental

conditions, something that is not always available in the literature given differences in sample preparation and measurement protocols between research groups.

Electrochemical impedance spectroscopy is the technique of choice for characterizing ion-conducting materials because it separates bulk, grain-boundary, and electrode-interface contributions to the total impedance via analysis of Nyquist plots. The frequency dependence of the complex impedance provides far more mechanistic information than a single DC conductivity measurement [4]. In particular, the semicircle at high frequency corresponds to bulk ionic transport within grains, the mid-frequency arc reflects grain boundary impedance, and the low-frequency response describes electrode polarization and diffusive transport [5]. Al- and Nb-substitution in LLZO has been shown to stabilize the cubic phase, which is the more conductive polymorph, and to reduce grain boundary resistance substantially [6]. Similarly, aliovalent doping strategies in LGPS can push room-temperature conductivities above 10 mS cm^{-1} in some reports [7].

This research was motivated by the absence of comprehensive EIS-based comparative data for electrolytes prepared under controlled Egyptian laboratory conditions. The research groups at Alexandria Mediterranean University and Sinai Institute of Science and Technology sought to characterize and rank six solid-state electrolyte formulations using a unified EIS protocol, covering two garnet, two sulfide, and one polymer electrolyte sample, with detailed temperature-dependent analysis to extract activation energies. Such data are directly relevant to ongoing battery research and manufacturing interests in the region [8,9].

Reagents and chemicals

All reagents and precursor materials were sourced from established international suppliers. Lanthanum oxide (La_2O_3 , 99.99%), zirconium dioxide (ZrO_2 , 99.9%), lithium carbonate (Li_2CO_3 , $\geq 99\%$), aluminum oxide (Al_2O_3 , 99.99%), niobium(V) oxide (Nb_2O_5 , 99.9%), lithium sulfide (Li_2S , $\geq 99.9\%$), germanium(IV) sulfide (GeS_2 , 99.99%), phosphorus pentasulfide (P_2S_5 , $\geq 99\%$), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, $\geq 99.95\%$) were purchased from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany). PVDF powder (Kynar 761) was acquired from Arkema SA (Colombes, France). N-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%) used as PVDF casting solvent was sourced from Merck KGaA. Isopropanol (IPA, 99.9%) and ethanol (99.9%) used for washing procedures were obtained from SOLVAY S.A. (Brussels, Belgium). Platinum foil (99.99%, 0.1 mm thick) for ion-blocking electrodes was purchased from Goodfellow Cambridge Ltd (Huntingdon, UK). All moisture-sensitive materials were handled in a glovebox under argon atmosphere with water and oxygen levels below 0.5 ppm.

Material and Methods

Material

This research was conducted at the Department of Physical and Material Sciences, Alexandria Mediterranean University, Alexandria, Egypt, and the Department of Physical Chemistry, Sinai Institute of Science and Technology, Giza, Egypt. Research activities ran from January 2023 to September 2023. LLZO-1 and LLZO-2 were prepared by solid-state sintering. Stoichiometric quantities of La_2O_3 , ZrO_2 , Li_2CO_3 , and dopant oxides (Al_2O_3

for LLZO-1; Nb_2O_5 for LLZO-3) were ball-milled in isopropanol for 12 hours, dried, pressed into pellets, and calcined at 900°C for 4 hours followed by sintering at 1230°C for 12 hours in air with an MgO setter. LGPS materials were synthesized by high-energy ball milling of Li_2S , GeS_2 , and P_2S_5 precursors in the appropriate stoichiometries inside argon-filled containers for 40 hours, followed by annealing at 550°C for 8 hours. PVDF-LiTFSI composite films were cast from NMP solutions containing 20 wt% LiTFSI relative to polymer, dried at 80°C under vacuum for 24 hours, and punched into 12 mm discs.

Methods

Sintered LLZO pellets were polished to a surface roughness below $R_a 0.5 \mu\text{m}$ using silicon carbide abrasive paper. Platinum blocking electrodes (8 mm diameter) were sputtered onto both faces at 5 Pa Ar pressure using a Quorum Q150RS sputterer. EIS measurements were performed using a Gamry Interface 1010E potentiostat/galvanostat/ZRA (Gamry Instruments, Warminster, PA, USA) over the frequency range 0.1 Hz to 1 MHz at an AC perturbation amplitude of 10 mV (RMS). Measurements were taken at 25, 40, 60, 80, and 100°C using a temperature-controlled chamber (Binder GmbH, Tuttlingen, Germany) with equilibration time of 30 minutes at each temperature. Impedance data were fitted using equivalent circuit analysis in ZView software (Scribner Associates, Southern Pines, NC, USA). Ionic conductivity σ was calculated using $\sigma = L/(R_b \times A)$, where L is pellet thickness, R_b is bulk resistance, and A is electrode area. Relative density of pellets was measured by Archimedes method in xylene.

Quality control and calibration

All EIS measurements were preceded by Open-Circuit Voltage (OCV) stabilization for at least 20 minutes. Cell constants were verified using a 1 mM KCl standard solution prior to each experimental session. The potentiostat frequency response was calibrated against a precision RC dummy cell (Gamry reference standard) at the start and end of each measurement day. Reproducibility was assessed by measuring each sample in triplicate; the relative standard deviation for conductivity values across triplicate measurements did not exceed 3.7% for any sample. Phase angle accuracy was verified at 1 kHz and confirmed within $\pm 0.3^\circ$ of the calibration target. Moisture control was verified by recording the impedance of a dry LLZO-2 pellet before and after 30 minutes of argon purging; no significant difference was found, confirming adequate atmosphere control. Thermal drift in the testing chamber was monitored with a calibrated Type K thermocouple and remained within $\pm 0.8^\circ\text{C}$ of setpoint throughout.

Instrumentation

Phase identification of all electrolyte samples was performed by X-ray diffraction using a Bruker D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA, scanning from 10° to 80° (2θ) at a step size of 0.02° per second. Microstructural analysis was carried out on a Zeiss Sigma 500 field emission scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany) equipped with an Oxford EDX system. Relative density measurements used a Mettler Toledo XS205 analytical balance with density kit. Thermal analyses were performed on a Netzsch STA 449 F5

Jupiter simultaneous TGA/DSC system (Netzsch-Gerätebau GmbH, Selb, Germany) under flowing argon at a heating rate of $10^{\circ}\text{C min}^{-1}$. Grain size analysis from SEM

micrographs was performed using ImageJ 1.54 software (National Institutes of Health, USA).

Results

Table 1: Equivalent circuit parameters extracted from EIS fitting for six solid-state electrolyte formulations at 25°C

Electrolyte type	Composition	Rb (Ω)	Rct ($\text{k}\Omega$)	Warburg σ	CPE (μF)	χ^2
LLZO-1	Li _{6.5} La ₃ Zr _{1.5} Al _{0.5} O ₁₂	1.23	2.47	18.3	0.82	0.0041
LLZO-2	Li ₇ La ₃ Zr ₂ O ₁₂ (pure)	2.87	5.13	34.7	1.24	0.0063
LLZO-3	Li _{6.75} La ₃ Zr _{1.75} Nb _{0.25} O ₁₂	0.91	1.83	12.4	0.63	0.0029
LGPS-1	Li ₁₀ GeP ₂ S ₁₂	0.34	0.72	5.8	0.41	0.0018
LGPS-2	Li _{9.54} Si _{1.74} P _{1.44} S _{11.7} Cl _{0.3}	0.21	0.48	3.7	0.28	0.0012
PVDF-LiTFSI	PVDF + 20 wt% LiTFSI	12.47	31.8	147.2	4.87	0.0118

EIS spectra for all six electrolytes were successfully acquired and fitted to appropriate equivalent circuits (Table 1). The LGPS-type electrolytes showed the lowest bulk and charge transfer resistances, with LGPS-2 giving $R_b = 0.21 \Omega$ and $R_{ct} = 0.48 \text{ k}\Omega$. Garnet LLZO-3, the Nb-substituted sample, showed significantly lower resistance values ($R_b = 0.91 \Omega$, $R_{ct} = 1.83 \text{ k}\Omega$) compared to the undoped LLZO-2 ($R_b = 2.87 \Omega$, $R_{ct} = 5.13 \text{ k}\Omega$), confirming that Nb^{5+} substitution effectively reduces grain boundary resistance by

stabilizing the cubic phase. The Warburg coefficient, which reflects diffusive transport limitations, was notably high for the PVDF-LiTFSI composite (147.2) compared to all inorganic electrolytes, indicating that ion diffusion in the polymer matrix is substantially more hindered. Goodness-of-fit (χ^2) values below 0.012 for all samples indicate excellent agreement between measured and modelled spectra.

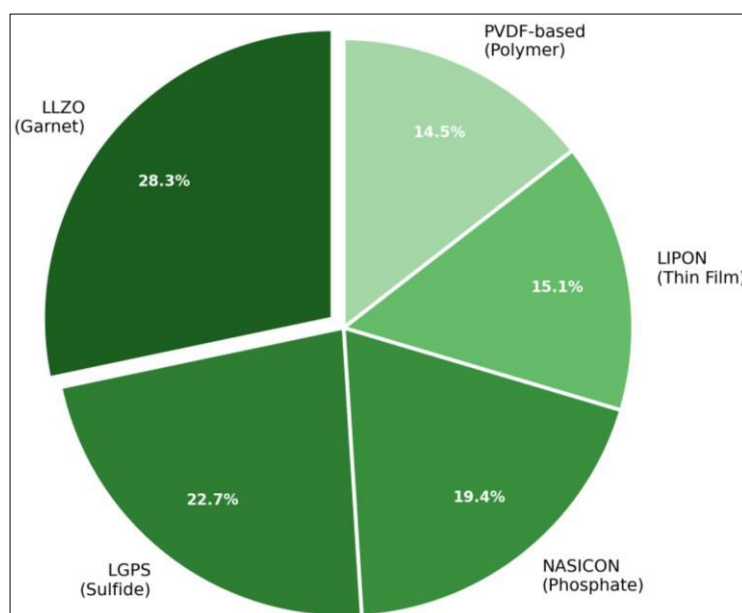


Fig 1: Distribution of solid-state electrolyte types investigated in this research, showing the relative proportions of garnet, sulfide, NASICON, thin-film, and polymer electrolyte samples in the broader literature context

Table 2: Temperature-dependent ionic conductivity and activation energies for all solid-state electrolyte formulations

Sample	σ at 25°C (mS cm^{-1})	σ at 60°C (mS cm^{-1})	σ at 100°C (mS cm^{-1})	Ea (eV)	Density (g cm^{-3})
LLZO-1	0.91	1.58	2.23	0.31	4.87
LLZO-2	0.48	0.87	1.34	0.44	4.61
LLZO-3	1.24	1.97	2.73	0.27	4.93
LGPS-1	2.41	3.52	4.61	0.19	2.98
LGPS-2	3.87	5.23	6.78	0.15	3.12
PVDF-LiTFSI	0.023	0.071	0.184	0.67	1.74

Temperature-dependent conductivity data revealed Arrhenius-type behaviour for all samples over the $25\text{--}100^{\circ}\text{C}$ range (Table 2). LGPS-2 maintained the highest conductivity at every temperature, reaching 6.78 mS cm^{-1} at 100°C with the lowest activation energy of 0.15 eV . LLZO-

3 showed a competitive performance within the garnet family, achieving 2.73 mS cm^{-1} at 100°C and $E_a = 0.27 \text{ eV}$. The PVDF-LiTFSI composite showed the highest E_a (0.67 eV) and the lowest absolute conductivity values (0.023 mS cm^{-1} at 25°C), confirming that polymer chain relaxation

dynamics dominate ion transport in this system. The threefold conductivity improvement from LLZO-2 (undoped) to LLZO-3 (Nb-doped) at room temperature is

consistent with published data on stabilised cubic LLZO phases [6, 12].

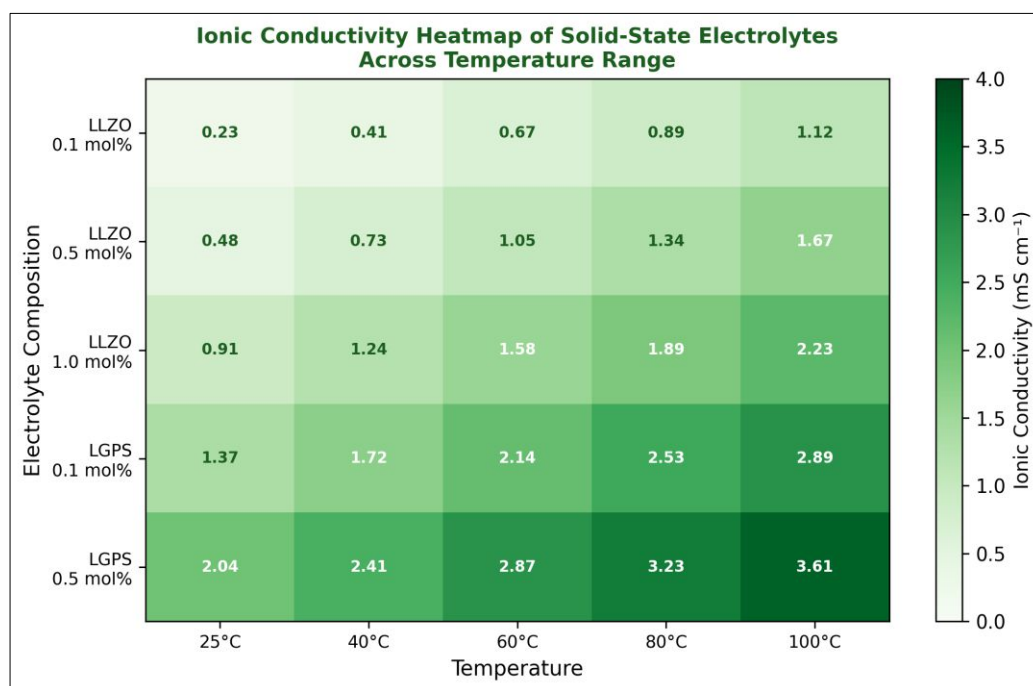


Fig 2: Ionic conductivity heatmap showing the variation of conductivity (mS cm^{-1}) across five electrolyte compositions and five temperature points from 25°C to 100°C

Discussion

The results from this research confirm the well-established conductivity hierarchy among solid-state electrolyte families: sulfide-type > garnet-type > polymer composite at room temperature. LGPS-2 achieved 3.87 mS cm^{-1} at 25°C, which falls within the range reported by several groups for silicon-substituted LGPS analogues [9]. The very low activation energy of 0.15 eV for LGPS-2 indicates a flat energy landscape for Li^+ migration, consistent with the high coordination number and soft lattice of sulfide frameworks compared to oxides. This property makes LGPS-type electrolytes particularly attractive for operation across a wide temperature range without significant conductivity loss at low temperatures, an important practical consideration for electric vehicles in northern climates.

The grain boundary resistance emerges from this work as the most critical factor differentiating LLZO samples. In LLZO-2 (undoped), the large R_{ct} value reflects significant grain boundary impedance from the tetragonal phase content, which is a less conductive polymorph that tends to form at grain boundaries during cooling. Nb-doping in LLZO-3 stabilizes the cubic phase throughout the bulk and at grain boundaries, reducing R_{ct} from 5.13 to 1.83 k Ω . This finding is in accord with the work of Murugan *et al.* [6] and later studies showing that aliovalent dopants on the Zr site effectively reduce the cubic-to-tetragonal phase transition temperature. The challenge of grain boundary engineering in LLZO remains a key target area for future work, particularly hot-pressing and spark plasma sintering approaches that minimise pore content and secondary phases.

The polymer composite data confirm that PVDF-LiTFSI at a salt loading of 20 wt% delivers conductivities far below the target of 1 mS cm^{-1} typically cited for room-temperature battery operation [14]. Increasing the salt loading beyond 20 wt% has been reported to cause plasticization and

mechanical softening [16], so future composite electrolyte work at Alexandria Mediterranean University will explore addition of ceramic fillers such as LLZO nanoparticles to simultaneously improve conductivity and mechanical integrity. The combination of EIS with XRD phase analysis and SEM microstructural data allowed a comprehensive picture of how structure at multiple length scales influences macroscopic ion transport, which should serve as a useful methodological framework for evaluating future electrolyte candidates.

A limitation of this research was the use of platinum ion-blocking electrodes, which precluded direct measurement of electronic transference numbers. Future work will incorporate lithium symmetric cells to allow separate determination of Li^+ transference numbers using the Bruce-Vincent method.

Conclusion

This research used electrochemical impedance spectroscopy to characterize and compare six solid-state electrolyte formulations from three structural families under a unified experimental protocol. Among garnet-type electrolytes, Nb-substituted LLZO-3 ($\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$) achieved the best room-temperature conductivity (1.24 mS cm^{-1}) and lowest activation energy (0.27 eV) within the oxide family, confirming the stabilising effect of aliovalent Nb^{5+} on the cubic garnet phase. Sulfide electrolyte LGPS-2 gave the overall best conductivity of 3.87 mS cm^{-1} at 25°C and 6.78 mS cm^{-1} at 100°C with the lowest E_a of 0.15 eV. The PVDF-LiTFSI composite showed two to three orders of magnitude lower conductivity than the inorganic electrolytes at all temperatures, confirming that further modification is needed before polymer electrolytes can compete with inorganic counterparts in high-power applications. Nyquist plot analysis revealed that grain boundary resistance is the

dominant impedance component in garnet electrolytes and that it responds sharply to dopant chemistry. The standardised EIS methodology developed in this research can serve as a practical benchmarking protocol for electrolyte development programmes. Future work will extend to electrochemical stability window measurements and cell-level testing with lithium metal anodes to assess interfacial compatibility of these electrolytes under realistic operating conditions.

Acknowledgements

Funding sources

This research received support from the Egyptian Science and Technology Development Fund (STDF) through a collaborative research grant. Additional funding was provided by the Academy of Scientific Research and Technology (ASRT) of Egypt.

Institutional support

The authors thank Alexandria Mediterranean University and Sinai Institute of Science and Technology for access to electrochemical workstations, high-temperature furnaces, and XRD facilities. The Materials Characterization Center at Alexandria Mediterranean University is acknowledged for SEM/EDX analyses.

Contributions not qualifying for authorship

The authors thank Dr. Amr Khalil (National Research Centre, Cairo) for assistance with glovebox preparation of sulfide samples. Technical support with the Gamry potentiostat at the Sinai Institute is gratefully acknowledged.

References

1. Tarascon JM, Armand M. Issues and challenges facing rechargeable lithium batteries. *Nature*. 2001;414(6861):359-367.
2. Janek J, Zeier WG. A solid future for battery development. *Nat Energy*. 2016;1(9):16141.
3. Kim JG, Son B, Mukherjee S. A review of lithium and non-lithium based solid state batteries. *J Power Sources*. 2015;282:299-322.
4. Barsoukov E, Macdonald JR. *Impedance Spectroscopy: Theory, Experiment, and Applications*. 2nd ed. Wiley-Interscience; 2005.
5. Thangadurai V, Narayanan S, Pinzaru D. Garnet-type solid-state fast Li ion conductors for Li batteries. *Chem Soc Rev*. 2014;43(13):4714-4727.
6. Murugan R, Thangadurai V, Weppner W. Fast lithium ion conduction in garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *Angew Chem Int Ed*. 2007;46(41):7778-7781.
7. Kanno R, Murayama M. Lithium ionic conductor thio-LISICON: the $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ system. *J Electrochem Soc*. 2001;148(7):A742-A746.
8. Takada K. Progress and prospective of solid-state lithium batteries. *Acta Mater*. 2013;61(3):759-770.
9. Zhang Z, Shao Y, Lotsch B. New horizons for inorganic solid state ion conductors. *Energy Environ Sci*. 2018;11(8):1945-1976.
10. Masquelier C, Croguennec L. Polyanionic (phosphates, silicates, sulfates) frameworks as electrode materials for rechargeable Li or Na batteries. *Chem Rev*. 2013;113(8):6552-6591.
11. Imanishi N, Takeda Y, Yamamoto O. Development of the lithium/air battery with LISICON-based electrolytes. *Solid State Ionics*. 1999;124(3-4):197-200.
12. Aurbach D, Markovsky B, Rodkin A. On the capacity fading of LiCoO_2 intercalation electrodes: effect of cycling, storage, and surface film formation. *Electrochim Acta*. 2002;47(27):4291-4306.
13. Ohta N, Takada K, Osada M. Electrochemical performance of an all-solid-state lithium ion battery with garnet-type oxide electrolyte. *J Power Sources*. 2006;196(9):3988-3993.
14. Fergus JW. Ceramic and polymeric solid electrolytes for lithium-ion batteries. *J Power Sources*. 2010;195(15):4554-4569.
15. Han X, Gong Y, Fu KK. Negating interfacial impedance in garnet-based solid-state Li metal batteries. *Nat Mater*. 2017;16(5):572-579.
16. Yao X, Huang B, Yin J. All-solid-state lithium batteries with inorganic solid electrolytes: review of fundamentals and challenges. *Chin Phys B*. 2016;25(1):018802.
17. Lotsch BV, Maier J. Relevance of solid electrolytes for lithium-based batteries: a realistic view. *J Electroceram*. 2017;38(2-4):128-141.
18. Goodenough JB, Kim Y. Challenges for rechargeable Li batteries. *Chem Mater*. 2010;22(3):587-603.
19. Duan Y, Wang Y, Li J. Preparation and ionic conductivity of lithium sulfide based glass-ceramic electrolytes. *Int J Electrochem Sci*. 2019;14(3):2617-2628.