Theory and Practice of Science and Technology
2025, VOL. 6, NO. 4, 170-173
DOI: 10.47297/taposatWSP2633-456930.20250604

EIS response characteristics and Randles modeling analysis of typical solid electrolytes at low temperatures

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ABSTRACT
Solid-state batteries, due to their high safety and high energy density, have gradually become a key technology to promote the development of new energy vehicles, aerospace and renewable energy storage systems. However, its capacity decay and rate performance decline are common problems at low temperatures, which are mainly limited by the decrease of ionic conductivity and the increase of interface impedance of solid electrolyte materials. In order to further understand the electrochemical characteristics of different electrolyte materials at low temperatures, three representative solid electrolytes - polymer PEO, sulfide LPS and oxide LLZO - were selected in this paper, and equivalent circuits based on simplified Randles model were constructed to carry out impedance frequency domain simulation analysis. The transport resistance and interface behavior of the three materials at −20 °C were compared by using the simulated Nyquist diagram. The simulation results show that LPS exhibits the lowest interfacial impedance and excellent ion conductivity, LLZO achieves a good balance between conductivity and stability. At the same time, PEO has the highest interfacial reaction resistance, limiting its cryogenic application potential. This study provides the theoretical basis and technical support for material selection and structure optimization of solid-state batteries in cold environment.

KEYWORDS
Solid-state electrolyte; low temperature; impedance; Randles model; EIS

1 Introduction

As an important part of the new generation of energy storage systems, the safety and high energy density of solid-state batteries have been verified in several studies. However, at low temperatures, solid electrolytes generally have problems such as decreased ionic conductivity and interface reaction hysteresis, especially in terms of battery capacity and rate characteristics [1-2]. Therefore, it is of great theoretical and engineering significance to study the conductivity of solid electrolyte at low temperature. To deal with the above problems, the behavior difference of different types of solid electrolyte materials at low temperatures has gradually become the focus of research. Polymer materials (such as polyethylene oxide, PEO) are often used in solid electrolyte systems because of their good flexibility and film forming ability, which can create continuous ion conduction channels at low temperatures. However, its ionic mobility is highly sensitive to temperature, and chain segment motion is significantly weakened at low temperatures, resulting in a substantial decrease in overall conductivity. To improve the conductivity, it is often necessary to doping lithium salts (such as LiTFSI) in PEO to provide a carrier source, but excessive doping is easy to induce crystallization phase precipitation, but hinder ion migration. Sulfide electrolytes (e.g. $Li_{10}GeP_2S_{12}$, Li_6PS_5Cl) exhibited a room temperature ionic conductivity of up to 10^{-2} S/cm and maintained good conductivity at low temperatures. The solid-solid interface contact is better than that between oxide and polymer, so it is favorable for interfacial charge transfer reaction. However, this kind of material is extremely sensitive to humidity, easy to react with water in the air to produce H_2S gas, there are stability and environmental adaptability problems, usually need to be prepared and operated in an inert atmosphere. Oxide electrolytes (e.g. $Li_7La_3Zr_2O_{12}$, LLZO) are widely used in high safety battery systems due to their high mechanical strength, wide electrochemical window and excellent chemical stability. Its dense crystal structure helps to inhibit the penetration of lithium dendrites and improve long-term cycle stability. However, LLZO material has a high interface impedance, especially at low temperature, which is prone to significantly limit ion migration due to poor interface contact or formation of barrier layer [3-5]. Through the comparative study of these three representative materials, the difference of their electrochemical behavior at low temperature can be deeply explored, which provides a theoretical basis for material optimization.

In order to further reveal the impedance response characteristics of different solid electrolytes under low temperature conditions, this paper takes three representative materials, PEO, LPS and LLZO, as the research objects, builds an equivalent circuit based on the classical Randles model, and carries out frequency-domain simulation analysis combined with the principle of electrochemical impedance spectroscopy (EIS). The research focuses on the difference of bulk conductivity and interface transport behavior of materials at −20 °C, providing theoretical basis for selection and interface optimization of solid-state battery materials in low-temperature application scenarios. The following paper will focus on the modeling principle, simulation process, result analysis and method evaluation.

2 Modeling principle and method

The aim of this study was to evaluate the ion conductivity and interface behavior of three typical solid electrolytes (PEO, LPS, LLZO) at −20 °C by constructing an equivalent circuit model and combining with electrochemical impedance spectroscopy (EIS) analysis.

Electrochemical Impedance Spectroscopy (EIS) is an analytical technique to obtain the behavior of complex impedance at different frequencies by applying small AC voltage perturbations and measuring the system response current. EIS can reveal key processes such as ion migration, charge transfer, interfacial polarization and diffusion in lithium batteries, and is especially suitable for modeling and analyzing reaction mechanisms under different time constants. Its non-destructive, high sensitivity and frequency-domain modeling capabilities make it an important means to evaluate the properties of solid-state battery materials [6-7].

As an important tool for EIS analysis, the equivalent circuit model can be used to equivalent the physical-chemical process inside the battery to the combined form of electrical components. Randles model is a classical first-order approximate modeling method, which can reflect the resistance and polarization characteristics of the interfacial charge transfer process and has been widely used in liquid and solid systems.

The Randles model consists of the following three typical components:

Rs: The solution resistance represents the ion migration impedance of the electrolyte body.

Rct: The interfacial charge transfer impedance reflects the difficulty of lithium-ion transfer at the electrode-electrolyte interface.

Cdl: Double layer capacitance, which describes the polarization effect of double layer formation, is closely related to the interface contact state.

The total impedance expression is: $Z(\omega) = R_s + \frac{R_{ct}}{1 + j\omega R_{ct} C_{dl}}$

Where $\omega = 2\pi f$ is the angular frequency, the expression is used to describe the complex impedance behavior of the system in the frequency domain and can reflect the electrochemical response characteristics of the solid electrolyte under multiple time constants. To enhance the adaptability and expression accuracy of modeling, model extension elements such as Warburg impedance or CPE (constant phase element) can be introduced in subsequent studies to characterize diffusion control behaviors or non-ideal interface effects [8].

When the model is used in solid electrolyte system, Rs corresponds to the bulk phase conductivity of the material, Rct is mainly affected by the interface structure and reaction rate, and Cdl is related to the interface contact area and surface energy. Therefore, by adjusting these three parameters, the conduction and polarization performance of different electrolytes at specific temperatures can be well reflected.

Three representative electrolyte materials were selected in this paper, namely polymer PEO (high compliance but weak conductivity), sulfide LPS (excellent conductivity but strong interfacial activity), and oxide LLZO (high stability but high structural rigidity). According to existing experimental values and literature reports, material parameters are set as shown in the table below [9-11]:

Table 1 Modeling parameters of three solid electrolytes at −20 °C

Material type	Rs (Ω)	Rct (Ω)	Cdl (μF)	Temperature
PEO	20	150	0.5	−20 °C
LPS	8	50	1.0	−20 °C
LLZO	12	80	0.8	−20 °C

The experiment and simulation process is as follows:

Parameter setting: Set the impedance parameters of the three types of materials at −20 °C regarding literature and experimental data.

Frequency scanning: Equal interval logarithmic frequency points are constructed in the range of 10 Hz-1 MHz, covering charge accumulation, polarization behavior and ion migration processes.

Model calculation: Use MATLAB language to calculate impedance expression and draw Nyquist diagram to extract semi-circle features corresponding to Rct and Cdl.

Performance comparison: the difference of interface impedance and conductivity of the three materials is analyzed by real and imaginary part responses.

Model verification: Interface additional resistance elements were further introduced into the LLZO model to test the sensitivity of the model to impedance response under different contact states.

The frequency range of 10 Hz to 1 MHz is selected to cover all key processes involved in the polarization layer response (low frequency) to the bulk phase conductive behavior (high frequency), ensuring that the simulation results are representative. Through this modeling process based on physical parameter setting, it can be applied to solid electrolyte systems with different temperature, thickness, doping mode or interface structure, and has good reproducibility and

universality in material screening and interface optimization design.

3 Simulation results and analysis

Nyquist diagram is the most common way to display the impedance spectrum. As shown in Figure 1, the comparison of Nyquist diagram of three typical solid electrolytes (PEO, LPS, and LLZO) at −20 °C can reveal the differences in their interfacial electrochemical behavior by analyzing the semicircle shape and height of corresponding curves of different materials in the diagram.

In the figure, the horizontal axis is the real part of the complex impedance Re(Z), which represents the ohmic resistance in the system. The vertical axis is the imaginary part −Im(Z), reflecting the interface polarization and capacitance effects. The horizontal diameter of the semicircle represents the charge transfer impedance Rct, and the curvature is affected by the double layer capacitance Cdl. When the Cdl value is small, the semicircle curvature in the Nyquist diagram becomes smaller, which means that the system responds slowly to high-frequency signals and the interface polarization is enhanced, indicating that the electrode/electrolyte interface reaction process is limited. In other words, the polarization layer formed by the electrode/electrolyte interface during charge and discharge is more obvious, indicating that the electrolyte material has more significant charge accumulation and transmission delay at low temperature [6].

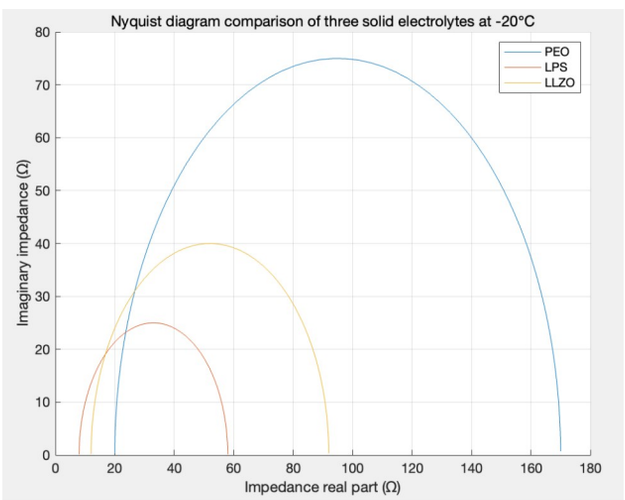

Figure 1 Nyquist plots of PEO, LPS, and LLZO at −20 °C showing impedance behavior under low-temperature conditions. In the figure, blue is PEO, orange is LPS, and green is LLZO. The corresponding semicircle sizes successively reflect the interface impedance differences.

The simulation results show that:

LPS (sulfide) has the smallest semicircle and the lowest Rct (50 Ω), showing excellent interfacial transport ability and fast dynamic response. This shows that its interface charge transfer reaction is faster, suitable for high power output scenarios, and its large Cdl value also means that it forms sufficient contact with the electrode, which is conducive to inhibiting polarization and stabilizing the conduction path.

LLZO (oxide) has a moderate performance with an Rct of about 80 Ω, moderate conductivity but stable interfacial capacitance. This reflects the performance balance between structural stability and ion mobility, which is suitable for scenarios where the interface reaction is not high, but the long-term stability of the material is important.

PEO (polymer) has the largest impedance arc, Rct up to 150 Ω, and interface transmission is limited. The high impedance is mainly due to the limited movement of the chain segment at low temperature, which restricts the migration of lithium ions. At the same time, the low Cdl indicates that the interface charge storage capacity is insufficient, and it is difficult to form an effective conduction channel. Suitable for battery systems that prioritize safety but do not require high low temperature performance.

At the starting point of the real part, the Rs of LPS is the lowest, indicating that the bulk ion conductivity of LPS is the best. However, PEO is limited by the increase of molecular chain rigidity and the decrease of electrical conductivity. The Cdl values of LPS also affect the curvature of the impedance arc, and the Cdl of LPS is the largest, indicating that it forms a better polarization structure at the electrode-electrolyte contact interface.

4 Model applicability and limitation analysis

Although Randles model can effectively characterize the frequency domain impedance behavior of three solid

electrolytes at low temperature in this study, its nature is a first-order approximation, which still has some limitations. First, the Warburg impedance term is not introduced into the model, so it is difficult to describe the diffusion control behavior at the electrode/electrolyte interface, especially in the middle and low frequency band, there will be deviation from the actual fitting. Secondly, the default capacitor behavior of Randles model is an ideal plate capacitor. However, porous structure and non-uniform charge distribution often exist in the actual solid-solid interface, which presents a frequency-dependent phase response, requiring the introduction of a constant phase element (CPE) for correction [12]. In addition, the interface states between different samples are significantly different (such as interface defects, contact gaps, etc.), resulting in sample dependent parameter setting, which is difficult to be directly generalized to multi-batch comparative analysis.

Based on the above limitations, future research can build a composite equivalent circuit structure with multiple time constants since Randles model, introduce temperature related parameters and structural constraints, and realize the modeling and prediction ability in a wider frequency domain and a wider temperature region. Further, the combination of EIS experimental data and parameter inversion algorithms (such as least square fitting or Bayesian optimization) is expected to improve the accuracy and adaptability of the model and provide a more practical modeling framework for material screening, interface optimization and performance prediction of solid electrolyte systems.

5 Conclusion

Based on the classical Randles equivalent circuit model, electrochemical impedance spectroscopy (EIS) was used to systematically analyze the conduction behavior and interface reaction characteristics of three representative solid electrolytes, PEO, LPS and LLZO, at −20 °C. The results show that:

- LPS has the lowest interface impedance and optimal low temperature conductivity for high-rate applications.
- LLZO is a compromise choice with medium conductivity and good stability.
- PEO needs to be modified or doped to improve its usefulness at low temperatures.

The results of this study can provide theoretical support for material selection and interface optimization of solid-state batteries in extreme environments in the future. At the same time, the modeling process based on Randles model has good parameter adjustability and adaptability, which is suitable for the performance simulation analysis of different types of solid electrolytes. In future work, the model structure can be further expanded by introducing the diffusion impedance or interface non-ideal behavior characterization mechanism to achieve a more refined dynamic process modeling and linkage with experimental data for model verification, thus improving its accuracy and reliability in the performance prediction of solid electrolyte systems.

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