

Temperature-Dependent Electrochemical Impedance Spectroscopy (EIS) of Li/MnO₂ Batteries

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Developing next-generation batteries with high energy and power densities requires extensive research into the optimization and characterization of metallic lithium anodes. Metallic lithium has the highest theoretical gravimetric and volumetric energy density compared to other materials, making it an attractive choice for high-performance batteries. Additionally, metallic lithium has a very negative reduction potential, enabling it to store and release energy more efficiently than other materials[1]. Yet, lithium metal anodes are still not commercially available due to a number of problems they face, almost all of them related to the interface between the lithium metal anode and the electrolyte.

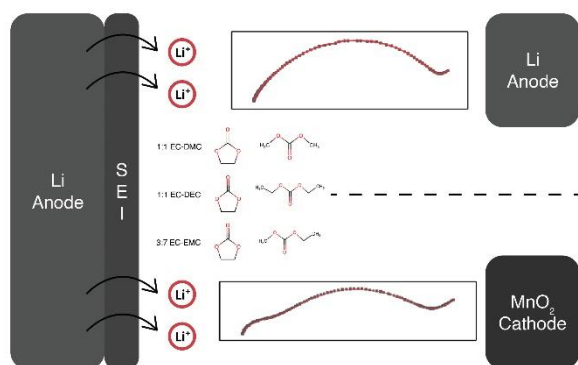


Figure 1. Impedance responses of symmetric and battery-type cells.

Electrochemical Impedance Spectroscopy (EIS), is a non-destructive analysis tool used in electrochemical research. The main principle is applying a sinusoidal excitation voltage (in potentiostatic mode) and analyzing the current response. As the famous Ohm's Law states, voltage is equal to the multiplication of the current and the resistance. The impedance (resistance with alternating current) can be acquired from this equation. In this research, EIS was employed to measure the activation energies of Li⁺ transport across the solid electrolyte interface (SEI). EIS facilitates the measurement of critical parameters such as charge transfer resistance, solution (electrolyte) resistance, double-layer capacitance, and mass transport resistance independently in a battery while keeping the battery intact[2]. Measured spectra are fitted with an equivalent circuit fit composed of resistances and capacitors (constant phase elements). These fit values correspond to

fundamental processes in the batteries, either belonging to one of the electrodes or the interfaces throughout the battery.

This study utilized EIS to measure batteries with different electrolyte compositions, using 1 M LiPF₆ in EC-DMC, EC-DEC, and EC-EMC solutions in Li/Li symmetric cells and Li/MnO₂ cells. The symmetric cells enable the isolation of the metallic lithium electrode on both sides, whereas battery-type cells exhibit a complete anode/cathode behavior. By comparing the two spectra, the effect of the cathode on the impedance response can be investigated. This comparison allows for unequivocal assignments of the various features of the impedance spectra to the phenomena in the batteries. The measurements were taken in a temperature-controlled chamber, ranging from 15°C to 65°C, to determine the activation energy of charge transfer resistance across the SEI. Using the Arrhenius equation, the resistance values obtained were then used to calculate activation energy.

The results demonstrate the dependency of SEI resistance and charge transfer activation energy (E_A) on electrolyte composition and battery architecture. It is also revealed that activation energy is related to the electrolyte compositions and the aging of the cell. Therefore, different electrolytes showed varying impedance results and activation energies.

In addition, the architecture of the cell (symmetric vs. battery-type) also had an impact on the activation energy of the charge transfer through the SEI. The Nyquist and Arrhenius plots of two types reveal the characteristics of the charge transfer.

Further developments in battery engineering will require a deeper understanding of how these electrolytes can affect the SEI and how they change as the battery is cycled. As a result, this study fills the gap in the literature on the SEI investigation concerning electrolyte composition and cell architecture with EIS.

References

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