

Advanced Characterization of Solid-State Batteries: Deconvoluting Interfacial Impedance by Distribution of Relaxation Times

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Abstract. All-solid-state batteries have attracted broad interest because they can improve battery safety and provide high energy density. But their performance is still limited by large interfacial resistance and complex failure processes caused by solid-solid contact. These interfacial processes need careful analysis. But conventional electrochemical impedance spectroscopy is often difficult to interpret in all-solid-state batteries. The main problem is that the time constants of grain boundaries and electrode interfaces can strongly overlap. Because of this, traditional equivalent-circuit models can get similar fitting results, but they end up with different physical meanings. This makes interpreting impedance spectra way less reliable than it should be. This paper centers on the distribution of relaxation times method. This method can help us look at these problems, and it needs far fewer pre-set model assumptions to work. It changes an impedance spectrum into a new spectrum that shows relaxation-time distribution. In this new format, bulk transport, grain-boundary response, and interfacial charge-transfer processes can all be split apart much more clearly. This paper explains the basic mathematical thinking behind the distribution of relaxation times method. It also talks about how the method is used in solid electrolytes, which covers both oxide and sulfide systems, plus in composite cathodes as well. We also look at how distribution of relaxation times analysis can work together with machine learning. Machine learning helps stabilize the tricky ill-posed inversion process. It can also pick out distribution of relaxation times peaks, and keep track of how peak position and peak area change when the cell goes through cycling.

Keywords: Solid State Batteries, Electrochemical Impedance Spectroscopy, Distribution of Relaxation Times, Machine Learning

1. Introduction

The growing use of electric vehicles and portable electronic devices has increased the need for safer batteries with higher energy density. Conventional liquid-state lithium-ion batteries have been used with great success for many years. But these batteries still rely on flammable organic liquid electrolytes. This electrolyte can cause leakage, thermal runaway, and fire. It also limits further

increases in energy density [1]. During long-term cycling, conventional cathode materials can also react with the liquid electrolyte. These reactions gradually lower the stability of the electrode [2].

For this reason, all-solid-state batteries have been studied as an alternative battery system. In these batteries, a nonflammable solid electrolyte replaces the liquid electrolyte. This design lowers the risks of leakage and flammability, which further can improve battery safety [3]. These properties make the use of lithium metal anodes more practical. Since lithium metal has a high specific capacity, all-solid-state batteries may reach much higher energy density, possibly above 500 Wh kg⁻¹ [4].

The change from a liquid electrolyte to a solid electrolyte also changes the nature of the interface. In conventional lithium-ion batteries, the liquid electrolyte can wet the porous electrode. Figure 1a shows the schematic of effects of the liquid electrolyte. In all-solid-state batteries, the electrode and the electrolyte contact each other as two rigid solids, as shown in Figure 1b. Compare to the liquid one, the local voids, gaps and weak bonding can remain at the interface. These defects may decrease the real area for ion transport. As a result, the interfacial contact resistance can be high [5].

Ion transport in all-solid-state batteries is not limited to one electrode/electrolyte interface. Lithium ions may need to pass through grain boundaries in the cathode active material, the cathode/electrolyte interface, and grain boundaries in the solid electrolyte [6]. Therefore, the chemical side reactions can form new interfacial phases at these interfaces or boundaries. Meanwhile, the possible space charge layers can also change the local ion distribution and concentration, which would lead to the generating cracks during long term measurements. Due to the above complex processes, it is difficult to interpret the impedance response into the special one [3]. This problem becomes more serious in composite cathodes. Since both ionic and electronic transport paths must remain continuous during in practical operations [7].

This problem creates a clear need for interfacial characterization. A useful method should measure the total impedance of the battery. It should also identify the main sources of resistance, including bulk ionic conduction, grain-boundary transport, and interfacial charge-transfer reactions. These processes occur on different time scales. But in practical cells, their impedance responses often overlap.

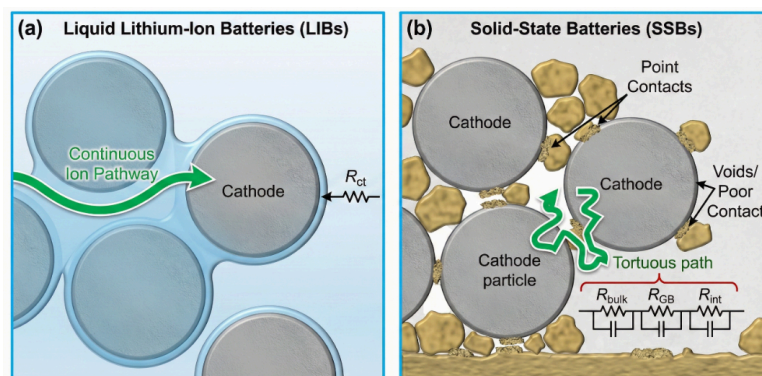


Figure 1. The schematic of ion transport pathways and interfacial contacts in (a) LIBs and (b) SSBs

2. Electrochemical impedance spectroscopy: principles and limitations

2.1. Fundamentals of EIS in solid-state batteries

Electrochemical impedance spectroscopy (EIS), owing to its nondestructive nature and broad frequency response window, typically spanning from MHz to mHz, has become a gold-standard

technique for probing the kinetic processes of electrochemical systems. In the field of all-solid-state batteries (ASSBs), EIS has been widely employed to quantify the ionic conductivity of solid electrolytes, evaluate the charge-transfer resistance (R_{ct}) at the cathode/electrolyte interface, and monitor the growth and evolution of interphase layers such as the solid electrolyte interphase [5].

Its basic principle relies on applying a small sinusoidal voltage or current perturbation to the cell and measuring the corresponding response. The resulting complex impedance contains information on the characteristic time scales of the different physicochemical processes occurring within the system. Ideally, each kinetic process in the battery, such as bulk conduction, grain-boundary transport, and interfacial charge transfer at the electrode/electrolyte interface, should appear as a distinct semicircle in the Nyquist plot, with its characteristic frequency, f_c , determined by the corresponding relaxation time [2].

2.2. The challenge: overlapping time constants and model ambiguity

Doing EIS analysis on practical solid-state battery systems is still really challenging, though. Solid-state batteries are not like liquid-based ones, because they have multilevel microstructures, and the capacitive behavior of each separate part works better with non-ideal constant phase elements instead of ideal capacitors. The biggest basic problem is the overlap of time constants. If you look at Fig. 2a, the relaxation times for grain-boundary impedance and interfacial resistance in solid-state batteries are usually really close to each other, they most often fall between 10^{-4} and 10^{-2} s. When this happens, you can't reliably tell where the impedance contributions come from just by looking at the Nyquist plot with your own eyes [8]. To split these overlapping signals apart, the usual method is to build equivalent circuit models (ECMs). But analysis that uses ECMs is naturally not clear-cut. Looking at Fig. 2b, one single experimental impedance spectrum can often get equally good fitting results, just from a pure math point of view, from multiple circuit models that have totally different topologies, for example Voigt-type or Maxwell-type setups [1]. This creates a big scientific problem: if we pick the wrong circuit model before we start testing, the resistance numbers we get might not actually match what's physically happening. This whole method, which relies on picking a model first, makes it really hard to get a deeper understanding of the complicated interfaces inside solid-state batteries. This problem gets even worse when the system has unknown ways of breaking down, or when we're working with new composite cathode materials [7]. In these kinds of situations, we really need an analysis method that doesn't depend on a pre-set model and is still mathematically solid. That's exactly why the DRT is so useful right now.

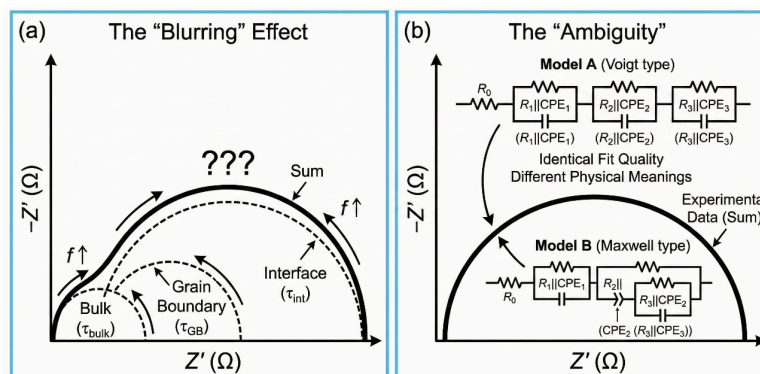


Figure 2. The challenge of spectral overlap and model ambiguity in EIS analysis of solid-state batteries. (a) Schematic drawing of overlapping time constants. (b) The problem of non-unique equivalent circuit models (ECMs)

3. Distribution of relaxation times: a high-resolution diagnostic tool

3.1. Theoretical framework: from discrete to continuous

To overcome the ambiguity and subjectivity inherent to conventional equivalent circuit model analysis, the distribution of relaxation times introduces a purely mathematical framework for impedance interpretation. Unlike ECM, which assumes a finite number of discrete circuit elements, for example, several RC or R-CPE subcircuits, DRT treats the electrochemical system as a continuous superposition of elementary relaxation processes with different time constants, τ .

Mathematically, the impedance, Z , can be expressed as the integral transform of a distribution function:

$$Z_{DRT}(f) = R_{\infty} + \int_0^{\infty} \frac{g(\ln\tau)}{1+j\omega\tau} d(\ln\tau) \quad (1)$$

where R_{∞} is the high-frequency ohmic resistance, $g(\tau)$ represents the distribution function associated with the relaxation processes in the system. By deconvoluting the experimentally measured impedance spectrum, typically through Tikhonov regularization to stabilize this ill-posed inverse problem, one can reconstruct the variation of $g(\ln\tau)$ with relaxation time and thereby obtain the DRT spectrum [8].

As you can see in Fig. 3, this transformation can turn the wide, overlapping arcs you see in the Nyquist plot into sharp peaks that are easy to tell apart in the DRT spectrum. The area under each peak matches up to how much resistance that specific process adds, while where the peak sits, measured with the value τ , shows what the typical kinetic time scale of that process is. This means DRT gets rid of the need to use a pre-set circuit model ahead of time, and instead lets the impedance data on its own show how many big electrochemical processes are actually there in the system.

3.2. Deconvoluting interfacial processes in SSBs

While solid-state batteries are used in practical settings, DRT can do a really good job checking the interface by separating the physical and chemical processes that happen at different time scales. The most confusing impedance signals usually show up in the low-frequency part of the data, where cathode charge movement, anode interphase reactions, and diffusion-linked processes get mixed up really closely together. When working with composite cathodes, DRT can separate two different kinds of resistance: one is the interfacial contact resistance between the active cathode material and solid electrolyte, and the other is electrochemical charge-transfer resistance. If a coating layer or buffer layer is added to the system, the corresponding mid-frequency peak can shift position, or the area of that peak can get smaller. Usually, these kinds of changes mean that interfacial reactions happen more easily, and the related resistance is lower [9]. When we talk about lithium metal anodes, DRT can also show early changes that happen at the lithium/electrolyte interface. A good example is when lithium dendrites grow or when interfacial contact gets worse, this can create a totally new peak in the low-frequency area. It can also make an existing peak wider than it was before. These changes give us helpful information we can use to analyze how the interface degrades over time [10]. With this kind of analysis that relies on peaks, DRT can split up the total resistance into the contributions that come from each different part of the battery. It also helps us figure out which part is causing most of the performance loss. A response that shows up at high frequency might be connected to the solid electrolyte not being dense enough. A response at mid-frequency is

often connected to the interface between cathode and electrolyte. This is how DRT can give useful practical guidance to help improve the materials and interfaces used in solid-state batteries.

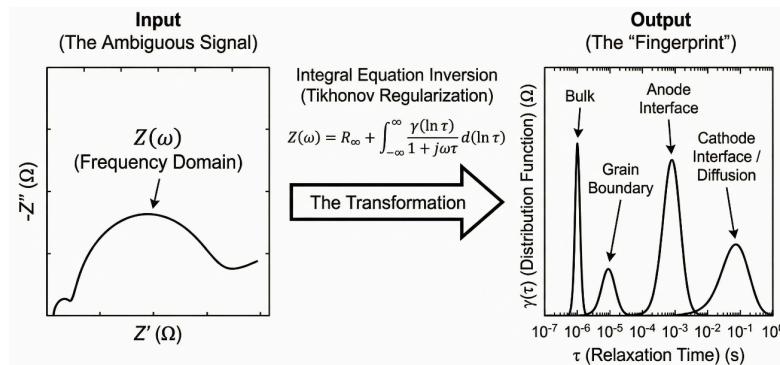


Figure 3. Transformation from the EIS to the DRT

4. Future perspectives: towards intelligent diagnostics

With the rapid development of computational science, the integration of advanced data-analysis methods into electrochemical characterization has become an inevitable trend. This is particularly true for all-solid-state batteries, which constitute highly complex and nonlinear systems, where interpretation of EIS data based solely on manual expertise is increasingly insufficient to meet the demands for long cycle life and high safety.

Machine learning (ML) is a computational approach that identifies patterns from large datasets and uses them for prediction. Unlike conventional physics-based modeling, machine learning can predict long-term battery degradation behaviors, including capacity fade, state of health, and remaining useful life, by analyzing information such as charge-discharge data and temperature variation. In battery systems, ML models have been widely applied to predict performance degradation and to assist battery management systems in identifying potential failure risks at an early stage. These approaches have already been extensively explored in the testing and health monitoring of both lithium batteries and fuel cells. For example, in lithium battery research, Severson *et al.* demonstrated the great potential of data-driven approaches [11]. By using time-series data obtained from early cycling tests, including voltage, current, and temperature, they trained machine learning models that successfully predicted the capacity degradation trajectories of batteries over hundreds of subsequent cycles. Their study showed that such models can achieve highly accurate prediction of battery lifetime, thereby substantially improving the effectiveness of battery management systems by enabling early identification of potential failure points.

If machine learning can be used to predict battery lifetime, then combining it with DRT, which can resolve microscopic electrochemical processes, offers a pathway to much deeper mechanistic insight. This strategy has already achieved promising progress in solid oxide fuel cell systems and thus provides an excellent paradigm for all-solid-state battery research. For degradation studies of perovskite cathode materials, Yang *et al.* [12] employed a machine-learning-based approach to predict performance decay induced by chromium poisoning. As shown in Fig. 4, they combined electrochemical impedance spectroscopy with machine learning and developed a Deep-DRT model, in which distribution of relaxation times analysis was used to further decouple the contributions from different electrochemical processes. By feeding short-term experimental data into this DRT-assisted machine-learning framework, the authors were able to predict long-term degradation behavior. More importantly, they identified the characteristic time scales related to the underlying

degradation mechanisms. This result shows that machine-learning models can infer long-term degradation trends from limited experimental data. It also shows that this strategy can reduce the total data requirement and improve prediction accuracy and efficiency.

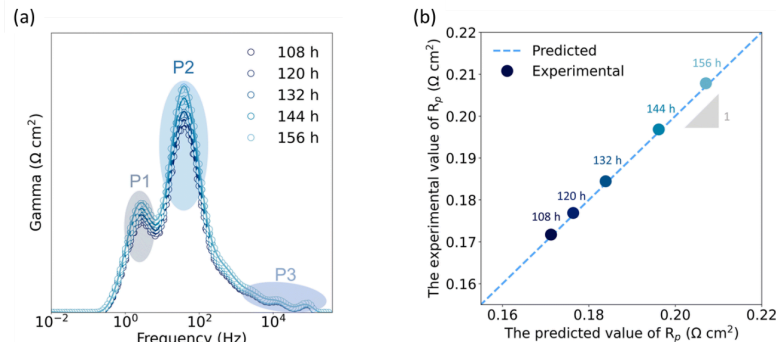


Figure 4. (a) DRT spectra of SFCO obtained by the deep-DRT model at 700 °C over 108-156 h, (b) comparison between deep-DRT-predicted values and experimental results at 700 °C within 108-156 h. Experimental data are shown as scatter points, and model-predicted DRT spectra are displayed as colored curves

A similar DRT-machine-learning strategy may also be useful for all-solid-state lithium batteries. In these batteries, interfacial failure processes, such as contact loss, lithium dendrite growth, and interfacial side reactions, may appear in DRT spectra as peak shifts or changes in peak area. This basic idea is really similar to how poisoning causes things to break down in solid oxide fuel cells. Later on, people could build a smart diagnostic system that uses the EIS-DRT-ML work process. In this system, DRT will take out high-dimensional features from EIS signals that overlap each other. After that, machine learning can build the quantitative connections between these features and specific types of failure that happen in solid-state batteries. The possible failure types include the breakdown of sulfide electrolytes caused by air, and the buildup of dead lithium on lithium metal anodes. This kind of work process does not just help us find when a battery starts breaking down. It can also help us guess which interface is going to fail sooner, and when that failure will probably happen. Because of that, putting EIS, DRT and machine learning together might give a good way to do rational design and smart management for solid-state batteries.

5. Conclusion

All-solid-state batteries can improve battery safety and energy density. But their practical use is still limited by interface problems. Bad contact between solid and solid materials, extra side reactions, and damage to the mechanical structure all can make the internal resistance of the battery get bigger. These same issues also make it harder to figure out how the battery actually fails. EIS is one good method that people use to study these kinds of processes. Conventional EIS analysis, though, often doesn't work well enough for solid-state batteries. The main problem is that multiple different processes can show up in around the same frequency range. Because of this, the Nyquist plot often can't show a clear separation between bulk transport, grain-boundary transport, and interfacial charge transfer. What's more, equivalent circuit fitting can end up with different circuit models that all have pretty similar fitting quality. This leaves the physical meaning of the fitted parameters unclear, we don't know exactly what they represent. DRT is a strong method that can help analyze these overlapping impedance signals. It works because it can make different electrochemical

processes show up as separate peaks on the plot. Where each peak sits tells you the characteristic time scale of that process, and from that you can get its contribution to total resistance. This info makes it easier to find where the main impedance comes from, like whether it is from the solid electrolyte, the grain boundary, or the interface between electrode and electrolyte. DRT also works pretty well together with machine learning tools. Machine learning can keep track of how peak positions, peak areas, and the whole peak pattern change when the battery goes through cycling. With this machine-learning-supported DRT method, we can get new understanding of how batteries degrade over long periods of time, and also do a deeper analysis of the actual failure mechanisms that are happening under the surface.

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