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Review Article

Impedance response simulation strategies for lithium-ion battery models

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Abstract

The battery is an electrochemical system that may be considered a black box with no practical way of observing processes occurring within in a nondestructive manner at an affordable cost. Fortunately, most physical and chemical processes in electrochemical systems can be distinguished by their distinct characteristic time constants. Electrochemical impedance spectroscopy (EIS) is a powerful technique to distinguish internal processes within batteries based on their frequency response. EIS has been successful at identifying relevant electrochemical mechanisms and battery parameters and therefore can be integrated with model-based battery management systems (BMS) which are critical for improving the battery life and performance. In this article, we provide our perspective on different simulation strategies for modeling the impedance response of lithium-ion batteries, implementation of EIS models in BMS, and some challenges associated with achieving a computationally efficient approach.

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Keywords

Lithium-ion batteries, Impedance modeling, Multiphysics modeling, Single particle model, Pseudo-two-dimensional model.

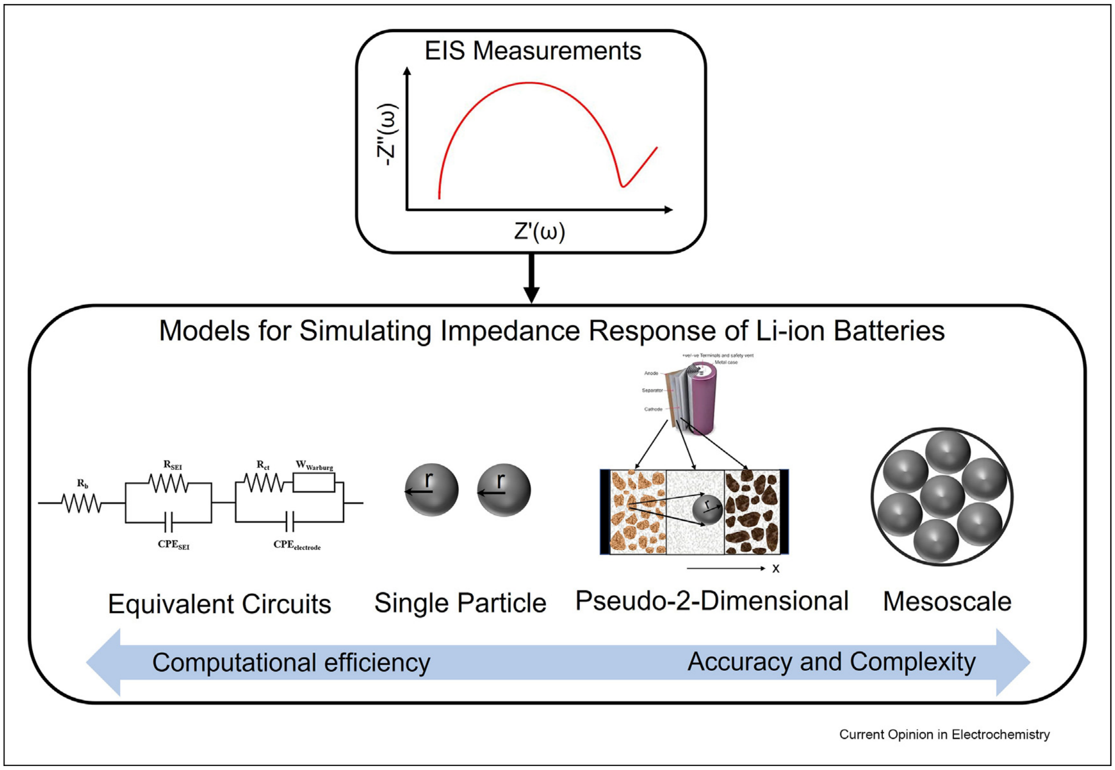
Introduction

The lithium-ion battery is a pivotal technology in the emerging sustainable energy landscape. Having dominated the electronics industry as a power source, it is now advancing toward the automobile and transportation sector. The optimization of a battery's design for a given application requires a fundamental understanding of the processes occurring inside it as precisely as possible. Electrochemical impedance spectroscopy (EIS) being a non-invasive technique [1] (due to the small amplitude input modulation) is a powerful diagnostic and prognostic tool for batteries. EIS deconvolutes electrochemical processes occurring simultaneously based on their characteristics phenomenological time scales [2]. In batteries, EIS has been used to measure the kinetics and transport properties of electrode materials [3,4] and evaluate degradation and capacitive loss mechanisms [5,6]. Several other studies reported the use of impedance spectra as a prediction and simulation tool for the estimation of state parameters, viz., state-of-charge (SOC) [7], state-of-health (SOH) [8], etc. The measured impedance data are influenced by physically distinct processes, including porous electrode effects [9], transient and nonlinear responses [10], and superposition of impedance response of different battery components [11]. Apart from these effects, there are additional data artifacts originating because of current collectors, battery terminals, and other peripheral components [12,13]. The major challenge associated with the use of EIS in a battery management system is the development of battery models that are computationally efficient, robust, and sufficiently accurate to predict and analyze the measured impedance response. This review first summarizes some of the recent research efforts that have been proposed to develop battery impedance models and then discusses different simulation strategies in the light of EIS's integration into model-based battery management systems (BMS).

Models for batteries

This section summarizes various impedance models available for lithium-ion batteries, evaluating the

Figure 1



Schematic representation of impedance models for lithium-ion batteries.

research efforts that have been introduced to improve these models. Figure 1 depicts the ways in which impedance models differ with respect to mathematical complexity, computational efficiency, and accuracy of their predictions.

Empirical models

Empirical models are based on a heuristic approach where the internal behavior of the battery is predicted by fitting sets of experimental data without considering physicochemical principles. Periodical measurement of impedance spectra of lithium-ion cells at different cycles, temperatures, and states of charge results in a vast amount of data that can be employed to find material parameters for implementation in a BMS. Samadani et al. [14] developed a Laplace transfer time-based model to predict the voltage of a Li-ion cell by fitting the impedance data with equivalent circuits (EC) considering each circuit element to be a function of SOCs and internal battery temperatures. Andre et al. [15] developed two empirical electrical models based on the parameters estimated by fitting impedance data recorded for a high-power 6.5 Ah lithium-ion cell in the temperature range from −30 °C to 50 °C for the entire SOC range. Several other empirical models have been developed based on EIS data to predict the remaining useful life [16], capacity fade [17], influence of different temperatures, C-rates on the charge—discharge profiles [18], etc. The low mathematical complexity of empirical models makes them computationally efficient. However, these models are constrained by their low accuracy and limited physical insights. Further, these models are based on fitting experimental data obtained under specific conditions; therefore, a high degree of empiricism is involved.

Single particle models

The single particle model (SPM) is considered a reasonable approach for understanding the battery impedance response. The basic SPM model considers intercalation kinetics and solid phase diffusion of electroactive species and ignores the diffusion of electroactive species in the solution phase for simplification. Li et al. [19] developed an impedance model based on a modified SPM with the inclusion of capacitance dispersion and growth of an insulating film on the anode. Impedance tests were conducted on two lithium-ion battery cells at two SOC levels (50% and 100%) at ambient temperature to study aging effects. It was observed that the faradaic impedance increases with cycles. The impedance of batteries at 50% SOC was smaller than at 100% SOC. Fang and Li [20] developed an analytical mechanics-modified impedance model considering the electro-chemo-mechanics of a single particle in lithium-ion batteries to include the stress effects. A control-oriented model was proposed by Riemann et al. [21] where the SPM and EC models were combined to describe the dynamics for a wider frequency range (10^-4 rad/s to 10^4 rad/s). This model was validated with experimental data of half cell (LMO cathode) and compared to pseudo-two-dimensional (P2D) simulation data. Howey et al. [22] investigated the identifiability and estimation of parameters of the SPM for lithium-ion battery simulation. It was demonstrated that only six independent parameters are necessary for full parameterization of a SPM model. An estimation algorithm (least square method) was implemented to obtain the transfer function of the linearized SPM model from experimental impedance data. Vivier et al. [23] derived an analytical expression for the impedance of a single insertion particle considering the insertion of lithium-ion in the graphite electrode and then extended the model for the porous electrode. Although significant research efforts have been made to improve the SPM, its utility remains under-explored compared to empirical models.

Pseudo-two-dimensional model

The Doyle−Fuller−Newman model [24], alternatively called the pseudo-two-dimensional (P2D) model, is by far the most accepted physics-based model by battery researchers. It offers a better illustration of battery functioning, effects of different transport and kinetic limitations, and physical insights compared to SPM and empirical models. This model is characterized by coupled partial differential equations (PDEs) describing charge conservation and mass conservation in the solid electrode and electrolyte. In addition, nonlinear algebraic equations describe the lithium-ion movement between the solid electrode and electrolyte phases. Solving these equations is time consuming and requires substantial computational resources.

Researchers have made continuous efforts to establish adequate models with enhanced computational efficiency, either by using order reduction approaches or formulating new numerical methods to solve P2D models. Kim et al. [25] proposed a multi-scale multi-domain (MSMD) model where spatial domains are partitioned into three domains, viz., particle, electrode, and cell domain in the ascending order of length scales. This partitioning prevents solving a large set of differential equations simultaneously, therefore, reducing the computational cost for each step. The computational efficiency of the MSMD model is further enhanced by using a separation of time scales principle to decompose model field variables [26]. Pathak et al. [27] developed a novel hybrid analytical-collocation approach to simulate the impedance response of lithium-ion batteries using the P2D model. The results were compared to numerical solutions obtained using the commercial solver COMSOL Multiphysics, and it was established that the proposed approach was superior in terms of accuracy, robustness, and computational efficiency. Kong et al. [28] established a modified P2D model to investigate the macroscopic effects of micro-internal short circuits (ISCr) by modifying the boundary condition for charge conservation. An impedance identification method was introduced to understand the impact of ISCr on cell impedance. Rahimian et al. [29] presented a numerically efficient sequential full order model (SFOM) by employing the finite volume method (FVM). Using the proposed approach, PDEs for lithium-ion transport were solved only once for each step instead of for each iteration, thus, reducing the model's computational complexity. The proposed model showed better computational efficiency over the same model implemented in the commercial finite element software, COMSOL. Teo et al. [30] developed a computationally efficient approach to simulate the dynamic electrochemical impedance response of lithium-ion batteries during charging and discharging using the P2D model. The timescale of the slow DC charge−discharge of a battery was separated from the fast local time scale of impedance measurement. This approach helps in understanding the physical processes that drive the difference between the stationary and dynamic response of the battery. Dynamic EIS can be used as an SOC indicator for diagnostic and control as DEIS signals are more sensitive to the states and parameters compared to standard EIS.

The need for more fundamental models emerges from the contemporary push toward functional and design improvements, such as modeling SEI growth and material loss [31], fast-charging protocols [32], and new age systems, such as solid-state batteries [33]. Kant et al. [34] developed a modular theoretical approach for the impedance response of solid electrolytes describing the dynamics of various processes in grain and grain boundaries. The system was partitioned into various interfacial modules, and the constitutive equation for each module was derived through the phenomenological ab-initio approach. The overall impedance of the system was obtained by the superposition of the dynamic impedance of the individual modules. The proposed theory was validated with the measured impedance data of cubic Ta-doped and Al-doped lithium lanthanum zirconium oxide (LLZO) [35]. Yuan et al. [36] presented a simplified P2D model by employing modified boundary conditions for the electrolyte diffusion equations. A reduced-order transfer function was obtained by simplifying the transcendental impedance solution using Padé approximation method. Their approach reported good accuracy for the prediction of electrolyte phase concentrations, with 0.8% and 0.24% modeling error, respectively, when compared to rigorous model under 1C-rate and urban dynamometer driving schedule.

An extension to linear EIS is the use of current or voltage perturbations with moderately larger amplitude driving the battery into a weakly nonlinear regimes. These nonlinear EIS (NLEIS) measurements are complementary to EIS, but they are more exhaustive in their ability to sense internal processes occuring in the battery. A recent review summarizing the research efforts in this domain was published earlier [37]. Notable research includes work by Murbach et al. [38] who reported second harmonic nonlinear impedance spectra for a commercial lithium-ion cell (1.5 Ah LiNMC|C). NLEIS experiments were corroborated with a NLEIS P2D impedance battery model [39] to analyze cell aging. It was shown that the nonlinear response of aged batteries (capacity loss <1%) exhibits a fundamentally different signature due to asymmetric charge transfer kinetics. This variation in transfer coefficients is not identifiable with standard EIS which is mainly sensitive to changes in charge transfer rates. Wolff et al. [40] conducted a SPM-based investigation to study the transient and steady-state behavior of a battery by applying nonlinear frequency response analysis.

Mesoscale models

Understanding the mesoscale phenomena, viz., chemical and electrochemical reactions, structural stability, degradation, etc., is critical to improve the performance of electrochemical devices. The physicochemical processes occurring within the porous media and at the electrode/electrolyte interface at very small length scales, typically in the range of microns to millimeters, are considered mesoscale phenomena. Several experimental and theoretical studies have been conducted to understand the mesoscale phenomena in the context of Li-ion batteries.

Sangaranarayanan et al. [41] investigated the shape-dependent electrocatalytic performance of rose, splintery, chrysanthemum flower, and thorn-like structures of palladium deposited on indium-tin-oxide substrates using cyclic voltammetry and impedance spectroscopy. Kant et al. [42] proposed a method to estimate the surface roughness and morphological convexity based on in situ EIS method. Ansah et al. [43] developed a pseudo-mesoscale finite element model to study the effect of particle size and porosity considering the impedance and charge−discharge profile of an NMC622 cathode. Hein et al. [44] combined microstructure resolved simulations with impedance measurements on symmetrical cells to identify the influence of the carbon binder domain (CBD) distribution in Li-ion batteries. Al-Zubaidi et al. [45] worked on investigating aging mechanisms by combining impedance spectroscopy and finite element modeling, complemented by microscopy data [45]. Precision and accuracy are very important for meso-scale models, and a recent paper from our group shows the need for 1000x1000 grids for precise phase-field models for lithium-metal batteries [46].

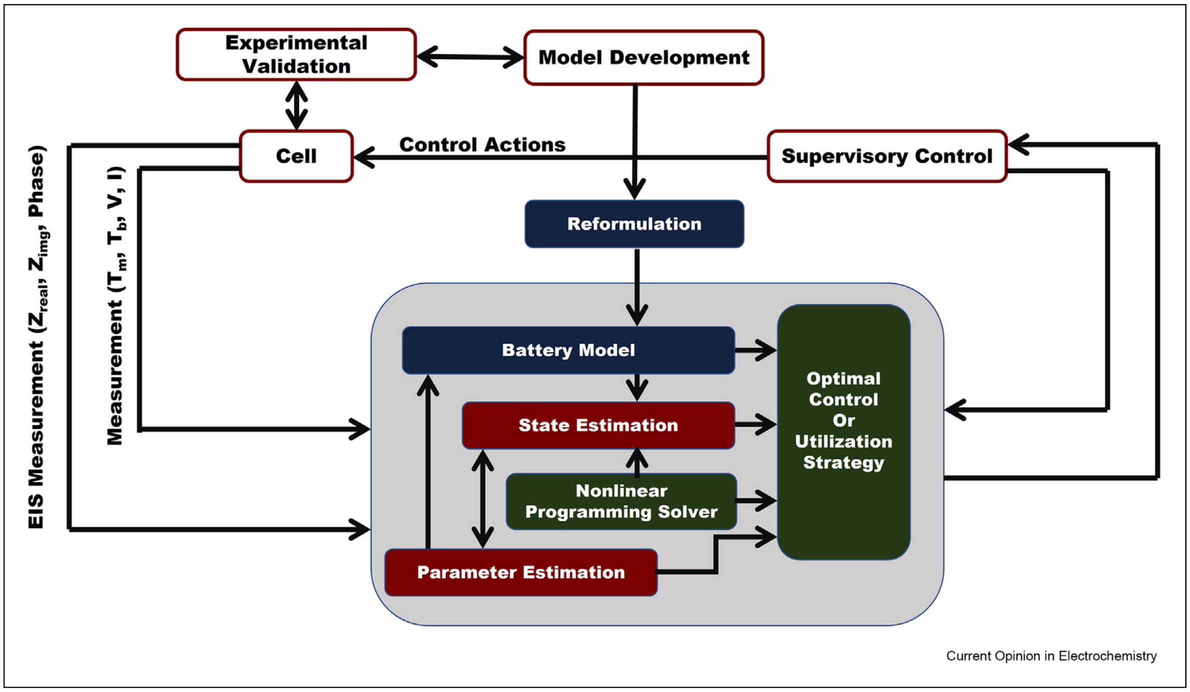
Analysis of impedance data using battery models to identify parameters and electrochemical mechanisms that describes the internal states of the battery under different operating condition is imperative to understand the overall dynamics of the battery. In the section, we discuss the integration of EIS data in a proposed model-based BMS.

BMS and state/parameter estimation

Model-based BMS provides essential life cycle monitoring and control for safe operation and improved performance of batteries/battery packs. The key job of a BMS is to monitor temperature and predict SOC, SOH, and level of degradation. Being a nondestructive battery characterization technique, EIS has a great potential to be integrated into a BMS. Data from EIS measurements can be readily interpreted using battery models to obtain key parameters, such as diffusivity, conductivity, activation energy, and reaction rate constants which are useful to obtain relevant battery metrics [47]. Figure 2 shows a proposed BMS architecture with integrated EIS measurement.

Critical components of the model-based BMS include the model, its efficient simulation, and parameter and state estimation approaches based on optimization. As discussed earlier, EC models are simple and computationally inexpensive which is ideal for a BMS. Some of the recent efforts have focused on the use of the distribution of relaxation time (DRT) technique that deconvolutes EIS measurements by magnifying the polarization effects overlapped in the frequency domain by a peak-based representation for analyzing EIS data [49,50]. Fractional order EC modeling has proven to be better than integer order EC modeling in accurately describing charge transfer, double layer, and mass transfer of species in the battery [51,52]. Recent efforts have reported low error margins as low as 1% in SOH estimation using this technique [53,54]. Physics-based models can be reformulated to reduce the computational complexities and cost by using fast numerical techniques [29] as well as reducing the full order models [36] as elucidated in section 2. Recent efforts in SPMs include applying metaheuristic approaches such as genetic algorithms to achieve lower computational cost [55]. Reformulated P2D models have been applied to simulate the EIS response of batteries in both linear and nonlinear regime [27,30]. Figure 3 shows the ability of the P2D model to replicate the charge-discharge behaviour as well as the EIS spectrum of batteries at different SOCs using robust and efficient parameter estimation algorithms developed in our group. Several

Figure 2



Proposed BMS architecture with integrated EIS. Note that depending on the equipment used, the impedance signals can be embedded into simple charge–discharge curves without the need for additional equipment. This requires more sophisticated model analysis and transient simulation of EIS. Fast simulation and efficient reformulation of models enables faster estimation of identifiable parameters as illustrated in a recent paper by Kolluri et al. [48].

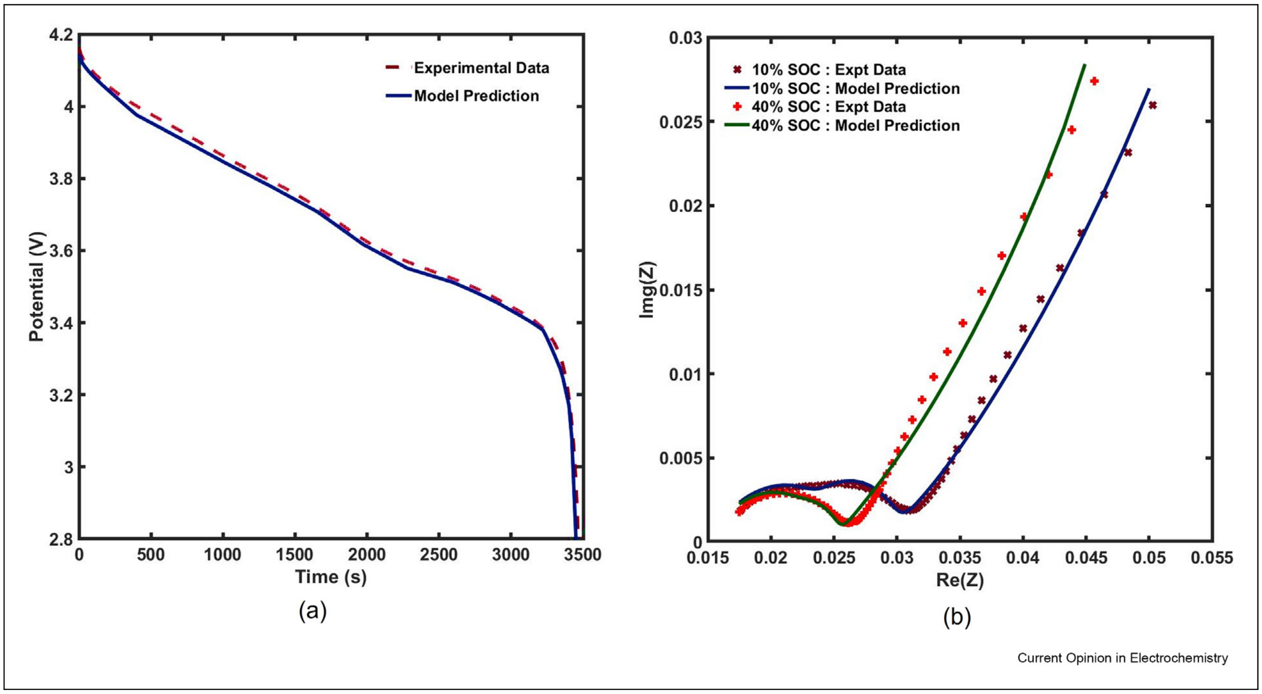
researchers have also worked on various experimental approaches and fitting algorithms for accurate parameterization of P2D models [56–58].

An interesting experimental approach have used a Newton–Raphson-based algorithm to obtain the phase of impedance at the zero-crossing frequency which was shown to corresponds to the internal temperature of a Li-ion battery [59,60]. Recently, Probabilistic machine learning (ML) models have been coupled with EIS to predict future capacities in batteries without prior knowledge of cycling activity [61,62]. ML techniques, such as Gaussian process regression [63], random forest [64], and deep neural networks [65], have been applied to the EIS data with varying degrees of accuracy in estimating SOC and SOH of batteries.

Perspectives on future research and challenges

1. If potential and concentration fields are solved simultaneously, this requires careful calibration of RC elements as described in a recent paper on ionic-electronic conducting electrodes [66]. In general, a more complicated model is required when there are more than one diffusing species in the system. Most binary electrolyte solutions can be recast as a standard model for the total electrolyte concentration [67]. But beyond binary electrolytes, models get more involved requiring a numerical simulation approach.
2. When there is more than one dimension involved with realistic boundary conditions, numerical approaches are needed. Challenges in moving to multiscale and multidomain models involve strategies for tackling local singularities, boundary layers, and/or moving boundaries [68].
3. For the next-generation chemistries, such as Li-metal and LiS, the development of mesoscale impedance models is imperative to account for the effect of the moving boundaries, phase separations, particle cracking, and surface roughness. This brings new challenges in terms of choice of the numerical approaches, parameters, underlying mechanisms, and insufficient grid resolution in multi-dimensions [46,69].
4. Future research will identify new hardware, software, and algorithms that would enable cheap and real-time simulations, robust parameter estimations, and online feedbacks. Accuracy of experimental measurement is important to correctly parameterize battery models which would require considerable efforts in experimental precision across a wide range of chemistries and battery/battery pack sizes [56,58].

Figure 3



Parameters estimation for (**a**) discharge curves and (**b**) impedance analysis. Parameters were estimated using the P2D model for the experimental data obtained from commercial cells. The experimental data and the relevant model parameters used for simulations are available from Battgenie Inc.

5. Nonlinear EIS in conjunction with EIS can prove to be a more effective diagnostic tool for the batteries. Nonlinear EIS can identify more information from higher harmonics. However, simulating impedance response in the nonlinear purturbation regimeinherently requires more sophisticated numerical approaches [30,37,40].
6. The emergence of data-driven predictive technique, such as ML, is proving as another tool in interpreting EIS data for estimating battery parameters. With increasing computational power, these techniques can potentially drive the future direction of EIS research in batteries [62].
7. EIS measurements are presently conducted in laboratories requiring significantly expensive equipment. Therefore, development of a low cost, power efficient chip-level technology that makes in-situ, real-time EIS measurements possible at the cell, module, and pack level is pivotal. A potential path forward is manufacturing of an EIS chip with strong noise rejection and the ability to measure AC μVolt excursions in real time.

Summary

EIS is a powerful, non-invasive technique to investigate a battery's electrochemical behavior. A significant research effort is being concentrated toward developing reduced-order multiphysics and multiscale models that are discussed in the present work. BMS is an indispensable part of modern battery systems in energy and storage applications, and EIS is expected to play a critical role either offline with a separate experiment/hardware or online with an integrated BMS architecture that is model-based and is built on real-time simulation and estimation of charge−discharge curves and impedance data.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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** of outstanding interest

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This publication provides a framework for the interpretation of dynamic impedance using the standard P2D model. Two interesting approaches based on: (i) Brute force time domain calculations of fully nonlinear equations and (ii) Time separated method that solves “slow” DC charge/discharge dynamics and “fast” AC dynamics separately are presented. The method allows for investigation into specific physicochemical processes that drive the difference between dynamic and stationary behavior of the battery.

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This publication reports a reduced order physics-based model for all-solid-state batteries. Padé approximation method is employed to transform the transcendental transfer functions into lower order fractional transfer functions. By analyzing frequency response of transfer functions, a third order Padé approximation is chosen to achieve better accuracy with a low computational cost. The calculation time per step was found to be within 0.2 ms.

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