



# Prediction of Electrolyte Conductivity: Results from a Generalized Molecular Model Based on Ion Solvation and a Chemical Physics Framework



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## ABSTRACT

Ionic conductivity is a foremost transport property that is extensively used to characterize and screen electrolyte systems. Although bulk measurements are done on the macroscopic scale, electrolytic conductivity has its foundation on molecular-scale interactions between solvent and ionic species. Correct interpretations of these molecular interactions and related quantities enable a balanced, comprehensive understanding of conductivity behavior with respect to system conditions (solvent composition, salt concentration and temperature). This work introduces a new methodology that achieves accurate predictions of electrolyte conductivity for a wide range of conditions, based on molecular, physical, and chemical terms. The formalism is universal, making it valid for aqueous and non-aqueous systems alike. The immediate application of the resultant model is candidate electrolytes for lithium-ion and sodium-ion batteries, although many other applications abound for systems that utilize liquid electrolytes. Conductivity predictions are compared to experimental data for a number of electrolytes over a wide range of conditions, demonstrating that exceptional accuracy is attained because the robust model captures multiple salient contributions to conductivity behavior. Model accuracy is well maintained over multi-solvent systems and for extended salt concentrations.

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## 1. Introduction

Without question, electrolytic conductivity is the chief transport property used to evaluate candidate electrolyte systems for a number of electrochemical energy storage devices (batteries, capacitors, etc.). Conductivity trends over electrolyte composition and temperature are a unique “thumbprint” of a given chemical system. However, conductivity can exhibit complex behavior that is often poorly understood or misunderstood, and thus was treated by empirical or semi-empirical methods in early works [1,2]. Thus, a more rigorous, robust approach is needed to describe electrolytic conductivity that accounts for key contributions stemming from molecular scale interactions. This work addresses this need by considering key phenomena that influence conductivity: solvent-ion interactions (ion solvation) and solvated ion sizes, ion-ion interactions (ion association and electrostatic interactions), viscosity, counter-ion transport, ionic hopping and ionic random motion effects. Conductivity predictions are performed within a larger electrolytes modeling package known as the Advanced Electrolyte

Model (AEM), a contemporary modeling tool developed under the US DOE Advanced Technology Development Program. One advantage of this modeling approach lies in its usage as an exploratory screening tool that can quickly determine optimal electrolyte compositions based on conductivity profiles or other parameters, as assessed over ranges of salt concentration, solvent composition, and temperature. Through the AEM, conductivity and other property predictions can now be made under numerous conditions for electrolytes that perhaps have not yet been studied or sparingly studied due to resource limitations. Within the larger modeling architecture developed by the author, conductivity is just one of many properties provided under a genomic-level investigation.

Herein the focus of the model predictions is battery electrolytes for Li-ion and Na-ion cells, although the modeling framework can be easily adapted to other non-battery applications. The systems of interest include solvents such as propylene carbonate (PC), ethylene carbonate (EC), mono-fluoro ethylene carbonate (FEC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), gamma butyrolactone (GBL), ethyl acetate (EA), 1,2 dimethoxyethane (DME), methyl butyrate (MB) and ethyl propionate (EP). Salts investigated include lithium hexafluorophosphate (LiPF<sub>6</sub>), lithium bis(fluorosulfonyl)imide (LiFSI), lithium

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bis(trifluoromethanesulfonyl)imide (LiTFSI), and lithium bis(oxalate)borate (LiBOB), as well as some Na-ion counterparts to these salts. The AEM component library contains these and other compounds relevant to battery applications.

## 2. Theoretical Basis

### 2.1. Overview of Approach

The passage of current through an electrolyte liquid is facilitated by the movement of free ions within the liquid. However, “free ions” experience a number of constraining influences as they move throughout the electrolyte region, wherein the environment imposes interactive molecular effects (solvent-to-ion, ion-to-ion, and solvent-to-solvent) that ultimately determine the efficiency of transport for a particular set of positive and negative ions. In a theoretical sense, capturing the realities of conductivity behavior for electrolyte systems is an enormous challenge using a molecular-based modeling approach. Accurate concepts are those that target the foremost parameters that describe the various molecular-scale interactions and how they impact bulk macro-scale properties such as viscosity, conductivity, activity coefficients, etc.

Fig. 1 shows the general approach developed by this work to predict solution conductivity, speaking to the complex interplay of parameters tied to this property. It is seen that ion solvation plays a seminal role in Fig. 1, emphasizing the importance of ion solvation phenomena in electrolyte behavior. Noteworthy influences on conductivity include solvent-ion interactions (sometimes termed as dielectric drag or friction), viscosity, ion association, counter-ion transport, random motion of ions, ion skipping (hopping) and other colligative effects. The modeling approach developed herein is universal in that it treats all electrolytes with the same set of governing equations, and hence, is unbiased toward the chemical system under investigation.

### 2.2. Chemical Physics Framework

Many important molecular processes involving battery electrolytes occur at spatial scales from 1–100 nm and timescales in the 1–100 ns range. Lithium desolvation and transport through surface-to-electrolyte interphase (SEI) films are examples of processes that can become rate limiting at particular conditions, such as at low temperatures or high cycling rates. In other cases, determination of macroscale properties (e.g., conductivity) by *ab initio* techniques may require an extensive sampling of molecular microstates to achieve adequate resolution of an average value at the chosen

conditions. Added to this is the high variability that electrolyte regions can undergo during cell operations, such as in the double layer (DL) wherein properties change over the span of several seconds, minutes or hours according to the electrolyte concentration gradients that develop therein. In general, *ab initio* techniques have practical limits not capable of resolving dynamic molecular interactions well into the ns region, and they can't be economically used to render a comprehensive list of properties over broad range of conditions seen within the DL or for other optimization tasks. Thus, a more robust approach is required to gain information of meaningful fidelity at a fraction of the computing time of DFT/MD methods to enable same-day evaluation of perhaps thousands of conditions for systems of interest. Contemporary chemical physics (statistical-mechanical) models provide a powerful approach toward quantifying molecular-scale behavior in multi-component electrolytes and other chemical systems [3–13], and can provide highly detailed analysis on a number of key metrics pertinent to electrochemical systems.

The chemical physics or statistical-mechanical basis of the modeling approach herein is found in the non-primitive non-restricted associative form of the Mean Spherical Approximation (NPNRAMSA), a powerful computational approach to accurate interpretation of chemical physics behind real electrolyte systems. The NPNRAMSA enables robust predictions over solvent composition, salt concentration, temperature, and permittivity domains. Associative forms of MSA have been used with good success in predicting properties of non-ideal aqueous and non-aqueous electrolytes that undergo noteworthy ion association [9]. The NPNRAMSA form captures explicit information regarding solvated ion sizes and incorporates an exponential modification to MSA that corrects for inherent inadequacies of the original MSA theory [12–16], and allows for application of MSA to very high salt concentrations.

Overall, molecular scale interactions are considered within a framework that incorporates pertinent chemical, physical, and colligative contributions of the various species. Foremost initial parameters for NPNRAMSA include solvated ion sizes, solution densities, permittivity, temperature, ionic number densities, and thermodynamic governing equations covering ion association (e.g., ion pair formation) under equilibrium conditions. Effects from ion solvation are explicitly considered in terms of reference solvent residence times and average ion-solvent ligand distances, both of which influence the effective solvated ionic radii. Regarding the “non-primitive” attribute of this modeling approach, the solution and solvent permittivity quantities are treated directly as colligative properties over salt concentration, wherein the change (decrease) of permittivity due to the presence of ions is explicitly derived and tied to Mass Action Law expressions for electrolyte species. Lastly, through NPNRAMSA the AEM estimates ion pair and ion triplet populations, as well as the onset of solid solvate formation. It is important to quantify these species because they can act as precursors to precipitated solids, and impact the effective ionic strength (and related conductivity) of an electrolyte solution. It should be noted that the NPNRAMSA as developed here is not limited to symmetric electrolytes (e.g., 1:1), but can be applied to any ionic stoichiometry in the native salt (1:1, 2:2, 1:2, 2:1, etc.). For example, the AEM has been successfully applied to electrolytes containing the salt  $\text{Li}_2\text{B}_{12}\text{F}_{12}$ .

Chemical physics models such as the AEM are inherently very fast and efficient on a computational basis. This is due to time-averaged values of metrics for key molecular interactions that are assigned up front. For example, the AEM provides accurate rendering of a large set of diverse properties on the order of  $\geq 10^6$  quicker than density functional theory (DFT) and molecular dynamics (MD) counterparts, and provides some macroscale properties typically out of reach of the *ab initio* techniques. With

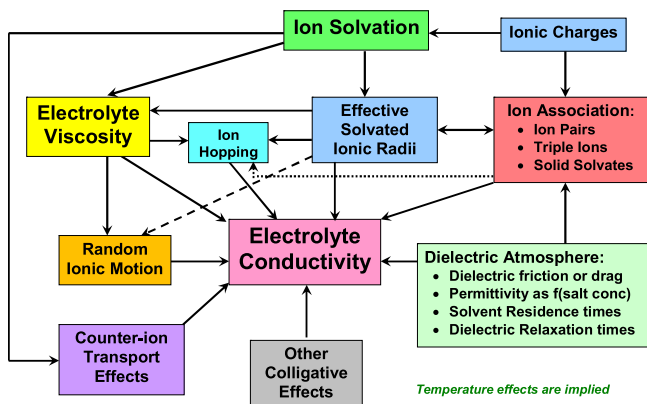


Fig. 1. Relationship of contributing factors to ionic conductivity, as incorporated into the AEM modeling approach. Ion solvation is a foundational attribute that underlies many aspects of electrolyte conductivity.

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