

COMMENTARY

The Electrolyte Frontier: A Manifesto

Chibueze V. Amanchukwu^{1,*}



Chibueze is currently an assistant professor at the Pritzker School of Molecular Engineering at the University of Chicago where his research group focuses on tackling the challenges (some of which are detailed here) related to electrolytes for energy storage and electrocatalysis. He obtained his PhD from the Massachusetts Institute of Technology (MIT), did his postdoctoral work at Stanford University, and was a visiting fellow at the University of Cambridge (UK). His PhD and postdoctoral work focused on understanding electrolyte instability and designing new electrolytes for lithium-air and lithium-metal batteries.

Introduction

From the oceans to the soil to our blood, electrolytes permeate our world. In simple terms, any medium with ions present is an electrolyte. In electrochemistry, the electrolyte supports ion transport and is a vital component of electrochemical energy storage and conversion systems. However, it is frequently less studied compared to the negative and positive electrodes. One reason may be because the electrochemical reactions happen at the electrode surfaces, albeit at the electro-

de:electrolyte interface. Decades of work have been funneled into fabricating novel nanostructures with shape, size, compositional, and morphological control—tuning electronic structures in the electrodes for both battery and catalysis applications. Unfortunately, most battery research today is limited by electrolyte design and selection. For example, lithium (Li)-air batteries have been touted as the holy grail of batteries (order-of-magnitude increase in energy density); however, electrolyte instability in the presence of reaction intermediates and product has stunted Li-air progress.¹ Electrolyte reactivity and consumption is a challenge for today's Li-ion batteries, limiting fast charging possibilities, as well as for silicon and Li metal-based anodes. Controlling ion (de)solvation is the rate limiting step in multivalent batteries (Mg^{2+} , Ca^{2+}) and in Li-sulfur batteries, where controlling polysulfide intermediate solubility is vital.² These challenges are not limited to batteries. For catalytic applications such as CO_2 reduction, increasing CO_2 solubility in the electrolyte (for improved mass transport) as well as extending the stability window of the electrolyte significantly affect achievable current densities and product selectivity. With all these challenges pointing toward the need for novel electrolyte design, we need to explore the electrolyte frontier and push our current understanding of electrolyte chemistry. Here follows a manifesto.

A Little Bit of Semantics

To enable an understanding of this piece, I will be making a distinction between two approaches to electrolyte design and analyzing how we can start exploring the frontier (Figure 1). I define *electrolyte engineering* as the combination (typically physical mixtures) of commonly used salts and solvents to obtain some linear improvement in properties such as viscosity, dielectric

constant, and ultimately, ionic conductivity. In contrast, *electrolyte chemistry* is the bottom-up design of novel compounds and salts that ultimately allow for finer control of properties such as electrochemical stability and mechanical properties beyond ion conductivity. I make this distinction because electrolyte engineering approaches often fail to give insight into molecule-property relationships beyond the exact compounds studied. Let me use the evolution of the Li-ion battery and the ethylene carbonate:propylene carbonate (EC:PC) debate to make this distinction.³ During the earlier development of Li-ion batteries, PC was heavily used as the solvent in the electrolyte because of its high dielectric constant and subsequently high ion conductivity. However, PC co-intercalation within graphite destroyed the weak van der Waals interaction holding the graphene sheets in graphite, leading to quicker capacity fade. An electrolyte chemistry approach was the switch to EC to prevent co-intercalation and to control the generated anodic solid electrolyte interface (SEI). An electrolyte engineering approach is the addition of diethyl carbonate (DEC) or dimethylcarbonate (DMC) to modulate viscosity, wetting, and ionic conductivity. The incorporation of additives (e.g., $LiPO_2F_2$, fluoroethylene carbonate) with sole focus on performance metrics such as “capacity versus cycle number,” but no understanding of the reaction mechanisms underlying the improved electrolyte, is an electrolyte engineering approach. While both approaches are vital for advancing and commercializing batteries, electrolyte chemistry should come first because a focus on understanding can spur entire new electrolyte classes. Then, new compounds (small molecules, polymers, ceramics, glasses) can be designed and synthesized to address the challenges of (de)solvation, electro(chemical) instability, mechanical (in)stability,

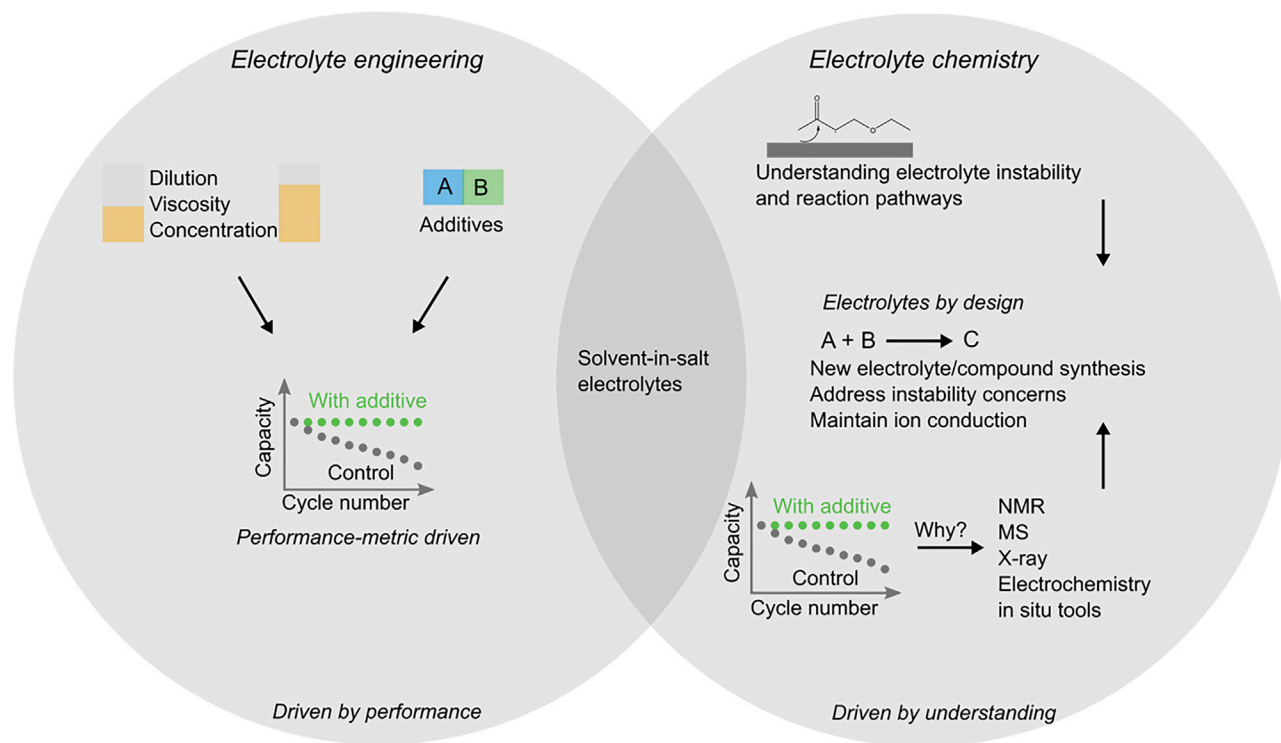


Figure 1. Electrolyte Engineering versus Electrolyte Chemistry

Venn diagram illustrating the differences between electrolyte engineering and electrolyte chemistry approaches for electrochemistry. Dilutions and concentration modifications to tune ionic conductivity and the blind use of additives solely focusing on performance metrics (e.g., capacity versus cycle number) is classified as *electrolyte engineering*. Meanwhile, *electrolyte chemistry* is motivated by an understanding of electrolyte instability and reaction pathways. Additives used with an understanding of *why* there is an improvement can lead to new electrolytes and compounds designed to address the limitations of current systems. Solvent-in-salt electrolytes intersect both definitions.

ion conductivity, etc. as the application demands. Once we have amassed an improved toolset, engineering approaches from mixtures to additives can then find fruitful ground.

A recent advance in electrolytes has been the development of “solvent-in-salt” or “solvate ionic liquid” that exploit high salt concentrations within the electrolyte to reduce the “free-solvent” concentration and modulate intermediate solubility and electrochemical stability even while giving up on some ion conductivity (Figure 1).⁴ This blends electrolyte engineering (typical salts, solvents, increasing salt concentration) with electrolyte chemistry (reduce free-solvent concentration, optimize properties beyond ion transport) and straddles my definition. While the semantics are arguable, the challenges facing electrolytes and

their importance in next-generation energy storage and conversion technologies are not. New ideas and approaches that push electrolyte science into a new frontier are urgently needed.

Instability as a Guide

Electro(chemical) instability has been the rule of law in both commercial and next-generation batteries to date, severely limiting capacity, power, and cycle life. Despite this, seldom works focus on understanding electrolyte degradation mechanisms and pathways. For example, functional group type (donor number, acceptor number, Hammett constant)¹ can be correlated to oxidative and reductive stability of electrolyte combinations (salt + solvent) instead of just solvent alone. It is known that salt choice and concentration play a significant

role in total electrolyte stability. Once degradation pathways are proposed, it is vital to start incorporating nuclear magnetic resonance (NMR) spectroscopy (solution and solid) and mass spectrometry (MS) to verify proposed mechanisms. Here, *in situ* methodologies (e.g., with combined differential electrochemical mass spectrometry [DEMS]) are quite important to decipher chemical (induced by O₂, HF) versus electrochemical stability (induced by potential).⁵ Molecular dynamics (coupled with density functional theory [DFT]) can then provide additional insight, energy barriers, and verification or rebuttal of proposed experimental pathways. Because electrolyte instability is often the most pressing barrier in electrolyte selection and longevity, it is important that a thorough understanding of (and hopefully predicting) electrolyte

reactivity will serve as an important first step in the electrolyte frontier.²

Compounds by Design

If instability were the only metric for electrolyte selection, then one would just use nonpolar compounds. But the requirement of ion dissociation and conductivity necessitates the presence of polar functional groups (e.g., carbonyl, nitrile, sulfone). Herein lies the dilemma. These polar functional groups, by virtue of their ability to solvate salts, are also susceptible to undesired oxidative or reductive reactions at the electrode surface. Decoupling instability from desired ionic conductivity is an important frontier in electrolyte design for both solid and liquid electrolytes. Innovative approaches such as the exploitation of molecular orientation and steric hindrance to “hide” vulnerable polar functional groups from the electrode surface, but still support ion transport, will be quite exciting. Tools such as sum frequency generation (SFG) would find great utility with this approach.⁶

Other important properties to decouple are mechanical stability from conductivity. As solid-state electrolytes have garnered fervent research and commercial interest, their benefits beyond nonflammability/safety need to be clearly elucidated.⁷ If nonflammability/safety is the key driver for solid-state electrolyte research, the use of ionic liquids or design of intrinsically nonflammable ionically conductive liquids should be of great interest because it will allow use of current manufacturing processes and expertise. Supramolecular polymer electrolytes to combine tailorable mechanical properties with the fluidity required for vehicular-assisted ion motion should also be pursued. Certain applications (e.g., wearables) may require solid-state electrolytes to enable different battery and application form factors. While the synthesis of new inorganic solid-state electrolytes is needed,

more work is needed in understanding the electrode-electrolyte interface (e.g., with *in situ* tools) and controlling reactivity between the anode (e.g., Li metal) and the inorganic electrolyte. An approach to modulate the solid-solid interface has focused on the study of hybrid solid-state electrolytes (polymer and inorganic). However, new approaches beyond the simple mixing of glasses/ceramics (which have high room temperature [RT] ionic conductivity but poor mechanical properties) with polymers (poor RT conductivity but robust mechanical properties) to form hybrids are needed because recent works have shown that conductivity is dominated by the poor polymer-phase ion mobility. One exciting approach involves glasses designed with controlled polymer “defects” to dissipate any strain-induced stresses to prevent fracture, while still supporting ion transport through the glass phase.

Regarding design, we can envision an electrolyte future that is not just passive (allow ion transport, don't degrade, stay mechanically stable) but active. “Smart electrolytes” can be designed to respond actively to changes in cell temperature, current rate, reaction intermediate/electrode dissolution, etc. The separator/electrolyte can also be engineered to provide insight into battery state of health and allow for prediction of cycle life.⁵

The Forgotten Half of the Catalyst: Electrolyte Interface

The strategies discussed above for electrolyte selection in energy storage can also be exploited in electrocatalytic systems. The availability of cheap renewable energy has galvanized interest in using electricity (instead of temperature and pressure) to convert raw materials into valuable products. One electrocatalytic process of great interest is CO₂ conversion because it eliminates the greenhouse gas from the atmosphere and also generates

valuable products. Aqueous CO₂ reduction is currently state of the art but is limited primarily by the competing hydrogen evolution reaction (HER) and mass transport limitations.⁸ While advanced catalyst designs such as alloys, nanostructure size, and crystal orientation are of great interest, it is often underappreciated that the electrocatalyst is always in contact with the electrolyte and that electrolyte design strategies can play a vital role in addressing these challenges. Using *instability as a guide*, nonaqueous electrolytes (e.g., acetonitrile, carbonates) with wider electrochemical stability windows should be explored. By suppressing HER, different catalysts previously discarded due to their propensity for HER can now be studied to tune product selectivity. Here, a *compound by design* strategy may allow for electrolyte selection depending on the valuable product of interest. Compared to water, CO₂ has an order-of-magnitude solubility in nonaqueous solvents that can mitigate mass transport limitations and increase CO₂ accessibility at the electrode surface. Furthermore, a vapor-fed CO₂ stream (avoiding solubility in any media) can be coupled with solid electrolytes to alleviate downstream separation costs. Understanding the influence of nonaqueous electrolytes on CO₂ reduction, reaction mechanisms, electrochemical stability, product selectivity, and faradaic efficiency among other figures of merit is the epitome of an electrolyte design strategy for electrocatalysis.

Garbage In, Garbage Out

The data revolution is upon us, and it behooves us as a community to seize the opportunities it provides. The ability to computationally screen millions of compounds has been a boon to materials science with success stories like the Materials Genome Project. More recently, the Electrolyte Genome Project was established by the same authors to tackle the challenges facing electrolytes for batteries by

Database consisting of *experimentally measured* electrolyte properties

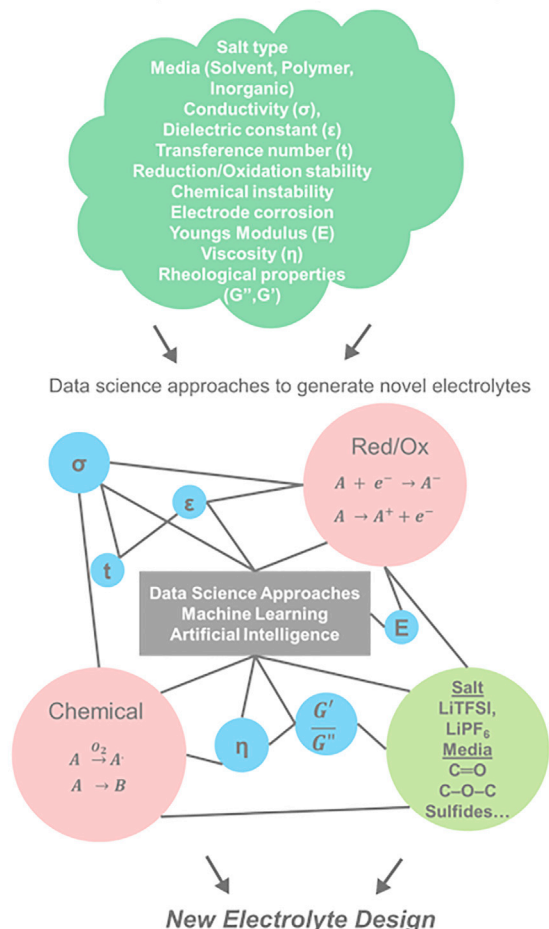


Figure 2. Data Science for Electrolyte Design

First, a database consisting of experimentally measured electrolyte properties must be created and curated with accurately measured data. Then, machine learning and artificial intelligence tools can be incorporated to generate new electrolyte designs.

using DFT and other computational techniques to better understand electrochemical stability, ionic solvation, SEI, and other properties of interest.⁹ While these computational approaches are excellent, they continually need to be validated and benchmarked by experimental studies. To push the electrolyte frontier regarding the data revolution, I make two proposals. First, measurement and reporting protocols need to be set for properties such as oxidative and reductive stability, lithium transference number, ionic conductivity, etc. to eliminate discrepancies between published work. The approach by the US Department of

Energy (DOE)-sponsored Battery 500 community to define protocols for measuring coulombic efficiency is a model approach that should enable comparisons among researchers around the world.¹⁰ Second, it is important to create a database consisting of all electrolytes with experimentally measured properties such as Red/Ox stability, conductivity, transference number, viscosity, and dielectric constant (Figure 2). This database will go beyond simple solvent properties that are currently tabulated in the Cambridge Structural Database and similar repositories. The recent paper by Jain et al.¹¹ that showed that natural lan-

guage processing (NLP) algorithms can be designed to “read” the published literature should allow for the use of Big Data techniques to scan the published electrolyte literature and collate all the required properties. Furthermore, high-throughput screening tools typically used in biological-based research can be deployed for rapid screening of electrolyte properties. With a database (with accurate datasets), emerging computational methodologies, like machine learning and artificial intelligence tools, can then be used to provide design principles for electrolyte design at both the chemistry and engineering levels based on the plethora of investigations done in the literature on electrolyte instabilities. In addition, approaches like AIRSS (*ab initio* random structure searching) could be explored to predict new electrolytes with structures that go beyond those currently known. One cannot truly begin to explore the electrolyte frontier until one knows, documents, and understands the past.

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¹Pritzker School of Molecular Engineering, University of Chicago, Chicago, IL 60637, USA

*Correspondence: chibueze@uchicago.edu
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