

# Towards More Stable and Ion-Conductive Organic Electrolytes for Rechargeable Batteries

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## Introduction

The global society urgently needs to remedy the effects of climate change resulting from burning fossil fuels and significantly increase the utilization of renewable energy. Rechargeable batteries are important enablers of sustainable energy use, as they can be employed to store energy generated from renewable but intermittent source. Enhancing the functionality of battery electrolytes, such as (electro)chemical stability and ion conductivity, can improve battery energy density, operation efficiency, and safety. This project explores strategies to improve the stability and ion conductivity of organic electrolytes for rechargeable batteries. Special attention is given to aprotic lithium-oxygen (Li-O<sub>2</sub>) batteries, which offer theoretical energy densities that are 2 to 4 times increase over the state-of-the-art Li-ion batteries (LIBs). Currently, the practical development of rechargeable Li-O<sub>2</sub> batteries is hindered by severe electrolyte degradations. Numerous families of organic solvents, polymers, and ionic liquids have been evaluated as electrolyte candidates; none are stable against the oxygen electrode in Li-O<sub>2</sub> batteries. Moreover, the decomposition pathways of many molecules are poorly understood. This project is aimed at understanding the fundamental principles underpinning the (electro)chemical stability and ion conductivity of organic electrolytes for high energy density batteries such as Li-O<sub>2</sub> and lithium-ion batteries, and exploring strategies to improve these functionalities.

## Results

We systematically investigated the chemical modification of the bis(trifluoromethanesulfonyl)-imide (TFSI) anion that leads to a family of new salts that we call FAST (Fluorinated Aryl Sulfonimide Iagged) salts.<sup>1,2</sup> This family of FAST salts employs alkoxy (-O-), piperidinyl (-N-), sulfide (-S-), sulfoxide (-SO-), and sulfone (-SO<sub>2</sub>-) functionalities, and allows us to systematically

study chemical and electrochemical stability as well as degree of salt dissociation, which correlates with charge carrier density, as a function of salt molecular structures. In particular, we observed excellent electrochemical oxidative stability and dissociation (i.e., high ion conductivity in organic solutions) in the sulfone-based FAST salts, highlighting their promising use in high voltage cathode Li batteries. Additionally, unlike TFSI which is chemically inert, FAST salts can be easily modified and incorporated into other molecules or polymers to obtain solid-state single-ion conducting electrolytes, which can find applications in potentially safer and more stable energy storage devices. Additionally, we explored the application of dissociative and stable FAST salts in equimolar mixtures with tetraglyme (G4) to form solvate ionic liquids (SILs). The stability of complexation between G4 and  $\text{Li}^+$  in these equimolar mixtures was quantitatively evaluated using thermogravimetric analysis (TGA). The strong complexation between G4 molecules and  $\text{Li}^+$  in such equimolar mixtures significantly enhances the thermal and electrochemical stability of the G4 solvent, and should improve the utility of G4-based electrolytes in Li batteries employing high voltage cathodes.

As discussed earlier, the practical development of rechargeable  $\text{Li-O}_2$  batteries is hindered by severe electrolyte degradations. To address these challenges, we develop computational and experimental tests to aid the search and design of stable and ion-conductive organic electrolytes for aprotic  $\text{Li-O}_2$  batteries. To understand structure-stability relationships, we first developed a comprehensive stability framework, called BANE,<sup>3</sup> based on four descriptors: Bond dissociation energy (BDE), Acidity or deprotonation free energy ( $\Delta G_{\text{deprot}}$ ), Nucleophilic reaction free energy ( $\Delta G_{\text{nuc}}$ ), and Electrochemical stability window (i.e., redox potentials). These stability descriptors were selected based on in-depth literature review on the dominant parasitic reaction pathways reported in aprotic  $\text{Li-O}_2$  batteries thus far. We utilized hybrid functional Density functional theory (DFT) to compute the aforementioned stability descriptors associated with a library of commercially available molecules with varied functionalities. Additionally, the chemical stability of the molecules was investigated experimentally under conditions mimicking the oxygen electrode environment in a typical aprotic  $\text{Li-O}_2$  cell. The DFT-predicted and experimental results were in great agreement. This comprehensive computational framework and experimental data set were used to identify vulnerable and reactive chemical moieties at the molecular level and to provide insight into the design of new electrolytes that would be stable in  $\text{Li-O}_2$  battery environment.

Utilizing the stability framework, we designed and characterized three sulfamide- and sulfonamide-based solvents<sup>4,5</sup> with enhanced chemical and electrochemical stability. These compounds were shown to be stable in the presence of commercial  $\text{Li}_2\text{O}_2$  and  $\text{KO}_2$  powders as

well as under galvanostatic, full discharge conditions, likely due to the suppressed solubility of discharge reaction intermediates (e.g.,  $\text{Li}^+\text{O}_2^-$ ) resulting from low electrolyte donor numbers (DNs). In contrast, DMSO decomposes significantly under the same testing conditions. Additionally, the sulfonamide-based solvents are considerably more stable against electrochemical oxidation ( $V_{\text{ox}} > 4.5 V_{\text{Li}}$ ) than DMSO and the sulfamide-based solvent, which can be attributed to the electron-withdrawing effect of the  $-\text{CF}_3$  moiety. Differential electrochemical mass spectrometry (DEMS) measurements show  $\text{O}_2$  as the vastly predominant gas evolved on charge in Li- $\text{O}_2$  cells employing sulfonamide-based electrolytes, which, notably, exhibit ~50% higher overall  $\text{O}_2$  evolution than the DMSO cell. In particular, Li- $\text{O}_2$  cells employing our sulfonamide-based electrolyte have been cycled for 90 times without capacity decay. The results presented in this study demonstrate that sulfamide- and sulfonamide-based electrolytes are promising for aprotic Li- $\text{O}_2$  battery electrolytes. In addition, this work highlights the power of molecular design in the context of Li- $\text{O}_2$  battery chemistry.

### **Impact and Perspective**

The results presented in this project demonstrated important structure-property relationships governing the (electro)chemical stability and ion conductivity of organic electrolytes for rechargeable batteries and effective strategies to improve these properties. Results in this project suggest additional areas of research. Firstly, utilizing the key lessons learned in the design of stable and dissociative FAST salts, one could expand the design library to include anions with vastly different structures, which potentially employ other scaffold(s) than the aromatic ring to further improve electrochemical oxidative stability.

Additionally, electrolyte instability against lithium metal electrode is a critical issue that has attracted tremendous research attention in the past decades. This project placed an emphasis on the molecular design of electrolytes with improved electrochemical oxidative stability (i.e., stability against high voltage cathode), and future research should explicitly address the challenge of enhancing electrolyte reductive stability against lithium metal anode. Numerous reports have indicated that lithium fluoride, LiF, is an important component of a stable and effective interfacial layer (SEI) between Li metal and organic electrolytes. In light of this, a few open questions remain: will electrolytes containing FAST salts (which contain multiple fluorine atoms) and/or the sulfonamide-based solvents form stable SEI on Li metal surface? How can we design fluorine-containing electrolyte components (salts, additives, and/or solvents) to ensure the formation of a stable and effective SEI? In other words, how can we probe the effectiveness of the SEI *a priori*

based on the electrolyte composition? These questions may be answered through careful *in situ* experimental characterizations that can elucidate the molecular compositions of the SEI layer as well as the development of descriptor-based computational screening tools to speed up the discovery of electrolyte formations optimized for stability against Li metal.

Lastly, regarding Li-O<sub>2</sub> battery stability, researchers<sup>6,7</sup> have reported Li-O<sub>2</sub> battery electrolyte degradation primarily due to the reactivity of singlet O<sub>2</sub> (<sup>1</sup>O<sub>2</sub>). However, the <sup>1</sup>O<sub>2</sub> formation mechanism(s) and onset (e.g., during discharge and/or charge, and at what potential, etc.) are not well-understood. Additionally, the techniques of detecting of <sup>1</sup>O<sub>2</sub> can be error-prone due to either low sensitivity or selectivity, or false negative results stemming from the instability of probe molecules. Additional research is needed to develop more reliable techniques for <sup>1</sup>O<sub>2</sub> detection and to understand <sup>1</sup>O<sub>2</sub> formation mechanisms and conditions at a molecular level, both of which are critical steps towards the development of strategies to prevent and/or suppress the formation of <sup>1</sup>O<sub>2</sub>, and to design organic electrolytes stable against <sup>1</sup>O<sub>2</sub>.

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## List of publications that have acknowledged Link Foundation support

- S. Feng\*, M. Huang\*, J. Lamb, W. Zhang, R. Tatara, Y. Zhang, C. F. Perkinson, J. A. Johnson, and Y. Shao-Horn, "Molecular design of stable sulfamide- and sulfonamide-based electrolytes for aprotic Li-O<sub>2</sub> batteries," *Chem* **2019**, 5(10), 2630-2641.
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## How the discretionary Funds was utilized?

The fund was used as the fellow's stipend during the award period. Due to the fellow's graduation in June 9, the fellowship was terminated before the intended award period ended, and the remainder fun was returned to the Link Energy Foundation.

## How did the Fellowship make a difference?

Receiving the Link Energy Fellowship has reinforced my interest and pursuit of fundamental study of structure-property relationships governing the engineering of battery components, as well as the accelerated design and discovery of new materials with improved properties. It has also allowed me to attend various national conferences to introduce my project work to a broad audience.