California State University Chico

EECE 699T Master of Science in Electrical and Computer Engineering Thesis Proposal

Advanced Characterization Framework for the Empirical Study of Li-S Batteries

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Version 1 October 26, 2024 Version 2 November 2, 2024

Version 3 November 5, 2024 Version 4 November 6, 2024

Version 5 November 7, 2024

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1. Introduction

1.i Background

Batteries power many electronics, from wireless keyboards to medical devices and transportation like cars. When utilizing a battery in a system's design, key considerations must be addressed, such as operational lifetime, typical operating conditions, charging time, and expected output. Several battery chemistries are currently commercially available, including the lithium ion battery (LIB) [1]. Barriers to the widespread adoption of electric options for transportation, machinery, and appliances include the cost to replace the battery, expected operational lifetime, and lengthy charging times.

While many LIB chemistries exist, the emergence of lithium-sulfur (Li-S) as potential commercial options has been hampered by the drawbacks with these configurations, such as the dramatic loss of cathode material, polysulfide shuttling, and the resulting short life cycle [1,2]. However, interest in these chemistries has increased mainly due to the theoretical energy per volume being significantly higher than currently available LIB options and reduced cost due to the accessibility of sulfur. By overcoming these barriers, Li-S batteries will provide a pathway to large-capacity batteries capable of further powering the transition away from fossil fuels.

1.ii Significance and Objectives

Overcoming cathode material loss and restricting polysulfide shuttling would remove barriers to producing high-capacity Li-S battery options for future applications [1,2]. Polysulfide chemistry depends on the electrolyte's chemistry, so characterizing the interactions between the cathode-electrolyte and the polysulfide species is critical to understanding the specific polysulfide species within the battery cell. Polysulfide shuttling can be mitigated using a metal-organic framework (MOF) as a cathode layer and a permeable separator, such as Celgard. Pursuing the optimization of the MOF pore size for a specific polysulfide species in a known electrolyte is a promising avenue for reducing polysulfide shuttling.

However, challenges exist when attempting in operando characterization, such as mitigating the exposure of the materials to reactive elements in the atmosphere and designing experiments to remain within the limited form factor of a traditional coin-cell battery. These challenges present the opportunity to engineer novel approaches to performing in operando characterization systems for monitoring the chemical interactions between the cathode-electrolyte interfaces and lithium polysulfide species within Li-S coin-cell batteries.

The main objective of this thesis is to develop an advanced characterization framework for the empirical study of Li-S coin-cell batteries. This framework will be realized by following several steps:

1. Conduct an extensive literature review into characterization techniques that cutting-edge, current research groups are pursuing.
2. Design and fabricate novel fixtures for multiple characterization methods; see Section 2.ii. Characterization Methods.
3. Perform data collection and in-depth analysis of the cathode, electrolyte, and electrochemical interactions between the two in operando.
4. Identify modifications to the framework and repeat steps 2 and 3.
5. Communicate results and present framework in a thesis to be defended in the Fall 2025 semester.

2. Review of Current Research

2.i. Battery Cell Configuration

Battery configuration is critical when determining the characterization methods explored in this thesis research. There are several different battery cell configurations to consider, such as half-cell, full-cell, and symmetrical-cell [1]. In addition, configurations can use either 2 or 3 electrodes. The framework described by this thesis will focus on a full-cell, 2-electrode configurations and explore novel housings to enable the utilization of advanced spectroscopic, microscopic, and diffraction characterization methods.

2.ii Characterization Methods

Characterizing polysulfides in electrolytes is challenging since only the charge product S_8 and discharge product Li_2S are thermodynamically stable [2]. Many groups have studied the electrochemical interactions in situ using Raman [3], UV/Vis [4], X-ray absorption, and NMR [2,5,6]. The literature review completed through week ten has identified several advanced characterization methods that will be further considered for integration into the experimental portion of the framework.

In addition to understanding the type of data traditionally gathered by each technique, a literature review is being conducted to shed light on each technique's limitations and shortcomings. Each characterization method has unique considerations, such as specific sample preparation steps, overall sample stability during data collection, and a fixed form factor of equipment sample stages.

This thesis framework will employ multiple methods to characterize the electrochemical interactions between the cathode and electrolyte of Li-S coin-cell batteries. The framework aims to provide insight for future advanced characterization experiments and present a method for analyzing electrolyte additives and cathode surface morphology in operando to minimize polysulfide shuttling. This work will focus on determining the species of polysulfides present so that, the MOF pore size can be adjusted to maximize polysulfide capture and reduce shuttling.

2.ii.a) Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is used to characterize the change in impedance of a battery over a wide range of frequencies [7,8,9]. If included in the framework, EIS may help confirm the presence of specific polysulfide species.

2.ii.b) Fluorescence Imaging Spectroscopy

Fluorescence imaging spectroscopy would be used to determine the distribution of polysulfides and can provide a platform for visualization of the polysulfide shuttling effect in operando [10]. Other experiments, such as temperature mapping of the electrodes, can benefit from this advanced characterization method to determine relationships between temperature and polysulfide shuttling, anode dendrite formation, and cathode material loss [11]. Including this valuable technique in the framework would require engineering a novel optical battery cell, and additional research into inert fluorescent dyes to implement a probe tuned towards a specific polysulfide species.

2.ii.c) Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) is a technique used to characterize chemical bonds by exploring molecular vibrations [12]. Technical issues with this method include vibrational modes with nonzero dipole moments having overlapping signatures from one or more polysulfide species. Polysufides peak at wave-numbers ranging from ~500 - ~513 [cm^{-1}] with significant overlap between 490 - 530 [cm^{-1}] , according to literature [23]. Due to the challenges with finding chemically and electrically inert materials that are also transparent from the mid-to-far-IR to hold the electrolyte a novel fixture would need to be engineered to utilize the Chemistry Department's equipment. If included in the thesis framework, it would provide access to identifying the formation and decomposition of various polysulfide species and electrolyte additives [12, 13].

2.ii.d) Raman Spectroscopy

Raman spectroscopy, complementary to FTIR, provides access to molecular-level details and can be used to observe interactions in operando of the polysulfide species present and track the evolution of electrolyte composition through many charge and discharge cycles [14]. Tracking the polysulfide and electrolyte composition during numerous cycles and under various temperatures is critical to characterize the efficiency of MOFs designed to reduce polysulfide shuttling [15]. A critical advantage of this method is that the light source can be near the IR- Vis range, allowing glass to be implemented as a transparent, electrically/chemically inert window. Another advantage is that vibrational modes that are inactive in FTIR measurements can be probed with Raman. Including this characterization method in the framework would enable monitoring changes in the electrolyte and polysulfides but would require other methods to fully understand the chemical functionalities and interactions of interest in Li-S coin-cell batteries.

2.ii.e) UV-VIS Spectroscopy

Ultraviolet to visible (UV-VIS) spectroscopy is a characterization method that can be leveraged to explore electrolyte composition during cycling [16]. The disadvantages of this method include the equipment requiring transparent samples to collect data. This would require engineering a novel fixture to enable the use of the Chemistry Department's Agilent 8453 equipment or the portable setup accessible to the research group. Including this characterization method in the framework would allow access to information regarding mass transport mechanisms and concentration build-up of the polysulfides in the electrolyte and confirm adequate MOF trapping.[17].

2.ii.f) Energy Dispersive X-Ray Spectroscopy

Energy dispersive x-ray spectroscopy (EDXS) utilizes electrons instead of photons to capture maps of elemental distribution from scanning electron microscopy (SEM) images. Analyzing the electrodes' surface morphology after cycling provides information vital to improving battery performance. EDXS coupled with thermal and FTIR mappings of electrodes can provide information on the distribution of polysulfide species in the battery component [18]. The downside to this method is that collection would not be in operando since it is unlikely that the battery could be capped for continued operation after SEM images are collected. Including this characterization method in the framework, maps of the elemental distribution from the electrode surface can be acquired; however, the subsequent characterization methods would need to be carefully selected to ensure an in-depth analysis and characterization of the battery can be performed.

2.ii.g) X-Ray Diffraction

X-ray diffraction (XRD) is implemented in battery research to detect the crystalline structure of intermediate species in the amorphous electrolyte and detect changes in other crystalline structures of interest over time [19,20]. This method also has the potential to measure the structural changes of the MOFs as a function of battery cycling. One exciting question to consider is if the crystalline nature of the MOFs is constant during battery cycling. Including this characterization method in the framework would enable the identification and quantitative analysis of phases which can be used to calculate the amount of active material versus degradation products in the electrolyte during battery cycling [21].

3. Thesis

3.i. Methodology

To create an advanced characterization framework for the empirical study of Li-S batteries, an extensive literature review will be conducted to develop potential pathways toward the in operando characterization of electrochemical interactions that contribute to polysulfide shuttling. Pathways toward characterization are currently being determined, and the best combination of methods for battery chemistry will soon be selected to be further explored via laboratory experiments. In pursuing characterization data via laboratory experiments, engineering novel fixtures and designing a clearly defined standardized process will be significant sections in this proposed thesis. Fixture design will also heavily depend on the characterization techniques selected, such as the UV-VIS methodology requiring transparent cells. Developing a repeatable, standardized process is vital to the proposed framework so that accurate comparisons can be made across a wide range of battery chemistries and setups of future experiments. These fixtures will be optimized for the characterization methods selected for this thesis but will also attempt to accommodate methods not selected for potential future work. This thesis research framework will be developed for those interested in conducting research in electrochemical characterization.

Characterizing the cathode and electrolyte in operando during cycling will provide critical information on electrolyte additives' effectiveness in reducing polysulfide shuttling, how electrode composition mitigates cathode mass loss, and the evolution of species of interest during cycling. With the foundational steps completed, sample fixtures fabricated, empirical data collected, and results from the pathway selected being analyzed, this framework will prove to be a valuable tool for future characterization experiments on rechargeable, Li-S batteries. These results will be presented to my thesis committee and other parties of interest during the Fall 2025 semester.

3.ii Potential Contributions and Impact

Exploring the electrochemical interactions of Li-S coin-cell batteries as they cycle will provide valuable information in an area with many unknowns. While there is evidence that batteries have existed since 250 BCE, knowledge of the interaction mechanisms, such as those responsible for polysulfide shuttling and cathode mass loss, remains elusive. This thesis proposes developing a framework that would produce a standardized environment for testing, design novel fixtures to enable advanced characterization techniques, and develop a roadmap for conducting future advanced characterization work. Li-S batteries in the consumer market would accelerate the transition from fossil fuels by lowering the cost of high-capacity batteries. With battery costs low, consumer products such as electric planes and vehicles would overtake previous internal combustion engine options.

4. Conclusion

4.i. Summary

The transition from fossil fuel-based energy profiles requires a significant increase in electricity storage. Li-S batteries have been theoretically proven to provide more energy density than currently available LIB options. They would reduce costs since sulfur does not suffer from supply chain issues as other LIB chemistries may. This thesis aims to develop, test, and present a reliable framework for future experiments toward characterizing battery chemistries and electrochemical phenomena. The characterization method selection process for this thesis will utilize information presented in Table 1 to determine the best pathway forward. Values in Table 1 listed as ***TBD*** are currently being researched, values listed as maybe are theoretically possible but challenges exist between standardizing setups.

4.ii Future Work

Conducting experiments that implement the characterization methods not selected for this thesis and others presented in the literature to acquire a complete picture of the electrochemical interactions at work would be worthwhile. Because information on the interaction mechanisms and electrochemical interactions during cycling is lacking, any research into the evolution of polysulfide species in the electrolyte would provide the Li-S battery community with vital information. This information would guide the optimization of the electrode composition and electrolyte additives, likely leading to improvements within Li-S batteries. Once the required improvements are made to Li-S batteries, very few barriers will exist for this chemistry to become commercially available and continue the transition away from depending on unsustainable fossil fuels.

Table 1. Characterization Method Rankings

Method	Pros	Cons	Complexity	Can quantify total polysulfide concentration	Can quantify individual polysulfide concentration	Can measure general polysulfide presence
EIS	Confirms polysulfide presence	Sensitive to experimental setup	Challenging	No	No	TBD
Fluorescence Spec.	Determines distribution of polysulfide, shuttling visualization method	Challenges with obtaining fluorescent probe	Moderately Challenging	No	No	TBD
FTIR Spec.	Identifies the formation and decomposition of various polysulfide species	Challenges with obtaining chemically/ electrically inert materials transparent in the mid-to-far IR to contain samples	Easy	No	No	Yes
Raman Spec.	Light source can be near the IR-VIS range, allowing glass to be utilized as the chemically/electrically inert, transparent in the mid-to-far IR to contain samples	Signal optimization for each sample	Easy	No	Yes	Yes
UV-Vis Spect	Provides information on build-up of polysulfides, and transport mechanisms	Samples must be transparent to utilize portable ECE setup or the Chemistry Department's Agilent 8453 equipment	Easy	Yes	Yes	Yes
EDXS	Provides visual information on the cathode surface morphology	Unable to collect in operando since battery needs to be transparent to electrons	Easy	No	No	No
XRD	Detects crystalline structures of intermediate species and changes in crystalline structures during cycling	Thickness of MOF layer on Celgard and preparation of MOF powder may affect signal strength	Challenging	No	No	Yes

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