

# ***In Situ* FTIR Spectroscopy to Probe Effects of LiNO<sub>3</sub> on First Cycle SEI Formation and Electrolyte Decomposition in Li-Metal Batteries**

**CNF Summer Student: Ben Hodder Alexander**

**Student Affiliation: Physics, Haverford College (graduated spring 2024);**

**Physics Ph.D. Program, Stanford University (starting fall 2024)**

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*Principal Investigator(s): Dr. Hidenori Noguchi, Chief Researcher, Interface Electrochemistry Group, Battery and Cell Materials Field, Research Center for Energy and Environmental Materials (GREEN) at NIMS; Graduate School of Chemical Sciences and Engineering, Hokkaido University*

*Mentor(s): Wang Yushen, Research Center for Energy and Environmental Materials (GREEN) at NIMS; Graduate School of Chemical Sciences and Engineering, Hokkaido University*

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*Contact: benalex@stanford.edu, noguchi.hidenori@nims.go.jp, wang.yushen@nims.go.jp*

*Summer Program Website: <https://cnf.cornell.edu/education/reu/2024>*

## **Abstract:**

Anode-free lithium metal batteries have a high theoretical performance ceiling for next-generation energy storage. To better control the system, it is important to understand the behavior of the solid electrolyte interface layer, particularly during the first charge cycle. This work uses FTIR spectroscopy to examine the role of lithium nitrate additive in ether electrolytes. Lithium nitrate is found to promote the irreversible formation of organic SEI species during electrolyte decomposition in TEGDME.

## **Summary of Research:**

**Background and Motivation.** The commercial lithium-ion battery is a backbone of modern rechargeable energy storage, being found everywhere from electric vehicles to cellular phones. While improvements in storage capacity are ongoing, they are theoretically limited by the graphite anode used in the system — a limitation made more painful by ever-increasing demands for energy storage in pursuit of climate-friendly infrastructure.

Lithium metal anodes represent a theoretical order of magnitude improvement in specific capacity over their graphite counterparts in commercial batteries [1]. Significant challenges remain, however, in developing lithium metal battery (LMB) technology for commercial use. This includes poor cycle life and safety issues, often resulting from lithium dendrite growth and/or parasitic reactions [2]. Anode-free configurations (anode-free lithium metal battery: AFLMB), where lithium is electrodeposited directly upon a current collector, seek to improve cell capacity and enable easier manufacturing. In such conditions, lithium is plated on the electrode surface during the first charge cycle, motivating the attention of researchers.

The interface between the electrode and electrolyte is chemically unstable, resulting in the formation of a solid electrolyte interface (SEI) layer between the two. This study

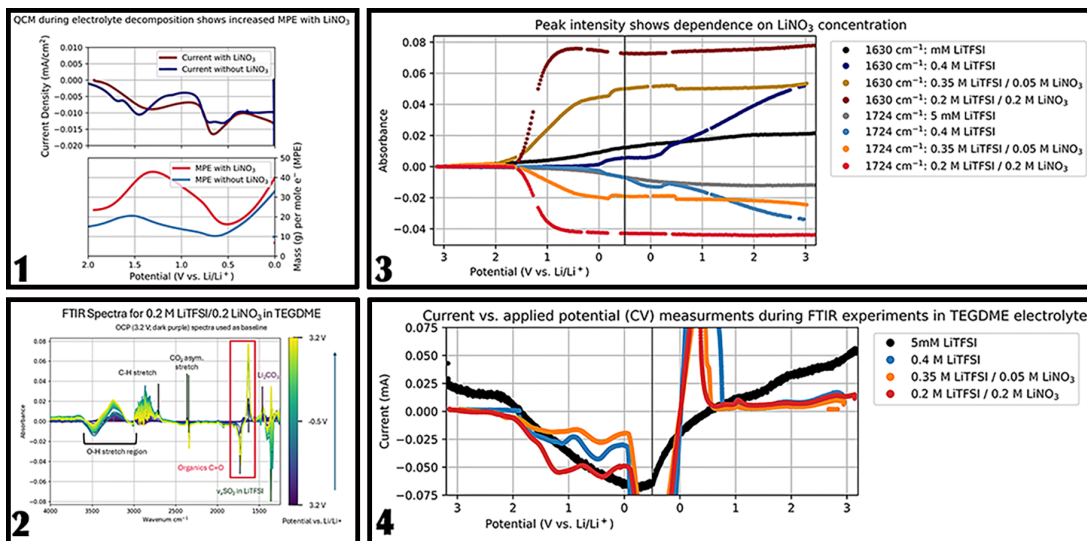
aims to understand the first cycle behavior of this layer in ether electrolyte systems, with a particular emphasis on the role of lithium nitrate (LiNO<sub>3</sub>) in the system, which is understood to improve stability as an additive [3].

**Materials and Methods.** Electrolyte solutions were prepared in glovebox using tetraethylene glycol dimethyl ether (TEGDME), which is commonly used in oxygen battery systems for its superior cathodic stability [4]; the common ether solvent dimethoxymethane (DME) was used for comparison measurements. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was added to these ethers as the primary salt at 0.4 M concentration. samples were tested without LiNO<sub>3</sub>, and to maintain a constant concentration of Li<sup>+</sup>, with an 0.05 M (functioning as an additive) or 0.2 M (as a co-salt) concentration of LiNO<sub>3</sub> replacing LiTFSI salt. All electrolytes were tested in a half cell with a copper working electrode and metallic Lithium reference and counter electrodes to examine anode behavior.

Characterization was primarily performed via Fourier Transform Infrared (FTIR) spectroscopy. Spectra were captured continuously, with a collection time of approximately 30 seconds while performing cyclic voltammetry tests of the first cycle behavior at 1 mV/s. Python code was written to analyze the large number of spectra produced by such a methodology.

Similar cyclic voltammetry tests were performed alongside quartz crystal microbalance (QCM) measurements of surface absorbed mass — after calibration, this allowed calculation of MPE (mass absorbed per mole of electrons of passed charge) values associated with the identified process.

**Results.** While data was collected to examine the entire first cycle anode behavior, the results presented here focus on the electrolyte decomposition process in TEGDME. They suggest that LiNO<sub>3</sub> accelerates the formation of organic surface species in the pre-SEI layer that are formed because of slightly decomposed TEGDME solvent.



The electrolyte decomposition process in solvents containing (0.4 M LiTFSI in TEGDME) and not containing (0.2 M LiTFSI/0.2 M  $\text{LiNO}_3$  in TEGDME) was first examined using a quartz crystal microbalance. Results are shown in Figure 1. Mass per electron values (technically an average over the entire system) increased from approximately 20 g/mole  $e^-$  to over 40 during electrolyte decomposition — note that this process identified with the first downwards peak in current, around 1.3 V vs.  $\text{Li/Li}^+$ . MPE values are notably high for electrochemical processes and likely correspond to either the deposition of organics or a chemical process, rather than a strictly electrochemical one; a chemical reaction not requiring electrons to deposit material has a theoretically infinite mass per electron value.

This process was examined in greater detail using FTIR spectroscopy. Figure 2 shows the spectra collected during the cycle of the half cell in TEGDME with  $\text{LiNO}_3$ . Various peaks were observed. This included hydrogen bonding;  $\nu_{\text{as}}\text{SO}_2$  bonds breaking in LiTFSI; signs of lithium carbonate, a common SEI species;  $\text{CO}_2$ ; and C=O bonding from organic species.

This work focuses on the last of these observations: the most unexpected result and one displaying a strong dependence on lithium nitrate. This can be most clearly seen in the heights of the absorbance peaks as a function of applied potential, shown in Figure 4. This shows peaks at 1724  $\text{cm}^{-1}$  and 1630  $\text{cm}^{-1}$ . Both are identified with C=O bonding, with the former believed to correspond to chemically decomposed TEGDME solvent and the latter thought to be a lithium-containing organic SEI species (e.g. ROCO<sub>2</sub>Li or Li-formate). Note that decreases in absorbance for the peak at 1724  $\text{cm}^{-1}$  correspond to increases in absorbance at 1630  $\text{cm}^{-1}$ , indicating that the former is consumed to produce the latter in all samples.

However,  $\text{LiNO}_3$  has clear effects on this process. Let us scrutinize the electrolyte decomposition region, identified to be at 1.3 V on the downwards potential scan by examination of Figure 3. Here, increasing concentrations of  $\text{LiNO}_3$  correspond to the acceleration of this process. Notably, this results in greater stability after the lithium plating and stripping process in systems with  $\text{LiNO}_3$ .

## Conclusions and Future Steps:

The ability of  $\text{LiNO}_3$  to accelerate organic deposition in the SEI layer in TEGDME may help explain its role as a stabilizing agent — as  $\text{LiNO}_3$  is known to quicken electrolyte decomposition, it may allow the system to reach near-equilibrium before plating and stripping. Alternatively, these results might indicate potential issues with the stability of TEGDME on the anode side. The organic deposition observed here may be undesirable and has not been the focus of previous studies with the solvent, which generally emphasize cathode interactions in  $\text{Li-O}_2$  systems.

In future studies, the effects of this organic deposition on later cycles could be combined with additional characterization techniques to obtain a more complete understanding of the system. Such an understanding aids in developing the stable SEI layers required for the success of Li-metal batteries. This work may also motivate study into native-SEI formation and chemical degradation of ether solvents. Such understanding could improve the precision of work throughout the field.

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