FAILURE MECHANISMS IN HIGH-VOLTAGE CATHODE MATERIALS FOR LITHIUM BATTERIES

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INTRODUCTION

- Lithium-ion batteries used in electric vehicles suffer from high cost and low energy density
- These obstacles are overcome by manganese oxide based batteries which present a promising high voltage alternative
- Manganese is cheap, abundant, and exhibits excellent rate capabilities [3]
- Unfortunately, lithium-ion batteries with manganese oxide cathodes suffer from accelerated capacity fade [1]

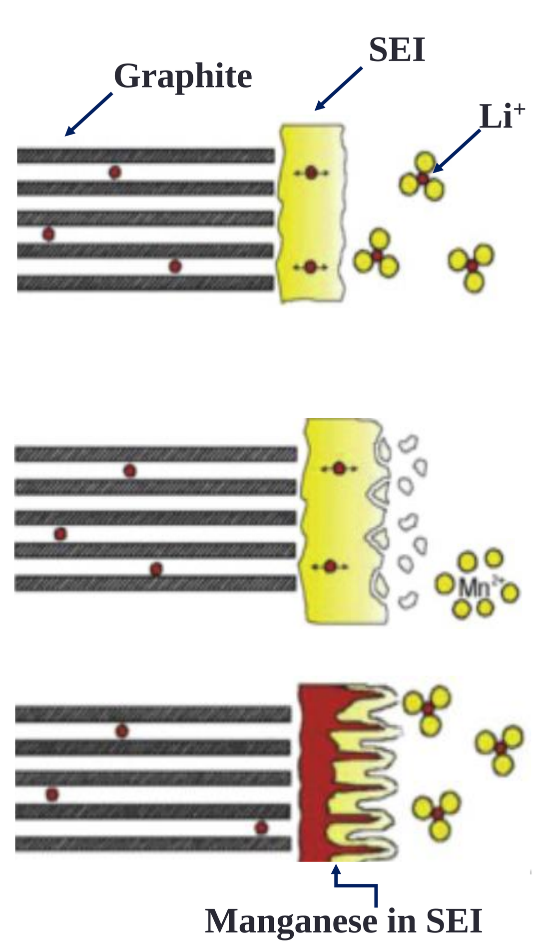
BACKGROUND

The solid electrolyte interphase (SEI) prevents electron tunneling and slows down the diffusion of electrolyte molecules

There are two theories in literature that try to explain the mechanisms by which manganese disrupts the SEI [2]

First theory: -
- Manganese dissolution electronically affects the SEI

Second theory: -
- Manganese integrates into the SEI structure, disrupting its morphology



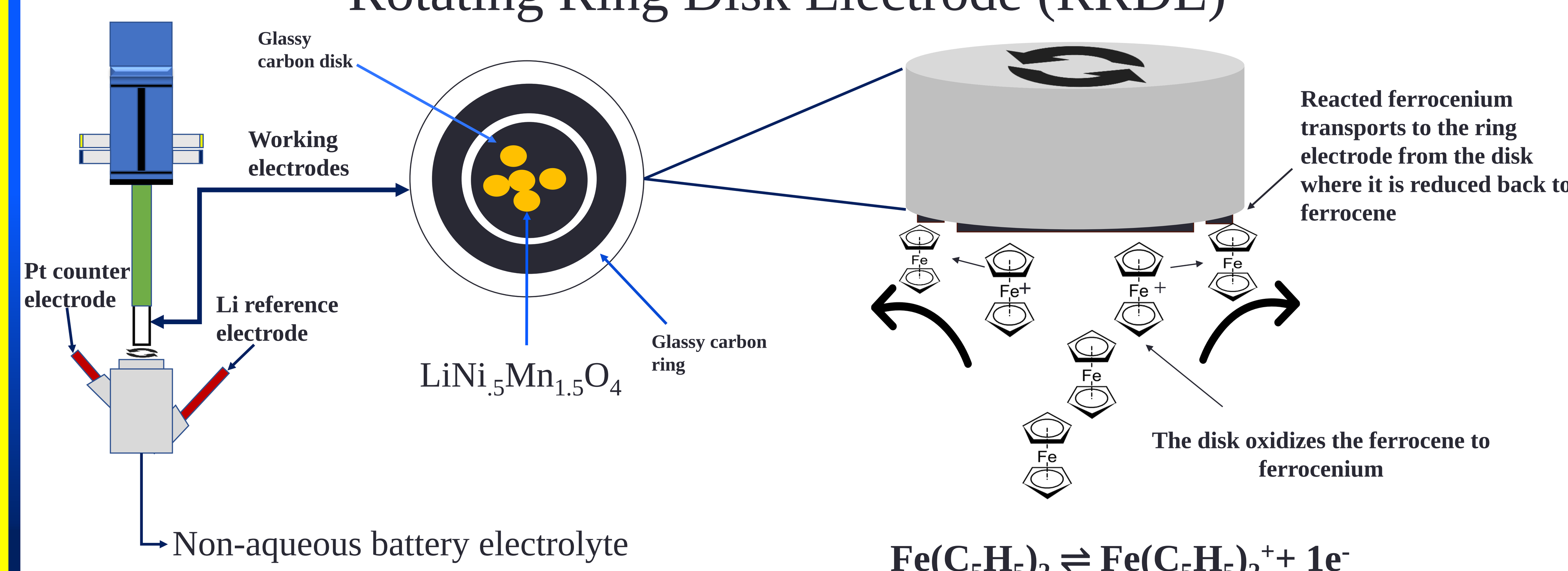
OBJECTIVES

- Using a rotating ring disk electrode to investigate the impact of manganese on the SEI
- Determine whether manganese ions form within the SEI's structure
- Explore if charged manganese ions displace components of the SEI

-Construct a microflow electrochemical flow cell to simulate a real battery
- Test the transport and electrical properties

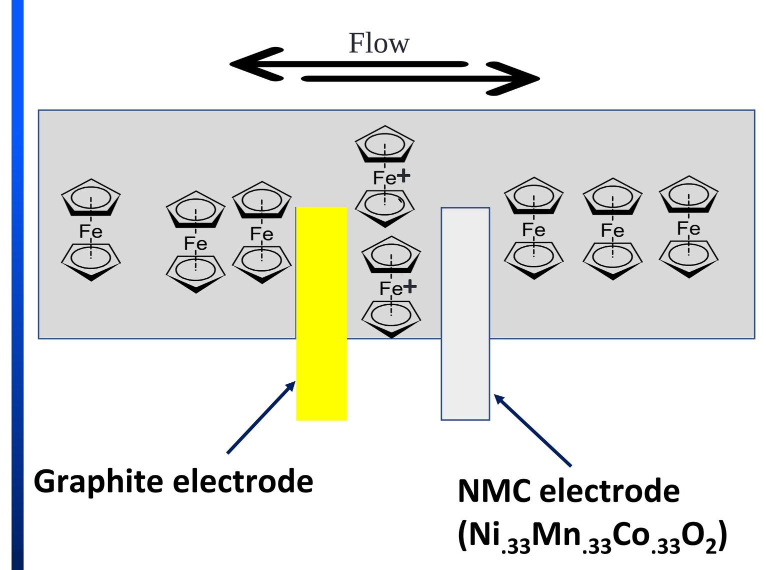
EXPERIMENTAL SET-UP

Rotating Ring Disk Electrode (RRDE)



$$Fe(C_5H_5)_2 \rightleftharpoons Fe(C_5H_5)_2^{+} + 1e^-$$

Microflow Electrochemical Flow Cell



DATA AND ANALYSIS

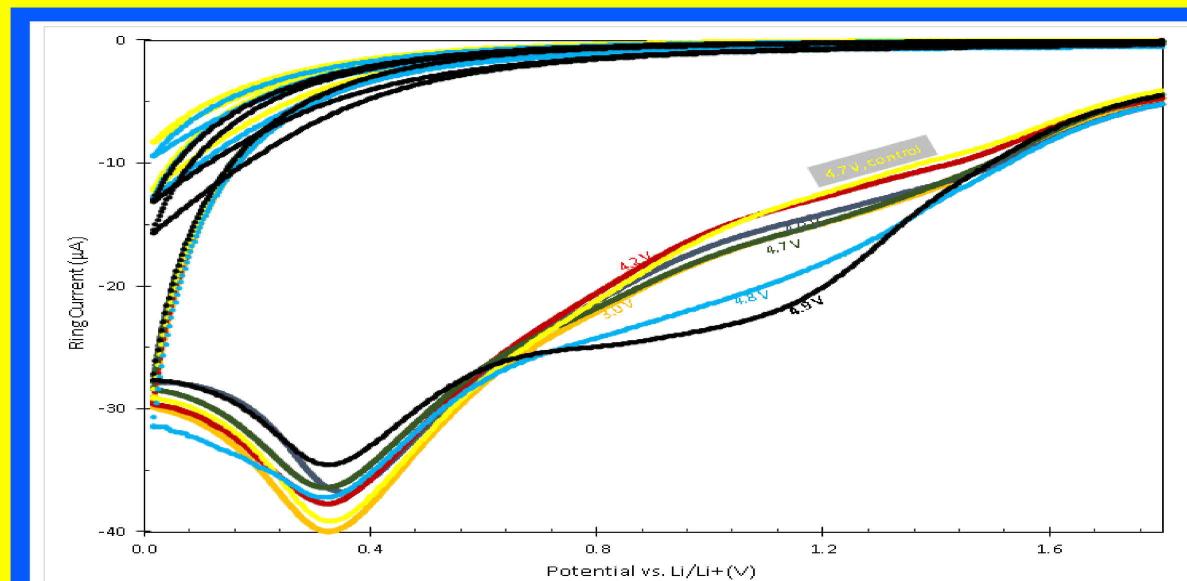


Figure 1: - Ring current in (μA) vs potential (V) during SEI formation.

SEI formation

- A different reduction peak starts to appear on the ring at around 1.2 V when the disk is held at potentials higher than 4.7 V
- The current decreases by approximately 57% after the first cycle indicating passivation
- Peaks that appear around 0.3 V indicate electrolyte reduction

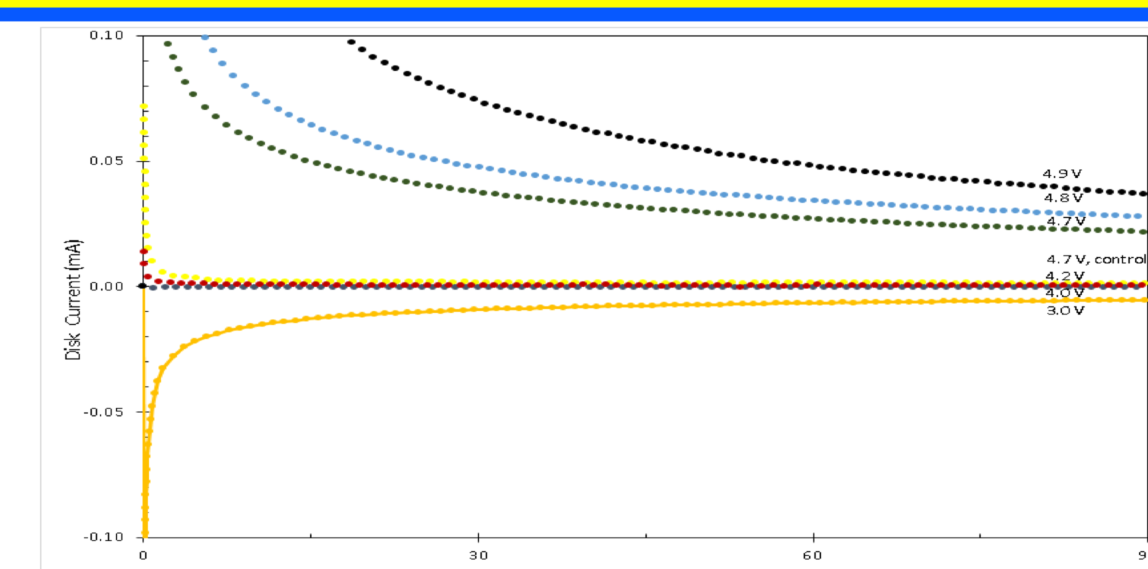


Figure 2: - Disk current (mA) vs. time at various applied disk voltages

Disk current during SEI formation

- The current follows an increasing trend as the applied voltage is increased
- 4.2 V and 4.0 V are indistinguishable from the control
- At 3 V, the measured current at the disk is below zero

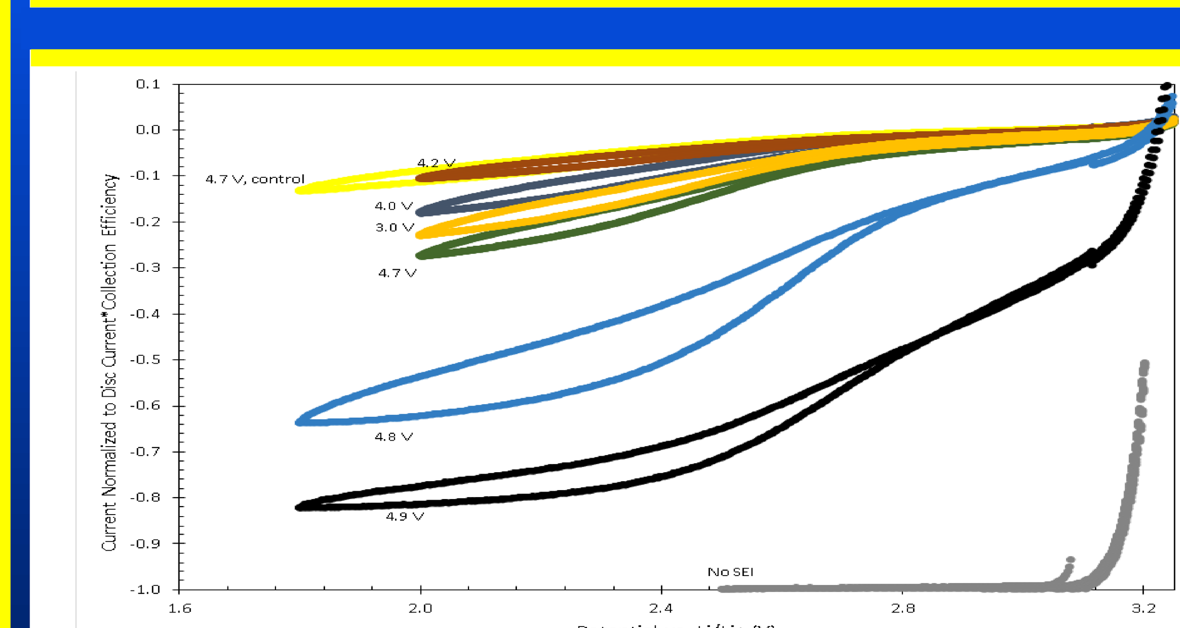


Figure 3:- Normalized ring current vs. potential (V) after SEI formation.

Cyclic voltammetry (CV) sweeps after SEI formation

- As the formation voltage is increased on the disk, the less passivating the SEI becomes
- For disk formation potentials of 4.7 V and higher, there are larger current gaps between each cycle

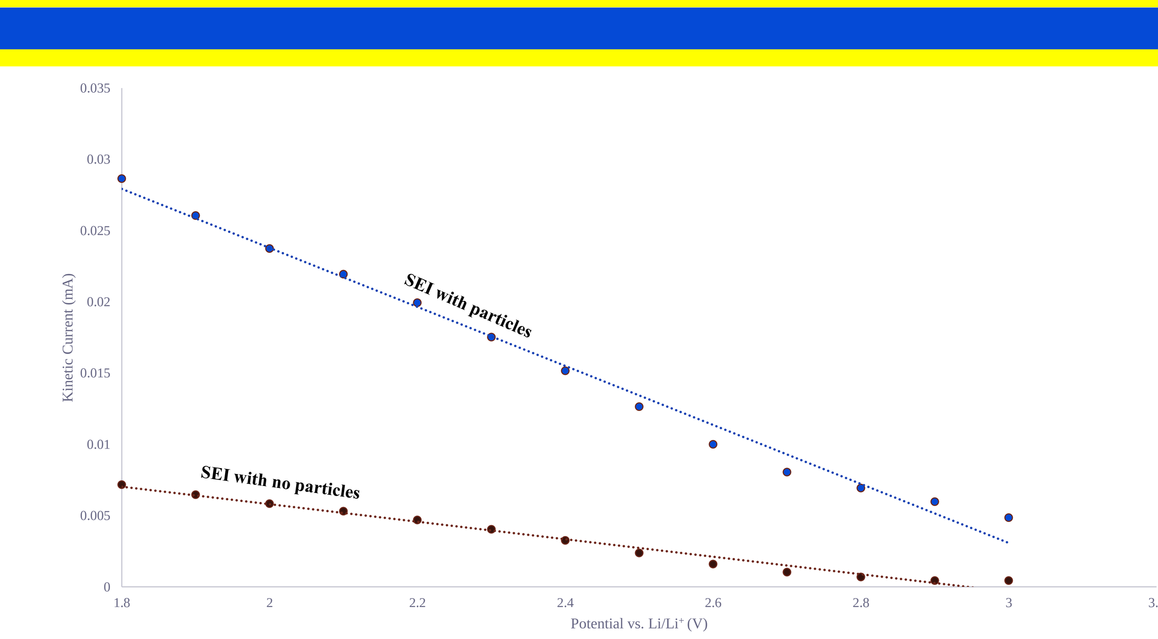


Figure 4: - Kinetic current vs. Potential

Kinetic Current with respect to potential

- At higher potentials, the kinetic current decreases for the SEI with particles and for SEI without particles
- The current voltage slope is steeper for the SEI formed in the presence of LNMO

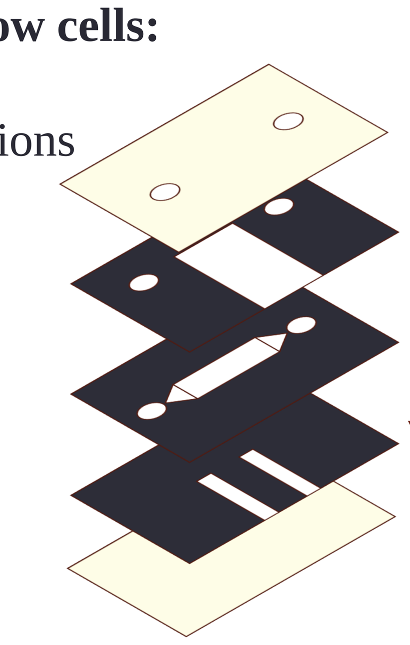
CONCLUSIONS

- Oxidation current on the disk increases with increasing potentials which may be indicating manganese dissolution
- The SEI with particles posses a higher kinetic current than the SEI with no particles
- Increased manganese dissolution during SEI formation causes the level of SEI passivation to decreases

FUTURE WORK

Determine if the effect of manganese on the SEI are predominantly electronic or morphological
- We know that manganese ions are incorporating into the SEI, but we still need to further investigate how the mechanism works

Microflow Electrochemical flow cells:
- Simulates real battery conditions
- Higher area: volume ratio
- Less electrolyte required



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[1] Jung Hyun Kim, Nicholas P W Pieczonka, Zicheng Li, Yan Wu, Stephen Harris, and Bob R. Powell. Understanding the capacity fading mechanism in LiNi0.5Mn 1.5O4/graphite Li-ion batteries. Electrochim. Acta, 90: 556–562, 2013. ISSN 00134686. doi: 10.1016/j.electacta.2012.12.069.
[2] Agubra, Victor A., and Jeffrey W. Fergus. "The formation and stability of the solid electrolyte interface on the graphite anode." Journal of Power Sources 268 (2014): 153-62. Web. June & july 2017.
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