Electrolyte and Electrode Passivation for Thin Film Batteries

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Overview

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  • Impedance spectroscopy
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Motivation

• Provide chemical stability at anode for high conductivity, low reductive stability electrolytes.
• Provide chemical stability at cathode for high conductivity, low oxidative stability electrolytes.
• Identify robust passivation film tolerant to humid air or wet processing for multi-step patterning of thin film batteries.
• Examine if other Li electrolytes could be nitrided.
Experimental

Film Preparation:
• RF sputtered from Li$_2$CO$_3$ target
• Power levels of 75-200 W for 3” target
• Sputter gas: blends of CO$_2$, O$_2$, N$_2$, Ar
• Li electrodes thermally evaporated

Characterization:
• Impedance spectroscopy
• DC breakdown
• XPS
• XRD
• TEM
Impedance Spectroscopy Results

Bode plot of Mo|Li₂CO₃|Mo

Complex plane plots of Mo|Li₂CO₃|Mo

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Impedance Spectroscopy Results

Equivalent Circuit Model

Arrhenius plot of Mo|Li$_2$CO$_3$|Mo

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DC Characterization Results

DC breakdown of Mo|Li$_2$CO$_3$|Mo

DC breakdown of Mo|Lipon|Mo
DC Characterization Results

Tafel Plots corresponding to Electrolyte Oxidation

Tafel plots of various liquid electrolytes
X-ray Diffraction: Li$_2$CO$_3$ Sputtered in N$_2$ and O$_2$

Collected at Stanford Synchrotron Radiation Laboratory

- Crystalline Li$_2$CO$_3$ Observed, Grain size ~ 20 nm

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X-ray Photoelectron Spectroscopy

Li$_2$CO$_3$ Sputtered in 100% O$_2$

- Al Kα Radiation used
- After 15 min ion etch
- Film Surface

- Li$_4$
- C
- O$_{3.7}$

- ~1/1 Combination of Li$_2$CO$_3$ & Li$_2$O

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Qualitative Trends

• Increase in air stability, repeatability with increasing power (less Li$_2$O)
• Increase in target decomposition, bonding failure with increasing power
• Little variation on film properties with sputter gas composition
• Conditions yielding low deposition rate favored resputtering
Alternative Passivation Films

- LiF: poor conductivity
- LiF/Li$_3$PO$_4$ (Ar/O$_2$ sputter gas) poor oxidative stability
- LiF/Li$_2$CO$_3$ poor air stability/target stability

![LiF/Li$_3$PO$_4$ film](image1)

![LiF/Li$_3$PO$_4$ film](image2)
Summary

- Passivation films for improved anodic and cathodic protection were examined.
- Films are to be used in conjunction with high conductivity electrolytes.
- \( \text{Li}_2\text{CO}_3 \) films prepared via sputtering bear \( \text{Li}_2\text{O} \).
- Fully amorphous films could not be obtained.
- RF sputter power level chiefly determined film stability, while sputter gas composition did not change film properties.
- Increased RF power resulted in higher stability films, but also resulted in target degradation.

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