In situ Observations of Lithium Dendrite Growth

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This presentation does not contain any proprietary or confidential information
Motivation

• Interfacial instability caused by dendrite formation limits cycle life and safety of lithium metal batteries
• Details of dendrite mechanism not fully understood
• Minimum lifetime 1000 cycles and 10 years
• Milestones:
  – The characterization of the effect of electrolyte composition and deposition conditions on Li morphology in the Li/liquid electrolyte system. (COMPLETED)
  – Fabrication of new test cells to study the C or alloy/liquid electrolyte and Li/polymer systems. (2nd Q 2008)
June 2006 Review

• New project
• Comments were all over the place from “nothing new” to “very interesting”
  – Available literature has no systematic study of dendrite formation in liquid electrolytes – the worse case scenario
• Move onto SPE and other electrolytes
  – Material issues slowed the transition to other electrolytes
Experimental Approach

• Combine *in situ* observations with electrochemical studies

• Microfluidic cells
  – Concentration and ohmic effects minimized
  – Good repeatability
  – Minimize electrolyte usage
  – Allows for the rapid changing of electrolytes, good for the study of additives
Sample Data

Watch this video at: http://lithiumdendrite.blogspot.com/

- This view is good for measuring dendrite growth rates

- Dendrite tip does not appear to be growing after 420 s

- Appears to be growing from the base

- This phenomena was also observed by Dolle et al.¹

- Signal sometimes becomes noisy after the formation of dendrites

Different Type of Picture

0.25 C cm\(^{-2}\)  
0.65 C cm\(^{-2}\)  
1.00 C cm\(^{-2}\)  
1.5 C cm\(^{-2}\)

Entire electrode is now viewable

Cannot obtain any info on dendrite velocity

Watch this video at: http://lithiumdendrite.blogspot.com/
Dendrite Propagation

- Dendrites rapidly spread over the electrode once formed
- Deposition does not always occur at tip as evident by the branching seen around 600s
- Large dendrite stops growing at 800 s
Time to First Observed Dendrite

- $t_{FOD}$ decreases linearly with PC content
- $t_{FOD}$ decreases logarithmically with increasing current density
Electrolyte Fluid Properties

• $t_{FOD}$ decreases with increasing PC content even though the limiting current increases.
• Does $t_{FOD}$ decrease with SEI resistance?
Effect of Flow

- Electrolyte flow delays the initiation of dendrites
- Flow at the start of deposition inhibits dendrites

Graph showing the effect of flow on time to dendrite deposition initiation.

- No flow
- Constant flow

Conditions:
- \(-4 \text{ mA cm}^{-2}\)
- \(1.0 \text{ m LiPF}_6\) in PC:DMC (75% DMC by wt)
- 5 mL h\(^{-1}\) when on

Time of flow shutdown [s]

\( t_{\text{FOD}} \) [s]
Dendrite Velocity

• Distance from dendrite initiation point is measured with time

• Can measure dendrite velocities in the axial and radial directions

all measurements in microns
Current Density at Tip

- Current at the tip is calculated using
  \[\dot{i} = \frac{v \text{ cm} \cdot \text{s}^{-1} \times 96487 \text{ C} \cdot \text{mol}^{-1}}{13 \text{ cm}^3 \cdot \text{mol}} \times \frac{1000 \text{ mA}}{1 \text{ A}}\]
- Calculated current at tip is lower than actual current due to branching
- Deposition is almost instantly mass transfer controlled
Dendrite Tip Velocity and Current

- Velocities are on the order of experimental data by Brissot et al.\textsuperscript{1} and theoretical results by Monroe and Newman\textsuperscript{2}

- Electrolyte with the higher interfacial resistance maintains a more consistent dendrite current and velocity

2008 Planned Work

• Microelectrode device to view *in situ* Li deposition in Li/gel-polymer and Li/polymer systems

• Microfluidic device to study additives in Gr or Alloy/Liquid electrolyte system
Summary

- *In situ* pictures of Li deposition are obtained using a microfluidic device.
- Mass transport does not seem to play a role in dendrite initiation.
- However, deposition quickly becomes mass transfer controlled after dendrite formation.
- High interfacial resistance inhibits dendrite formation, however, it also hurts battery performance due to slowed Li transport through the SEI.