In situ Observations of Lithium Dendrite Growth

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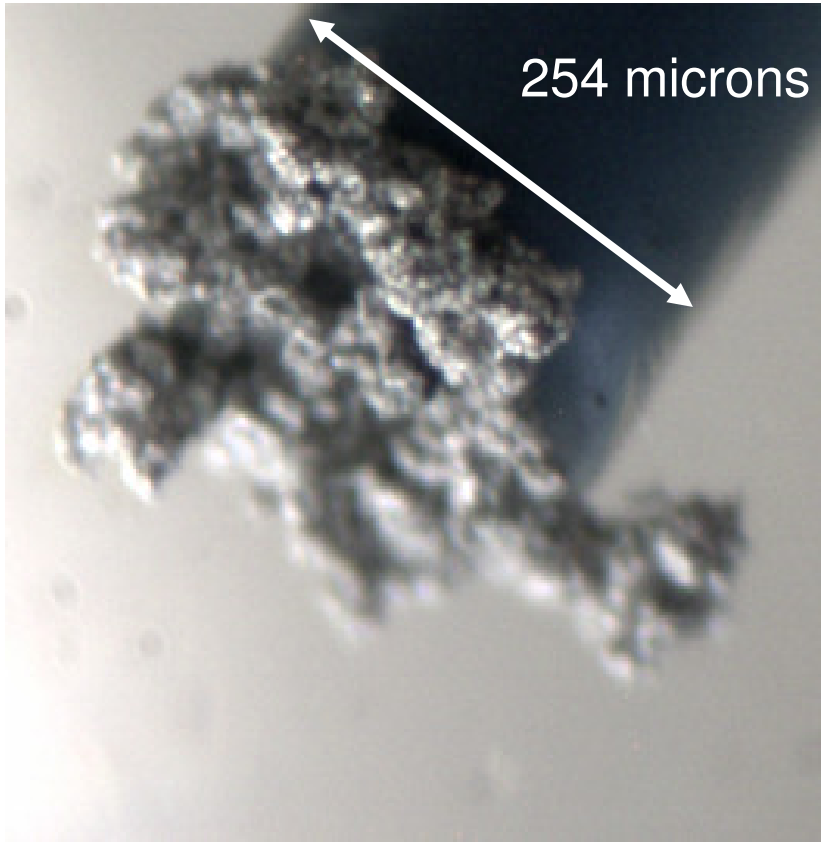
- Columbia University - Chemical Engineering
- February 27, 2008



This presentation does not contain any proprietary or confidential information

Motivation

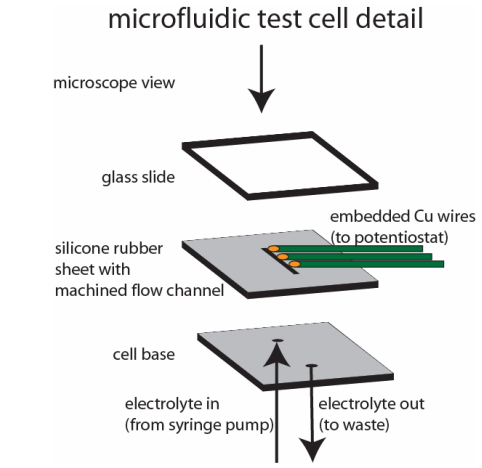
- Interfacial instability caused by dendrite formation limits cycle life and safety of lithium metal batteries
- Details of dendrite mechanism not fully understood
- Minimum lifetime 1000 cycles and 10 years
- Milestones:
  - The characterization of the effect of electrolyte composition and deposition 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. (2^{nd} Q 2008)

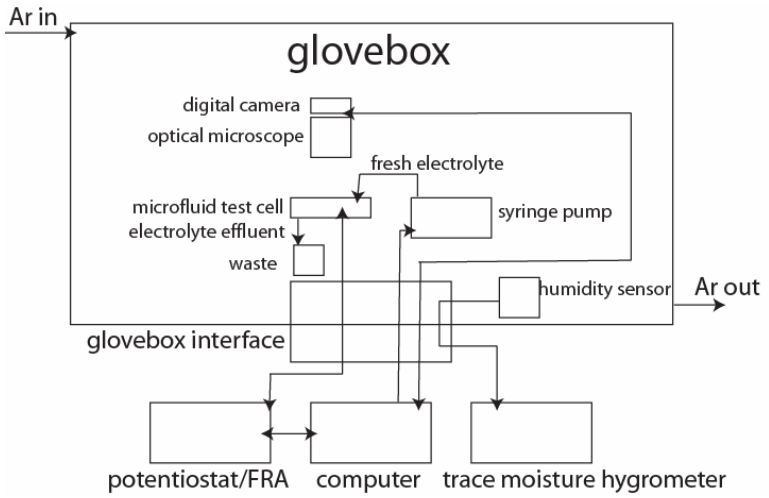
June 2006 Review

- 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

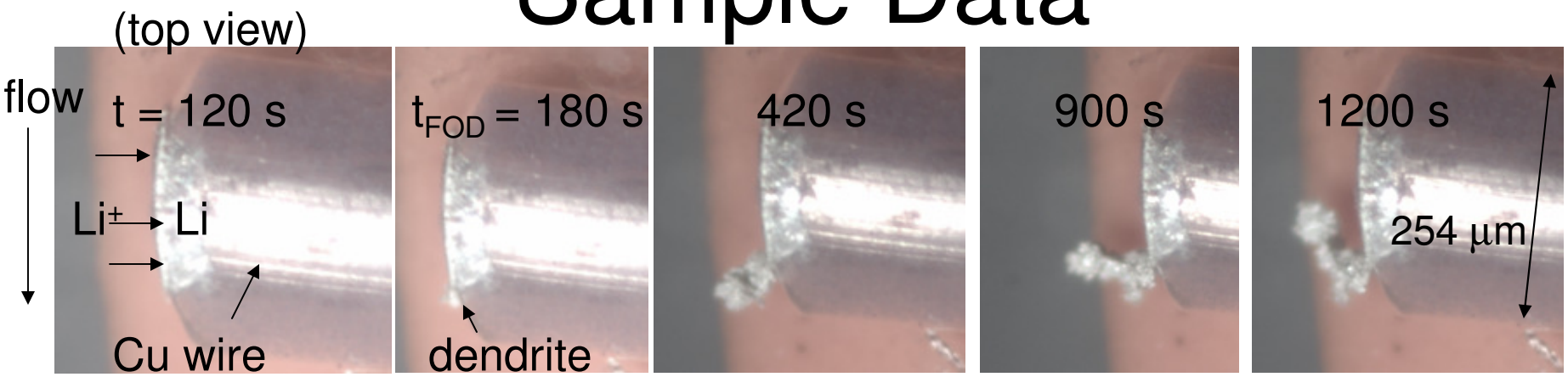
Experimental Approach

- 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**



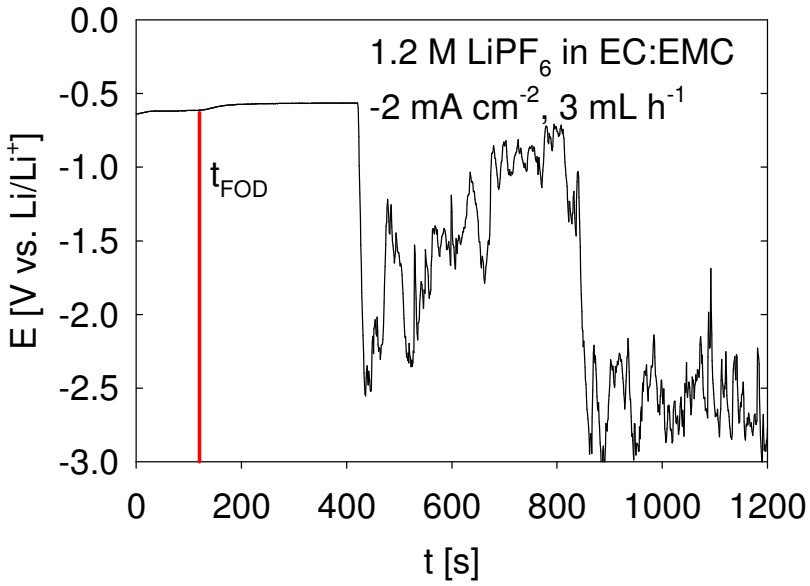


Sample Data



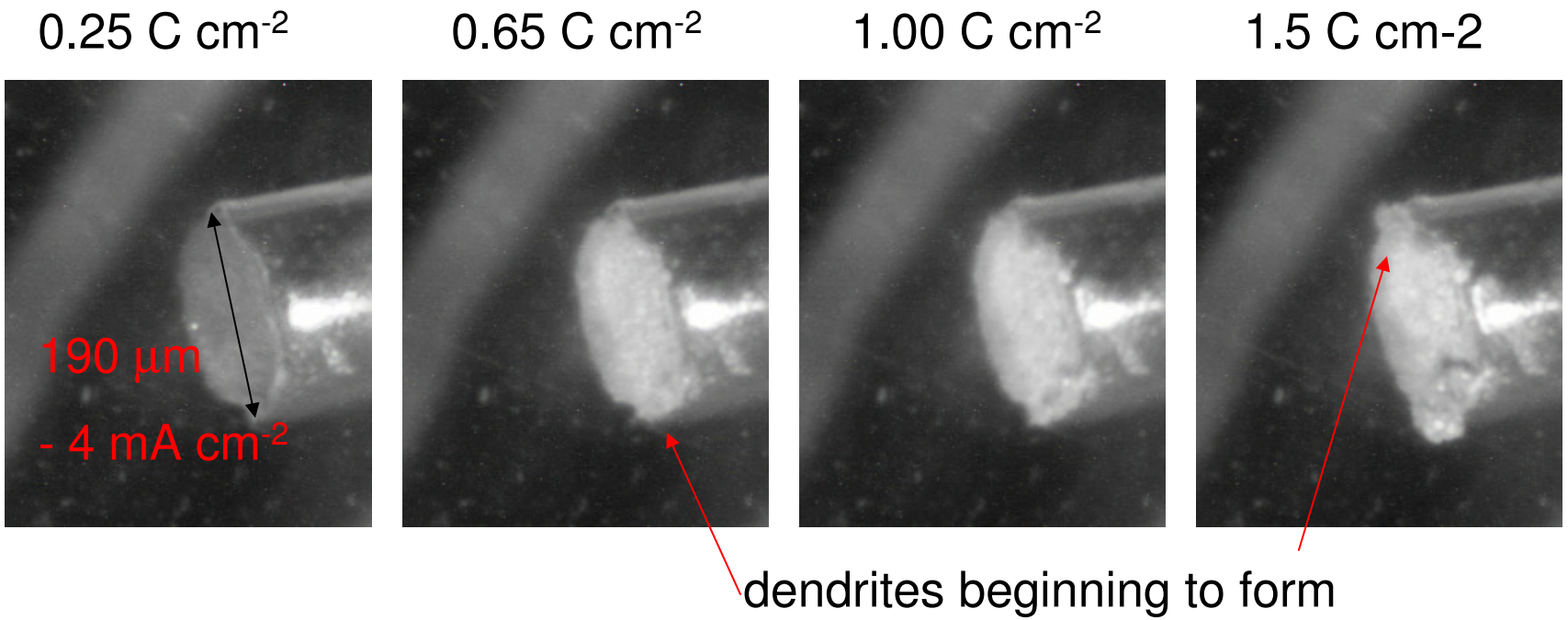
Watch this video at: http://lithiumdendrite.blogspot.com/

- 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



1. Dolle et al., *Electrochemical and Solid State Letters* **5** (2002) A 286.

Different Type of Picture

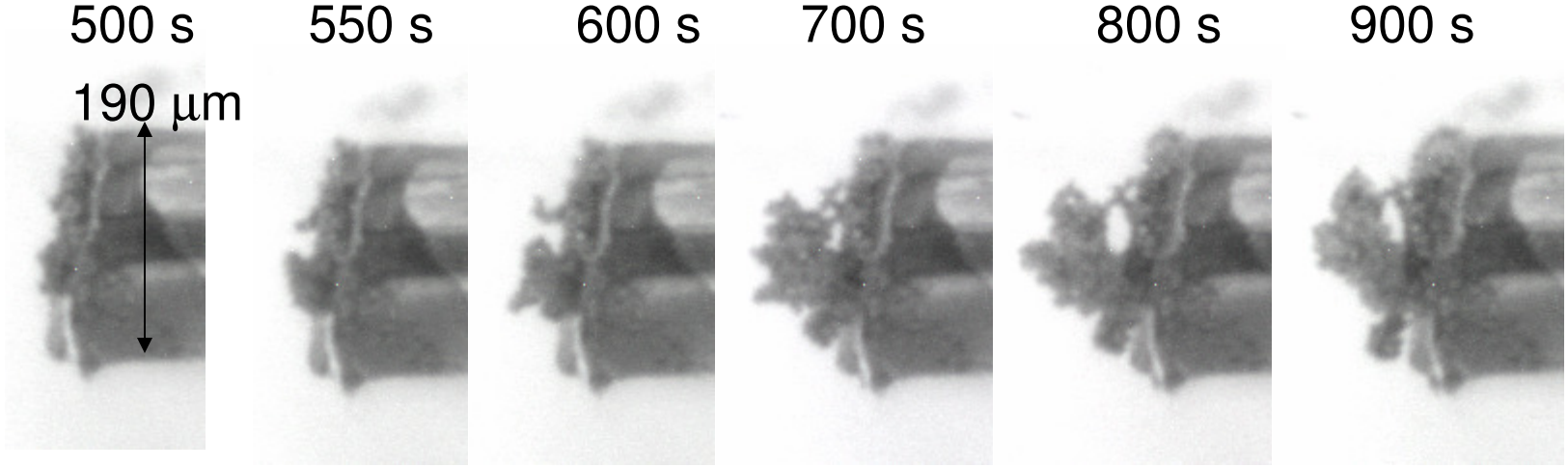


Entire electrode is now viewable

Cannot obtain any info on dendrite velocity

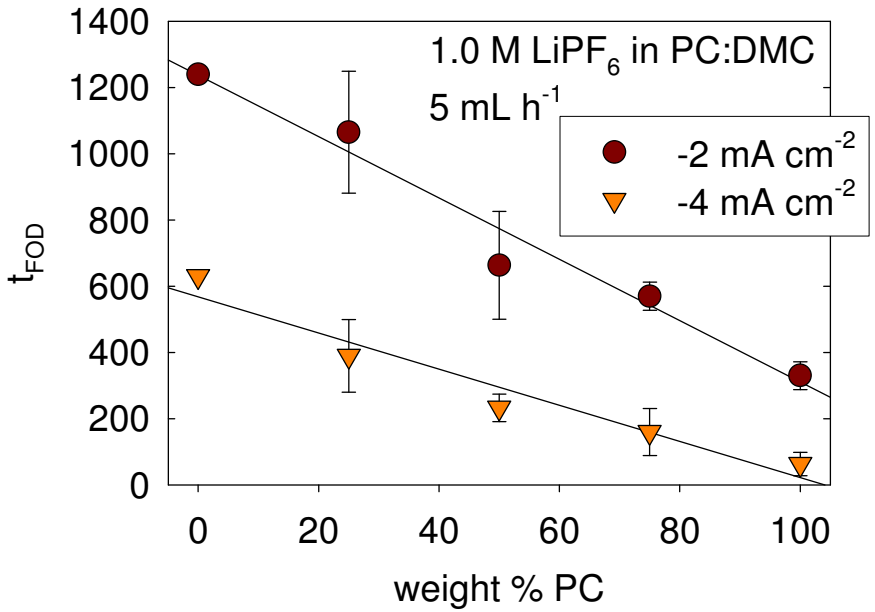
Watch this video at: http://lithiumdendrite.blogspot.com/

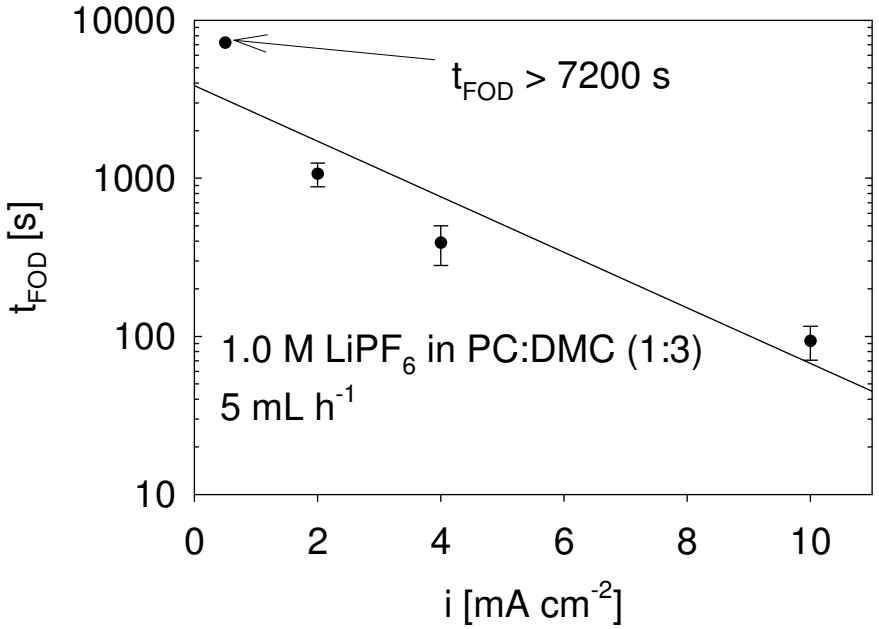
Dendrite Propagation



- 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

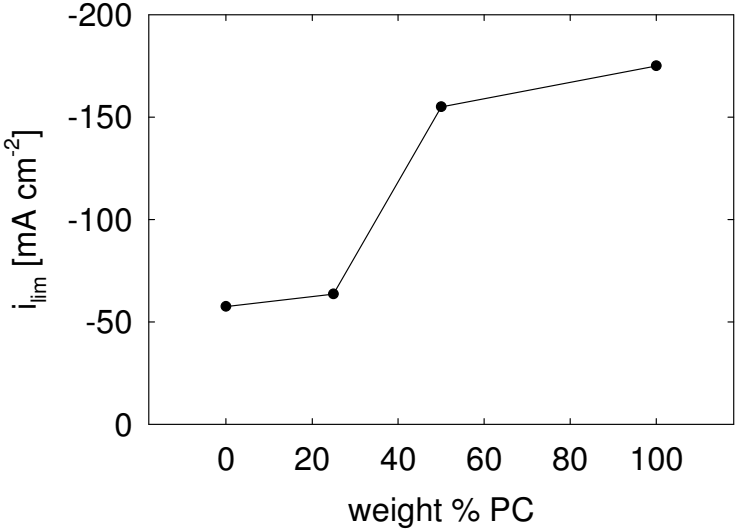
Time to First Observed Dendrite

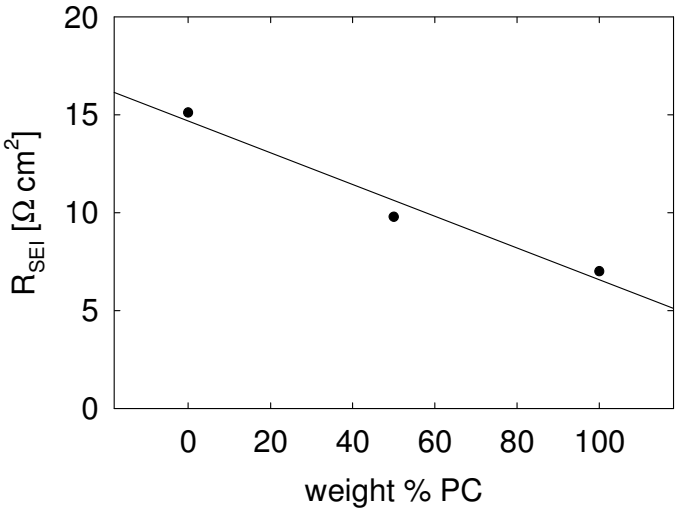




- t_{FOD} decreases linearly with PC content
- t_{FOD} decreases logarithmically with increasing current density

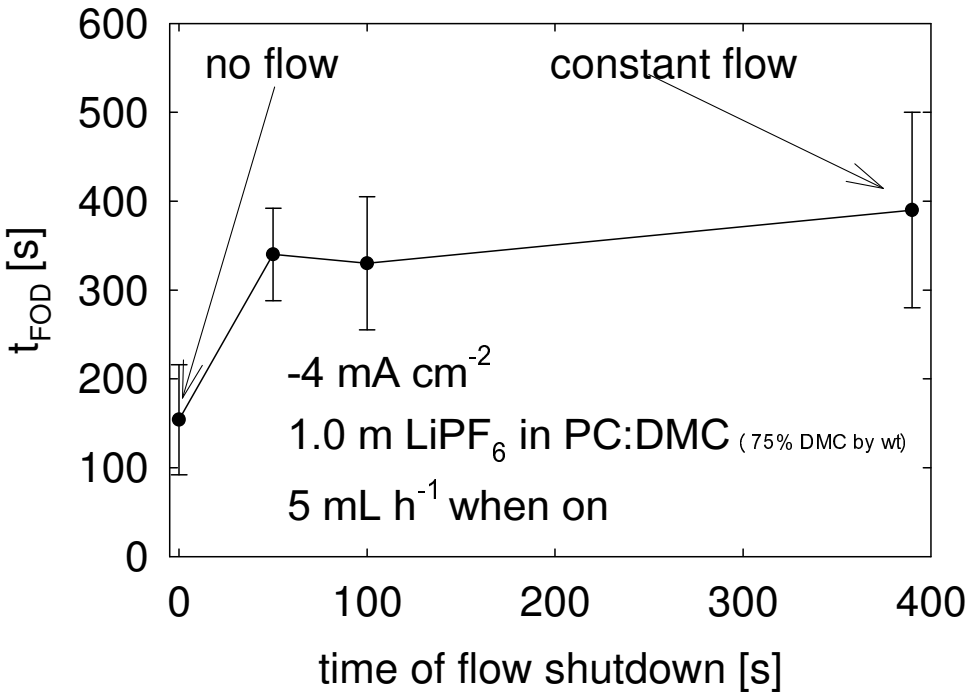
Electrolyte Fluid Properties





- t_{FOD} decreases with increasing PC content even though the limiting current increases
- Does t_{FOD} decrease with SEI resistance?

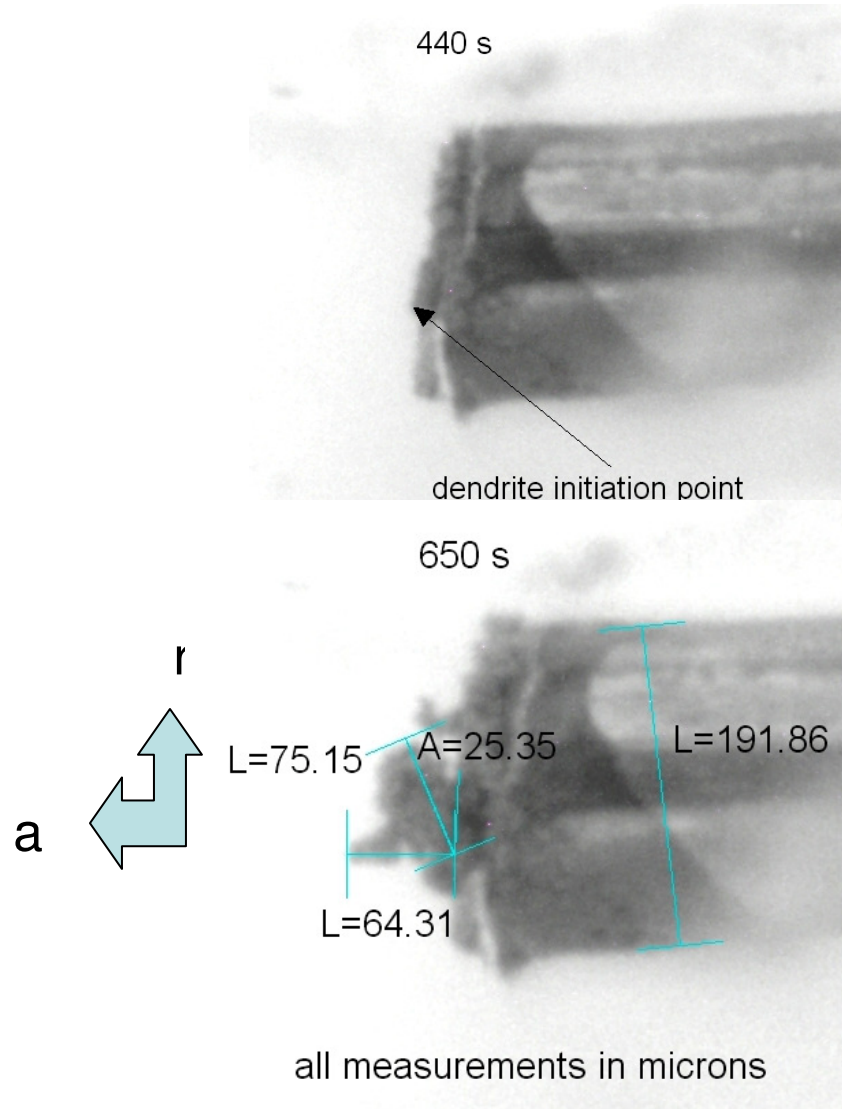
Effect of Flow



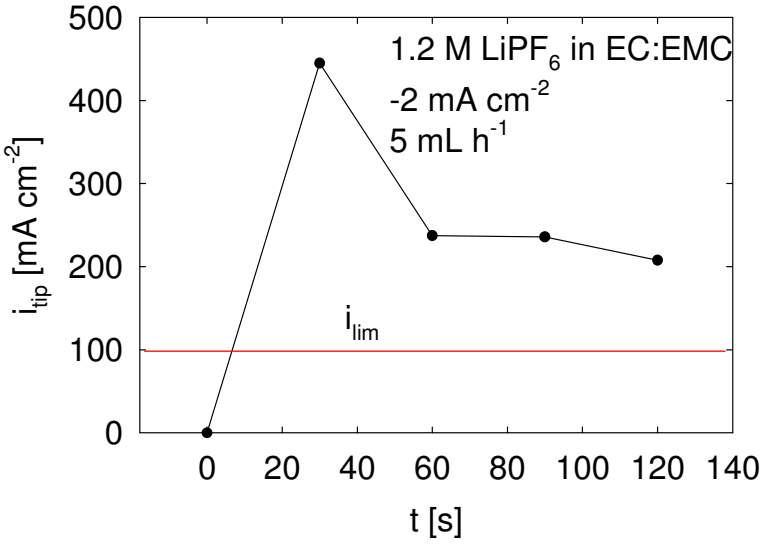
- Electrolyte flow delays the initiation of dendrites
- Flow at the start of deposition inhibits dendrites

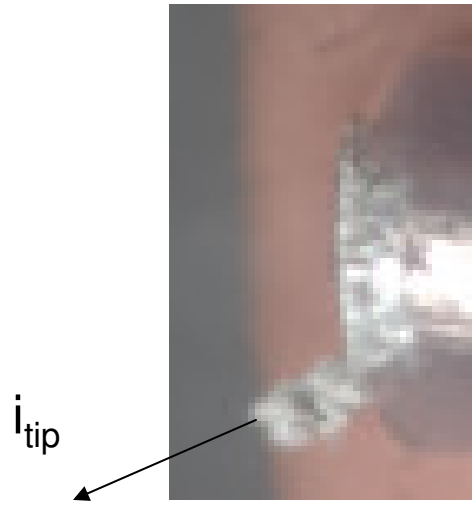
Dendrite Velocity

- Distance from dendrite initiation point is measured with time
- Can measure dendrite velocities in the axial and radial directions



Current Density at Tip



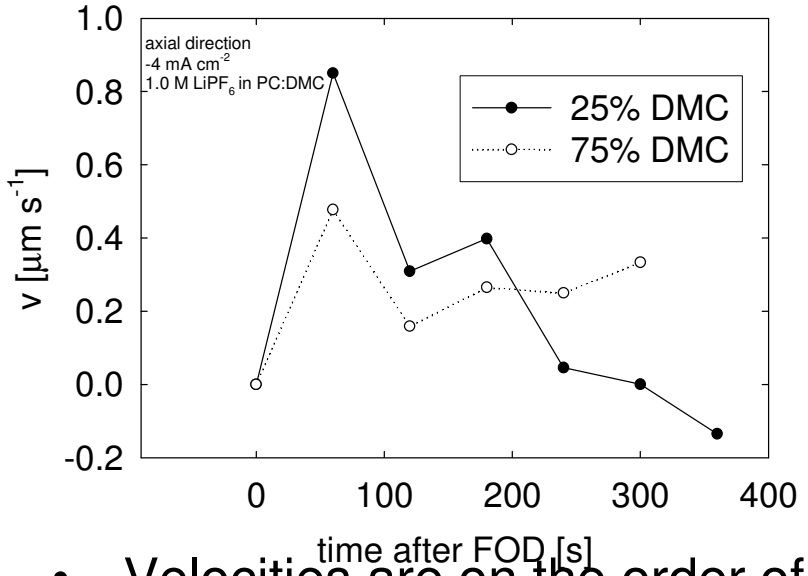


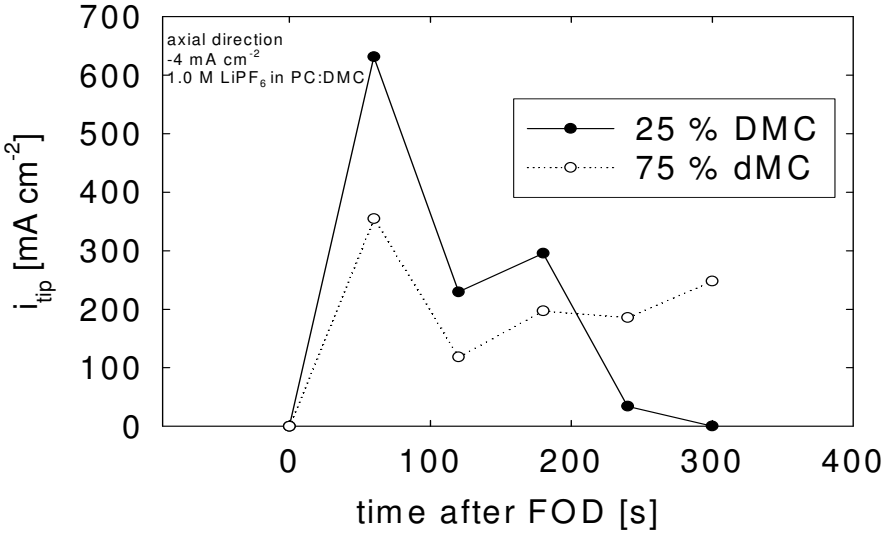
- Current at the tip is calculated using

$$i = \frac{v\left[\mathrm{cm \cdot s^{-1}}\right] \times 96487\ \mathrm{C \cdot mol^{-1}}}{13\ \mathrm{cm^3 \cdot mol}} \times \frac{1000\ \mathrm{mA}}{1\ \mathrm{A}}$$

- 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.[1] and theoretical results by Monroe and Newman[2]
- Electrolyte with the higher interfacial resistance maintains a more consistent dendrite current and velocity

1. Brissot et al., *Electrochimica Acta* **43** (1998) 1569.
2. Monroe and Newman, *Journal of the Electrochemical Society* **150** (2003) A1377.

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