# Protection of Li Anodes Using Dual Phase Electrolytes

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Project ID #
ES012

# Overview

## Timeline

- Project start date 10/1/2009
- Project end date 9/30/2012
- Percent complete 37 %

## Budget

- Total project funding
  - DOE share $832,215
  - Contractor share $1,996,639
- Funding received in FY10 $910,876
- Funding for FY11 $1,567,924

## Barriers

**Barriers addressed for EV application**

- Specific Energy >250 Wh/kg
- Thermal stability, Safety
- Cycle Life

<u>Target of Phase 2 Technology Development</u>

Demonstration of large format cells with high energy anode and dual-phase electrolyte systems

## Partners

**BASF SE, Germany**

- Development of Li-S battery materials

# Relevance. Project Objectives.

- Develop a unique electrolyte providing two liquid phases having:
  - Good lithium ion conductivity.
  - Self-partitioning and immiscibility.
  - Optimum chemical stability for each phase's respective negative and positive electrode.
  - Application to stabilize and protect lithium metal anodes.
- Demonstration of approach:
  - Lithium sulfur (Li-S) rechargeable battery:
    - Improve anode and cathode function.
    - Improve cycle life.
    - Increase thermal runaway temperature.

# Relevance. Project Milestones

- Success Criteria at Decision Points for 3 Phases of the Project:
  - Phase1 Criteria: Demonstration of anode unit specific capacity >750 mAh/g and > 50 charge/discharge cycles (03/31/2010).
  - Phase 2 Criteria: Demonstration of large format cells with high energy >250 Wh/kg and dual-phase electrolyte systems (07/31/2011).
  - Phase 3 Criteria: Large format cell manufacturing, test and evaluation. Demonstration of high energy, cycle life, and safety (thermal runaway temperature > 165$^{o}$C) (9/30/12).

# Relevance. Phase 2 Technical Tasks.

1. Gel Polymer Electrolyte Mixing/Coating Hardware System Development
2. Gel Polymer Electrolyte Coating Process Optimization
3. Large 2.5 Ah Format Cell Design, Optimization and Cell Manufacturing

# Approach/Strategy

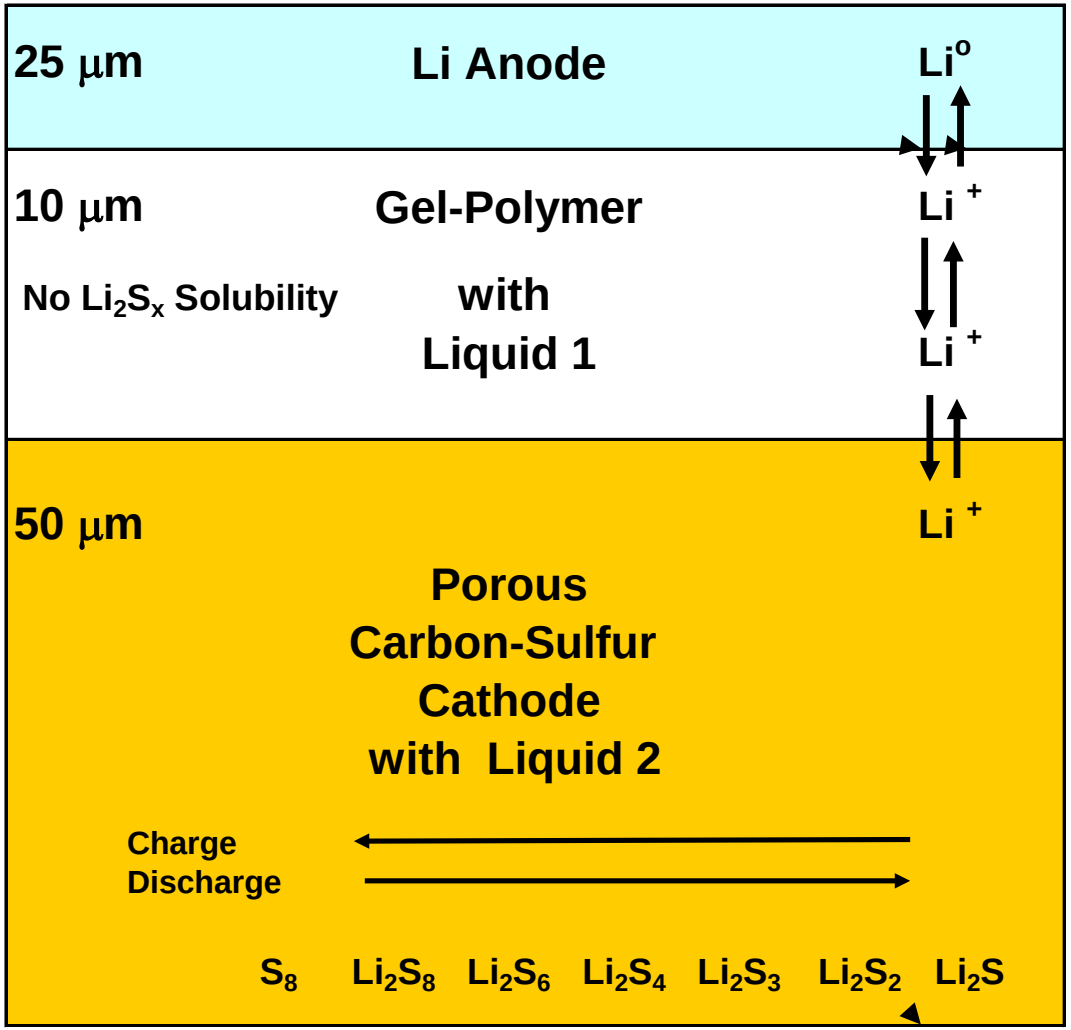
**“Anode” Liquid 1:**

- Immobilized within polymeric gel applied to anode.
- Stable with lithium preventing side reactions and dendrite growth.
- Immiscible with Phase 2 electrolyte and does not dissolve polysulfides.
- Polymeric gel can serve as coated separator.

**“Cathode” Liquid 2:**

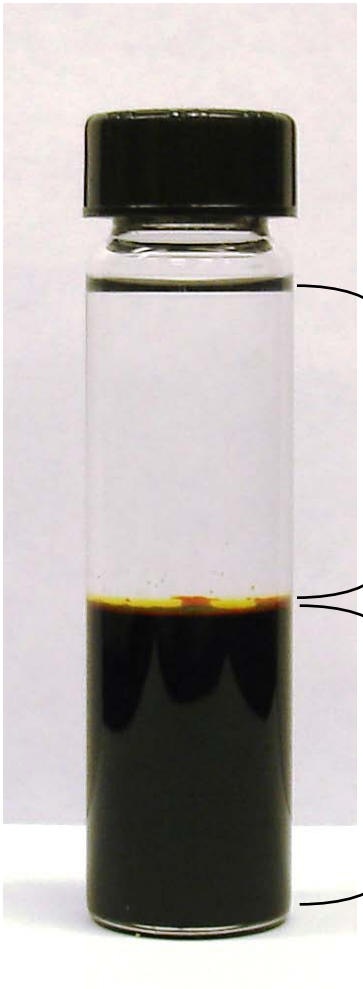
- Tailored to improve high energy Sion Power sulfur cathode performance.
- Immiscible with Phase 1 electrolyte.
- High ion conductivity and lithium polysulfide solubility.

## Dual Phase Electrolyte Li-S Battery



# Approach/Strategy

**Example of Dual Phase Electrolyte System**



"Anode" and "Cathode" electrolytes are immiscible liquids and both have Li ion conductivity

"Anode" Electrolyte:

Electrolyte can be immobilized within polymeric gel applied to anode.

$Li_2S_8$ is insoluble in this solvent.

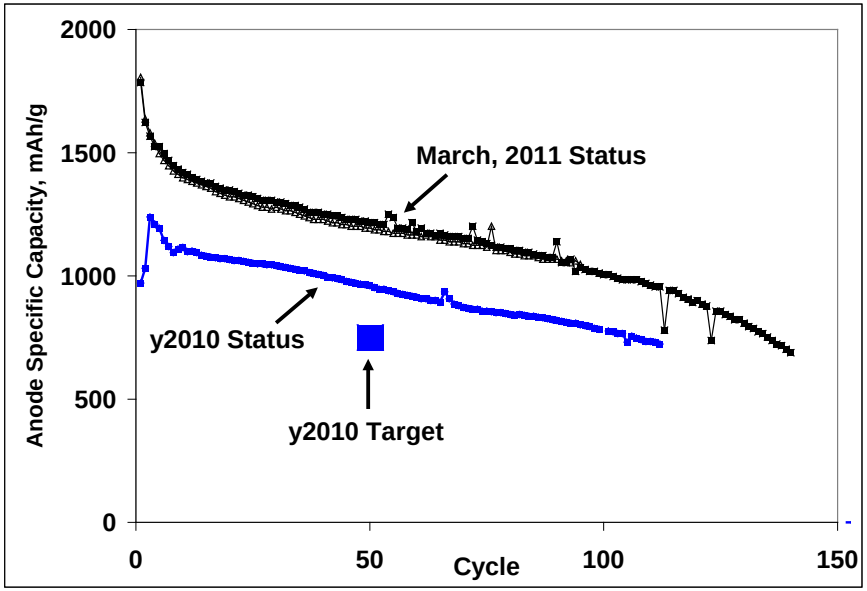
"Cathode" Electrolyte:

Readily solubilizes polysulfides

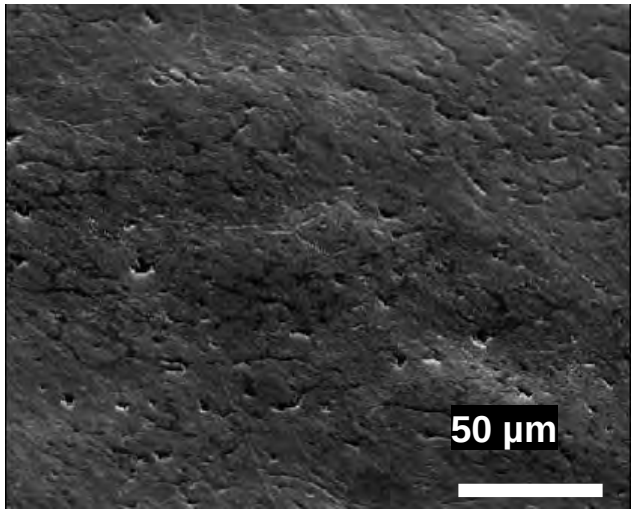
# Approach/Strategy

- Viability of dual phase electrolyte approach has been successfully demonstrated for the Li-S system for small 0.25 Ah cells.
- Approach to demonstrate large format 2.5 Ah cells with high energy >250 Wh/kg and dual-phase electrolyte systems included:
  - Modeling of large format 2.5 Ah Li-S cells and selection of optimal: electrodes sizes, substrates thickness, active materials loading and depth of discharge.
  - Large scale Gel Polymer Mixing/Coating Hardware System development and production of larger gel-polymer coated anodes and cathodes.
  - 2.5 Ah cells manufacturing and test.

# Technical Accomplishments and Progress




Anode specific capacity vs cycle.

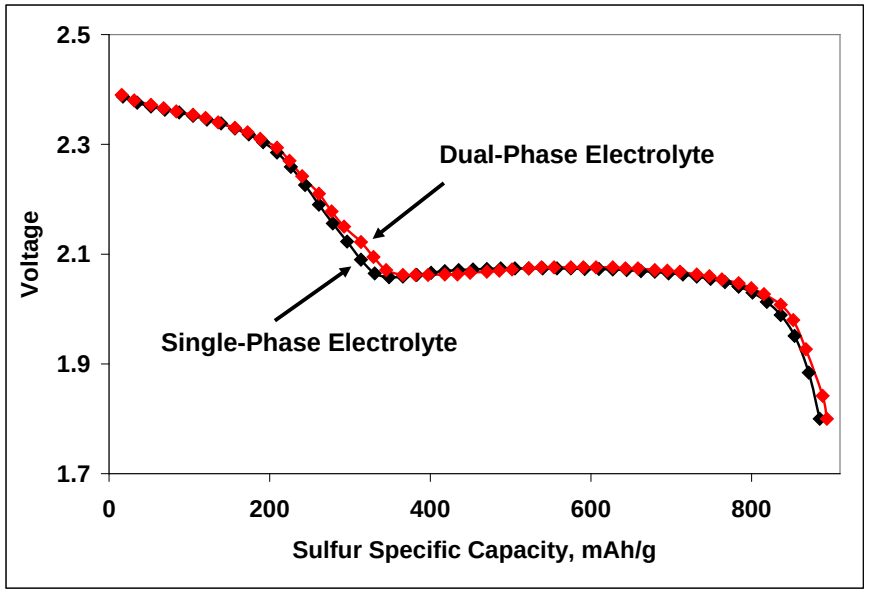



Anode surface after cycling.

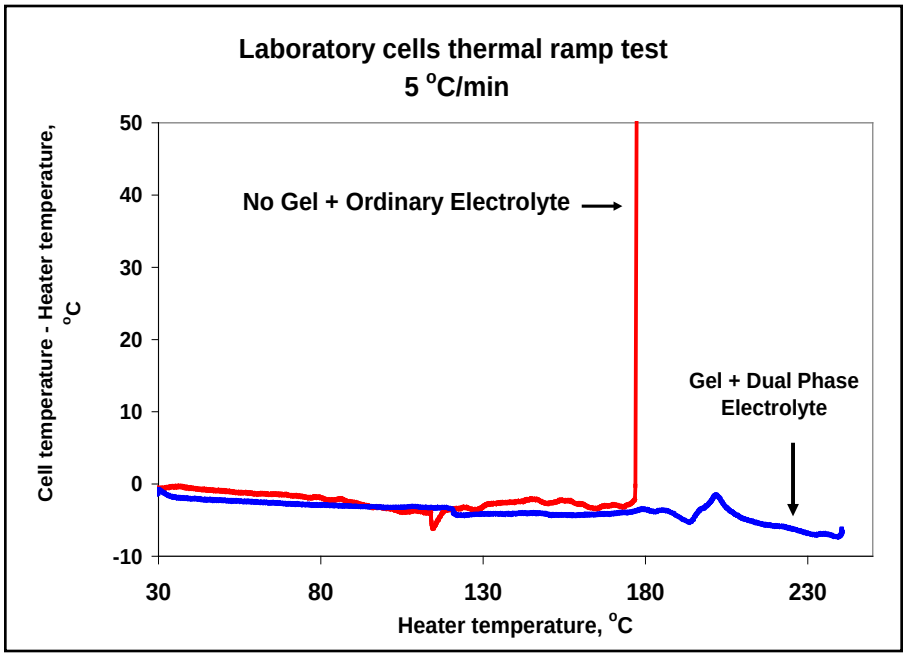
**We are still increasing cycle life of 0.25 Ah cells with Li anode protected with dual-phase electrolyte incorporated into gel-polymer. Cycle life reached 140 cycles at twice higher targeted anode specific capacity.**

**Application of gel-polymer combined with uniaxial pressure (part of ARPA-E project) eliminated development of mossy lithium and dendrites.**

# Technical Accomplishments and Progress



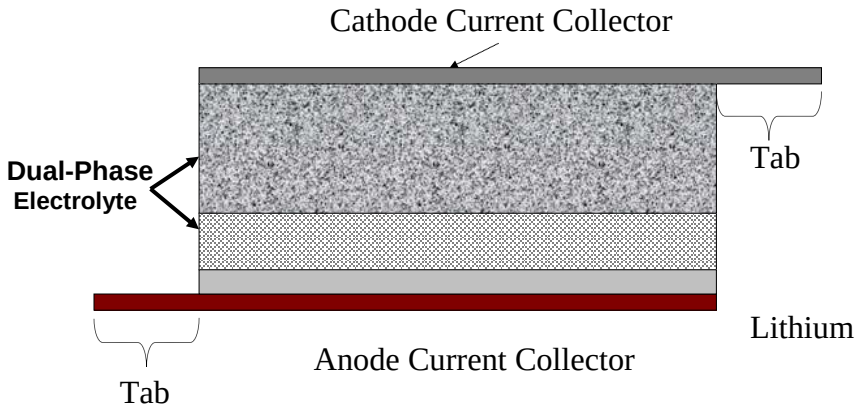

**Discharge profiles at 50th cycle at C/5 discharge rate**

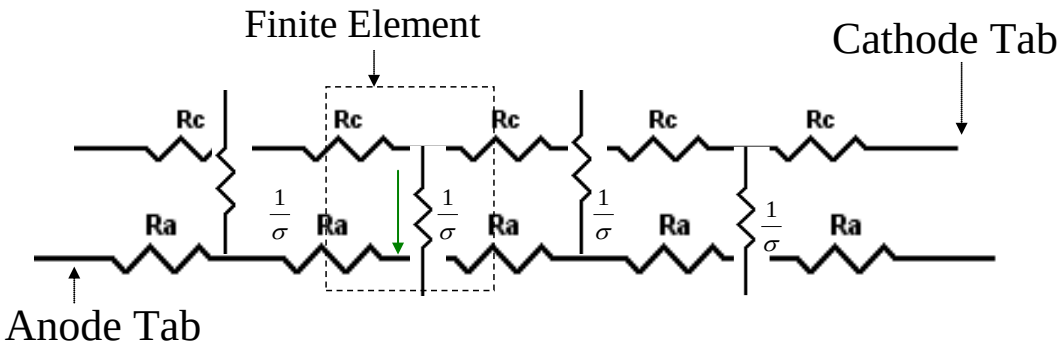



Introduction of dual-phase electrolyte did not cause additional cell polarization at discharge. We did not see rate/polarization limitations due to $Li^+$ migration from phase to phase.

Protection of Li anode with dual phase electrolyte and combined with uniaxial pressure (part of ARPA-E project) eliminated thermal runaway for 50% of the 0.25 Ah rechargeable Li-S cells tested at end of life.

# Dual-Phase electrolyte cell structural and electrical schemes for modeling




**$R_c$ = Cathode current collector's square resistance (Ohm)**

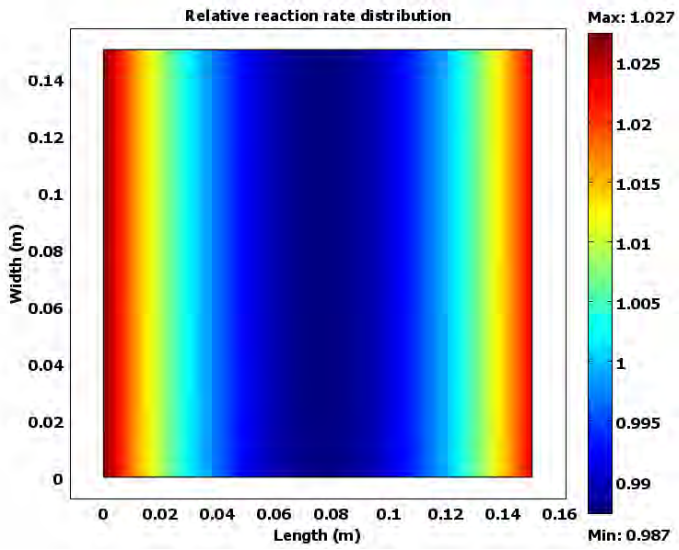
**$R_a$ = Anode current collector's square resistance (Ohm)**

**σ = Area specific conductance (due to electrochemical reactions at cathode and anode and Gel and Dual-Phase electrolyte conductivity)**

**σ = 1/ASR (Area Specific Resistance)**

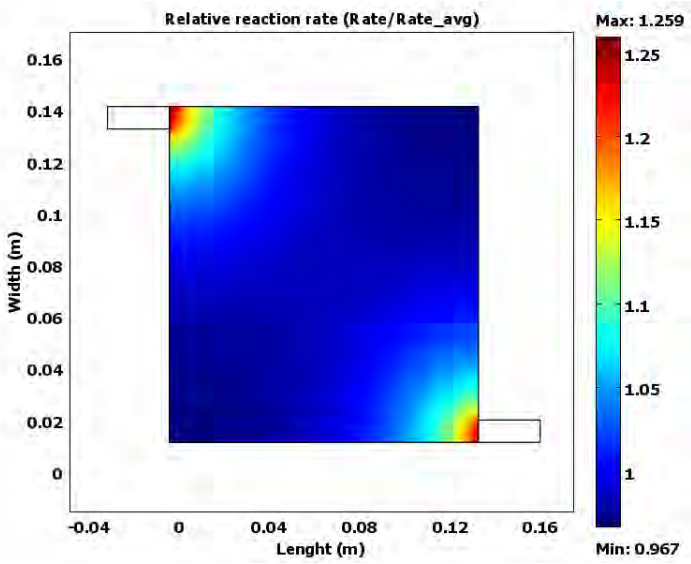
# Technical Accomplishments and Progress

- Modeling and selection of electrode terminal connection:




**Tabs along electrodes**

**(max-min)/max = 4%**



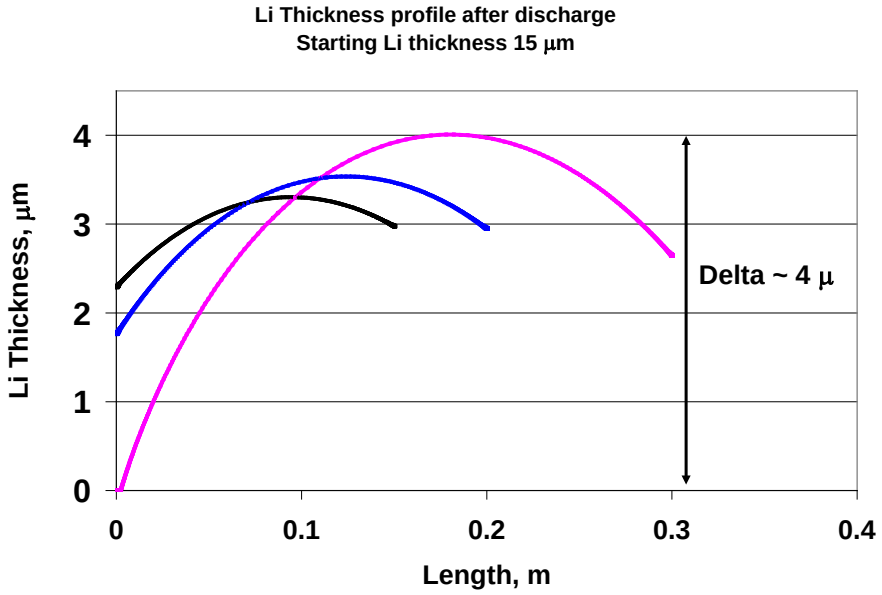

**One point connection**

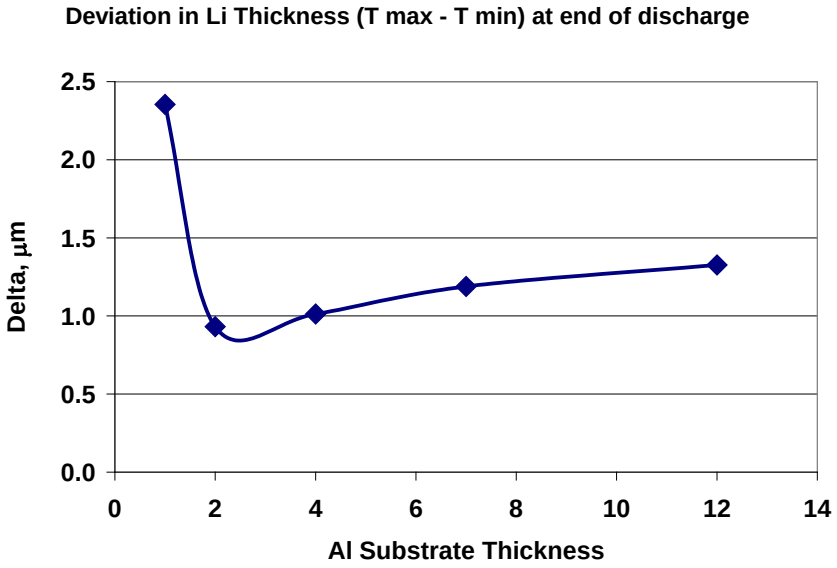
**(max-min)/max = 30%**

Single point terminal connection for cathode and anode electrodes results in ~8 times larger non-uniformity in the current distribution (right figure) compared with continuous terminal connection at one of the electrode sides.

# Technical Accomplishments and Progress

- Modeling and selection of electrodes length and cathode substrate thickness:



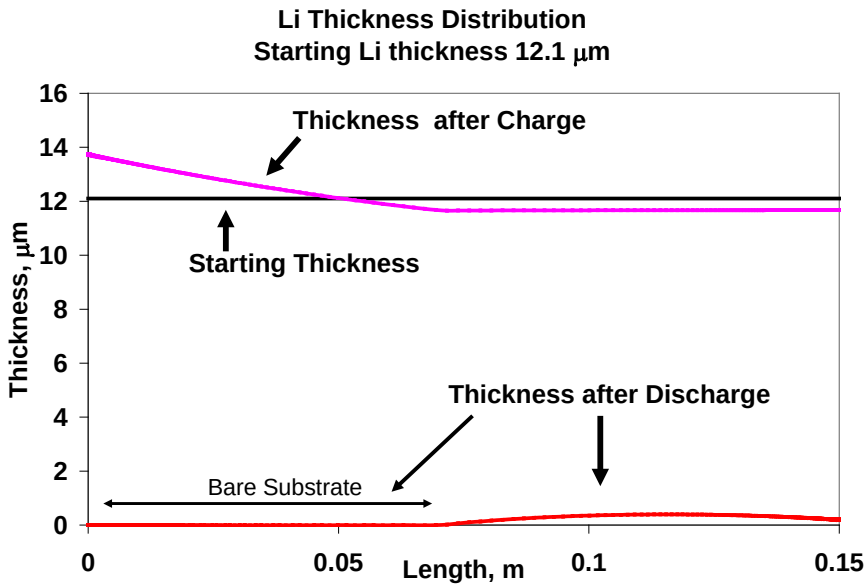



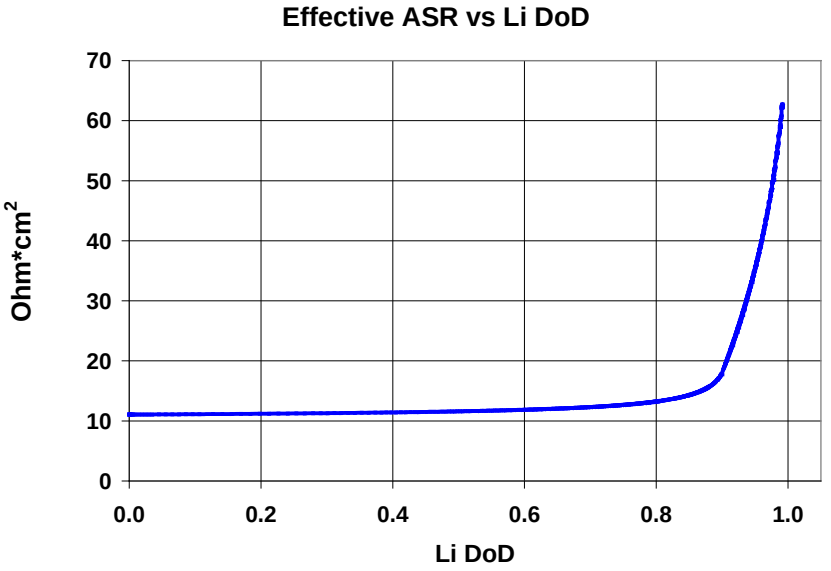

**Long electrodes will result in larger non-uniformities in the current distribution. Current will be concentrated near electrodes terminals and result in excessive Li stripping in these areas. At electrodes length less than 15 cm end of discharge lithium thickness non-uniformity will be less than 2 μm.**

**Very thin Al cathode substrates are attractive for low weight. However, too thin and resistive a substrate can cause large non-uniformities in the current distribution and lithium thickness at end of discharge. Minimal Li non-uniformity can be found in the 4-7 μm Al thickness range.**

# Technical Accomplishments and Progress

- Modeling and selection of optimal starting Li thickness and depth of discharge:




**At the end of discharge lithium can be stripped completely near the anode terminal, exposing bare substrate (left side of figure). Subsequent charge can result in thicker deposited lithium near the terminal. This problem can be solved by using thicker starting Li (> 15 μm) and avoiding exposure of the thin metalized substrate.**

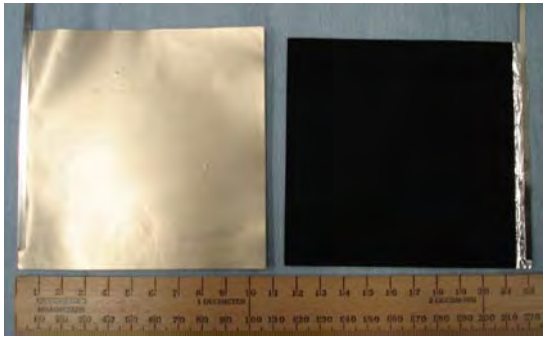
**At high Li anode depth of discharge (DoD) (>90%) thin metalized substrate can be exposed near the anode terminal (see left figure) and result in increased anode resistance and total cell Area Specific Resistance (ASR). The solution is to keep the starting Li thickness > 15 μm.**

# Technical Accomplishments and Progress

- **Gel Polymer Electrolyte Mixing/Coating Hardware System Development/Optimization:**
  - Gel-polymer mixing and silica filler dispersing hardware systems were upgraded and enabled production of up to 4 gallons of coating mixture.
  - Coating conditions were optimized for gravure and slot die techniques.
  - At optimal conditions Sion Power's pilot gel-coater produced gel-polymer films with thicknesses in the range from 2 –10 μm, with roughness less than 0.05 μm and at speeds of 1-1.5 m/min.

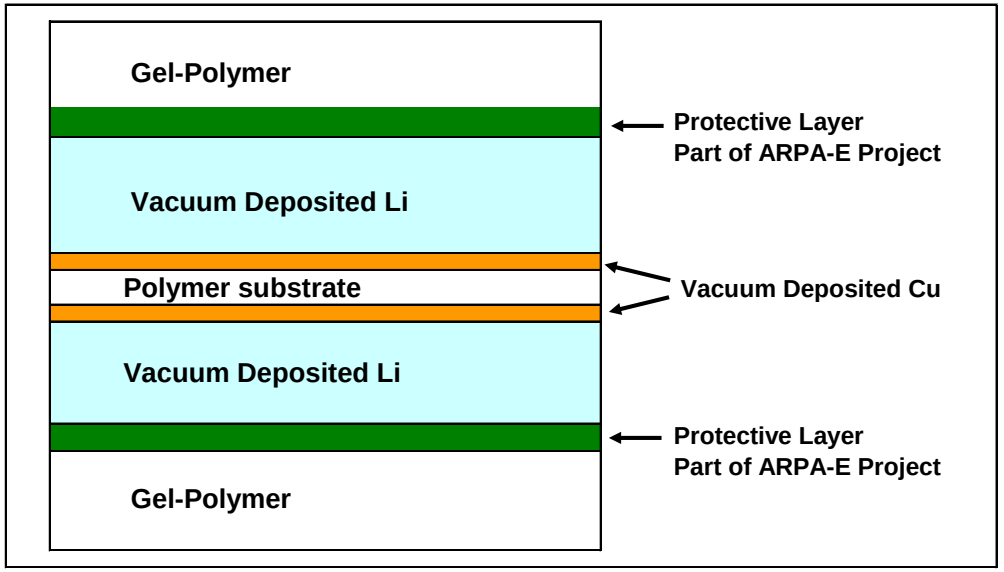
# Technical Accomplishments and Progress

## 2.5 Ah cells manufacturing started (March,2011 Status).



2.5 Ah cell anode and cathode images


2.5 Ah cell image




Dual-Phase Electrolyte Anode Structure

**Anode unit includes gel-polymer layer to hold "anode component" of dual phase electrolyte and can include other features (Protective layer, thin polymer substrate) related to ARPA-E project.**

**The protective layer, working together with uniaxial pressure, polymer-gel and dual-phase electrolyte is expected to increase cycle life to 500-1000 cycles.**

# Proposed Future Work

- Remaining Milestones of Phase 2 to be Achieved by July 31, 2011
  - 2.5 Ah cells electrolyte, gel-polymer and electrodes mass balance optimizations.
  - 2.5 Ah cells performance evaluations under USABC test conditions.
- Phase 3 Objective: Large format cell manufacturing, test and evaluation. Demonstration of high energy, cycle life, and safety (thermal runaway temperature > 165$^{o}$C) (9/30/12).

# Collaboration

Sion Power Corporation and BASF SE, Ludwigshafen, Germany, announced a Joint Development Agreement (JDA) to accelerate the commercialization of Sion Power's proprietary lithium-sulfur (Li-S) battery technology for the electric vehicle (EV) market and other high-energy applications.

The collaboration targets the development of battery materials to increase Li-S cycle life, energy density and safety to extend driving range of future EVs beyond 300 miles between charges.

- Relationship: Partner in JDA (not a sub-contractor).
- BASF collaborates with Sion Power outside the VT Program.
  - 14 BASF scientists report to Sion's Director of Materials Development and work full time on Li-S technology.

# Summary

- Cycle life approached 140 cycles at twice higher than targeted anode specific capacity.
- Lithium anode did not show development of mossy lithium or dendrites after cycling.
- Protection of Li anode with dual phase electrolyte eliminated thermal runaway for 50% of the 0.25 Ah rechargeable Li-S cells tested at end of life.
- Modeling and design of large format 2.5 Ah Li-S accomplished: optimal electrodes sizes, substrates thickness, active materials loading and depth of discharge selected.
- Large scale Gel Polymer Mixing/Coating Hardware System was developed and produced gel-polymer coated anodes for 2.5 Ah cells.
- 2.5 Ah cells manufacturing started (March, 2011 Status).