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Low Temperature Performance Characterization & Modeling

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U.S. Department of Energy

UChicago Argonne LLC

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Vehicle Technologies Program

Overview

Timeline

- Start: October 2003
- Finish: September 2008
- 100% Complete

Budget

- ~$600K per year

Barriers

- Lithium ion cells experience 20X increase in impedance at -30 °C.
- USABC HEV goal: three 5 kW pulses at -30 °C
- Must reduce ASI to ~100 Ω-cm² at -30 °C.

Partners

- Idaho National Laboratory
- Army Research Laboratory

Objectives

- Understand the extent of the poor low temperature performance of lithium-ion batteries by characterizing the behavior of a wide range of non-traditional solvents, salts, active materials, and surface morphologies.

- Use electrochemical modeling studies combined with experimental efforts to gain insights into sources of impedance and aging mechanisms.

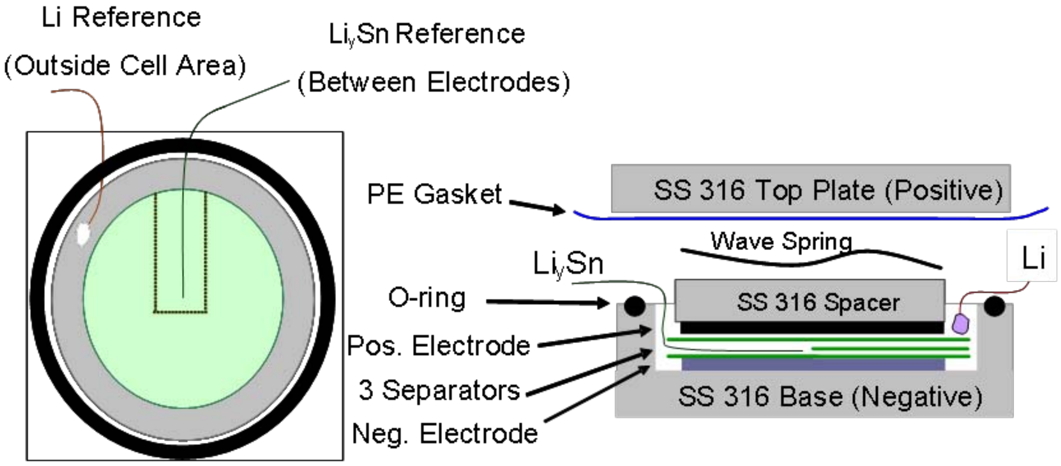
- Propose methods of mitigating effects of low temperature on lithium-ion battery performance.

Key Milestones

Developed low temperature reference electrode cell system	Dec-2003
Determined viscosity and density effects at low temperature	Mar-2006
Developed electrochemical model for anode and cathode	Sep-2006
Completed Butler-Volmer Kinetics study	Apr -2007
Completed of interfacial portion of the negative electrode electrochemical model	Sep-2008
Assessed microcalorimetry technique for lithium deposition	Sep-2008

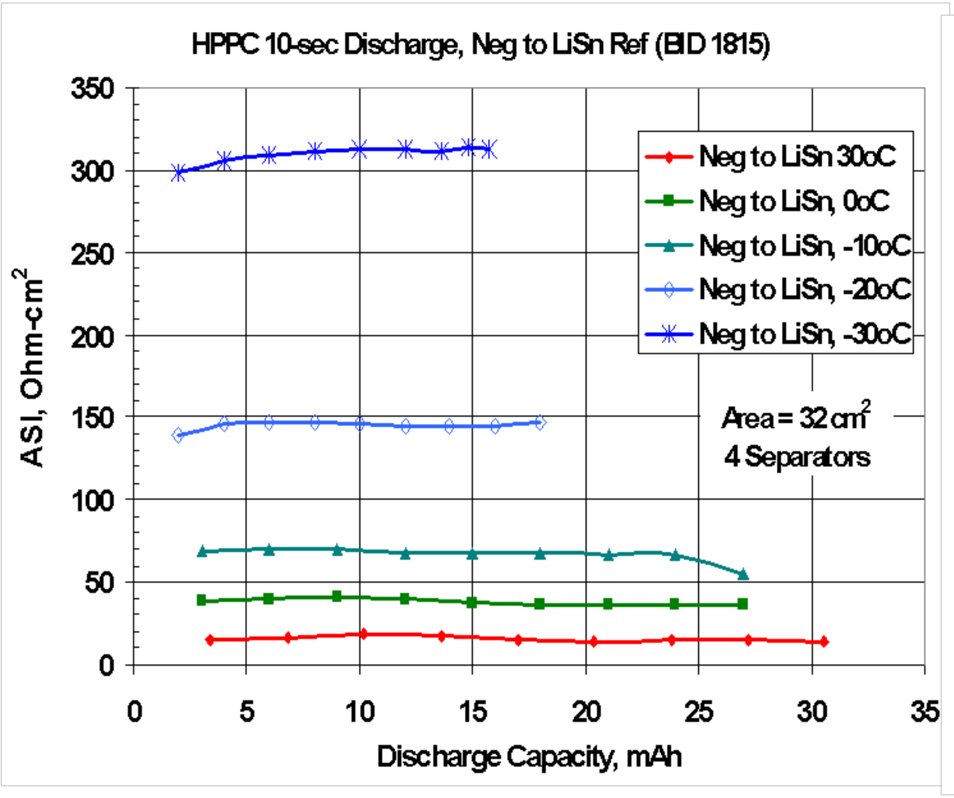
Approach

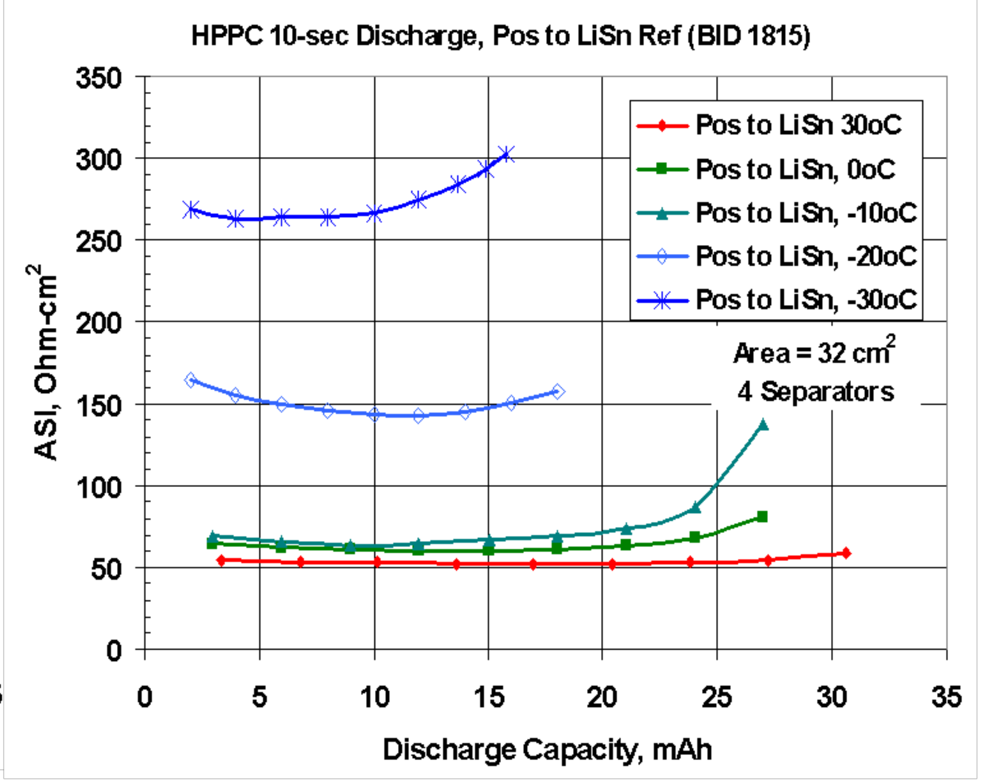
- Identify and systematically investigate physical and electrochemical properties that could influence low temperature performance using tailored test apparatus and electrochemical modeling
  - Active Material ☒
  - Conductivity ☒
  - Lithium Salt ☒
  - Charge or Discharge ☒
  - Salt Molarity ☒
  - Electrolyte Viscosity ☒
  - Binder ☒
  - Kinetic or Diffusion Limited ☒
  - Surface Area ☒
  - Carbonate Solvents ☒
  - Supporting Electrolytes
  - Inherent Lithium Redox Reaction Kinetics



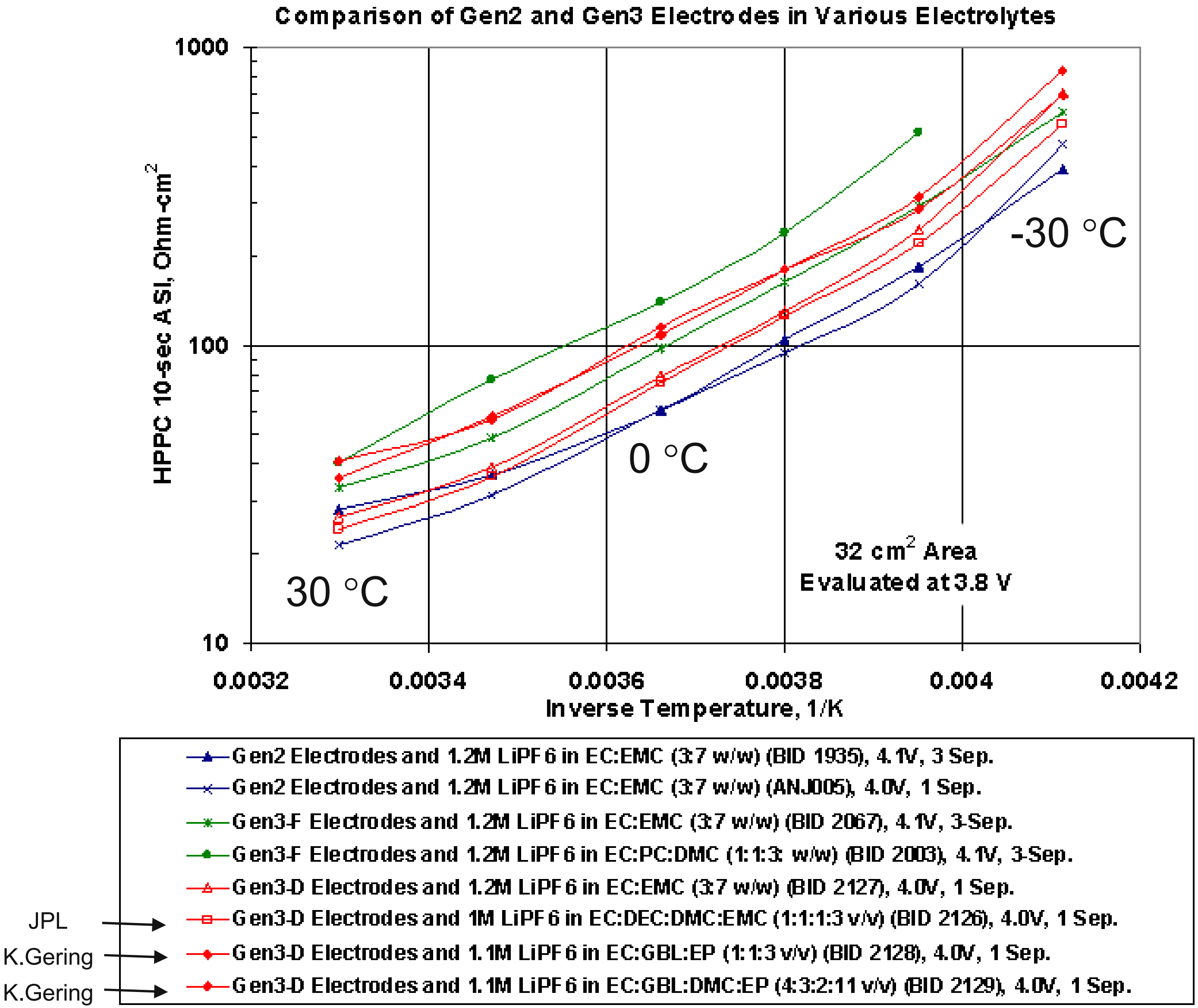
Negative and Positive Electrodes have Similar Power Loss at Low Temperature

Technical Accomplishments 2004





Li-ion Cells Lose Power when Cold



JPL
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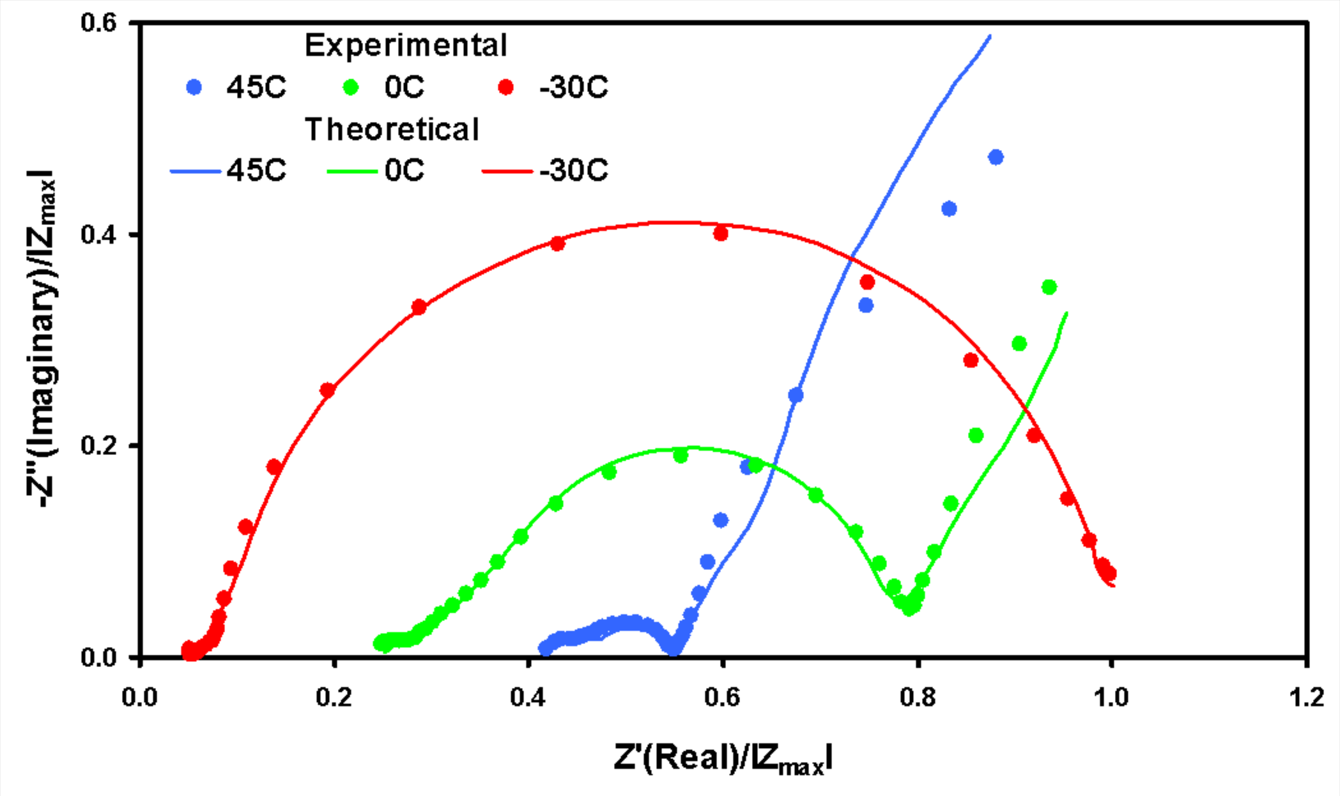
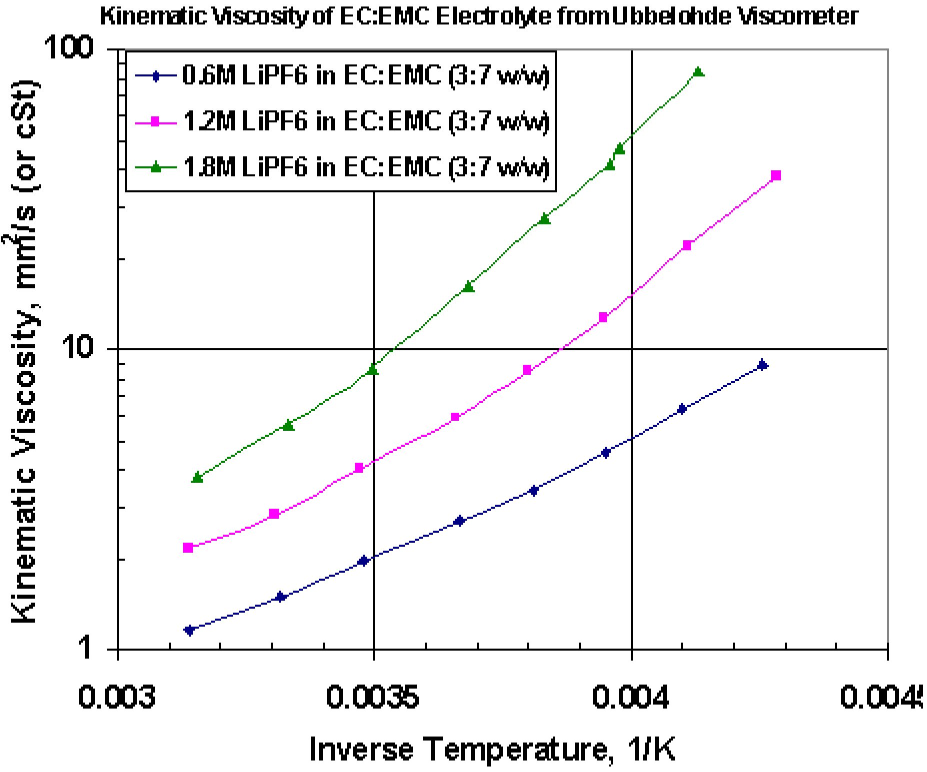
All cells have similar low temperature behavior (same activation energy).

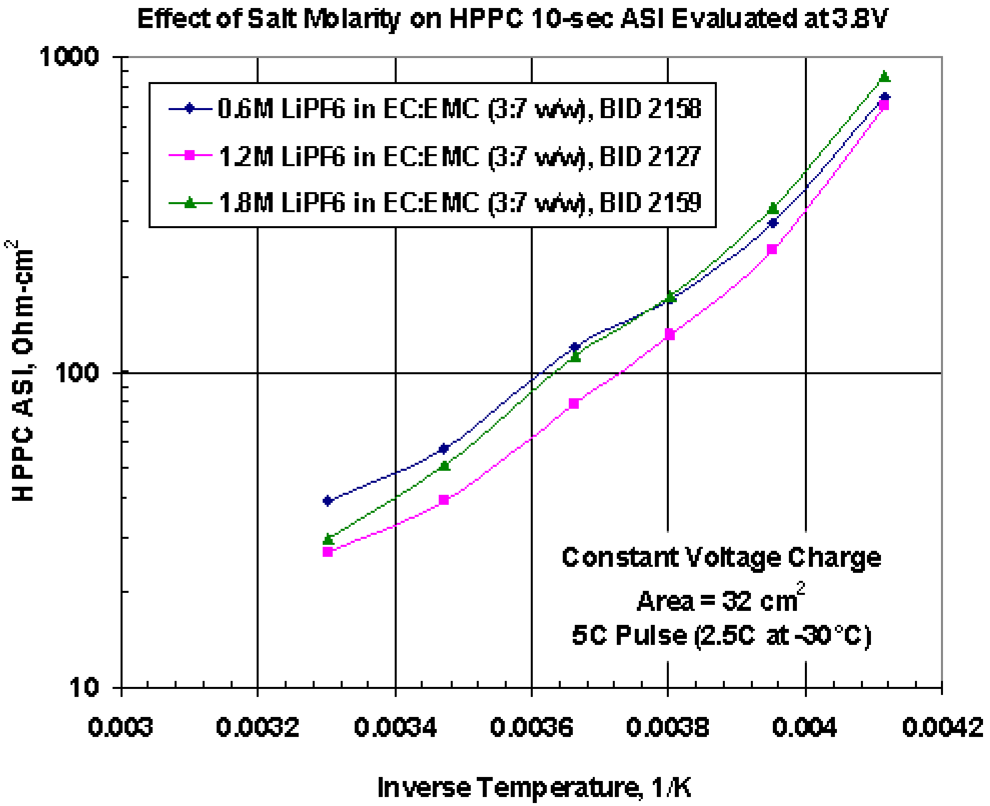
Simulation of Gen 2 NCA Positive Electrode AC Impedance Over Wide Temperature Range



- Generally, all interfacial parameters are relatively sensitive to temperature
- Of all the interfacial parameters, the kinetic exchange current density is shown to be the strongest function of temperature

Little Effect of Salt Molarity (and Viscosity) on Impedance

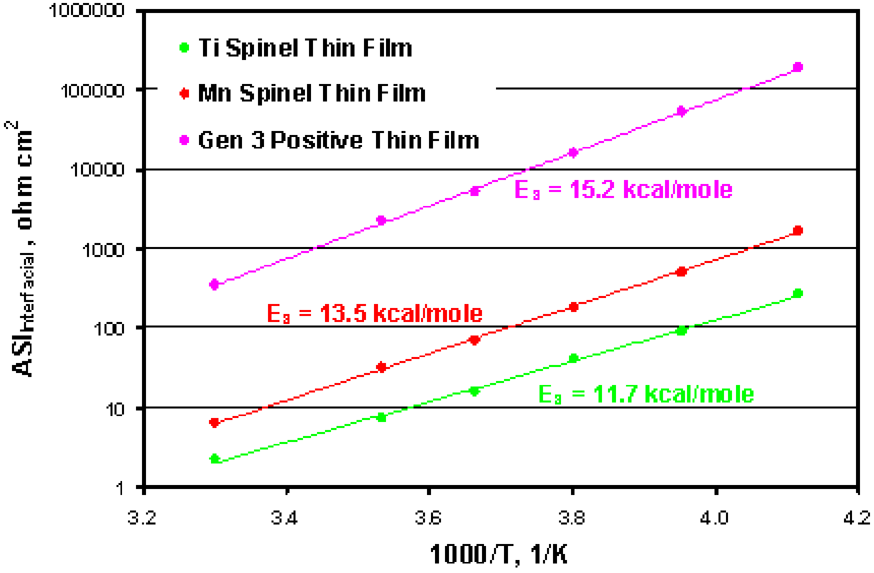

Kinematic Viscosity of EC:EMC Electrolyte from Ubbelohde Viscometer

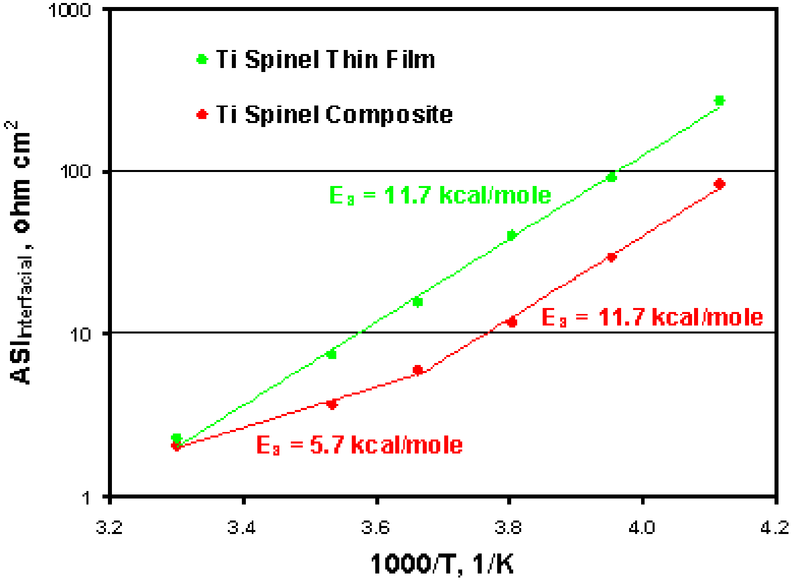

Effect of Salt Molarity on HPPC 10-sec ASI Evaluated at 3.8V

This further confirms that the power limitations at low temperature are not due to bulk electrolyte properties.

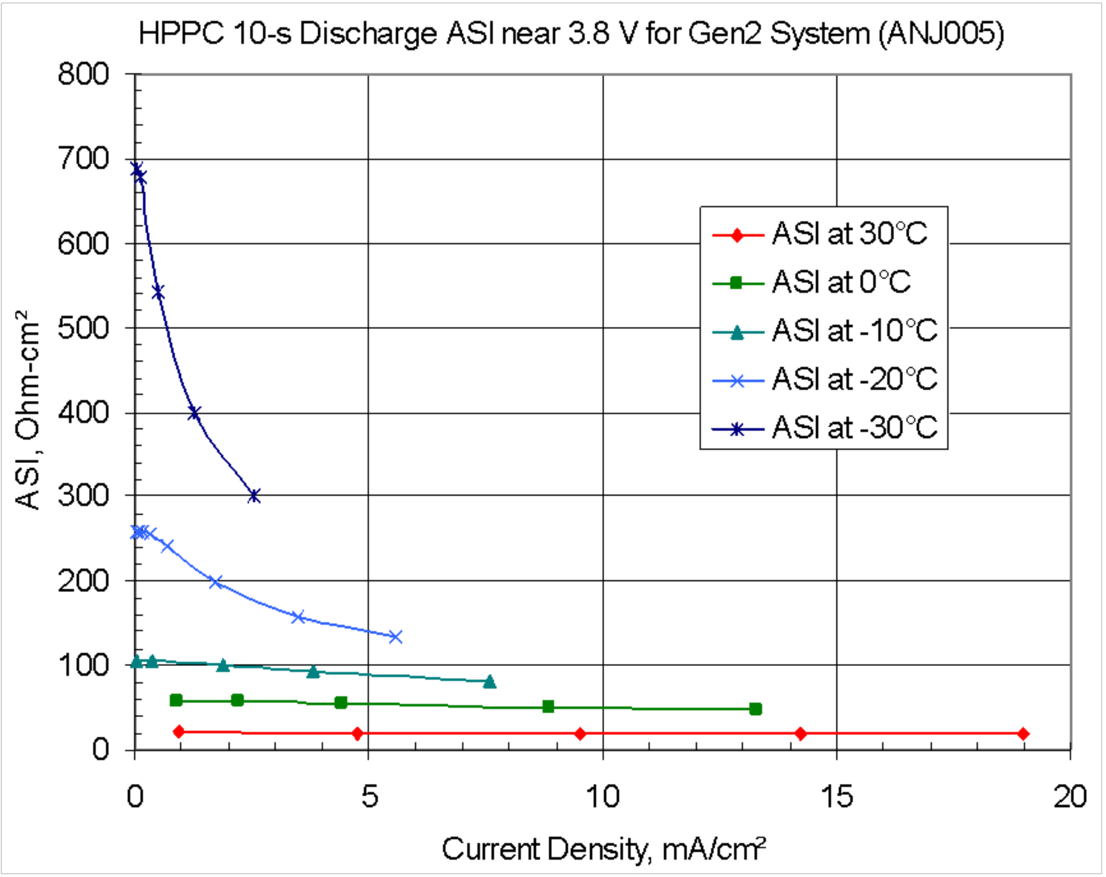
Thin Film Binder and Carbon Free Electrodes Also Suffer at Low Temperature

- The BCF electrode’s electrochemically active area can only be estimated (Ti Spinel > Mn Spinel > Gen 3 Positive)
- The interfacial impedance of all thin film BCF electrodes studied exhibit a strictly Arrhenius type behavior (i.e. no change in slope at 0°C)
- The interfacial impedance of all three oxides studied had similar Arrhenius activation energies (E_a), suggesting the active material’s role is minor.
- As shown for the Ti Spinel the E_a of the BCF electrodes agrees with the low-temperature E_a exhibited by conventional composite electrodes, which suggests the binder and carbon also play a minor role.

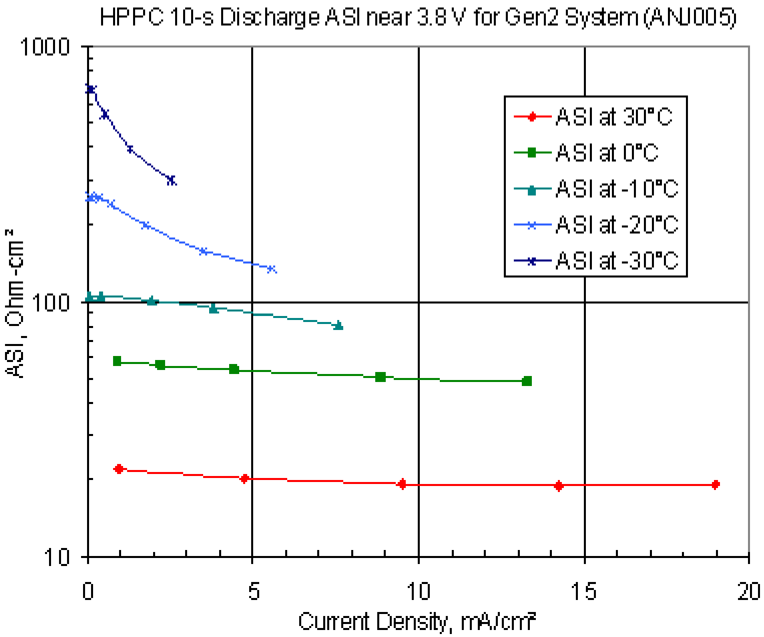




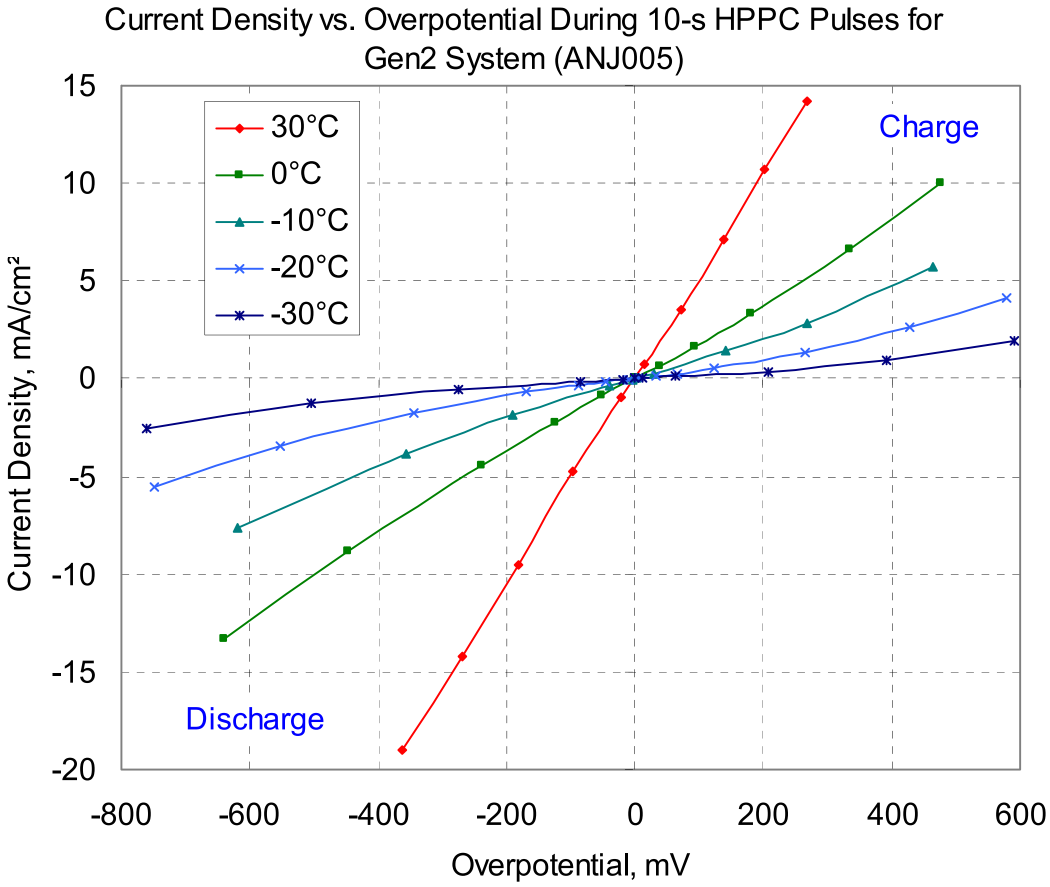
Impedance Depends Strongly on Current at Low Temperature

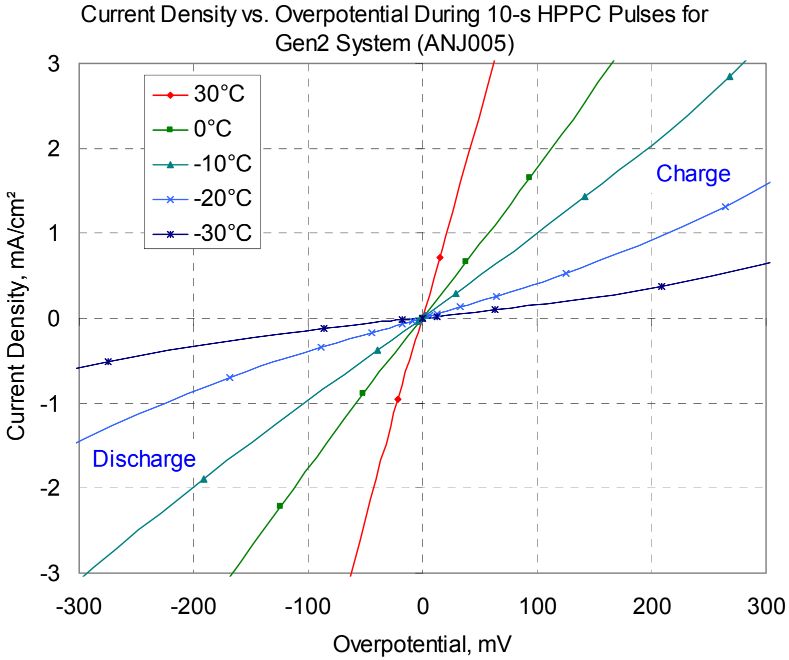


A decreasing resistance with increasing current may seem counter-intuitive, but this phenomena is fully explained by Butler-Volmer kinetics.



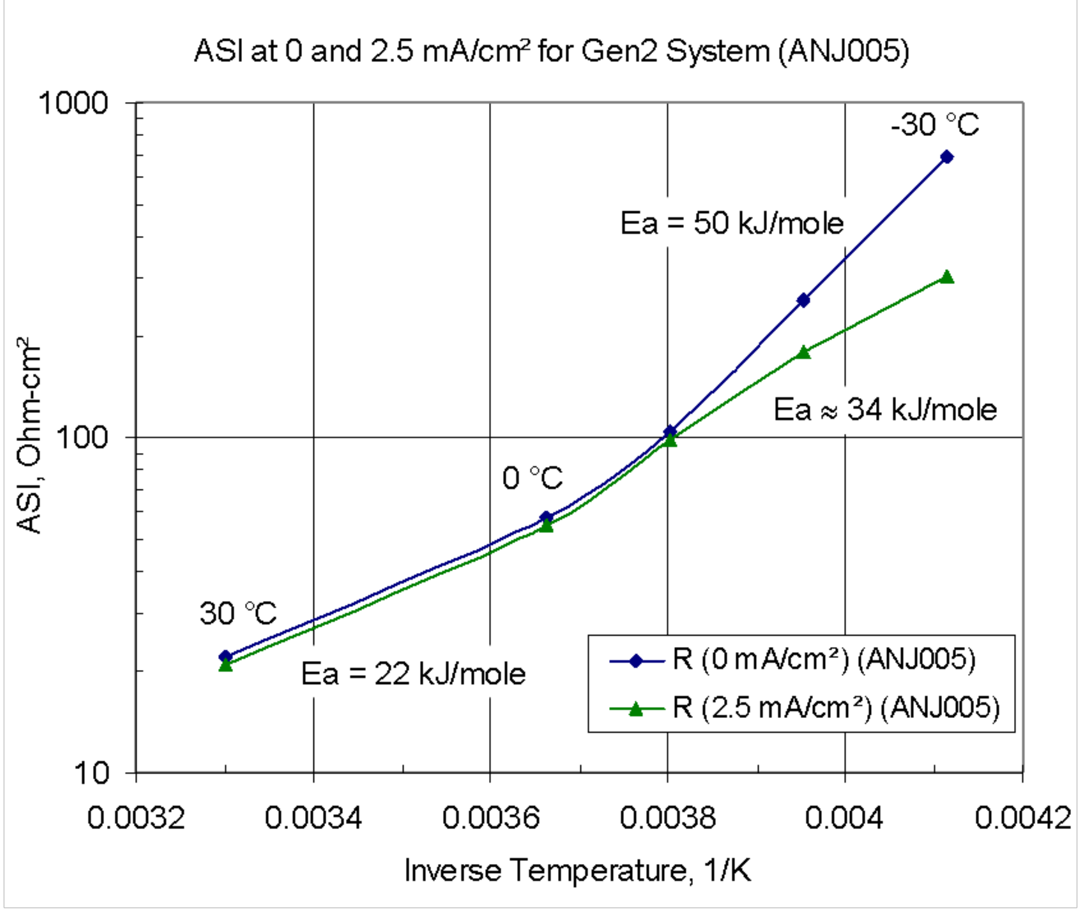
HPPC Data Obey Classic Butler-Volmer Kinetics


Current Density vs. Overpotential During 10-s HPPC Pulses for Gen2 System (ANJ005)


Current Density vs. Overpotential During 10-s HPPC Pulses for Gen2 System (ANJ005)

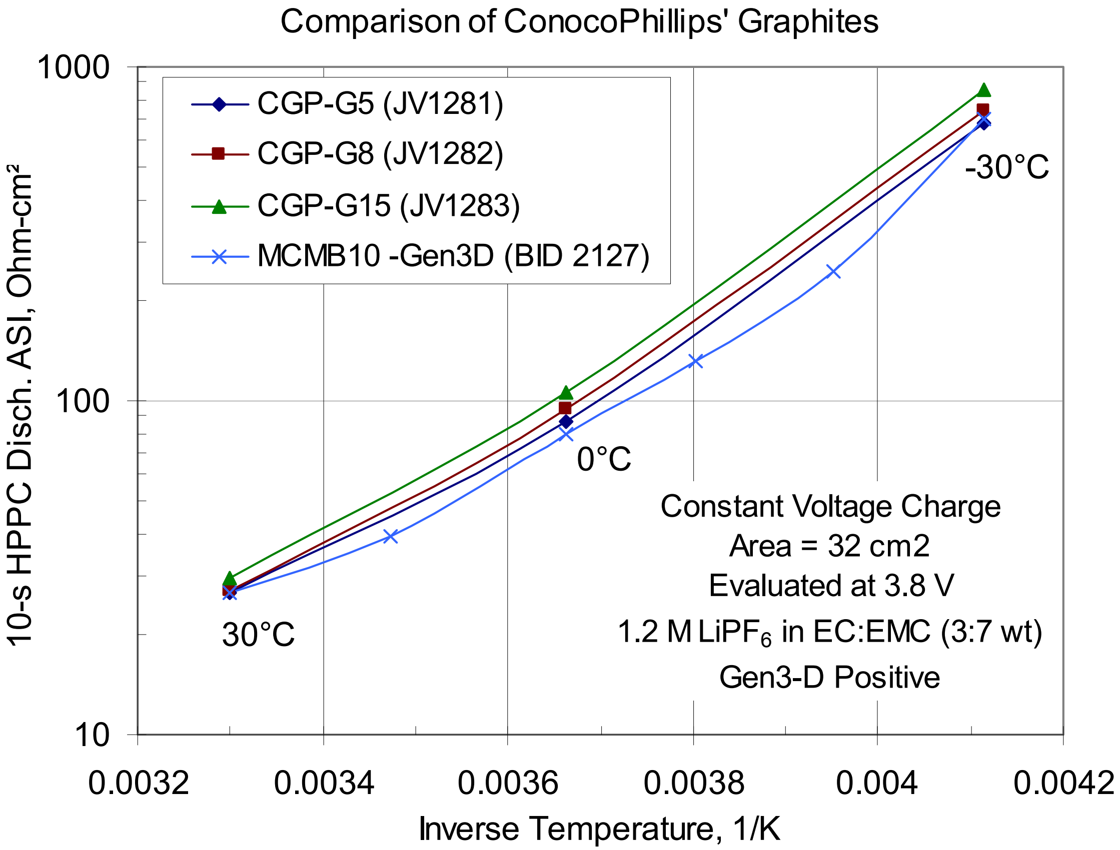
- Exchange current (i_0) increases with temperature
- Nearly symmetric current-overpotential response, *i.e.*, charge and discharge resistance are nearly identical

Activation Energy Clearly Increases Below 0 °C



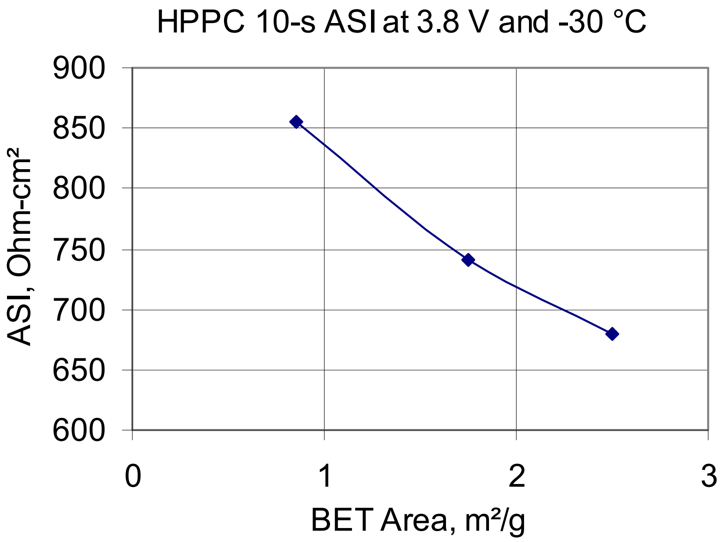
- The low temperature activation energy will decrease as the current (or overpotential) increases.
- It is generally bounded between 34 and 50 kJ/moles for normal operating voltages.

Higher Surface Area Improves Power, But Not Enough


Comparison of ConocoPhillips' Graphites

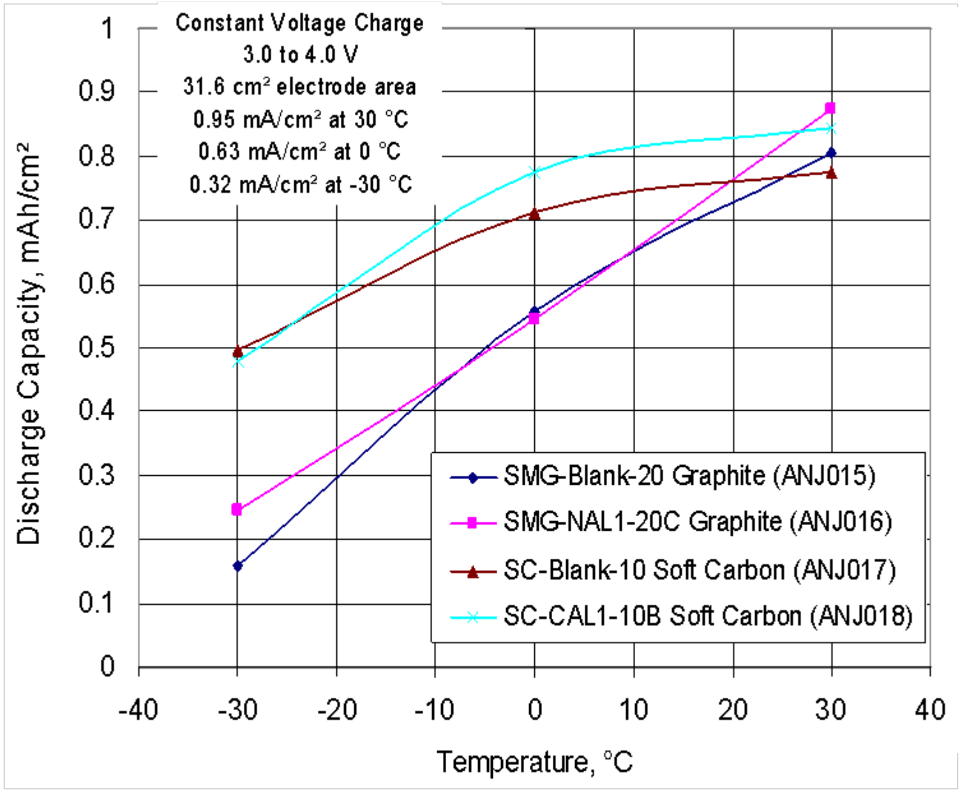
Constant Voltage Charge
Area = 32 cm2
Evaluated at 3.8 V
1.2 M $LiPF_6$ in EC:EMC (3:7 wt)
Gen3-D Positive

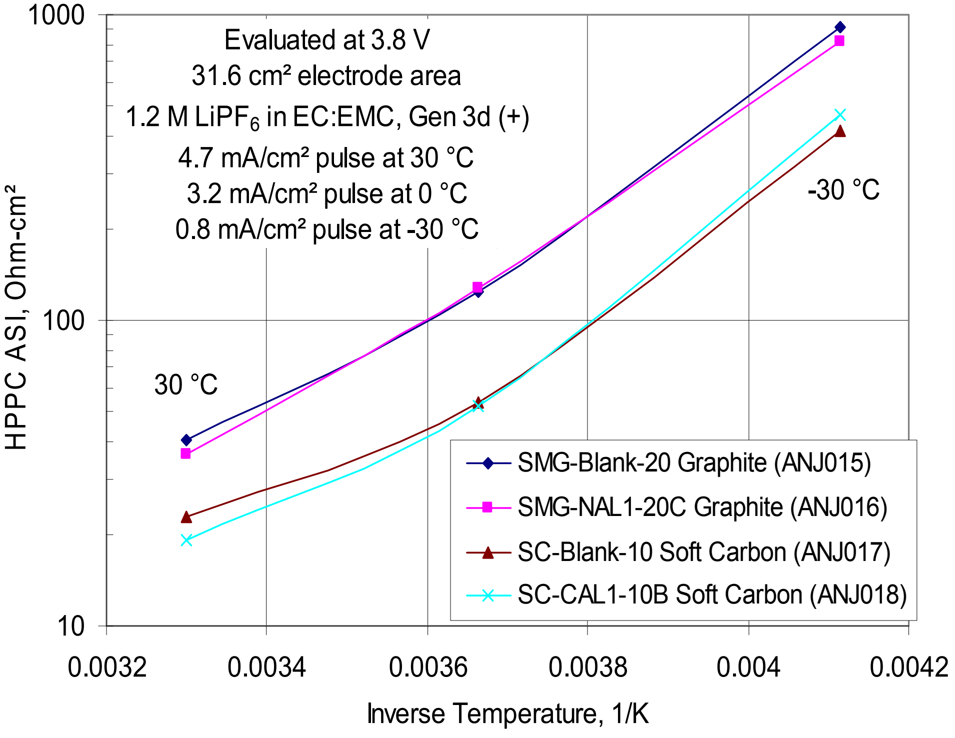
- ConocoPhillips' graphites have an impedance response very similar to the ATD's Gen3 graphite.
- Higher surface area will not by itself solve the low temperature problem.


HPPC 10-s ASI at 3.8 V and -30 °C

Surface Modifications Do Not Have a Significant Effect

Hitachi Chemical's natural graphite (SMG) and soft carbon (SC)

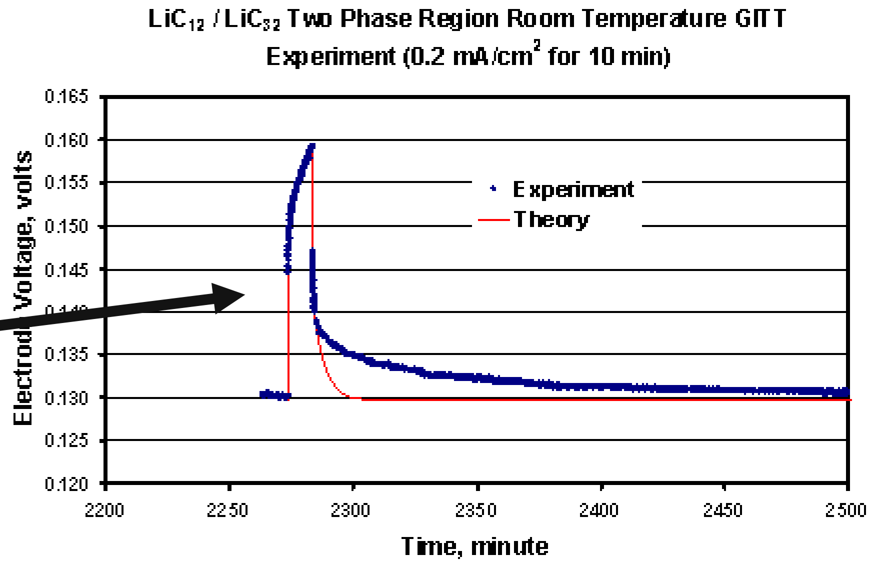




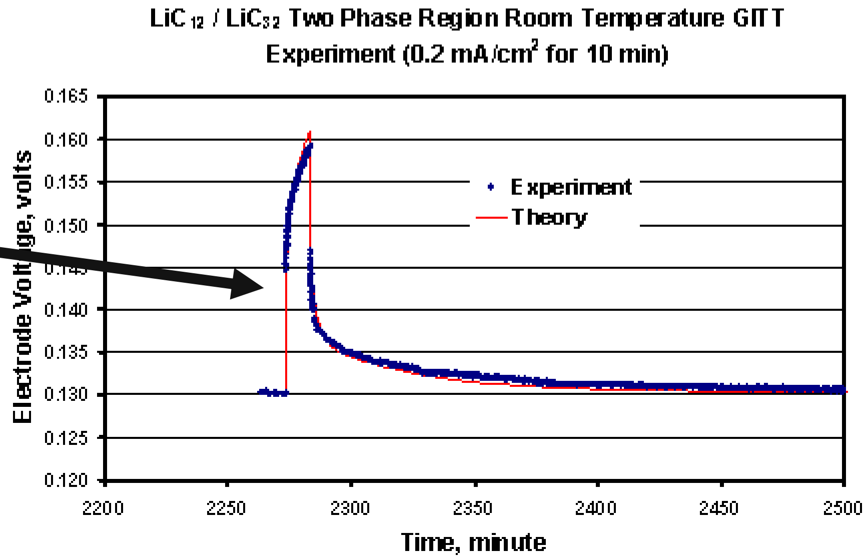
Soft carbon's better performance in this study is most likely due to its smaller jagged particles (exposed surface area and morphology).

Several Two Phase Active Material Electrochemical Models Examined for Graphitic Negative Electrode

- Shell and core phases in active material particle with lithium diffusion only in outer shell phase and fast phase transition reaction
  - Partial fit of GITT data
- Shell and core phases in active material particle with lithium diffusion in both shell and core phases with finite phase transition reaction and phase equilibrium at interface
  - Good fit of GITT data
- These studies where extended into a more general two phase reaction diffusion model under the PHEV modeling effort

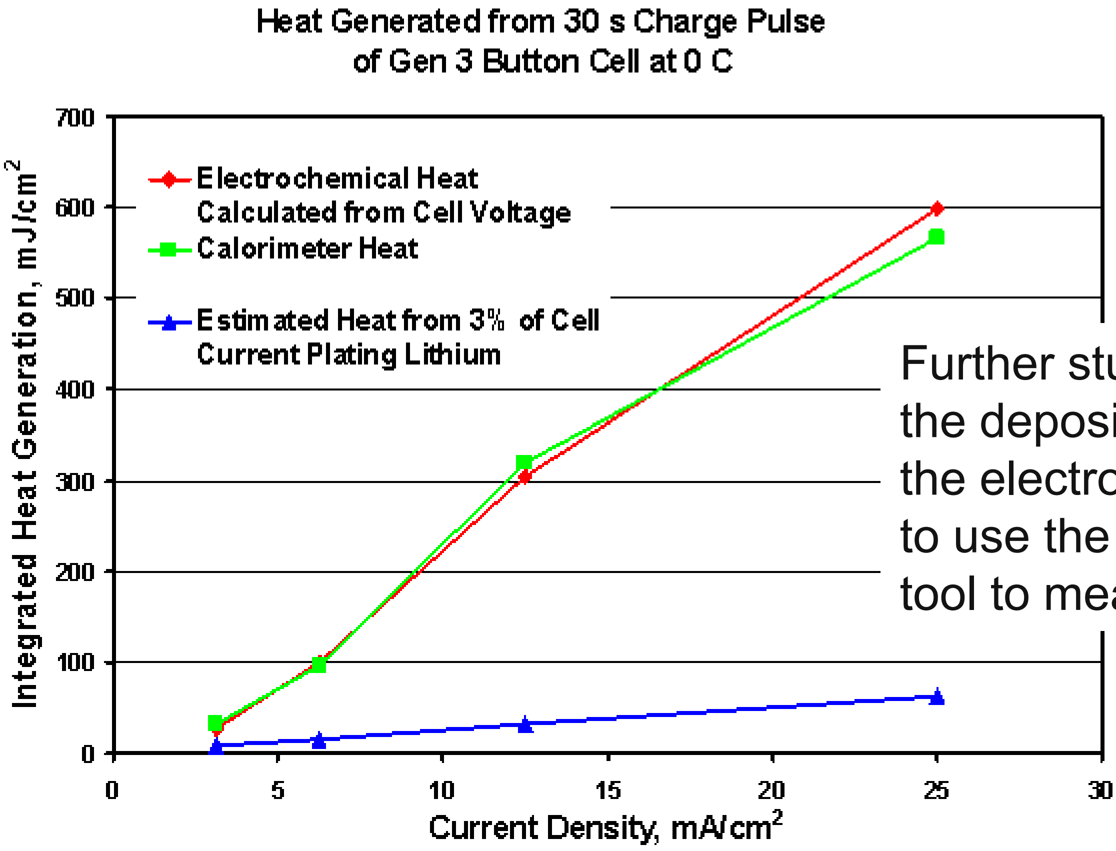


LiC_{12} / LiC_{32} Two Phase Region Room Temperature GITT Experiment (0.2 mA/cm^2 for 10 min)



LiC_{12} / LiC_{32} Two Phase Region Room Temperature GITT Experiment (0.2 mA/cm^2 for 10 min)

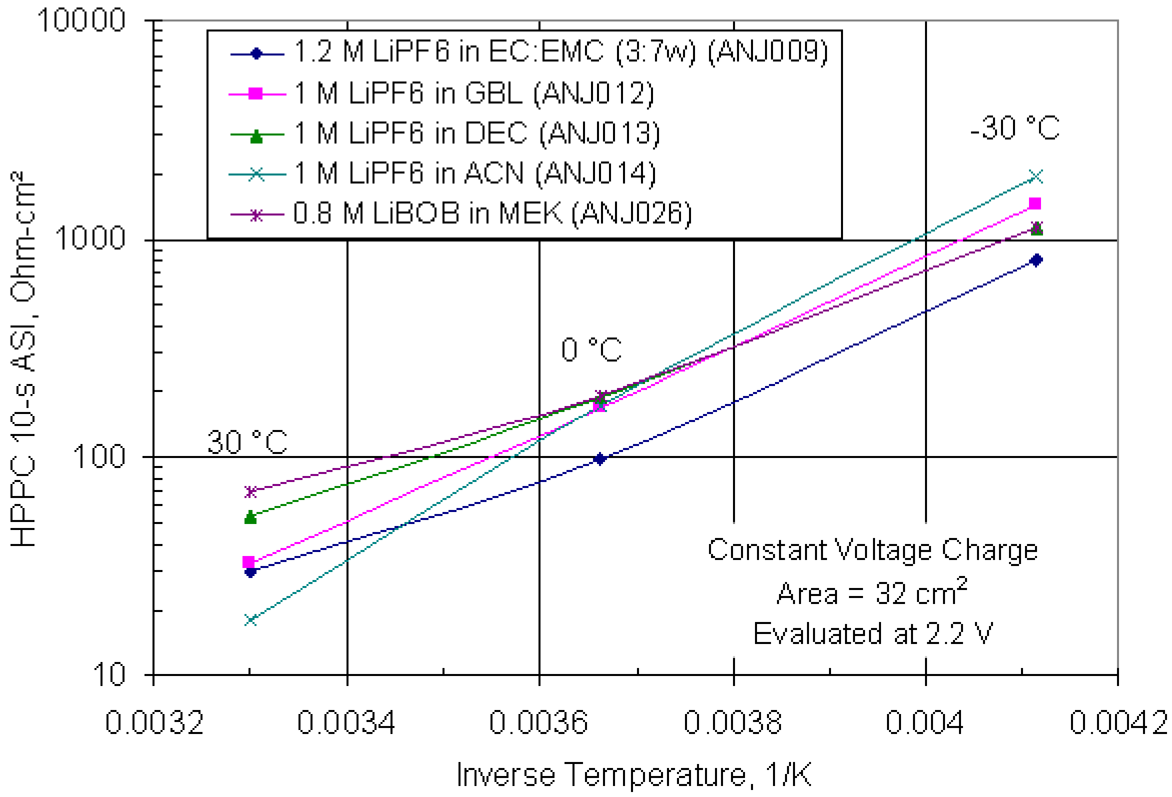
Electrochemical Microcalorimetry Study of Lithium Deposition on Graphite at Low Temperatures



Further studies indicated that very little of the deposited lithium actually reacted with the electrolyte, making it extremely difficult to use the microcalorimeter as a quantitative tool to measure the lithium deposition rate.

Electrochemical Calorimetry sensitivity to lithium plating estimated at a few percent of cell current

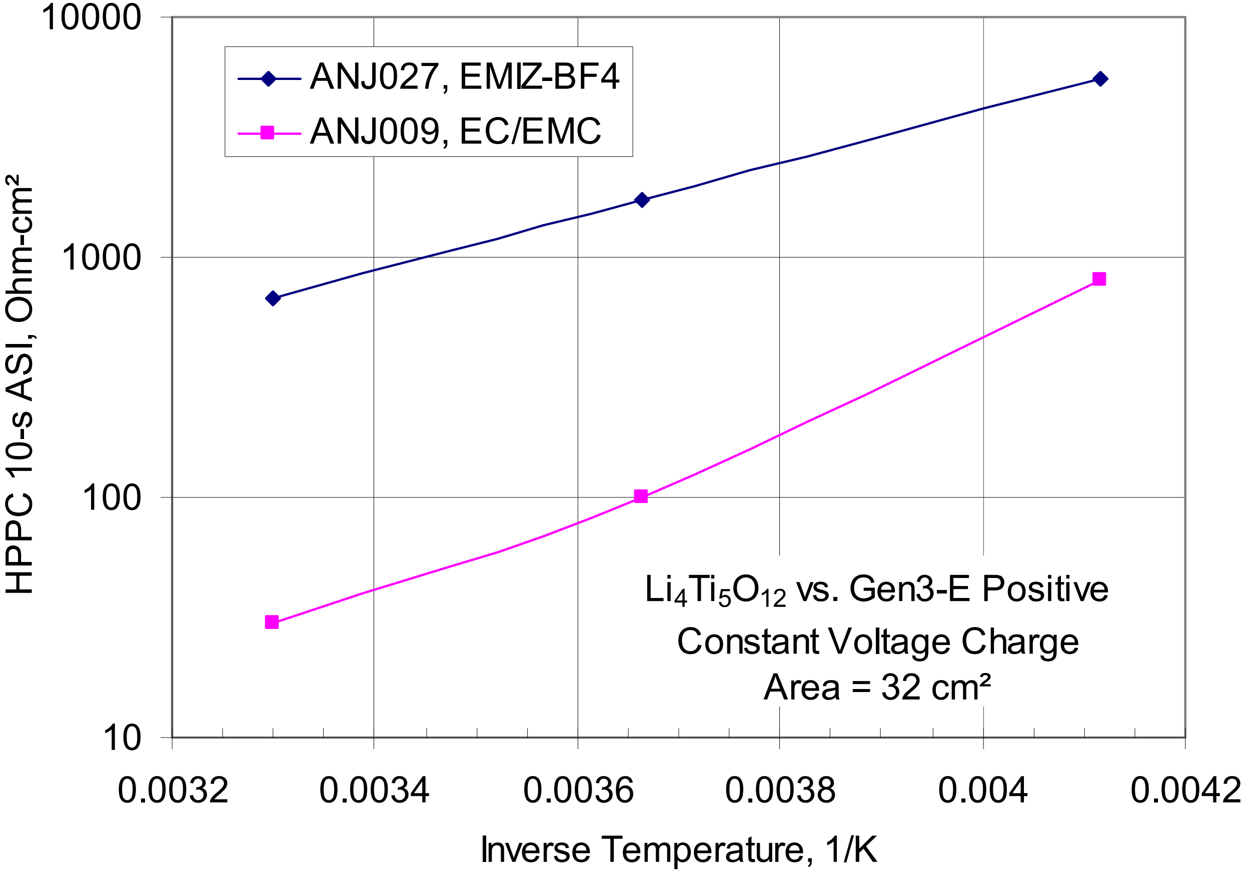
Non-Carbonate Based Electrolytes Also Suffer at Low Temperature


Comparison of Solvents with $Li_4Ti_5O_{12}$ (Kyorix) vs. Gen3-D Positive

- Other solvents suffer too:
  - Diethyl Carbonate
  - γ-Butyrolactone
  - Acetonitrile
  - Methyl Ethyl Ketone
  - Many others!
    - *Substituted furans*
    - *Oxazolines*
    - *Esters*
    - *Sulfolanes*
    - *Thiazolines*
- No solvent (or additive) system has been found yet that has a significantly lower activation energy.

Ionic Liquids Are Not Immune to Low Temperature Power Loss

1M $LiPF_6$ in ionic liquid 1-ethyl-3-methylimidazolium-BF_4 versus 1.2 M $LiPF_6$ in EC:EMC (3:7 w/w).



Future Work

- No specific future work is planned in the low temperature performance area since this project was brought to a close in September, 2008.

- Novel technologies that develop in the lithium-ion battery area will be evaluated for their low temperature performance in the Materials Screening Project (Task 1.3 of ABRT) if warranted.

Summary

Based on the many observations made (summarized below), it appears that the power loss experienced by lithium-ion battery systems at low temperature is inherent to lithium-ion kinetics with no fundamental solution identified as of yet. Engineering approaches will most likely be necessary in the design of HEV battery systems to mitigate the effects of low temperature.

- Electrochemical Impedance Spectroscopy studies indicated that the main rise in impedance occurs in the mid frequency range. Processes that occur in this frequency range are generally interfacial in nature.
- In situ micro reference electrode data indicated that the impedance rise at low temperature is shared nearly equally between the positive and negative electrodes and it is not significantly influenced by the direction of current flow.
- The choice of active material (carbon, graphite, metal-oxide, inter-metallic alloys, etc.) does not have a significant effect on the low temperature performance.
- Salt molarity and temperature were found to have a significant influence on electrolyte viscosity, but the influence of electrolyte viscosity on impedance was almost insignificant.

Summary (Continued)

- From Binder and Carbon Free thin film electrodes, it was found that the binder and carbon may play a significant role at room temperature, but only a minor role at low temperature.
- Higher surface area does improve the low temperature performance by providing more surface area for the electrochemical reactions to take place, but the power robbing mechanism still dominates – just over a larger surface.
- Alternative electrolytes (ACN, GBL, non-EC carbonates, ketones, sulfolanes, esters, ionic liquids, etc.) show similar low temperature behavior as typical carbonate-based electrolytes.
- Surface modification of graphite and soft carbon does not affect the low temperature performance.
- Pulse current level has a dramatic influence on impedance at temperatures below 0 °C, especially at -30 °C. A decreasing resistance with increasing current is fully explained by Butler-Volmer kinetics. Impedance response at low temperature is clearly dominated by Butler-Volmer kinetics at the electrode-electrolyte interface and not diffusion.

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