Argonne
NATIONAL LABORATORY

... for a brighter future

Low Temperature Performance Characterization

Presented by Andy Jansen
Chemical Sciences and Engineering Division

Tuesday, February 26th, 2008

DOE Vehicle Technologies Program
Annual Merit Review, FY2008
Hybrid Electric Systems
Energy Storage / Applied Battery Research
Bethesda, Maryland

This presentation does not contain any proprietary or confidential information.

U.S. Department of Energy

UChicago ▸ Argonne LLC

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

Vehicle Technologies Program

Outline

- Purpose of Work
- Address Previous Review Comments
- Barriers
- Approach
- Performance Measures and Accomplishments
  - Power pulse level
  - Surface area
  - Non-carbonate solvents
  - Surface modifications
- Technology Transfer
- Publications/Patents
- Plans for Next Fiscal Year
- Summary

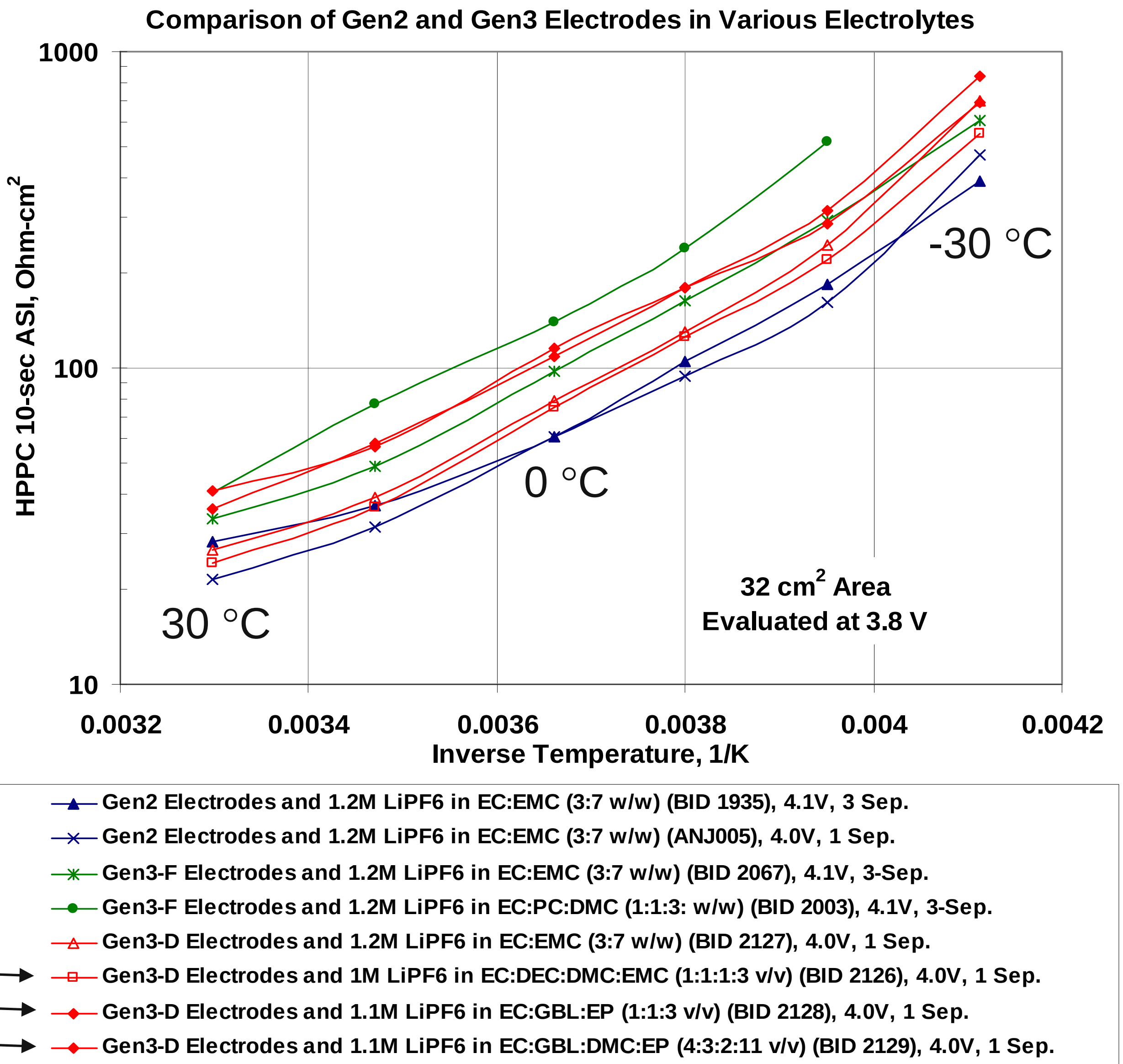
Purpose of Work

- 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.

Reviewer Comments from Aug.'06 Merit Review

- "Low temperature work should determine the root cause of the problem."
  - The ATD program continues to develop in-situ diagnostics techniques to determine the root cause(s) of low temperature performance degradation. Recent work proved performance is kinetic limited.
- "Investigate additives for low T, formation."
  - Additives are continuously evaluated and screened in ATD. Additives will also be screened for improved low temperature performance.
- "Vary electrode surface area to assess affect of interfacial impedance."
  - Studied graphites from ConocoPhillips that are ideal for this particular investigation.

Barrier: Li-ion Cells Lose Power when Cold

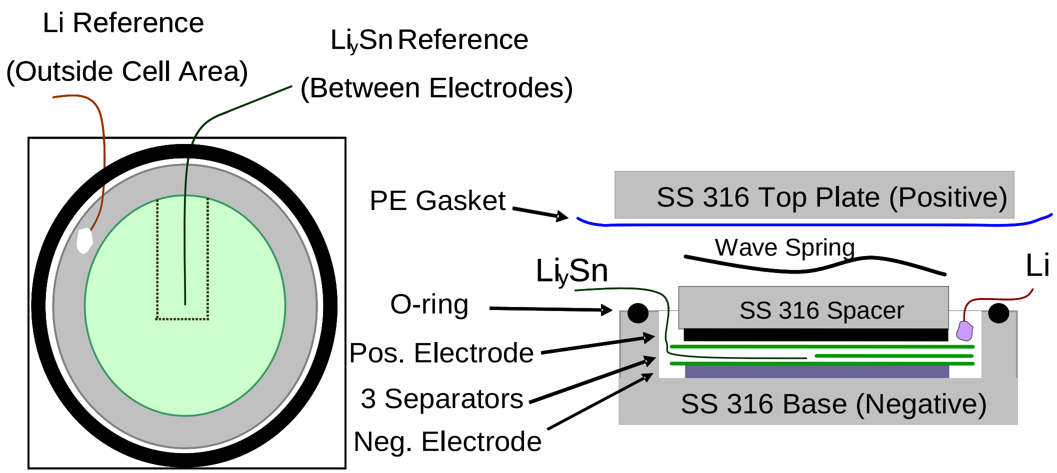


JPL
K.Gering
K.Gering

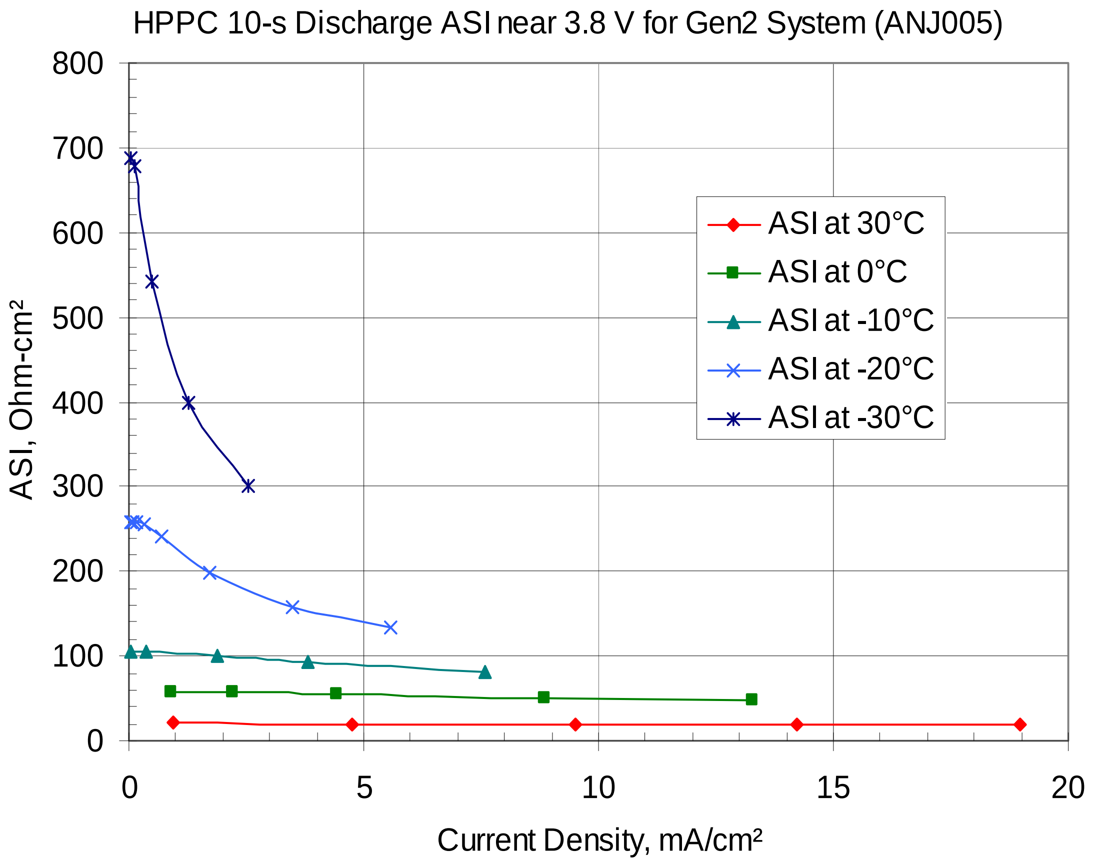
All cells have similar low temperature behavior (same activation energy).

Approach

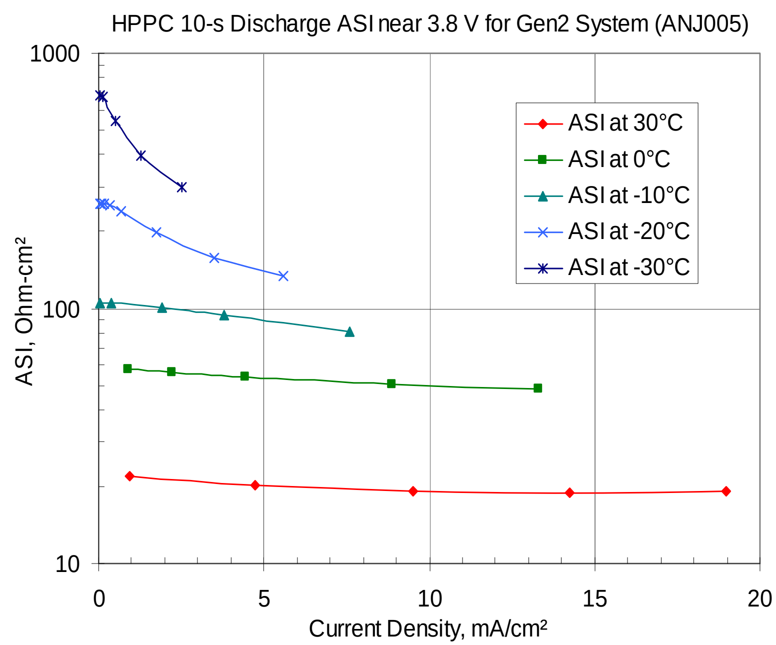
- Identify and systematically investigate physical and electrochemical properties that could influence low temperature performance using tailored test apparatus
  - Active Material ☒
  - Conductivity ☒
  - Lithium Salt ☒
  - Charge or Discharge ☒
  - Salt Molarity ☒
  - Electrolyte Viscosity ☒
  - Binder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



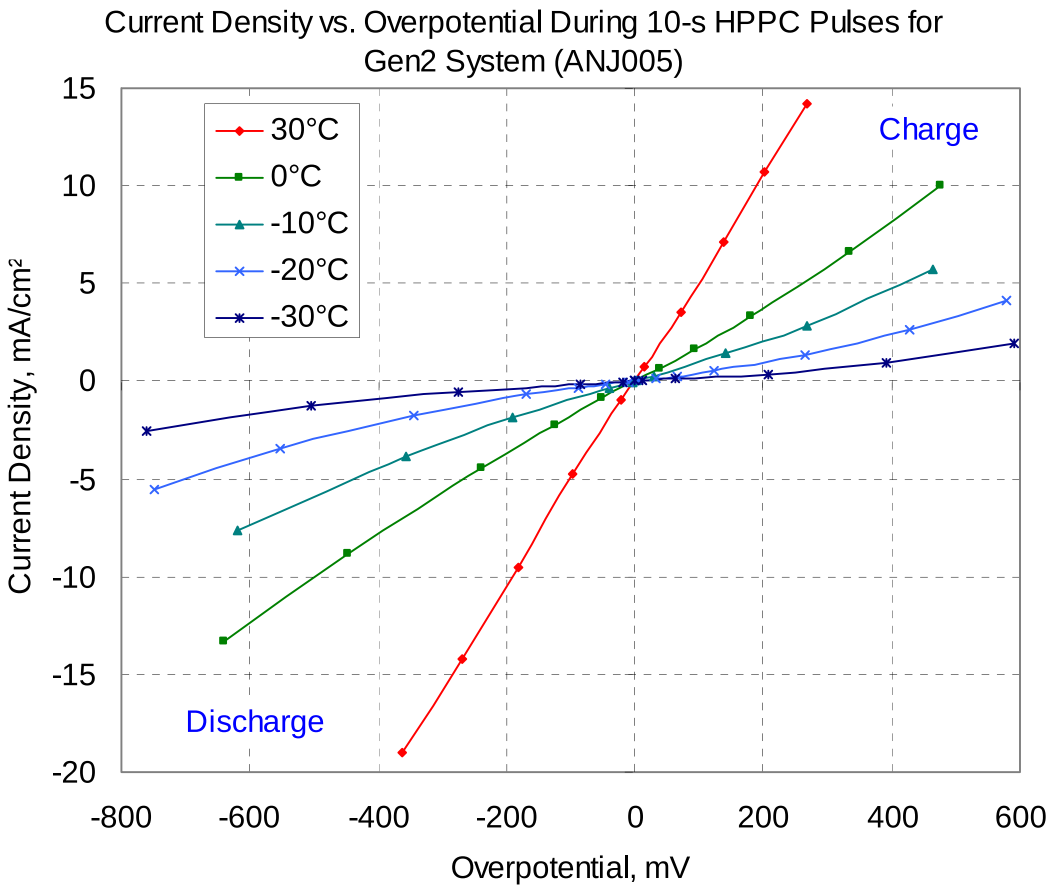
Impedance Depends Strongly on Current at Low Temperature

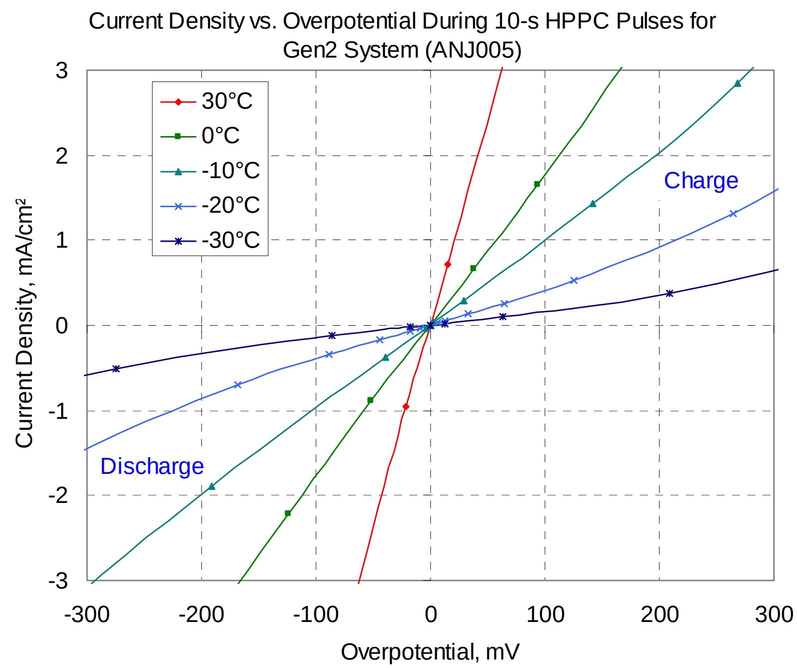


A decreasing resistance with increasing current may seem counter-intuitive, but this phenomena is fully explained by Butler-Volmer kinetics.



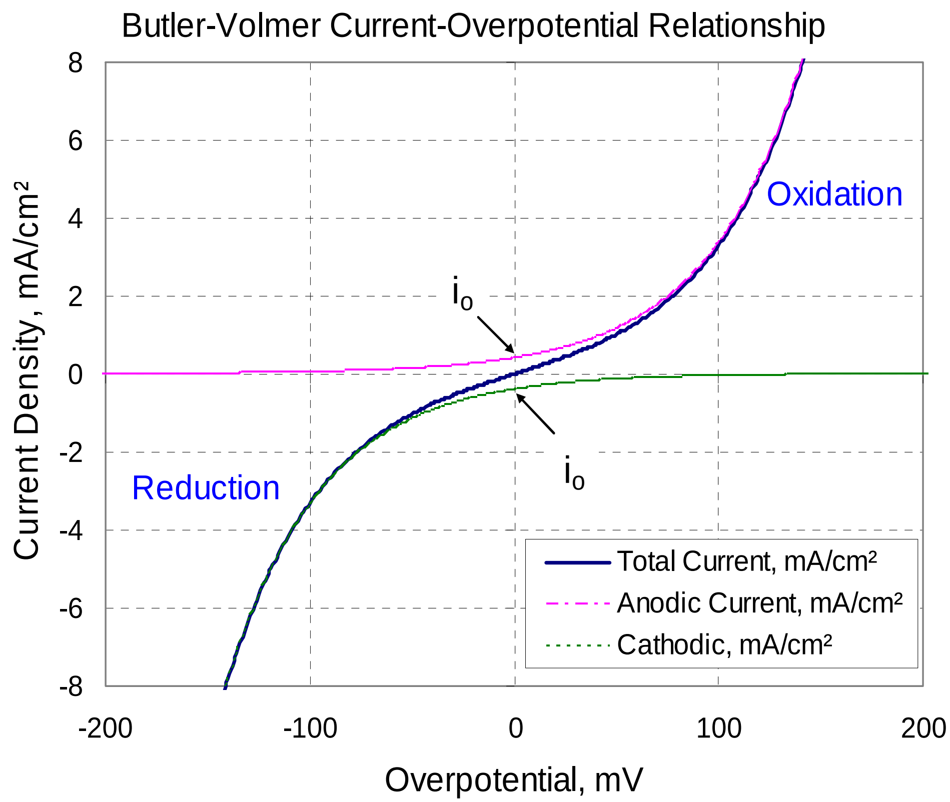
HPPC Data Obey Classic Butler-Volmer Kinetics





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

Butler-Volmer Kinetics Refresher



see "Electrochemical Methods" by Bard and Faulkner

$$i = i_0\left[e^{\alpha nF\eta/RT} - e^{-(1-\alpha)nF\eta/RT}\right]$$

$$\eta = \left(V - V_{eq}\right)$$

$$\frac{1}{R} = \frac{di}{d\eta} = \frac{nFi_0}{RT}\left[\alpha e^{\alpha nF\eta/RT} + (1-\alpha)e^{-(1-\alpha)nF\eta/RT}\right]$$

Linear Region

$$\eta \approx 0 \quad \frac{1}{R} = \frac{nFi_0}{RT}$$

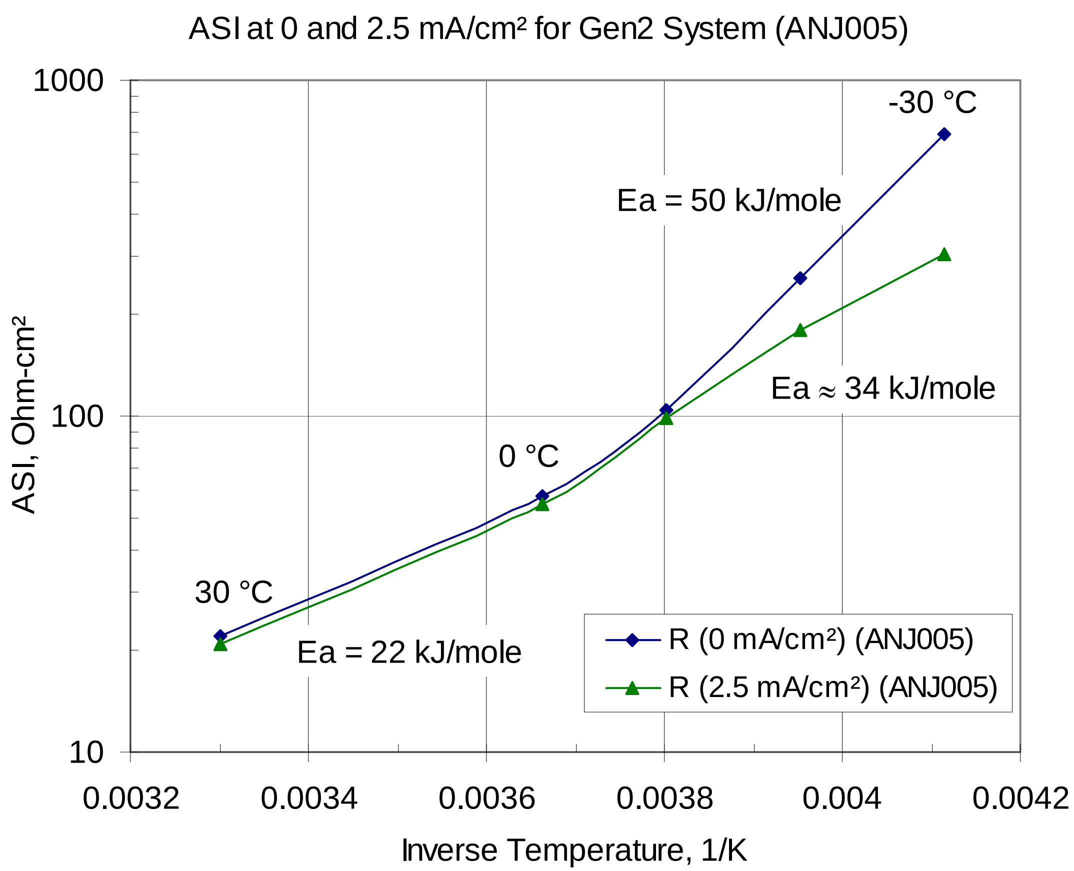
Tafel Region

$$\frac{1}{R} = \frac{\alpha nF}{RT}i$$

In real life, current does not go off to infinity with increasing overpotential – at some point mass transfer (diffusion) limits the current.

Limiting currents were not observed for these studies within the operating voltage used (2.9 to 4.3 V).

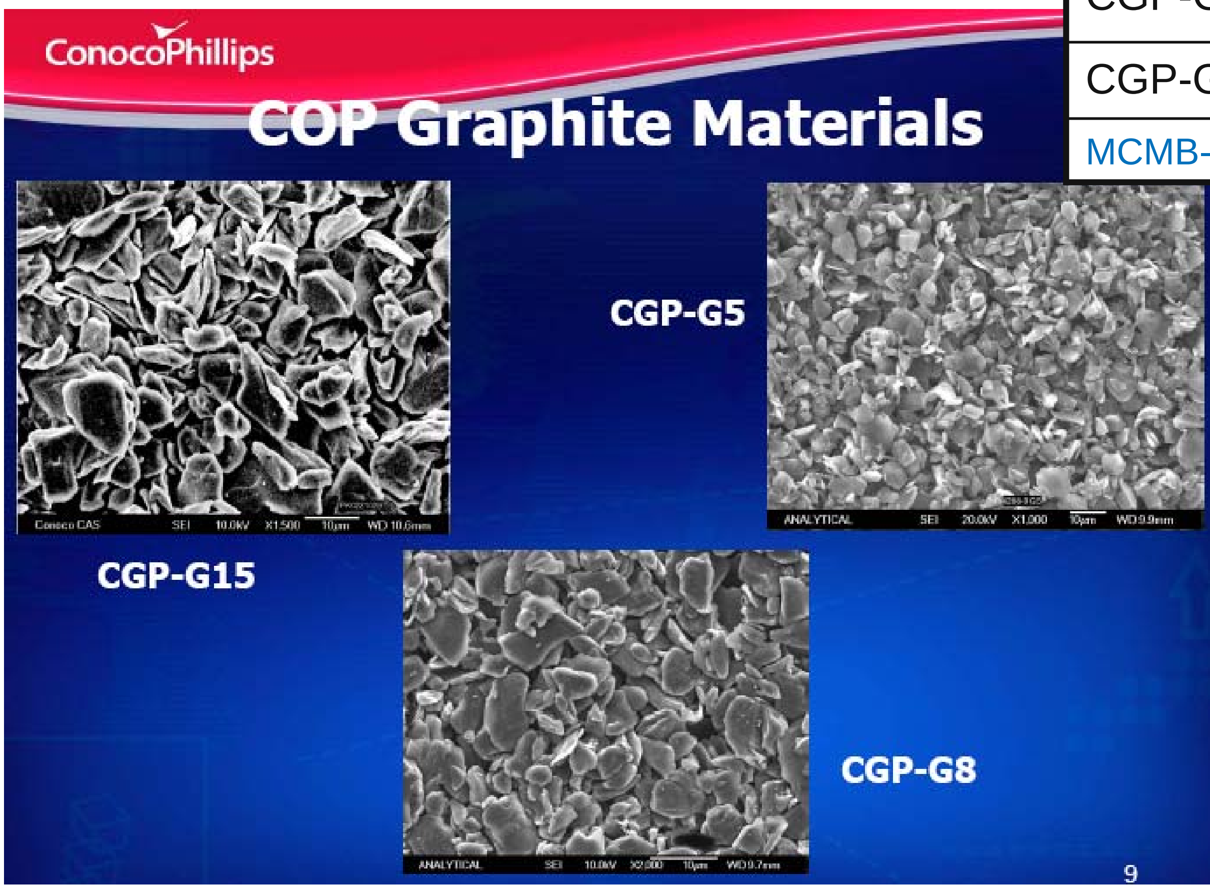
Activation Energy Clearly Increases Below 0 °C



- 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.

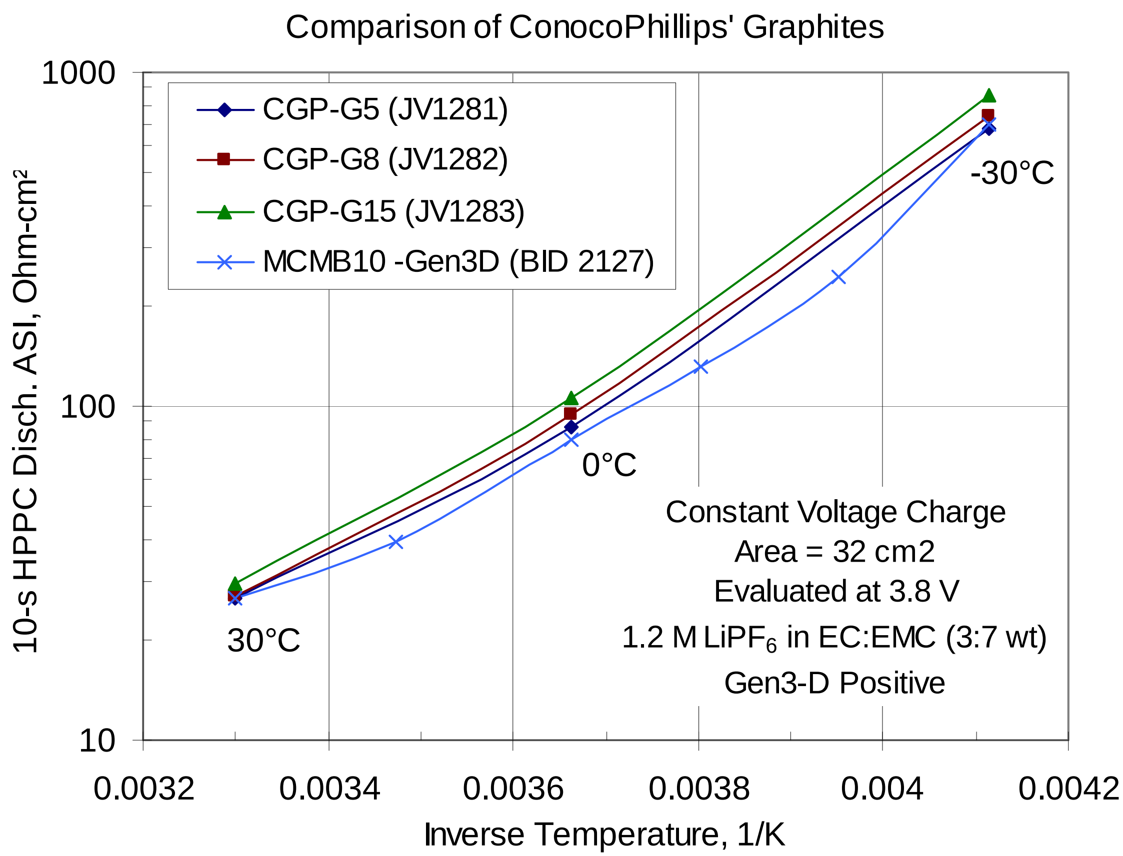
Explore Surface Area Effects with ConocoPhillips' Graphite

Material	Particle Size D50, µm	Surface Area BET, m^2/g
CGP-G5	4-6	2.0-3.0
CGP-G8	7-9	1.5-2
CGP-G15	13-17	0.7-1.0
MCMB-10	11.8	2.0

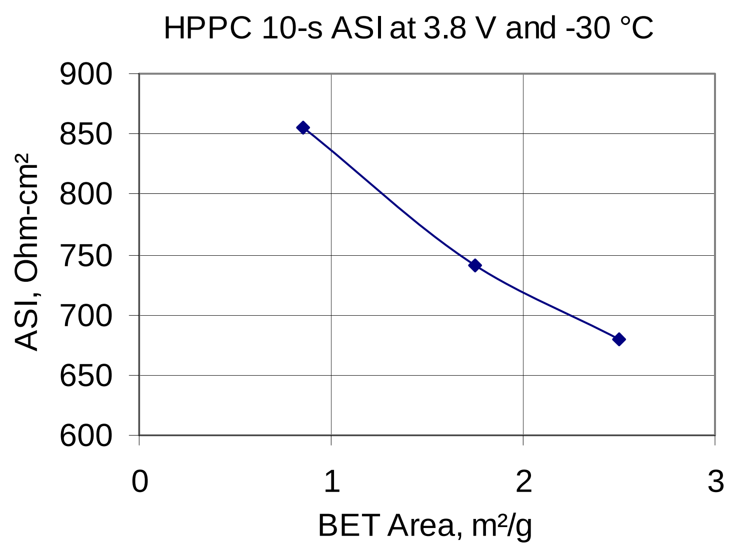


The graphites from ConocoPhillips are well suited for surface area studies because of their similar processing that results in nearly identical morphology.

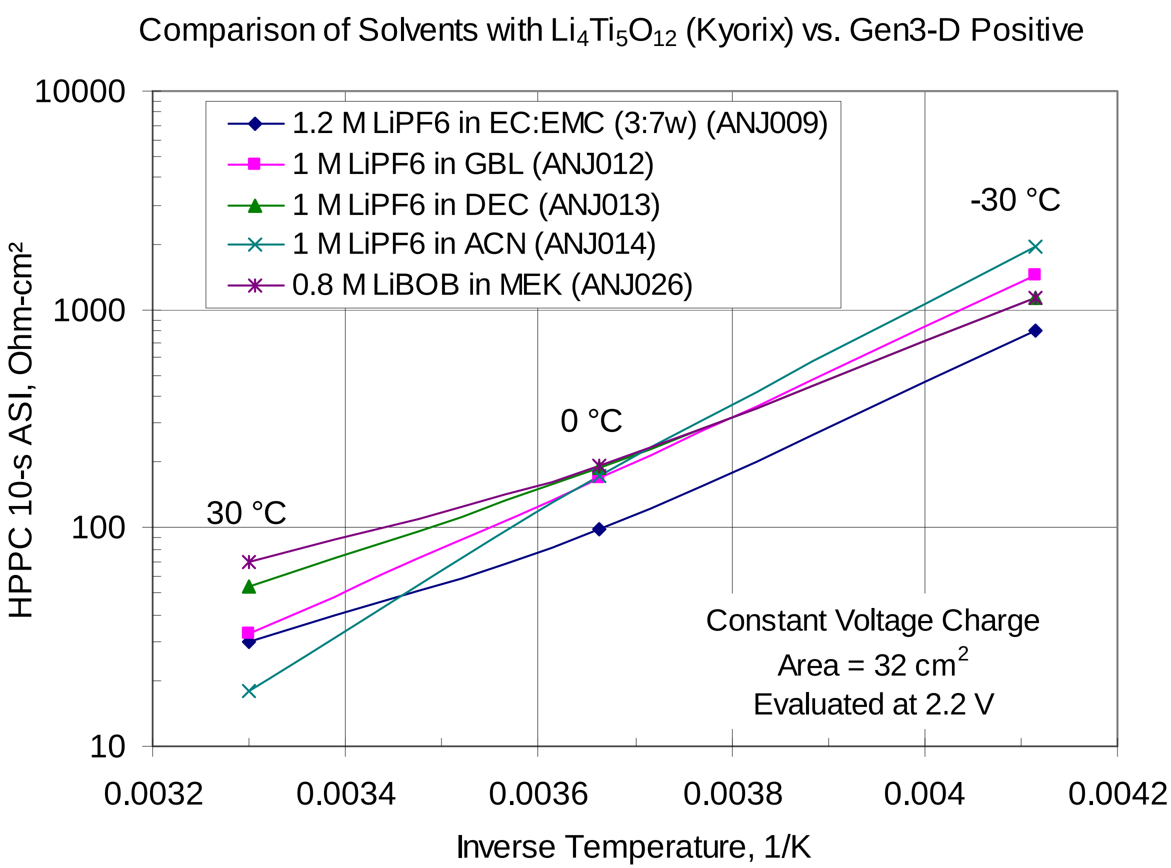
Higher Surface Area Improves Power at all Temperatures, But Not Enough



- 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.



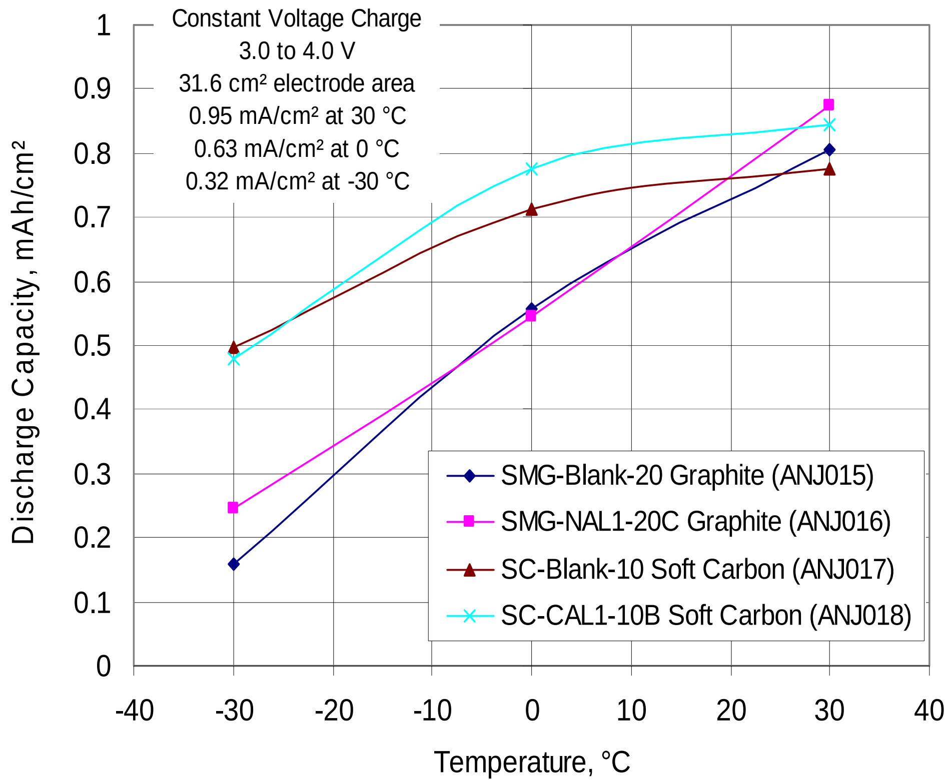
Non-Carbonate Based Electrolytes Also Suffer from Low Temperature Power Loss

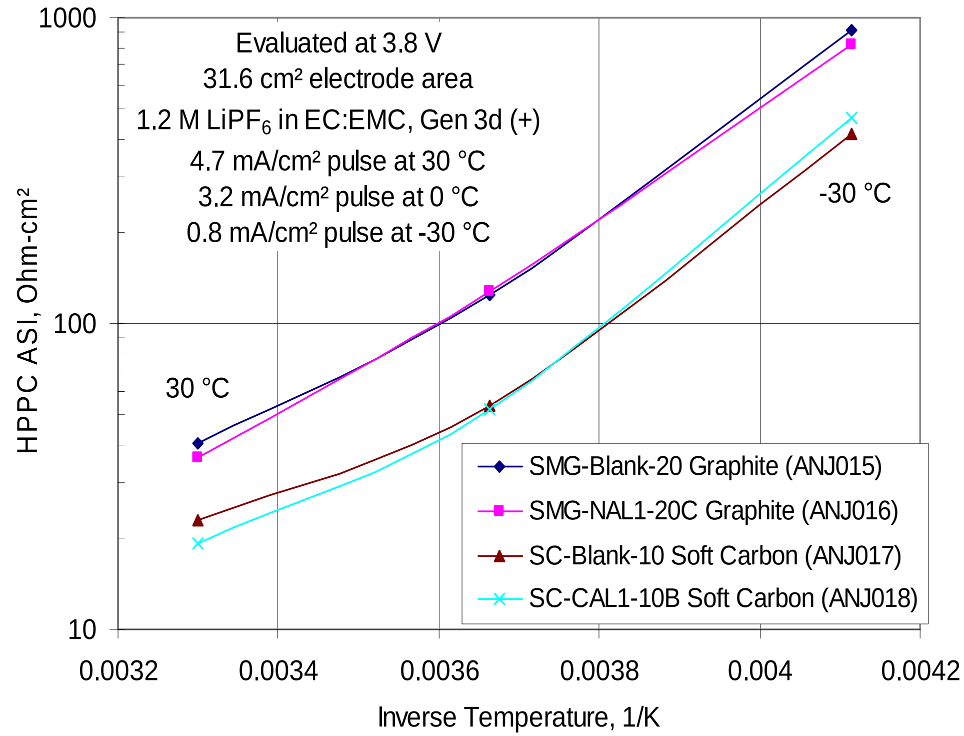


- Other solvents suffer too:
  - Diethyl Carbonate
  - γ-Butyrolactone
  - Acetonitrile
  - Methyl Ethyl Ketone
  - Many others!
    - *Substituted furans*
    - *Oxazolines*
    - *Esters*
    - *Sulfolanes*
    - *Thiazolines*
- No solvent (or additive) system has been found yet that has a significantly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

Surface Modifications Do Not Have a Significant Effect on Low Temperature Performance

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).

Technology Transfer

- Intellectual property generated under this project is available for licensing through Argonne's Office of Technology Transfer
- Results are made available to the DOE, USABC, and battery developers and suppliers at regular review meetings
- Results are made available to the general public via
  - Technical reports and journal articles
  - Presentations at technical meetings
  - HEV website (coming soon from Ira Bloom)

Publications/Patents

- **“**Low-Temperature Study of Lithium-Ion Cells using a Li_ySn Micro-Reference Electrode”, A.N. Jansen, D.W. Dees, D.P. Abraham, K. Amine, G.L. Henriksen, *J. Power Sources*, **174** (2007) 373.

- “Investigating the Low-Temperature Impedance Increase of Lithium-Ion Cells”, D.P. Abraham, J.R. Heaton, S.-H. Kang, D.W. Dees, A.N. Jansen, *J. Electrochem. Soc*., **155** (2008) A41.

- “Temperature Dependence of Capacity and Impedance Data from High-Power Lithium-ion Cells”, D.P. Abraham, E.M. Reynolds, P.L. Schultz, A.N. Jansen, D.W. Dees, *J. Electrochem. Soc*., **153** (2006) A1610-1616.

- “Theoretical Examination of Reference Electrodes for Lithium-Ion Cells”, D.W. Dees, A.N. Jansen, D.P. Abraham, *J. Power Sources*, **174** (2007) 1001.

- “Electrolytes for Lithium Ion Batteries”, John Vaughey, Andrew Jansen, and Dennis Dees (inventors), Filing Provisional Patent Application.

Future Plans

- Modify Double Layer with
  - Fluorinated carbonate electrolytes (FEC:EC:EMC)
  - Supporting electrolytes (modify double layer)
    - *$(Bu)_4NPF_6$, $(Bu)_4PPF_6$, $(Et)_4NPF_6$, $(CH_3)_4NPF_6$, NH_4PF_6, etc.*
    - *Cs_2CO_3 (cesium doesn't intercalate into graphite)*
- Investigate use of low temperature ionic liquids
- Explore Li-ion aqueous cell to shed insight on lithium kinetics at low temperature
- Consider cell system that uses sodium (or magnesium) as the active species also to shed insight on kinetics
- Continue NMR studies
- Assess feasibility of using ketone-based solvents
  - Size of organic groups (R-CO-R')
  - Non-HF forming salts or addition of Lewis Acid inhibitors

Summary

- Impedance response at low temperature is clearly dominated by Butler-Volmer kinetics and not diffusion
- Carbonate-based solvents are not likely responsible for the poor low temperature performance
  - Other solvents (ACN, GBL, ketones, sulfolanes, esters, etc.) had similar problems
- High surface area particles do improve the low temperature performance but are only part of the solution, and they may cause abuse tolerance concerns at higher temperatures
- Surface modification of graphite and soft carbon does not affect the low temperature performance (as expected)

Contributors and Acknowledgments

- Jack Vaughey (Argonne)
- Dennis Dees (Argonne)
- Kevin Gering (INL)
- Jun Liu (Argonne)
- Holly LaDuca (Argonne)
- Chris Joyce (Argonne)
- Nick Veselka (Argonne)
- Daniel Abraham (Argonne)
- Gary Henriksen (Argonne)
- John Muntean (Argonne)
- Chris Johnson (Argonne)
- Sun-Ho Kang (Argonne)
- Khalil Amine (Argonne)

- ConocoPhillips Co.
- Hitachi Chemical Co., Ltd.

Support from Tien Duong and David Howell of the U.S. Department of Energy's Office of Vehicle Technologies Program is gratefully acknowledged.