Low Temperature Double-Layer Capacitors With Improved Energy Density: An Overview of Recent Development Efforts

Erik J. Brandon*[1], William C. West[1], Marshall C. Smart[1], Gleb Yushin[2], Yair Korenblit[2], Adam Kajdos[2], Alexander Kvit[3] and Jacek Jagiello[4]

[1]Jet Propulsion Laboratory, California Institute of Technology
4800 Oak Grove Drive, Pasadena, CA 91109
*erik.j.brandon@jpl.nasa.gov

[2]School of Materials Science and Engineering
Georgia Institute of Technology, Atlanta, GA, 30332

[3]Materials Science Center & Materials Science Department, University of Wisconsin - Madison
Madison, WI 53706

[4]Micromeritics Instrument Corp
Norcross, GA 30093 USA

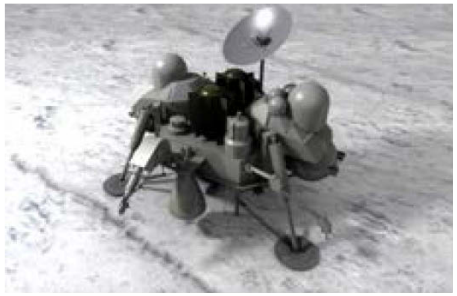
Power Sources Conference
Las Vegas Nevada
June 14, 2012

Copyright 2012. All rights reserved.

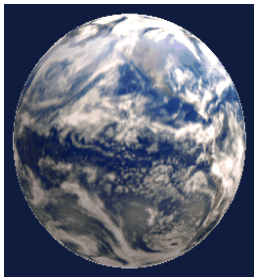
Outline of talk

- **Motivation**
  - Interest in low temperature energy storage
  - Potential applications in robotic exploration
- **Benchmark performance of commercial cells**
- **Approaches for designing low temperature systems**
- **Experimental results**
- **Summary**

Low temperatures encountered during Solar System exploration

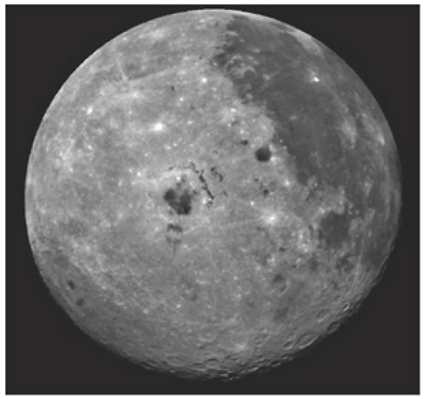


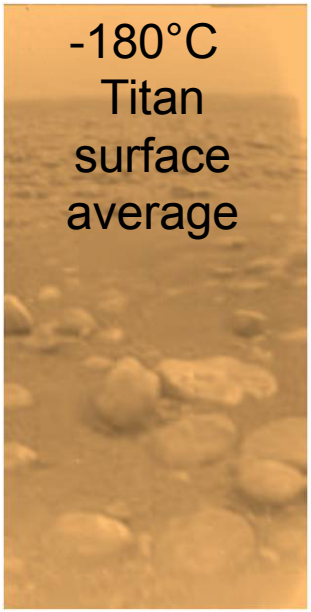
Europa surface average
-170°C



-55°C
Antarctica average

-233°C
Lunar Aitkin Basin Region



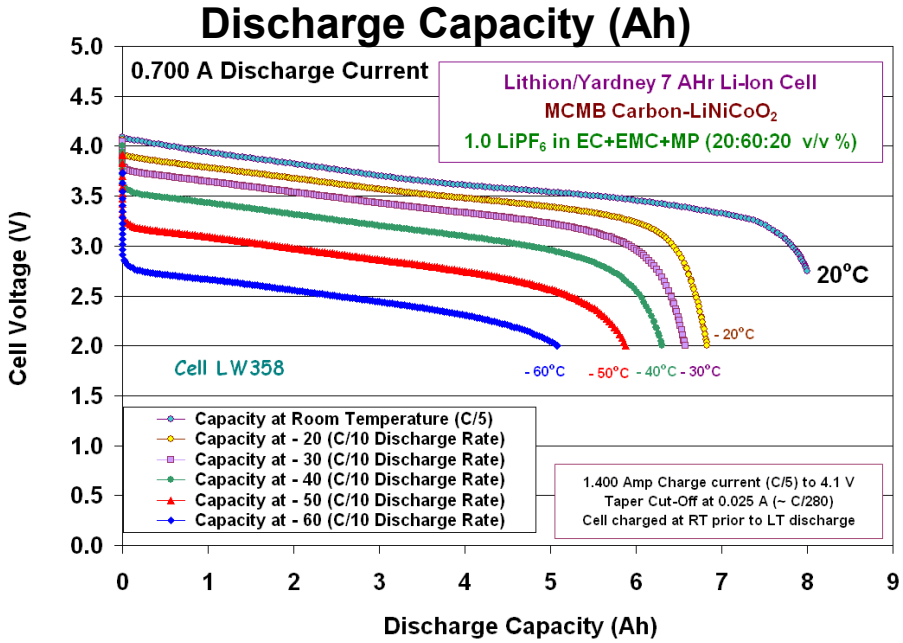


-180°C
Titan surface average

-120°C
+20°C
Mars surface temperatures

Low temperature Li-ion batteries for space applications

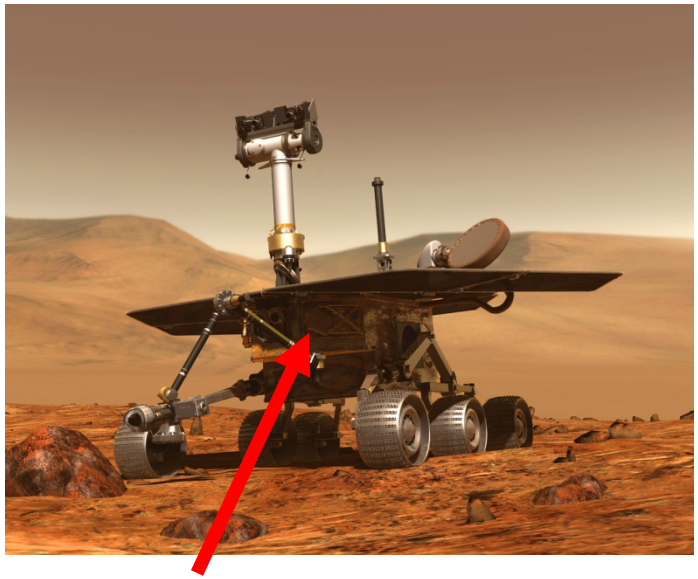
Yardney 7 Ah Prototype Cells with Advanced Electrolytes
Low Temperature Discharge Performance of Prototype Cells



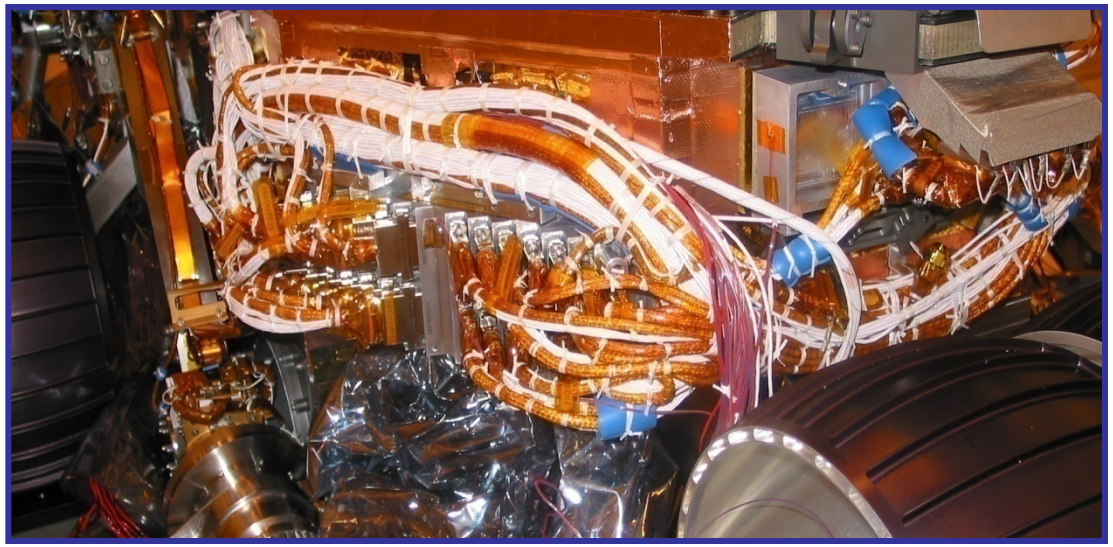
- Cells containing the methyl propionate-based electrolyte were observed to perform well down to -60°C using a C/10 discharge rate
- Other advanced electrolytes developed at JPL used in conjunction with different cell types enable operation to even lower temperatures and higher rates
- However, high rate discharge at very low temperatures remains a challenge
- Charging batteries at low temperature remains a challenge, due to Li plating concerns

Courtesy of Marshall Smart

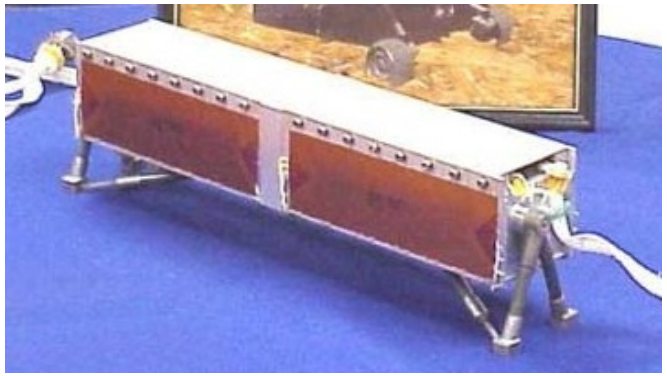
Need for low temperature power systems



Warm electronics box (WEB)



Cabling from the WEB



Mars Exploration Rover
Li ion battery

- **Current practice:** avionics in warm electronics box (WEB) with radioisotope heat source to maintain temperature between -40°C to +40°C
- Extensive cabling presents design, integration and test challenge
- Battery power de-rated at lower temperatures
- ***Possible solution: Hybrid low temperature battery-capacitor power systems***

Double-layer capacitors for low temperature energy storage and power delivery

Technology need

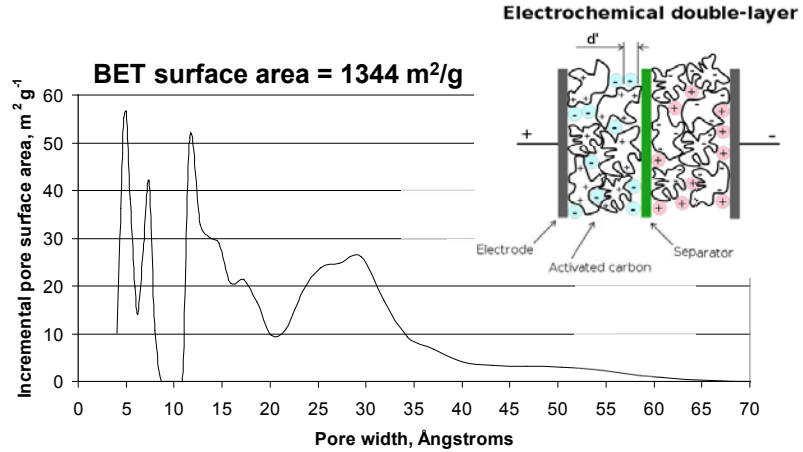
- Storing electrical energy and delivering power at low temperatures (<-30°C) remains a significant challenge
- Difficult to deliver high power effectively at low temperatures (batteries derated due to slow kinetics)

Objectives

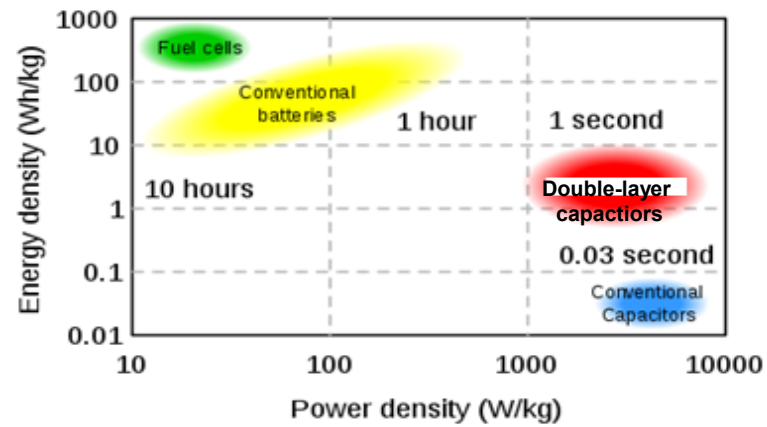
- Utilize the advantage of double-layer capacitors, which store energy *at the electrochemical double-layer* (rather than intercalation and redox processes, which are highly temperature sensitive)
- Develop low temperature electrolytes to extend beyond -40°C limit with commercial cells
- Target low equivalent series resistance (ESR) to effectively deliver power at low temperature

Potential applications

- Hybrid battery/capacitor low temperature power systems (with the capacitor providing pulse power at low temperatures)
- Capacitor-only power systems, for low duty cycle distributed sensor platforms on planetary surfaces (with limited thermal management)
- Fully testable thermal battery replacements

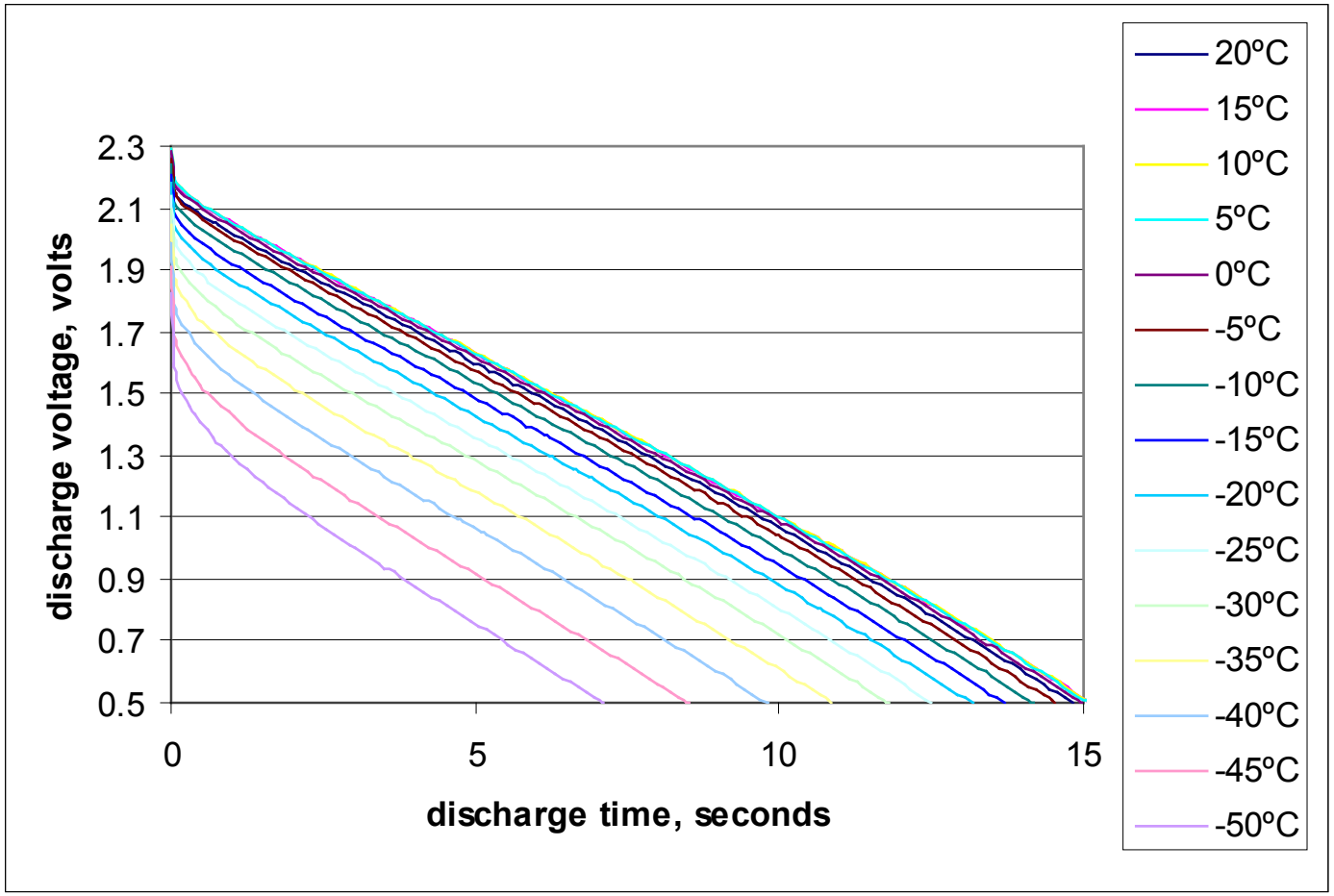


Incremental pore surface area vs. pore width for representative activated carbon electrode material



High power density/moderate energy density of double-layer capacitors can augment high energy density of batteries in low temperature power systems

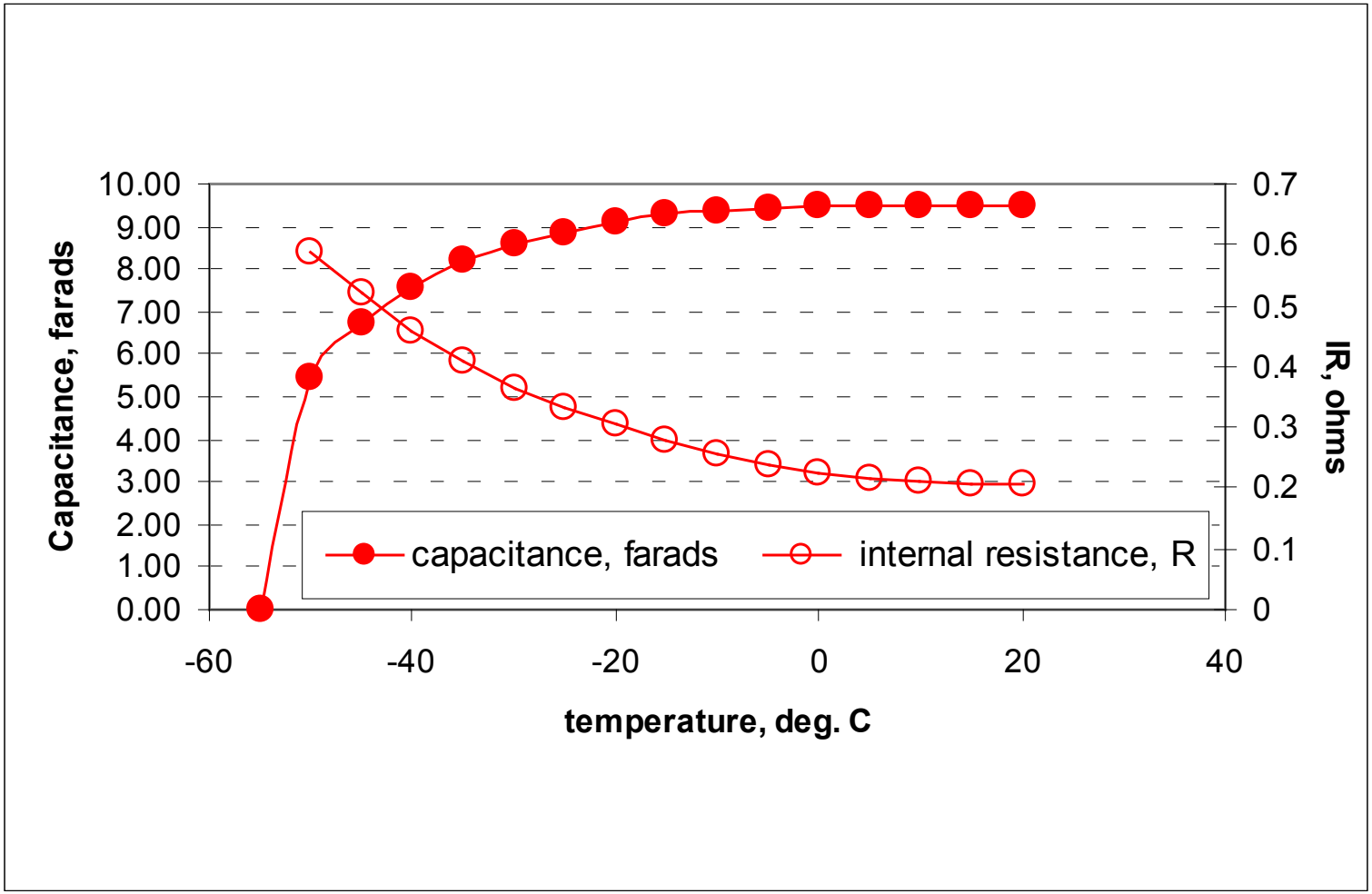
Representative data from commercially available cells



10 F cell

Discharge current = 1 A

Representative data from commercially available cells



10 F cell

Discharge current = 1 A

Approach for low temperature double-layer capacitor development

1. Develop electrolyte with melting point lower than standard acetonitrile/propylene carbonate based systems

2. Optimize salt type and salt concentration to eliminate salt precipitation issues and maximize conductivity (for maximum power delivery)

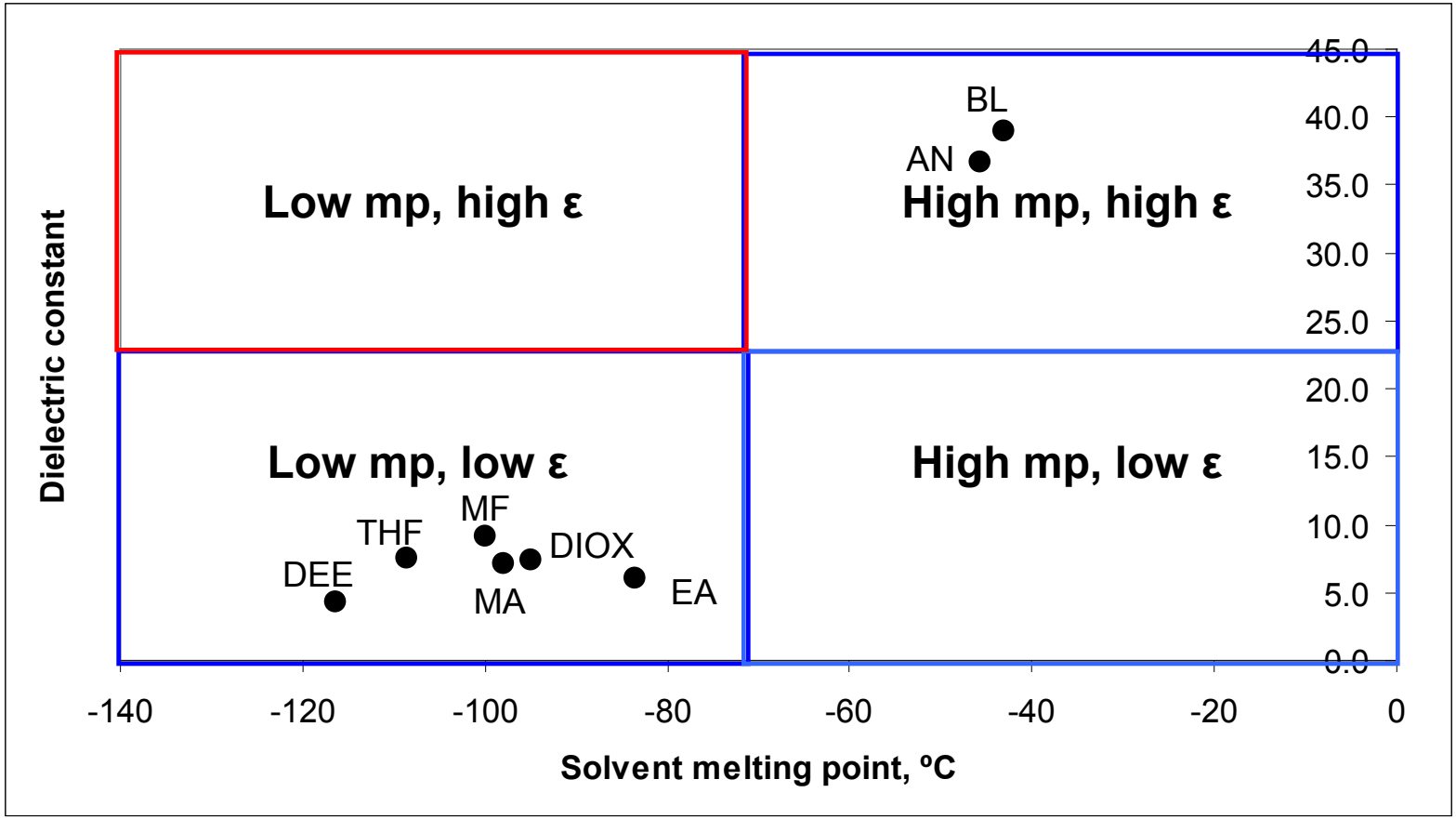
3. Evaluate performance of low temperature electrolytes in small cells using standard high surface area carbon electrodes

4. Optimize electrolyte systems

5. Evaluate influence of electrodes on performance, and tailor electrodes for optimal low temperature performance

6. Transfer electrolytes/materials to large cell format for more realistic evaluation/cycle life evaluation

Electrolyte design considerations

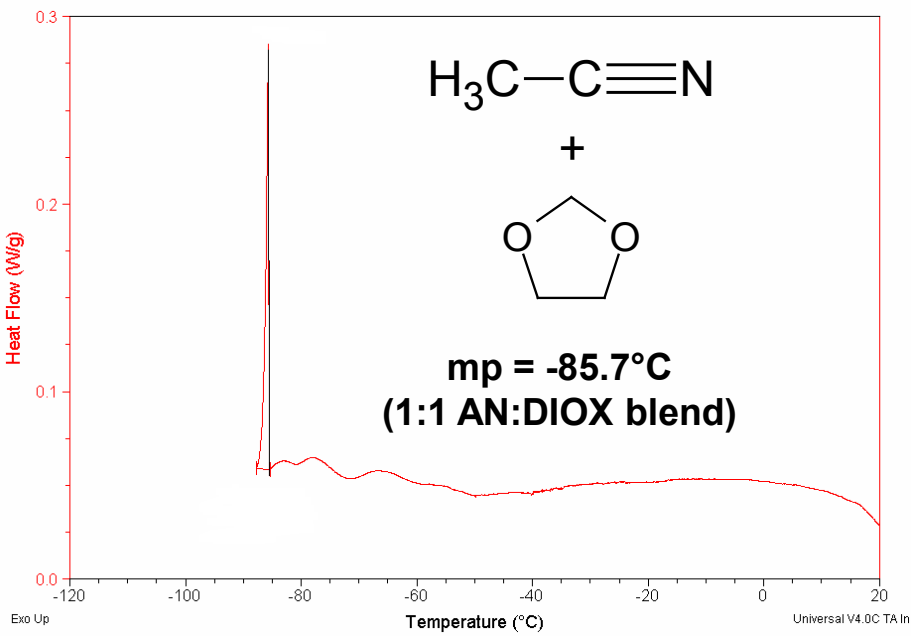


THF = tetrahydrofuran
BL = gamma butryolactone
AN = acetonitrile
MA = methyl acetate

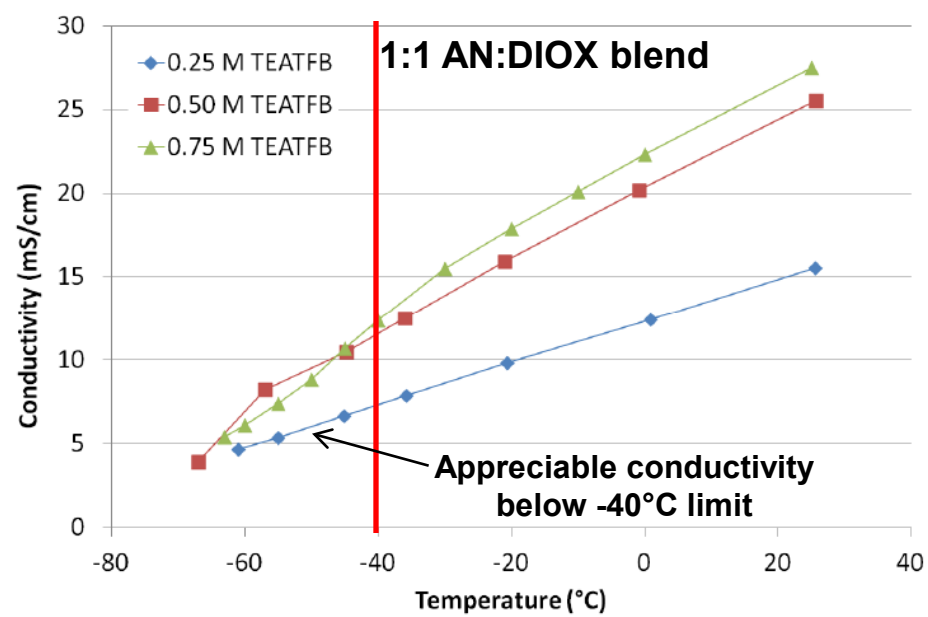
DIOX = 1,3-dioxolane
MF = methyl formate
DEE = diethyl ether
EA = ethyl acetate

1,3-dioxolane lowers melting point

Solvent	Freezing point (ºC)	Dielectric constant (ε)	Viscosity (cP)
acetonitrile (AN)	-43.84	37.5 (20°C)	0.33 (30°C)
1,3-dioxolane (DIOX)	-95	7.34 (25°C)	0.6 (20°C)
3:1 v/v% AN:DIOX	-67.9	27.1	N/A
1:1 v/v% AN:DIOX	-85.7	19.3	N/A



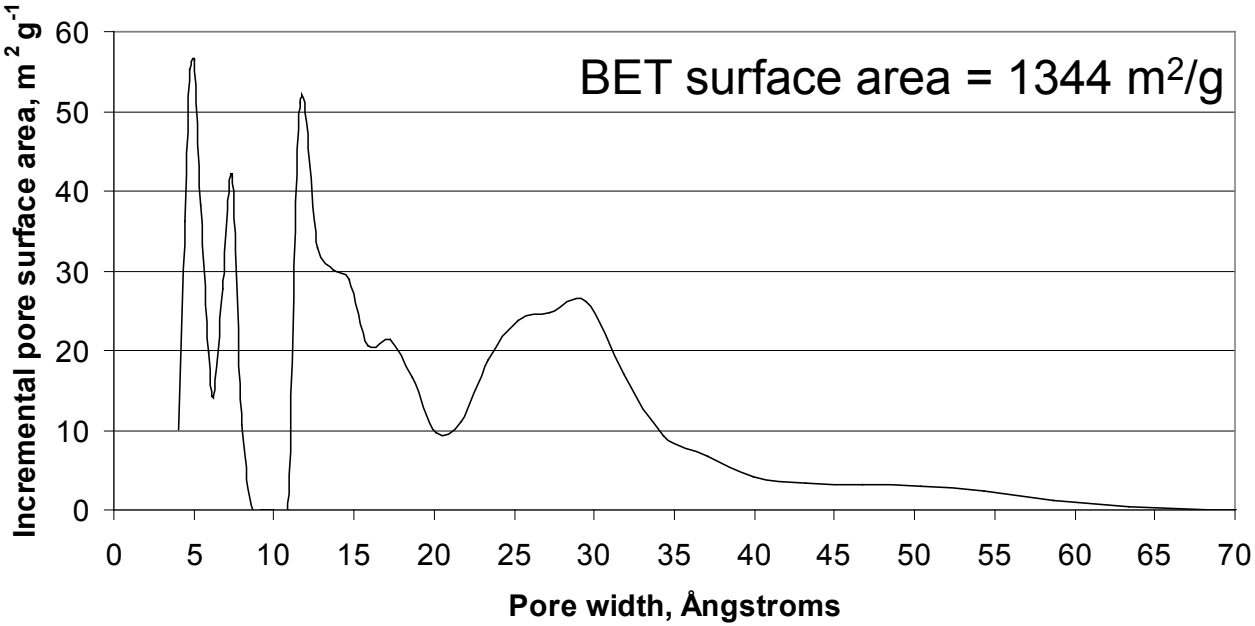
Differential scanning calorimetry data for low temperature electrolyte solvent system

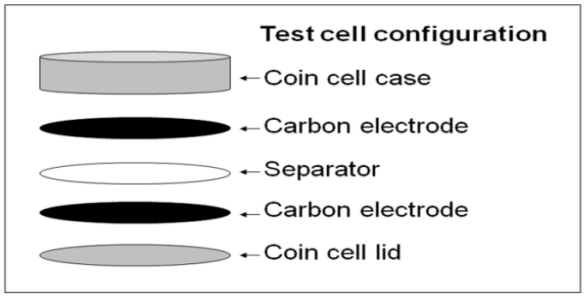


Conductivity for three salt concentrations

Coin cell assembly for experimental cells

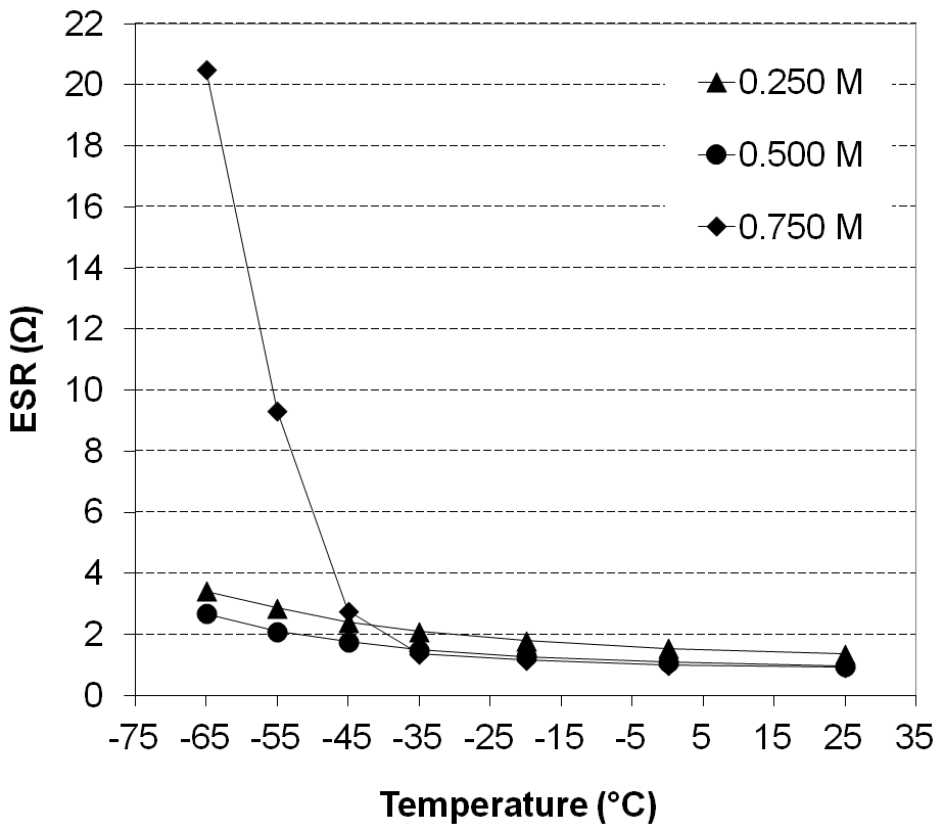
- **2032 coin cell**
- **Separator:** 25 micron polyethylene (Tonen)
- **Electrodes:** Activated carbon
- **Salt:** Quaternary ammonium salts

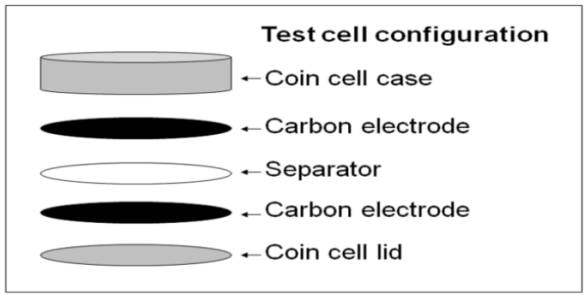




Incremental pore surface area vs. pore width for representative electrode material

Challenge maintaining low ESR at low temperatures

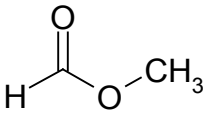




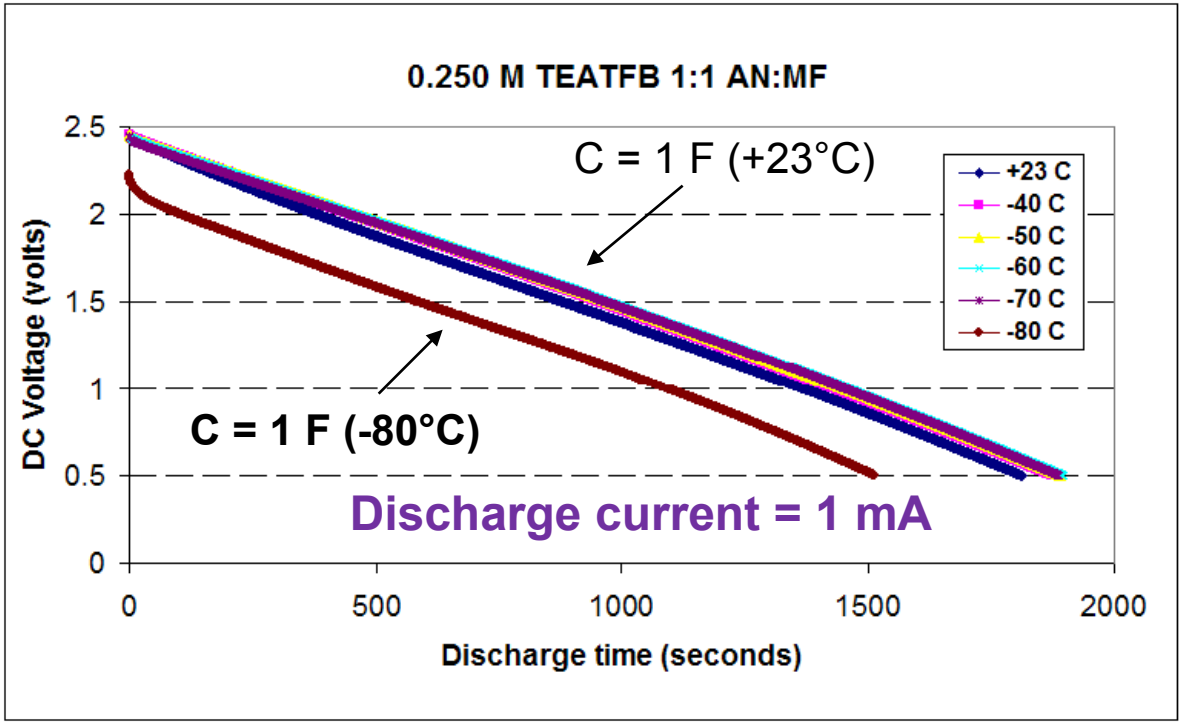
At low temperature and higher salt concentrations, ESR increases with temperature due to decreased salt solubility (coin cell data)

Methyl formate co-solvent enables operation to -80°C in experimental cell

- **2032 coin cells**
- **Separator:** 25 micron polyethylene (Tonen)
- **Electrodes:** PACMM 203 activated carbon
- **Salt:** Tetraethylammonium tetrafluoroborate

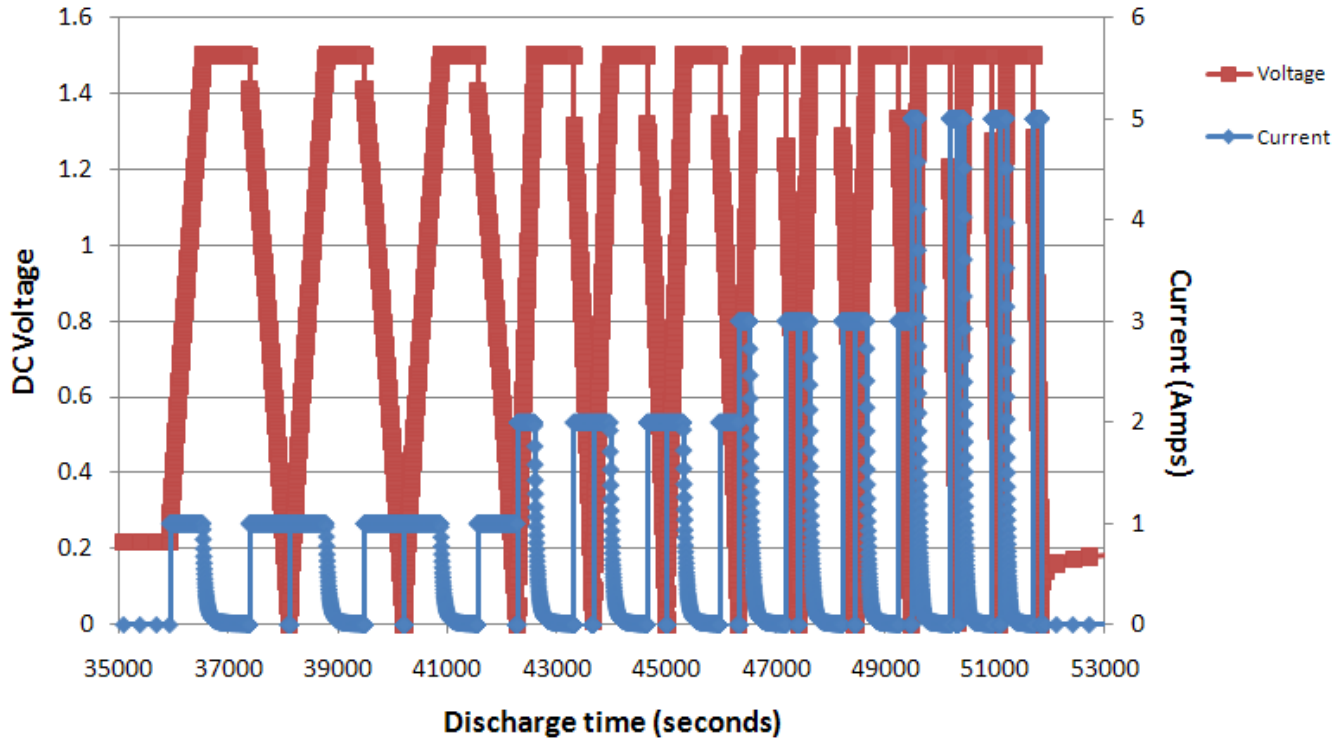
Solvent	Freezing point (ºC)
$H_3C-C\equiv N$ acetonitrile (AN)	-43.84
 methyl formate	-100

Electrolyte = 0.250 M TEATFB in 1:1 acetonitrile / methyl formate



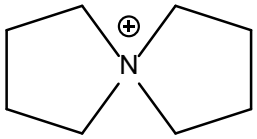
Performance of large double-layer capacitor cells at -70°C

- **Electrolyte:** 1:1 acetonitrile / methyl formate
- **Salt:** 0.5 M tetraethylammonium tetrafluoroborate

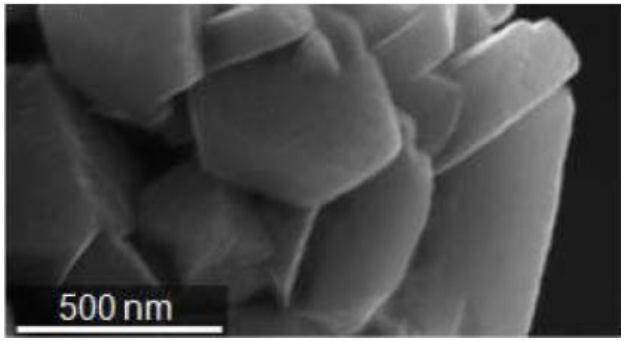


- At -70°C, cell displays ~520 F capacity at 1 A and V_{max} = 1.5 V with very linear discharge characteristics
- Large cell format facilitates long duration cycling studies

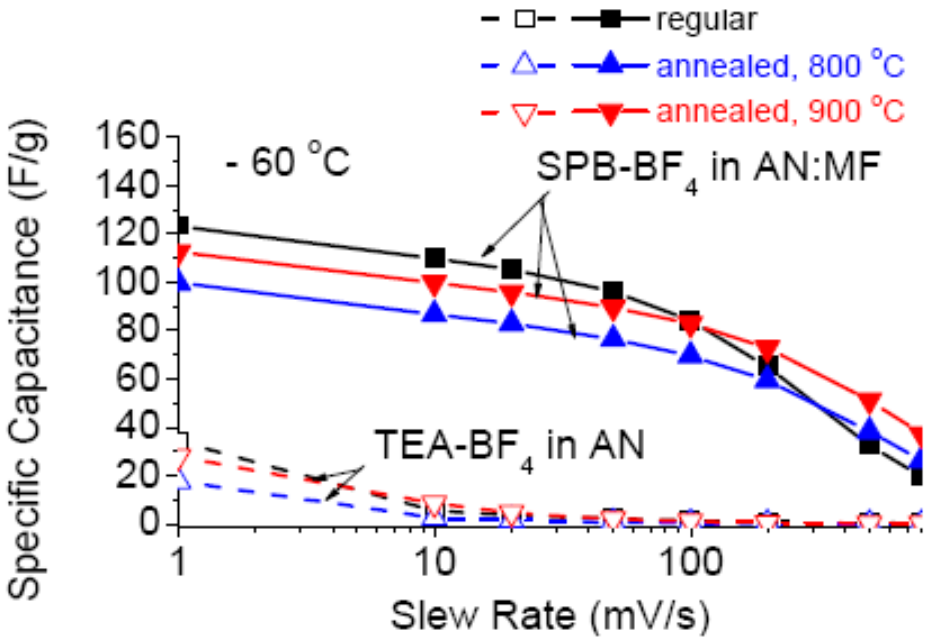
Optimizing salt and electrode materials for low temperature performance



SPB cation



SEM micrograph of Georgia Tech zeolite templated carbon powder electrode material



1 M TEATFB in acetonitrile vs. 0.5 SPB-TFB in 1:1 acetonitrile / methyl formate at – 60 ºC (coin cell using different zeolite templated carbon electrodes)

Collaboration with Professor Gleb Yushin at Georgia Tech

Summary

- **Demonstrated double-layer capacitor operation to at least -80°C**

- **Low temperature operation enabled by:**
  - Base acetonitrile / TEATFB salt formulation
  - Addition of low melting point formates, esters and cyclic ethers

- **Key electrolyte design factors:**
  - Volume of co-solvent
  - Concentration of salt

- **Continuing efforts**
  - Larger scale cells for life testing
  - Lower melting point blends (ternary, quaternary, PC blends)
  - Higher capacitance electrodes
  - Higher voltage blends
  - Hybrid cells

Acknowledgements

We would like to thank Gary Plett for the differential scanning calorimetry measurements and Larry Whitcanack for assistance with the dc cell measurements.

This research was carried out at the Jet Propulsion Laboratory (JPL), California Institute of Technology, funded through the JPL Research and Technology Development fund, under a contract with the National Aeronautics and Space Administration.