Improved Low Temperature Performance of Supercapacitors

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Outline of Talk

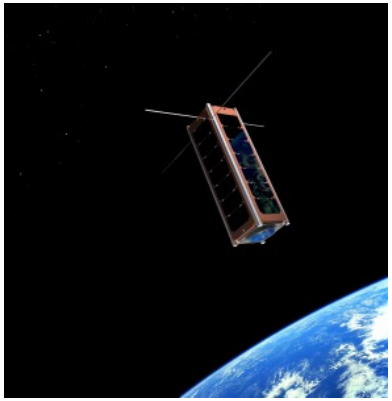
- **Motivation**
- **Benchmark performance of commercial cells**
- **Approaches for designing low temperature systems**
  - Symmetric cells (activated carbon electrodes)
  - Symmetric cells (zeolite templated carbon electrodes)
  - Asymmetric cells (lithium titanate/activated carbon electrodes)
- **Experimental results**
- **Summary**

Low Temperature Energy Storage Needs

Improved cold cranking in electric vehicles

Planetary exploration rovers and landers

Monitoring of critical assets in extreme environments



Cubesats and small satellites

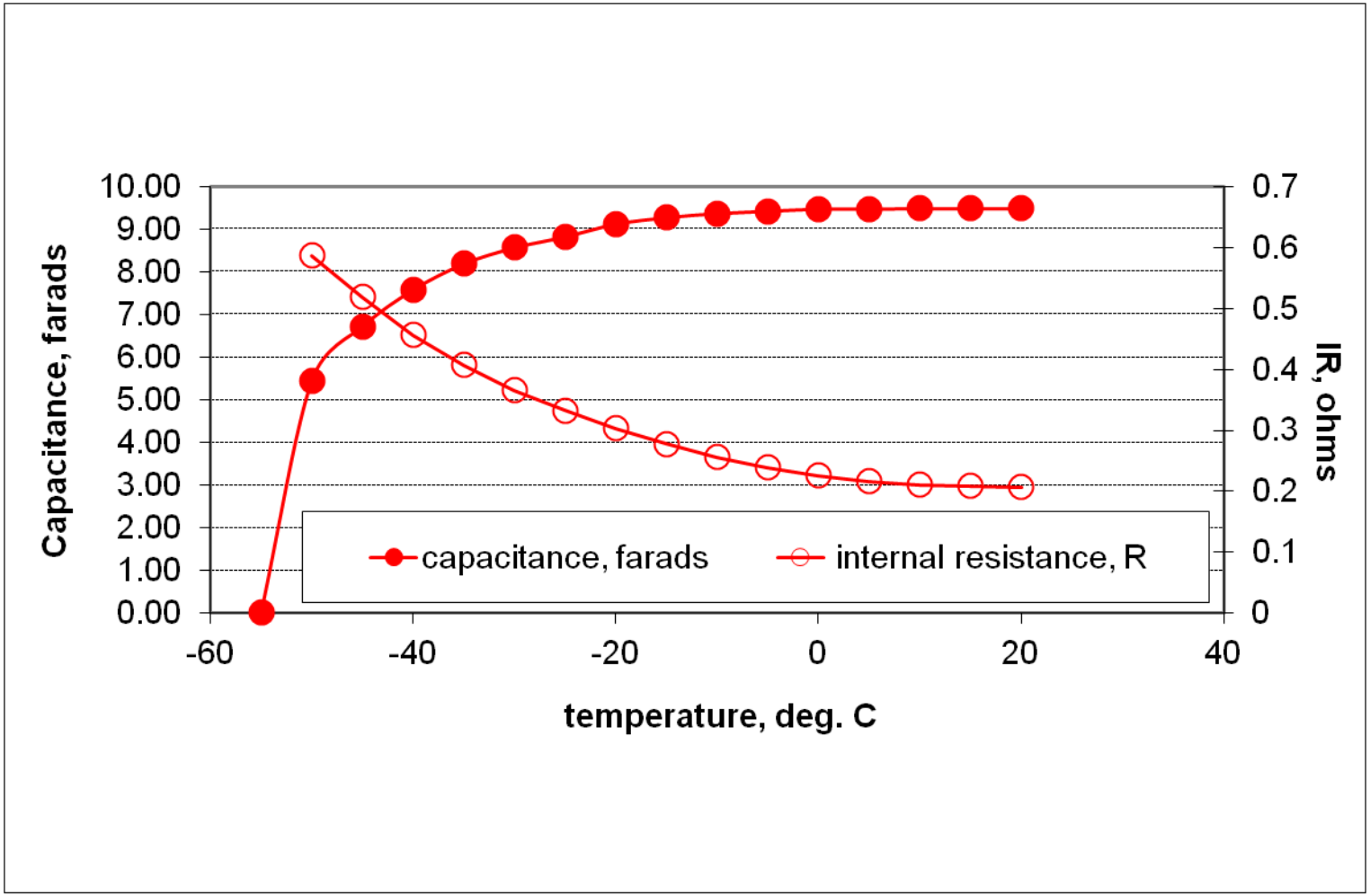
Unmanned aerial vehicles and high altitude vehicles

Polar region distributed environmental sensing

Double-layer Capacitors at Low Temperatures

- Low temperature battery charging and discharging rates limited by slow kinetics of intercalation process
- Concerns over lithium plating in Li-ion batteries when charged at low temperatures
- Double-layer capacitor charging/discharging only involves rearrangement of double-layer during each cycle
- Provides mechanism for charge storage and power delivery at low temperatures
- Require modified electrolytes to prevent freezing and salt precipitation at low temperatures
- Consider opportunities for increasing energy storage capacity

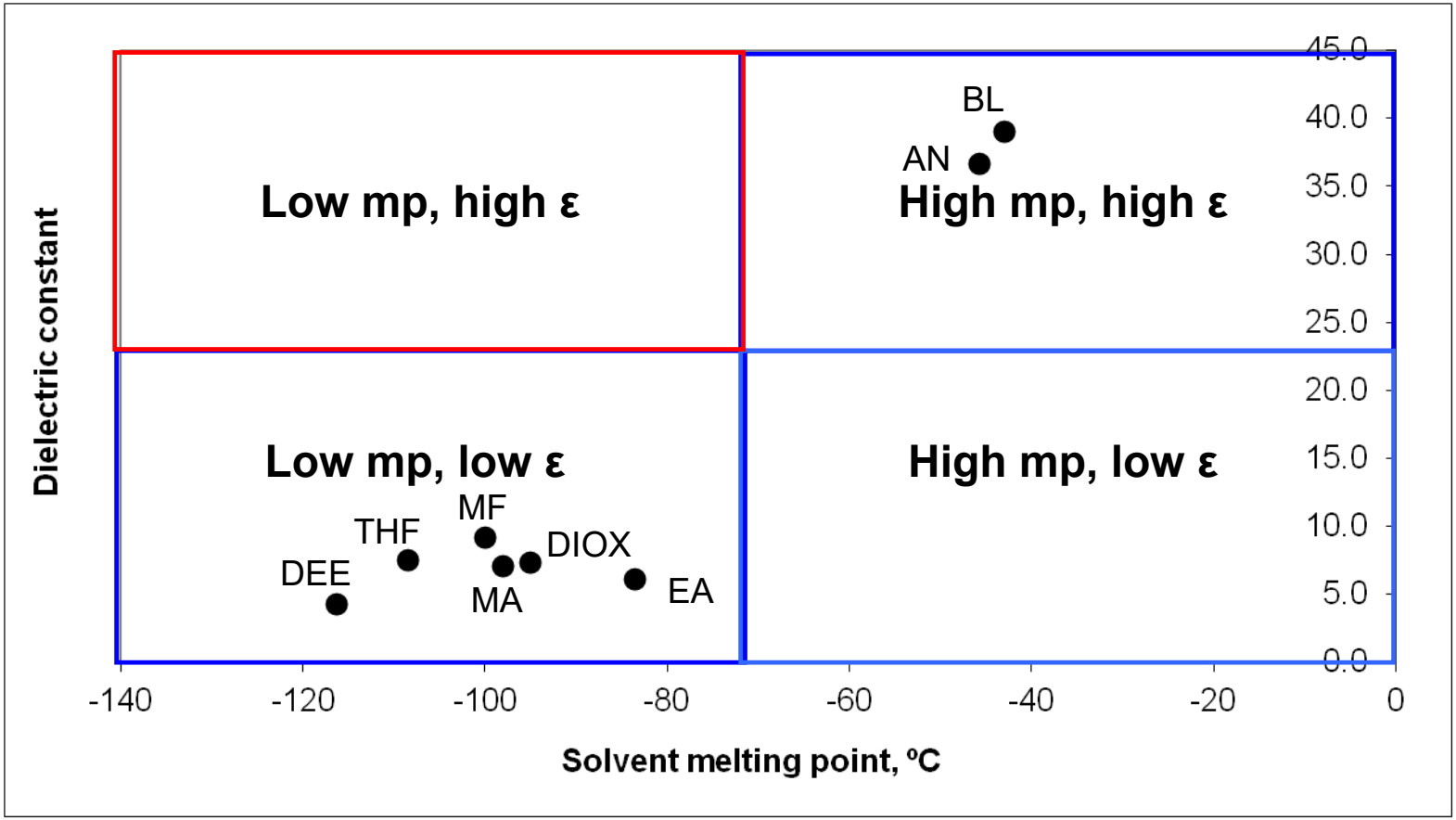
Representative Data from Commercially Available Cells



10 F cell

Discharge current = 1 A

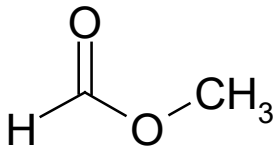
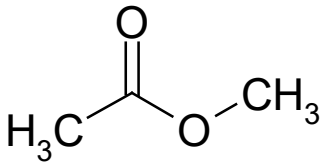
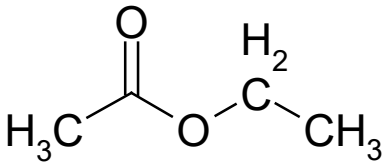
Electrolyte Design Considerations



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

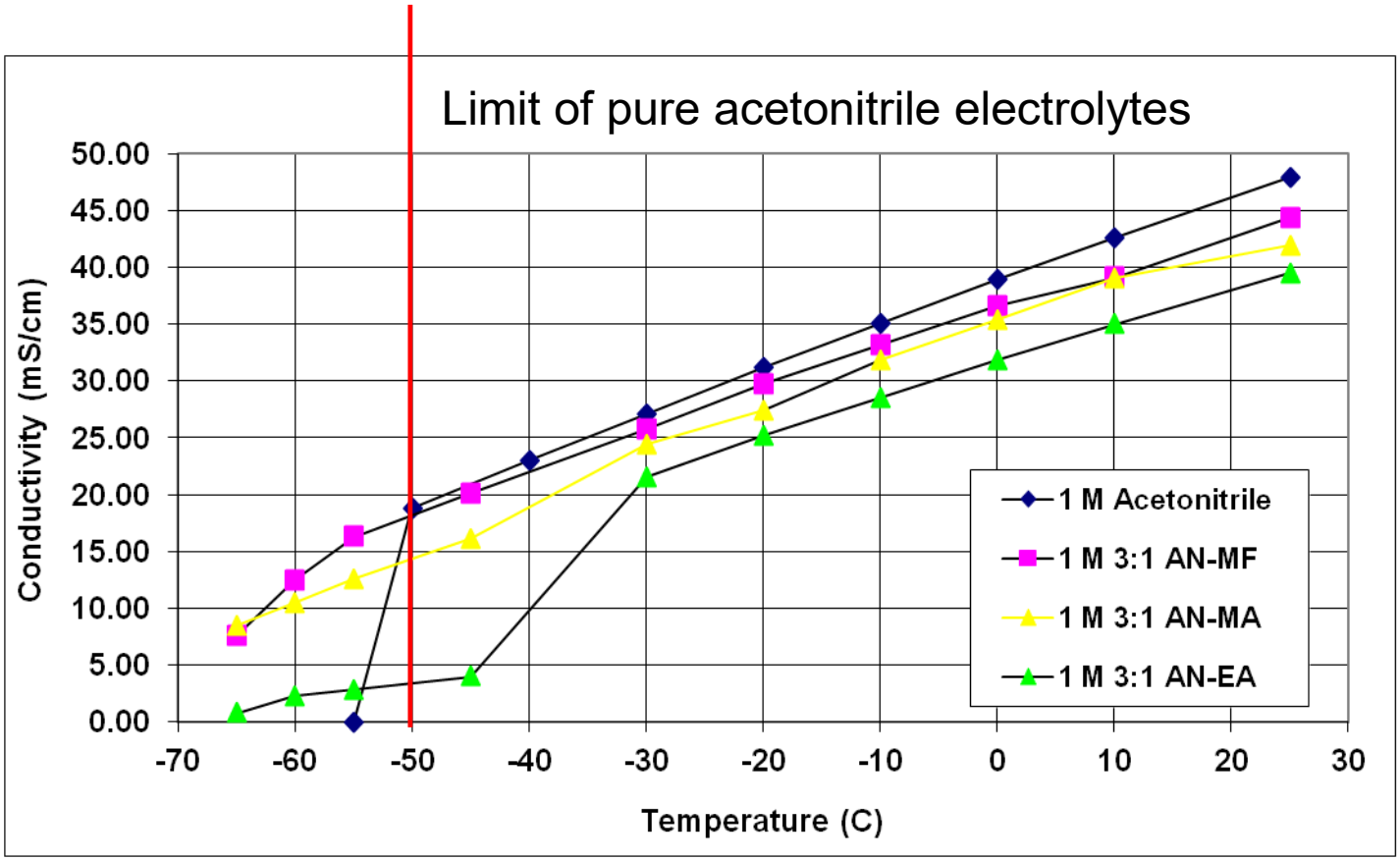
DIOX = 1,3-dioxolane
MF = methyl formate
DEE = diethyl ether
EA = ethyl acetate

3:1 Electrolyte Solvent Blends

Solvent	Freezing point (ºC)
$H_3C-C\equiv N$ acetonitrile (AN)	-43.84
 methyl formate	-100
 methyl acetate	-98
 ethyl acetate	-83.6
Acetonitrile : methyl formate (3:1 vol/vol%)	-70
Acetonitrile : methyl acetate (3:1 vol/vol%)	-71
Acetonitrile : ethyl acetate (3:1 vol/vol%)	-72

"Extending the low temperature operational limit of double-layer capacitors," E.J. Brandon, W.C. West, M.C. Smart, L.D. Whitcanack and G.A. Plett, *J. Power Sources*., 170, 225, 2007.

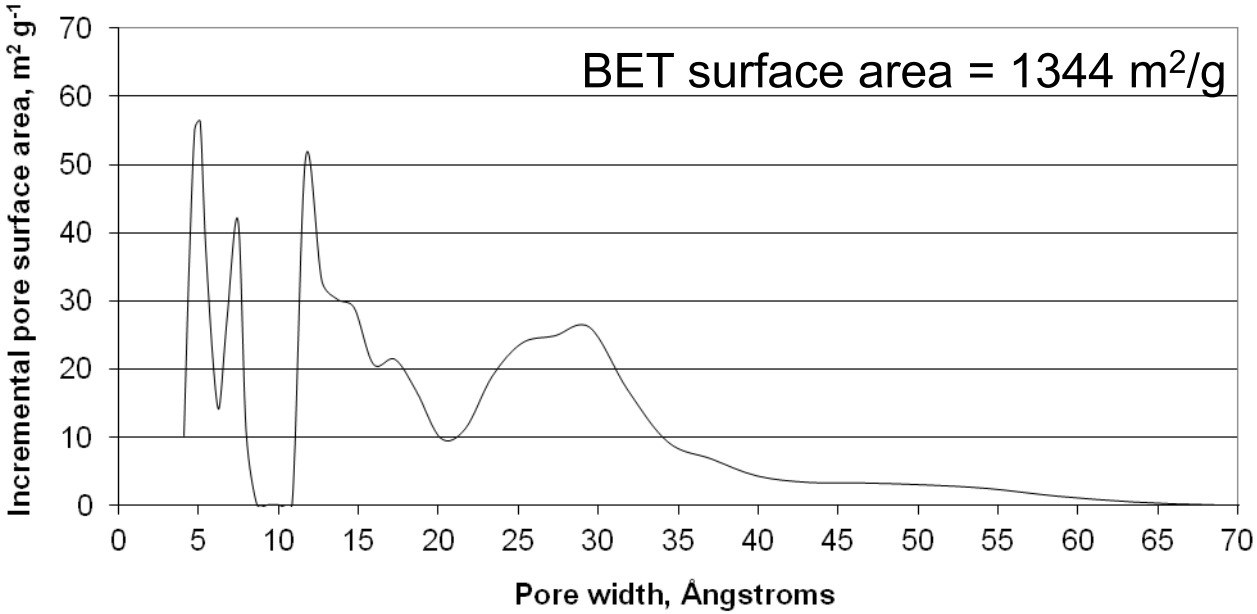
Conductivity of 3:1 Solvent Blends

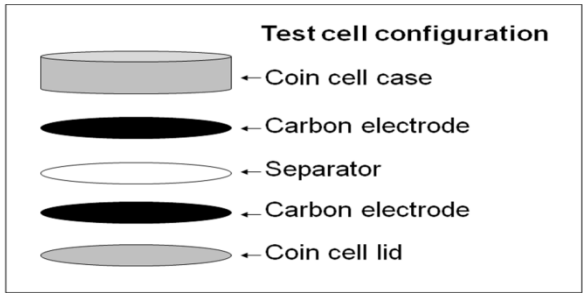


- 1 M TEATFB in 3:1 blends display appreciable conductivity below -40°C
- Methyl formate provides best performance relative to unmodified electrolyte
- Solubility studies and coin cell testing confirmed precipitation at these high salt concentrations was occurring at these temperatures

Test Cell Materials

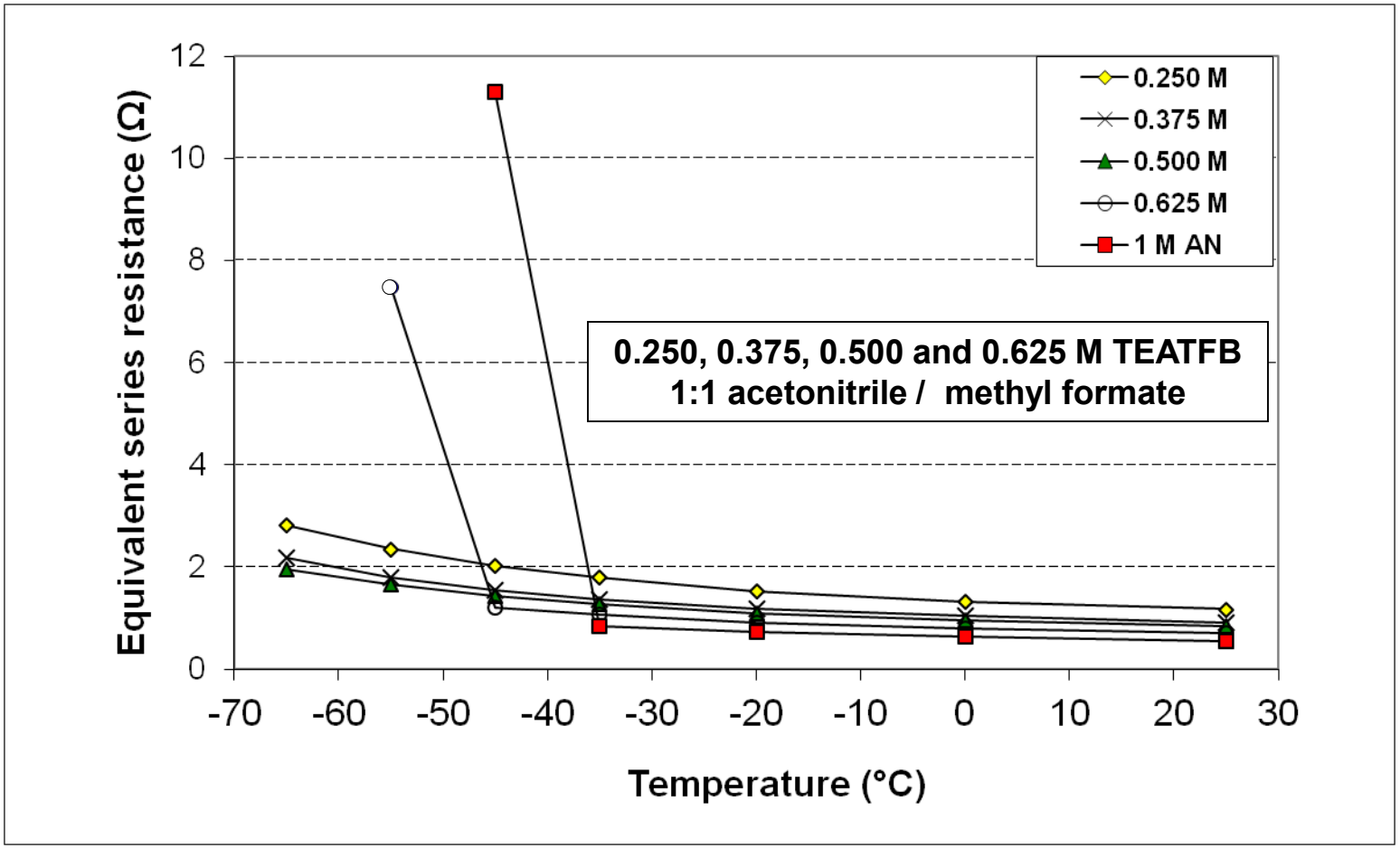
- **2032 coin cell**
- **Separator:** 25 micron polyethylene (Tonen)
- **Electrodes:** Activated carbon (PACMM203)
- **Salt:** Quaternary ammonium salts





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

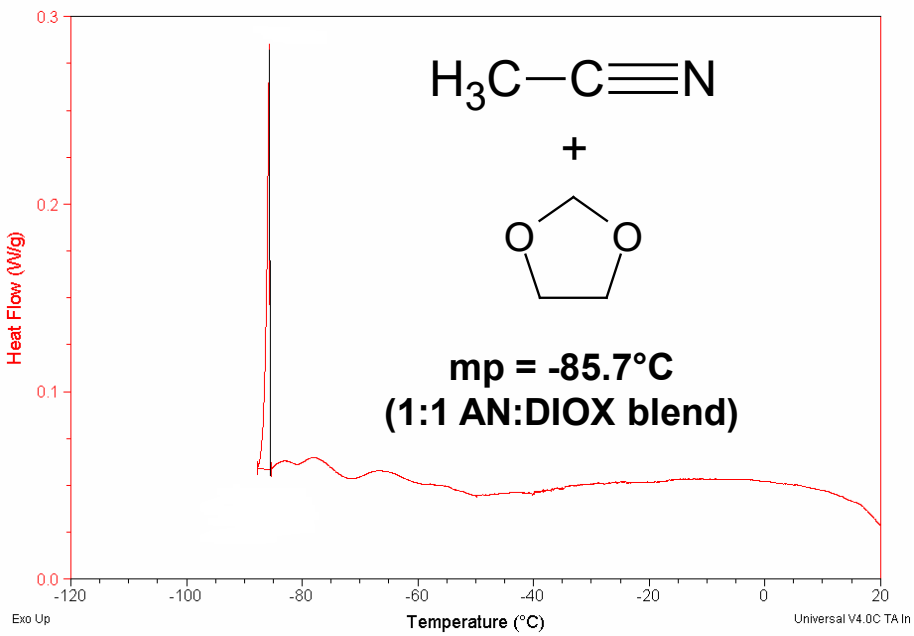
Conductivity vs. Salt Concentration



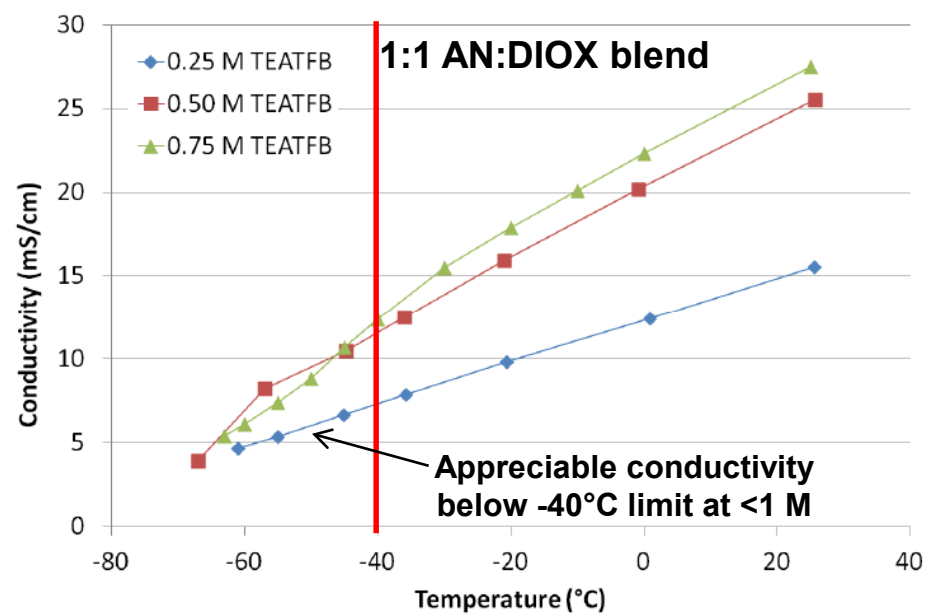
- 1:1 AN-MF blend supports lower temperature operation vs. 3:1 blend
- Salt concentration must be maintained at or below 0.5 M

1,3-Dioxolane As Alternative Co-Solvent

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

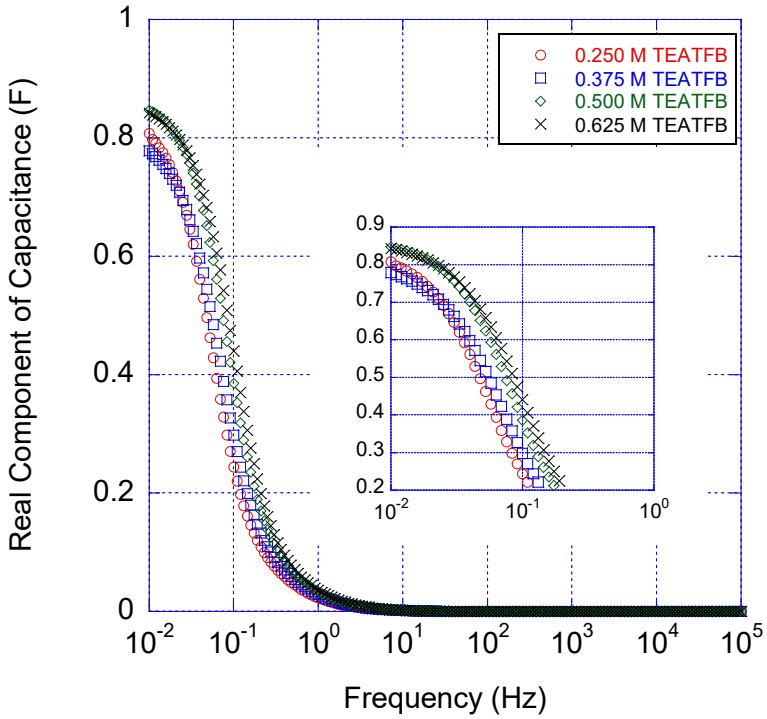


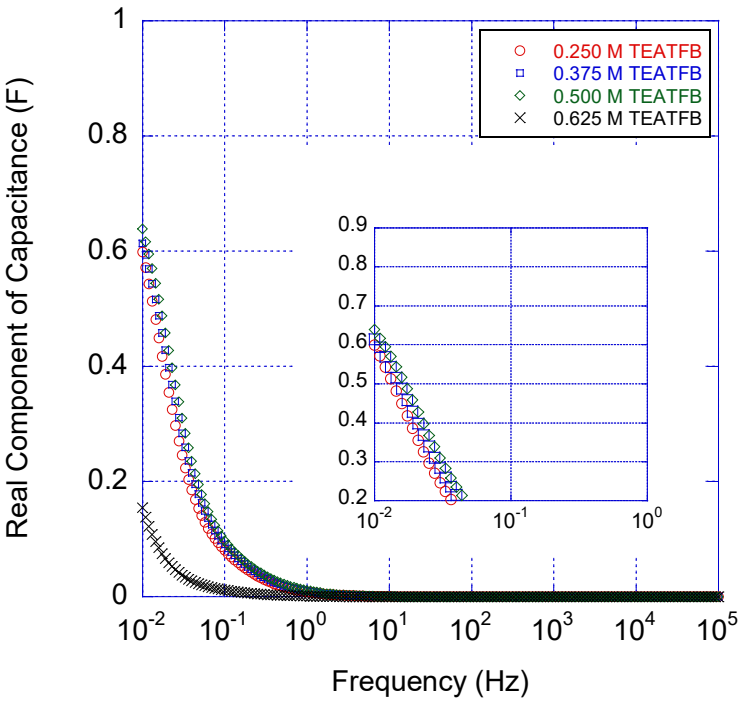
Differential scanning calorimetry data for low temperature electrolyte solvent system



Conductivity for three salt concentrations

Capacitance of 1:1 AN-DIOX Cells at Low Temperature





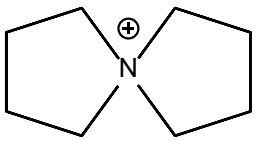
Capacitance vs. frequency for 0.250, 0.375, 0.500, and 0.625 M TEATFB electrolyte concentrations

"Double-Layer Capacitor Electrolytes Using 1,3-Dioxolane for Low Temperature Operation," W.C. West,* M.C. Smart,* E.J. Brandon, L.D. Whitcanack, and G.A. Plett, *J. Electrochem. Soc.*,155, A716, 2008.

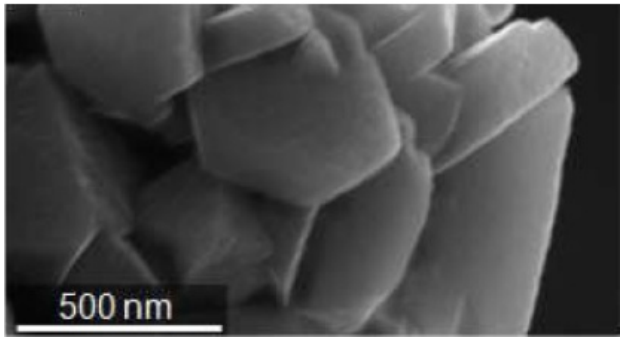
Strategies to Improve Specific Energy

- Improved high surface area carbons
  - Zeolite templated carbons
- Asymmetric cells
  - Intercalation electrode + high surface area carbon

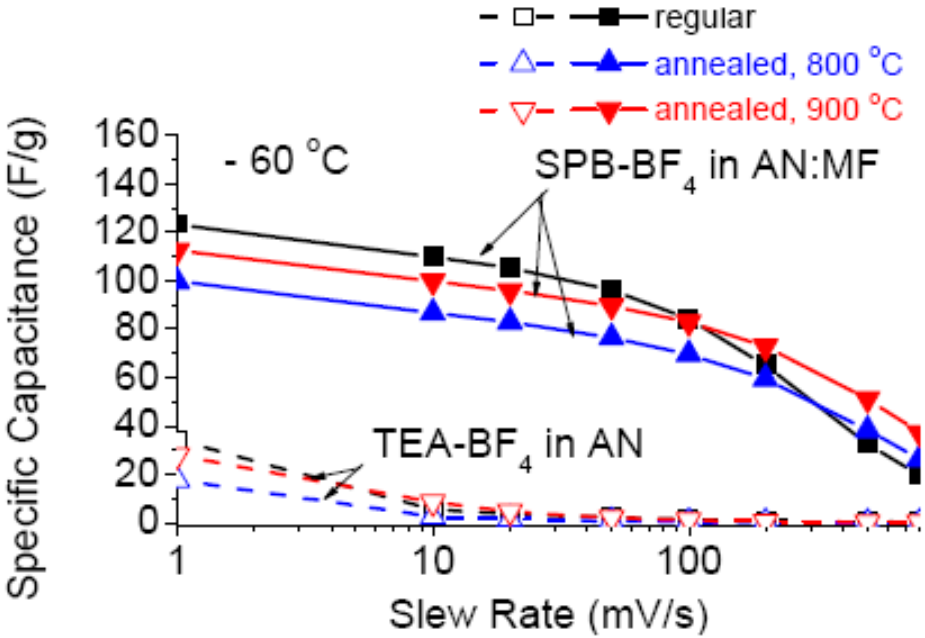
Optimizing Salt and Electrode Materials For Low Temperature Performance



SPB cation + BF_4 anion



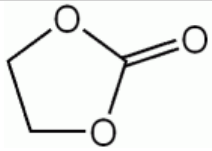
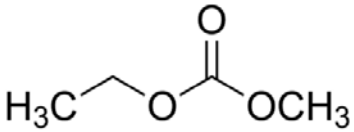
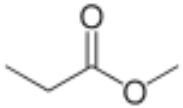
SEM micrograph of Georgia Tech zeolite templated carbon powder electrode material



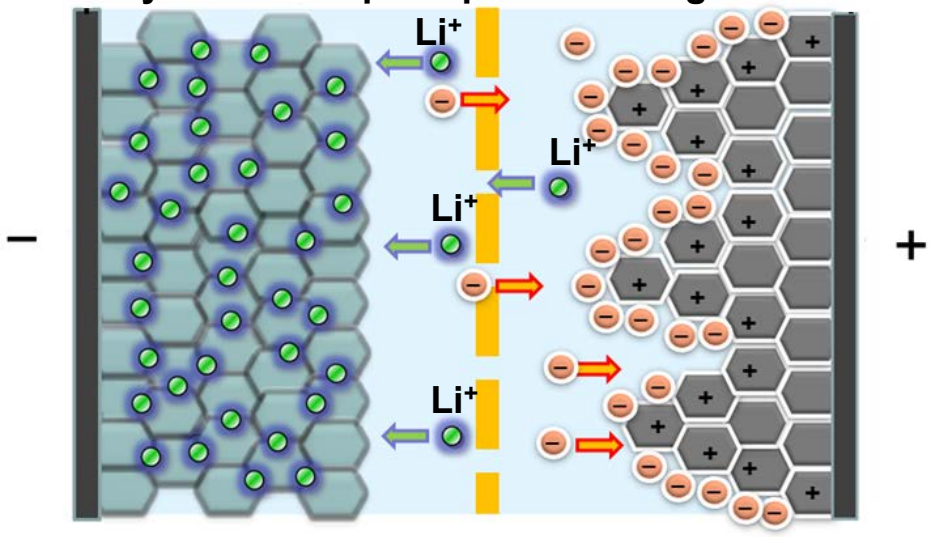
1 M TEATFB in acetonitrile vs. 0.5 SPB-TFB in 1:1 acetonitrile / methyl formate at – 60 ºC (coin cell using different zeolite templated carbon electrodes)

"In Situ Studies of Ion Transport in Microporous Supercapacitor Electrodes at Ultralow Temperatures," Y. Korenblit, A. Kajdos, W.C. West, M.C. Smart, E.J. Brandon, A. Kvit, J. Jagiello and G. Yushin, *Adv. Funct. Mater.*, 22, 1655, 2012.

Asymmetric Designs for Higher Capacity

Solvent	Structure	Melting Point (°C)
Ethylene Carbonate (EC)		34
Ethyl Methyl Carbonate (EMC)		-14.5
Methyl Propionate (MP)		-88

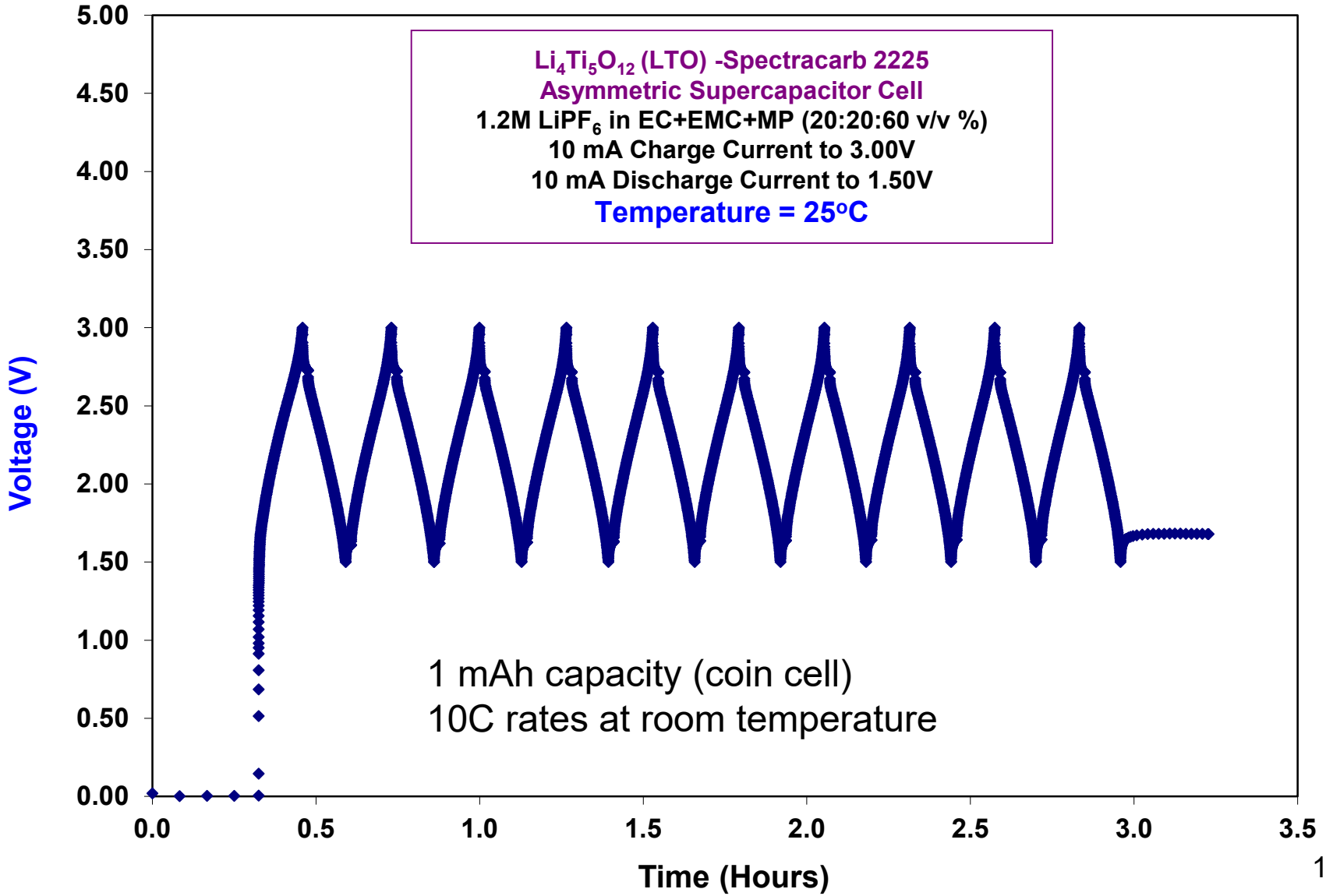
Asymmetric supercapacitor configuration



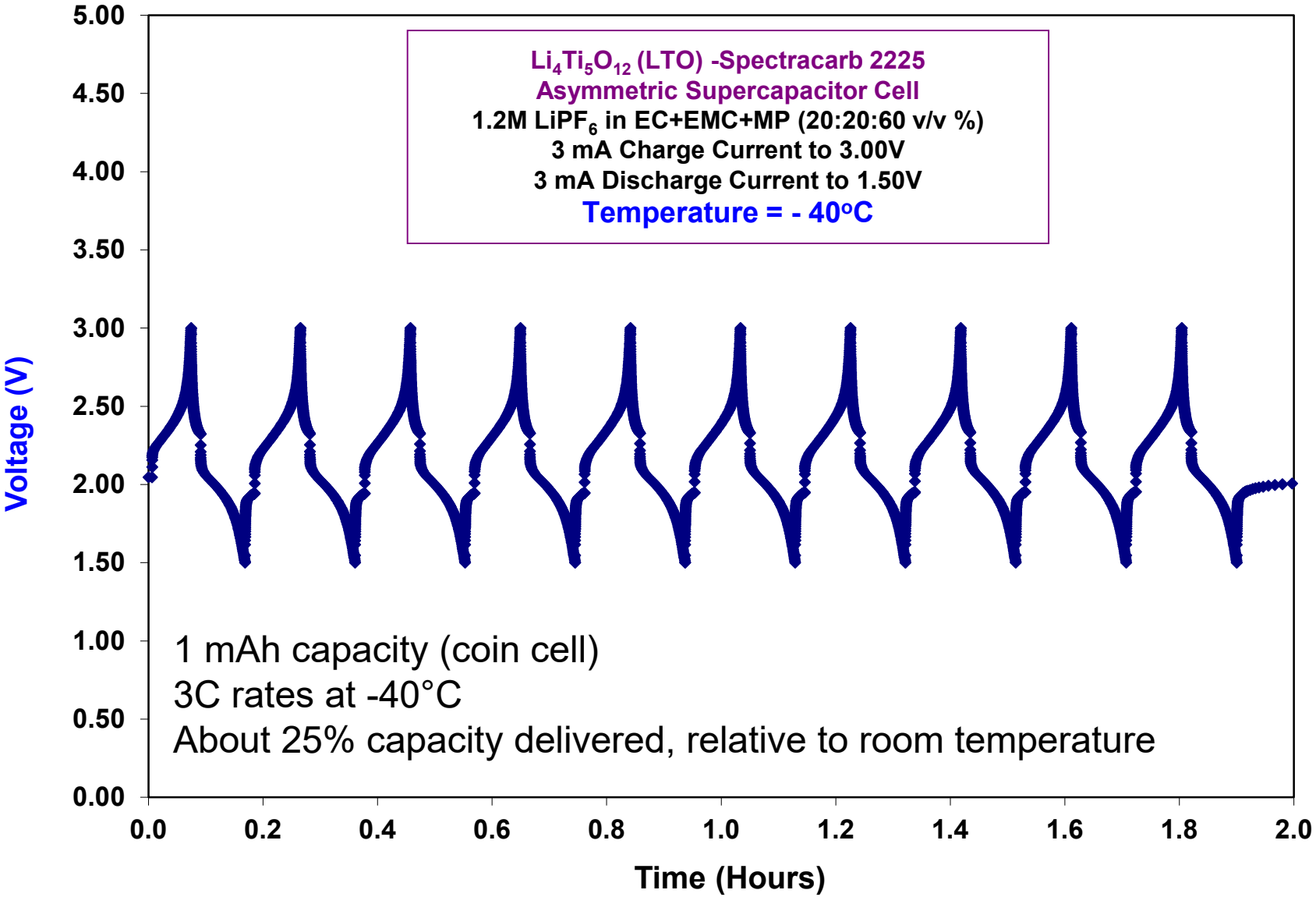
Lithium Titanate Electrode **High Surface Area Electrode**

- Coin cell geometry (2032)
- $Li_4Ti_5O_{12}$ (LTO) electrode
  - coated on copper current collector
  - 80% active material
- Activated carbon electrode (Spectracarb 2225)
  - Sputter coated with platinum
- Electrolyte:
  - 1.2M $LiPF_6$
  - EC+EMC+MP (20:20:60 v/v %)

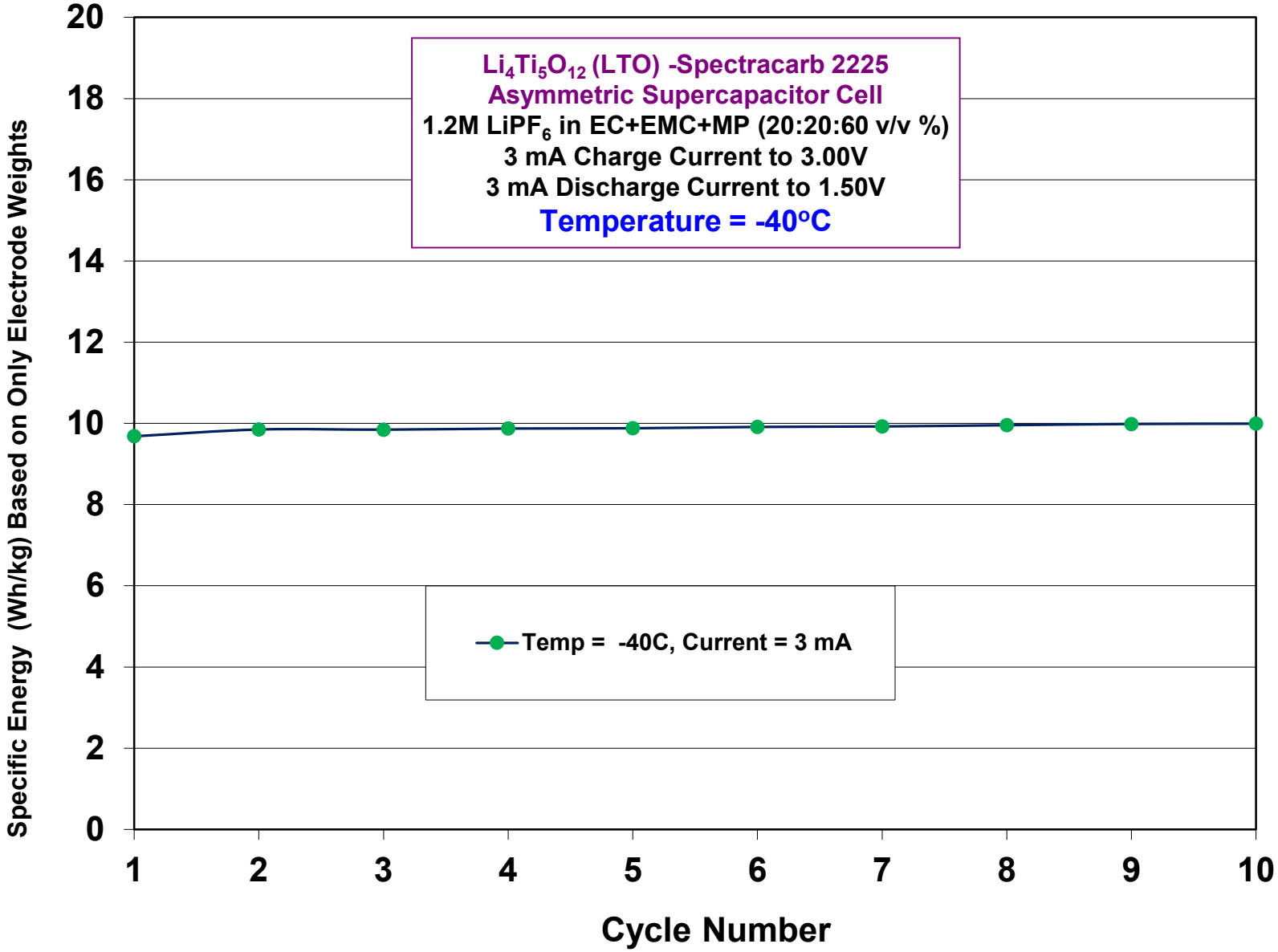
LTO/Carbon Asymmetric Supercapacitor



Constant Current Discharge at Low Temperatures



Specific Energy vs. Cycle (Active Electrode Materials Basis)



Summary

- **Low temperature double-layer capacitor 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

- **Capacity increased through higher capacity electrodes:**
  - Zeolite templated carbons
  - Asymmetric cell designs

- **Continuing efforts**
  - Improve asymmetric cell performance at low temperature
  - Cycle life testing

Acknowledgements

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