Design of Supercapacitors for Wide Temperature Operation

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2019 Spring Materials Research Society Meeting

Phoenix, AZ

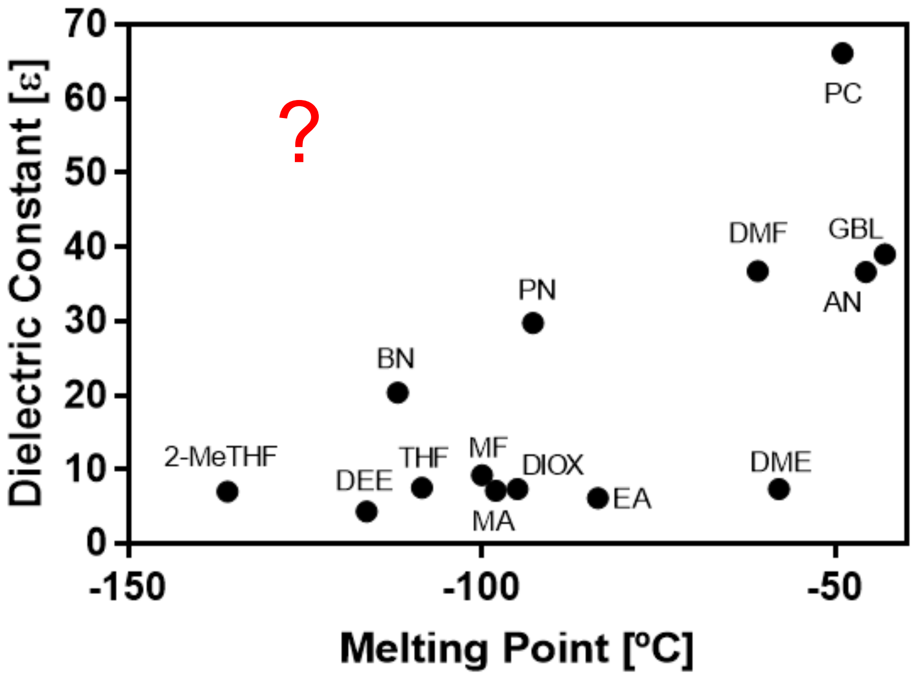
Wednesday, April 24, 2019

Wide Temperature Operation Design Considerations

- **Double-layer capacitors are well suited for wide temperature operation**
  - Non-Faradaic charge storage eliminates kinetic limitations associated with electrode diffusion processes
  - Solid electrolyte interface (SEI) stability not a concern at elevated temperatures
  - Typically operate in the -40 to +70ºC range
  - Limited largely by electrolyte *solvent properties*
- **Low temperature operation**
  - Acetonitrile electrolyte freezes between -40 and -50ºC
  - Decreasing solvent conductivity and increasing cell resistance at low temperature
- **High temperature operation**
  - Acetonitrile electrolyte boils at 82ºC
  - Reduced voltage window and electrolyte decomposition at elevated temperatures

CSUNSat1 Hybrid Battery
"FM1-2"
2.5 Ahr Nameplate

Solvent Blending Strategy for Low Temperature Operation



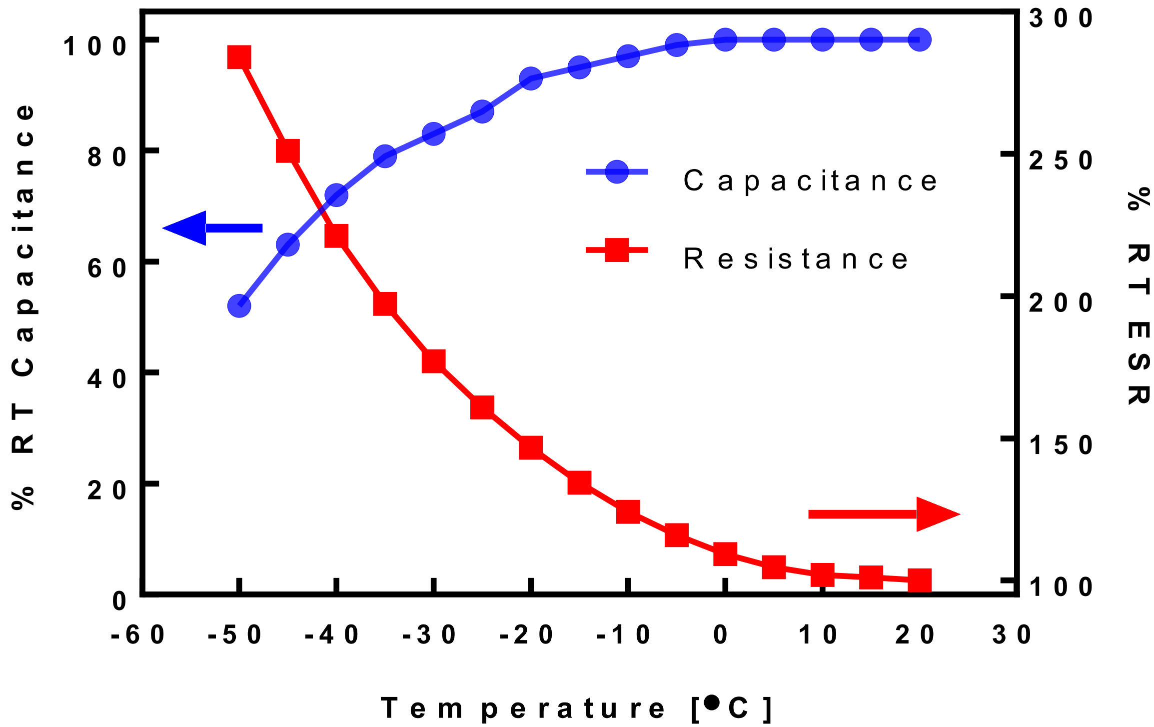
- Depress freezing point
- Maintain sufficient dielectric constant for high salt solubility

AN = acetonitrile
BN = butyronitrile
DEE = diethyl ether
DME = dimethyl ether
DMF = N,N-dimethyl formamide
DIOX = 1,3-dioxolane
EA = ethyl acetate
GBL = γ-butyrolactone
MA = methyl acetate
MF = methyl formate
PN = propionitrile
PC = propylene carbonate
THF = tetrahydrofuran
2-MeTHF = 2-methyl tetrahydrofuran

1. E.J. Brandon, W.C. West, M.C. Smart, L.D. Whitcanack, G. A. Plett, *J. Power Sources*, 170, 225 (2007).
2. W.C. West, M.C. Smart, E.J. Brandon, L.D. Whitcanack, G. A. Plett, *J. Electrochem. Soc.*, 155, A716 (2008).
3. Y. Korneblitt, A. Kajdos, W.C. West, M.C. Smart, E.J. Brandon, A. Kvit, J. Jagiello, G. Yushin, *Adv. Ener. Mater.* 22, 1655 (2012).

Cell Resistance More Sensitive to Temperature Than Capacitance

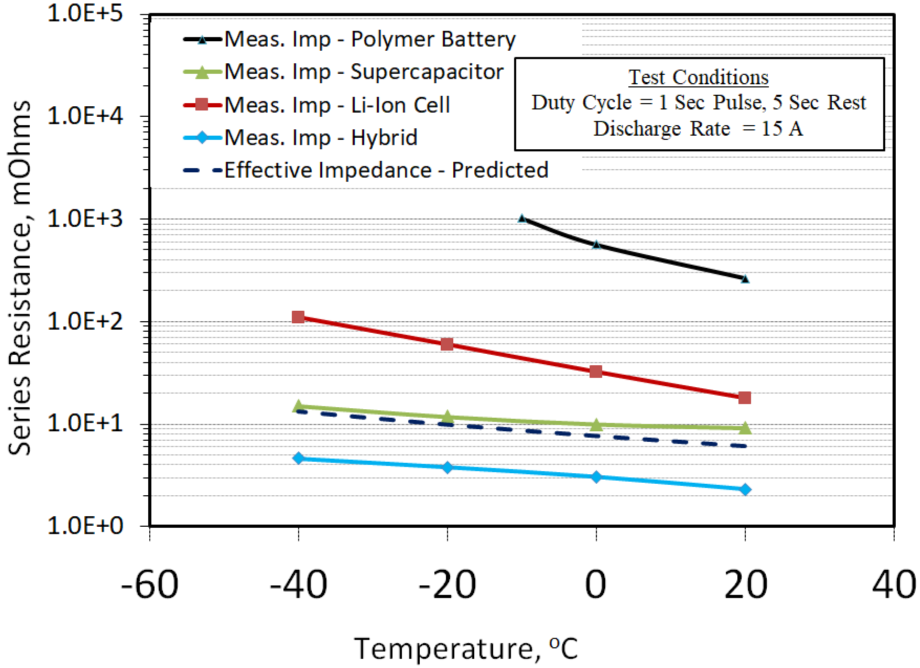
10 F Maxwell Boostcap cell
Discharge current = 1 A

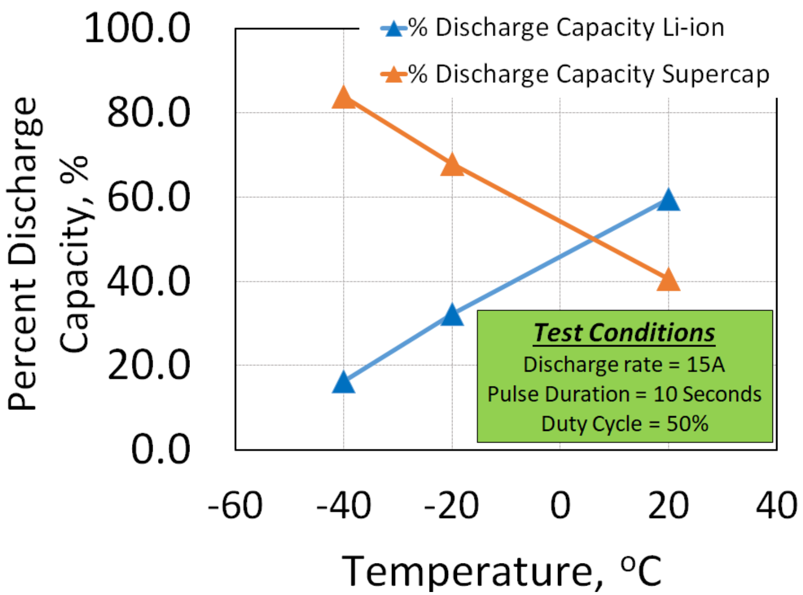


- Increase in equivalent series resistance (ESR) more significant
- Capacitance response less sensitive
- Requires managing resistance increases

Comparison of Series Resistance vs Supercapacitors (>300F)

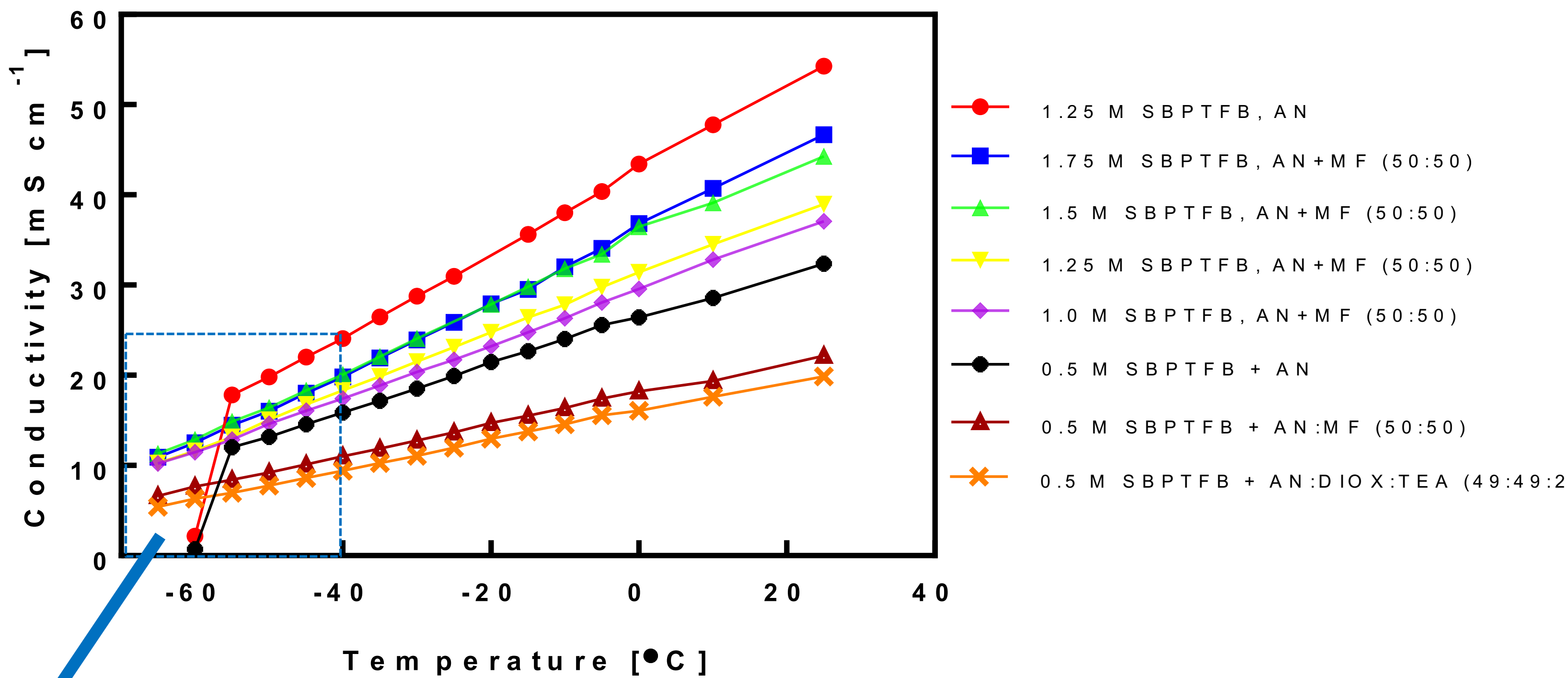
Cells tests below are >300 F Boostcap Cells

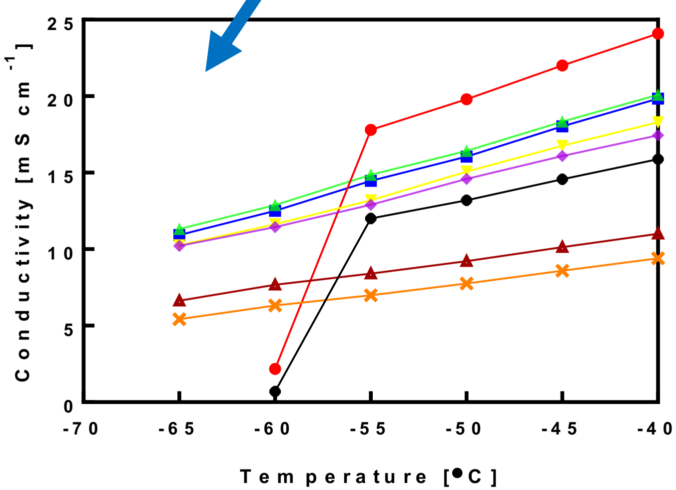




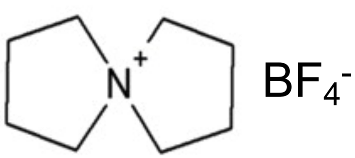
- Supercapacitors exhibit lowest series resistance compared to other conventional energy storage systems
- Supercapcitors enhance low temperature performance under high loads in hybrid energy storage systems
- Hybrid energy storage systems with supercapacitors exhibit excellent load-sharing qualities

Conductivity of Low Temperature Blends

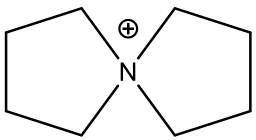




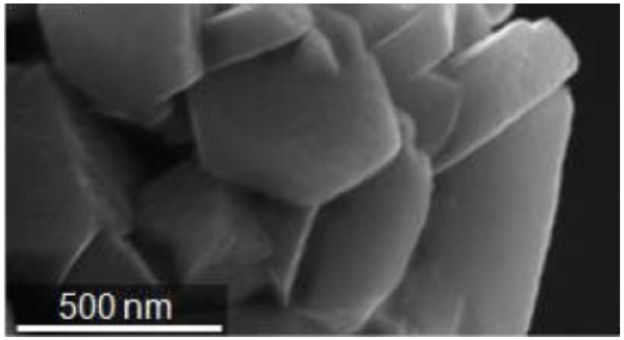
Used spiro-(1,1')-bipyrolidinium tetrafluoroborate (SBPTFB) in place of TEATFB salts



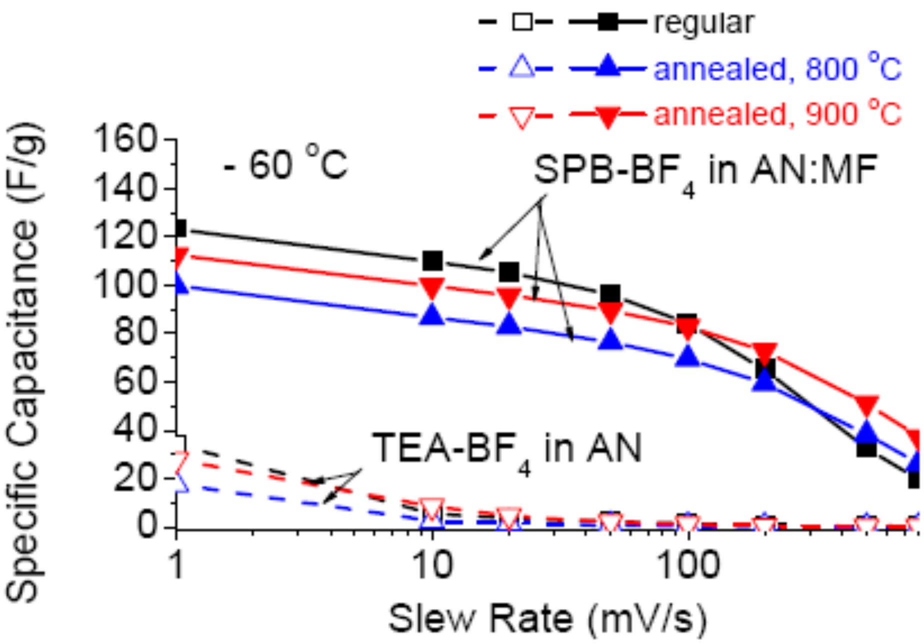
Optimizing Salt and Electrode Materials For Low Temperature Performance



spiro-(1,1')-bipyrrolidinium tetrafluoroborate salt



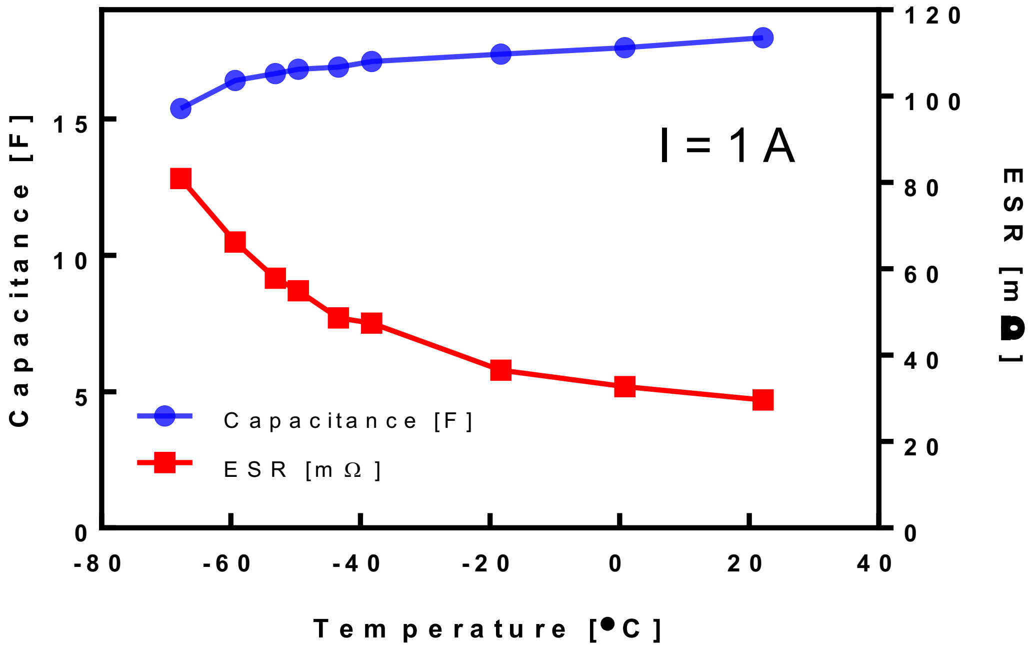
SEM micrograph of Georgia Tech zeolite templated carbon powder electrode material



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.

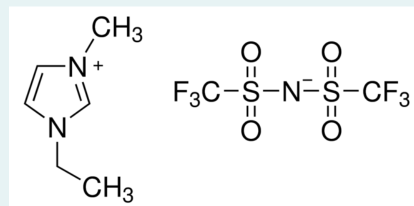
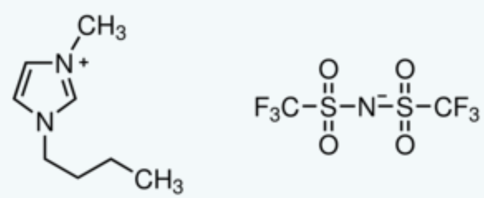
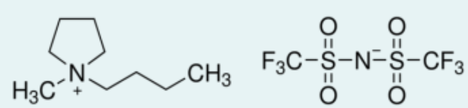
Operation of Cylindrical Cells to -70ºC



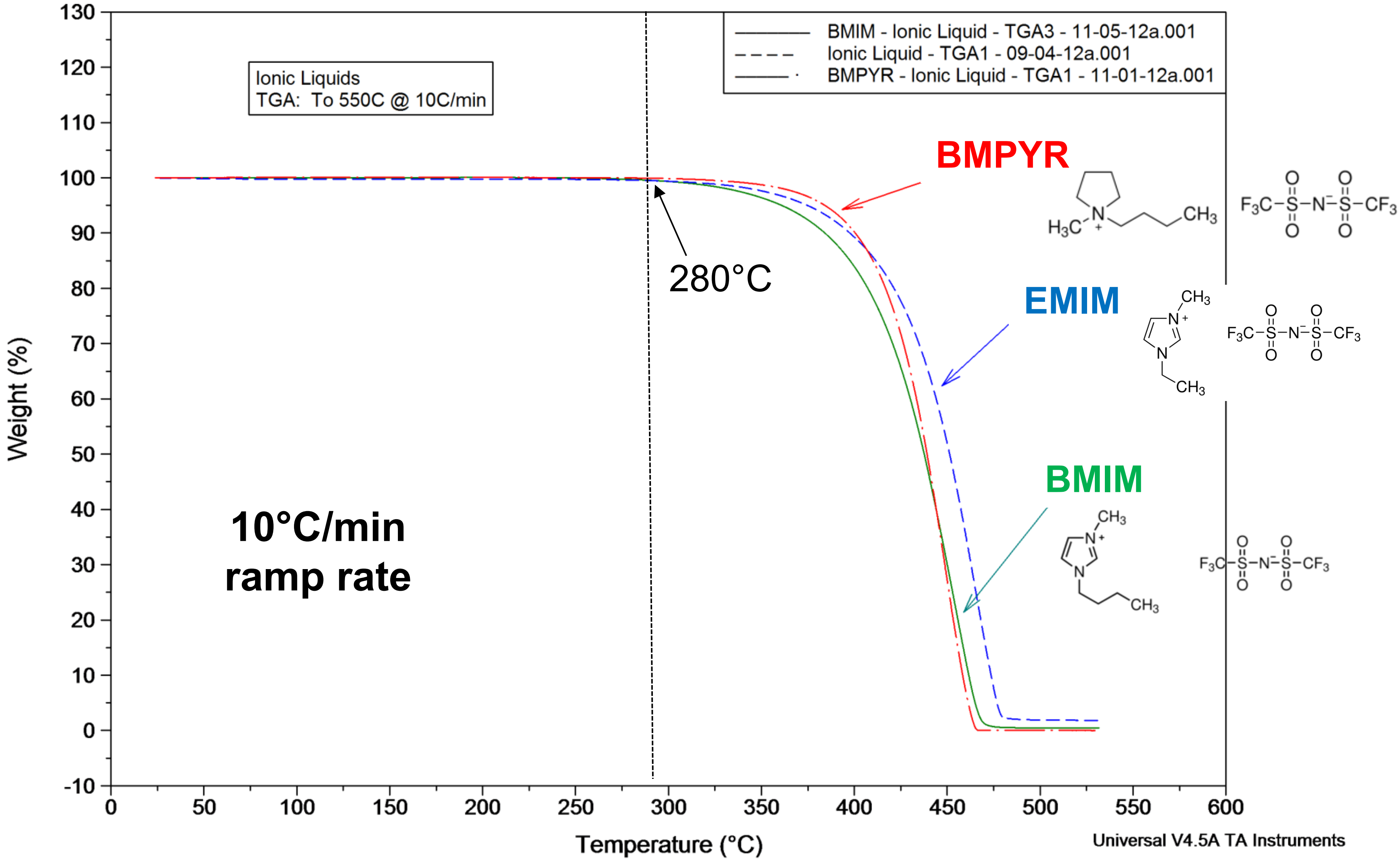
Operation to -70ºC through use of AN:MF modified electrolytes and standard high surface area carbon (YP-50)

Cells assembled at the Case Western University Electrochemical Capacitor Prototyping Facility (Robert Savinall and John Miller)

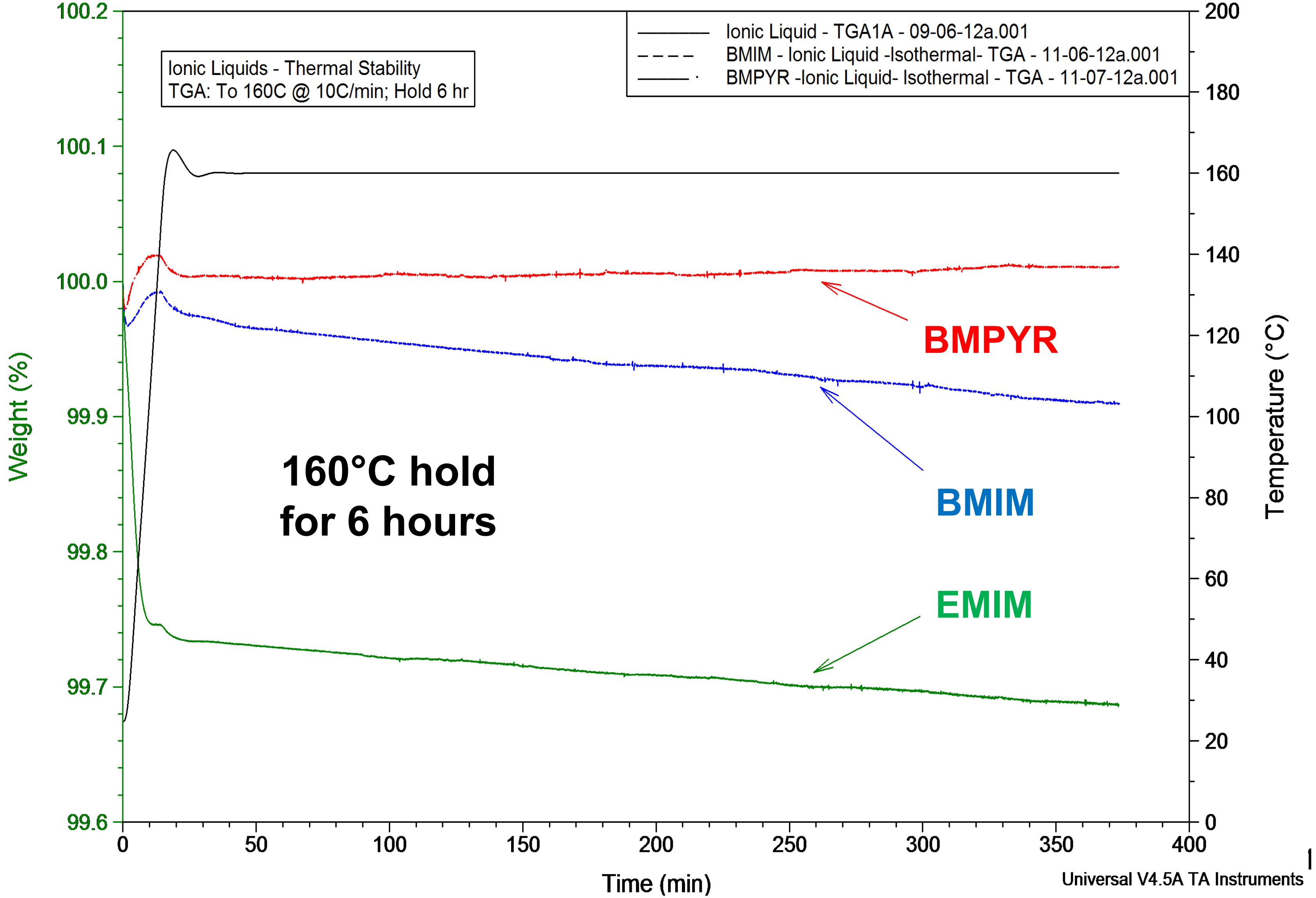
High Temperature Ionic Liquid Electrolyte Options

Solvent Name	Molecular Structure	Ionic Conductivity, mS cm^{-1} (25°C)	Viscosity, cP (25°C)
1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (EmIm)		8.8	34
1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (BMM)		3.9	52
1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) Imide (BMPYR)		2.2	85

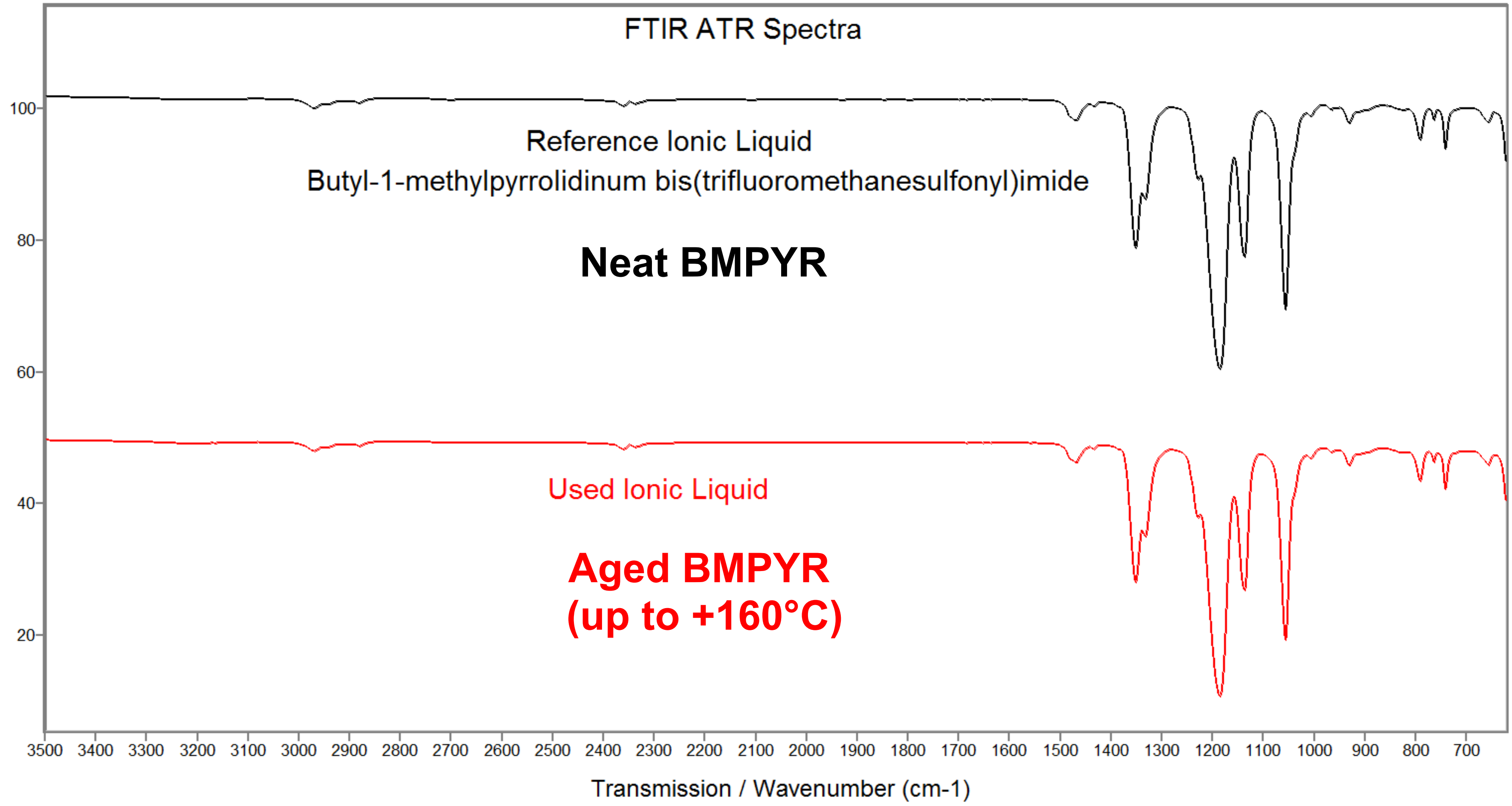
Ionic Liquid Thermogravimetric Analysis



Ionic Liquid Mass Loss at 160°C

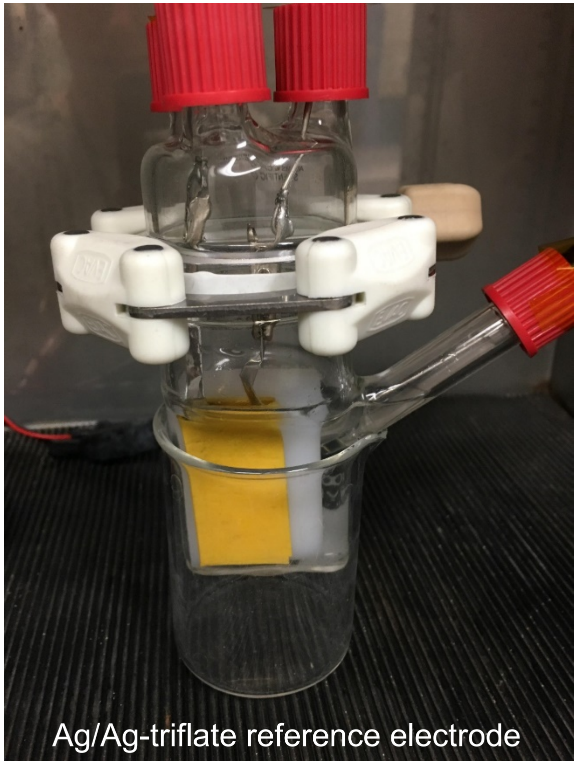


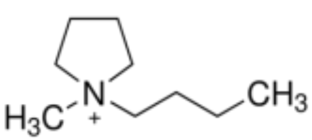
Stability of Ionic Liquid

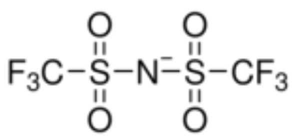


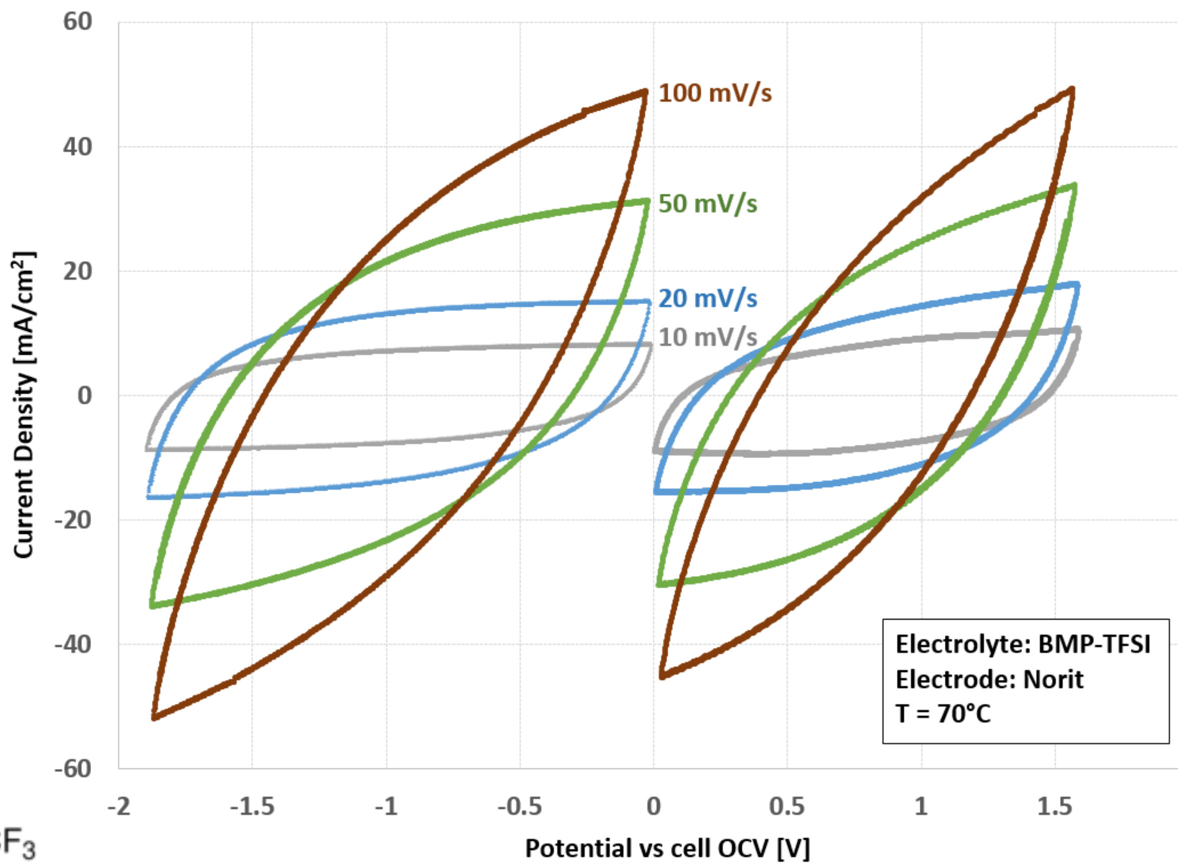
Extracted ionic liquid from 160°C treatment in Swagelok cell indicates no decomposition or reaction with cell components via FTIR spectroscopy (corroborated by NMR spectroscopy)

Voltage Stability of Ionic Liquids at Elevated Temperatures



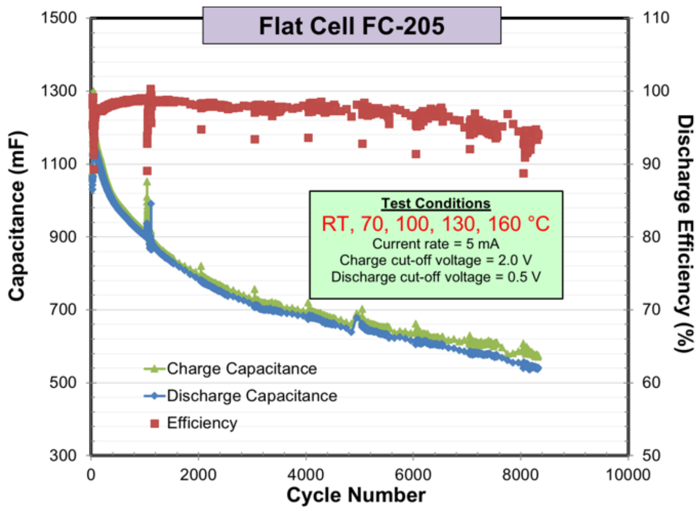


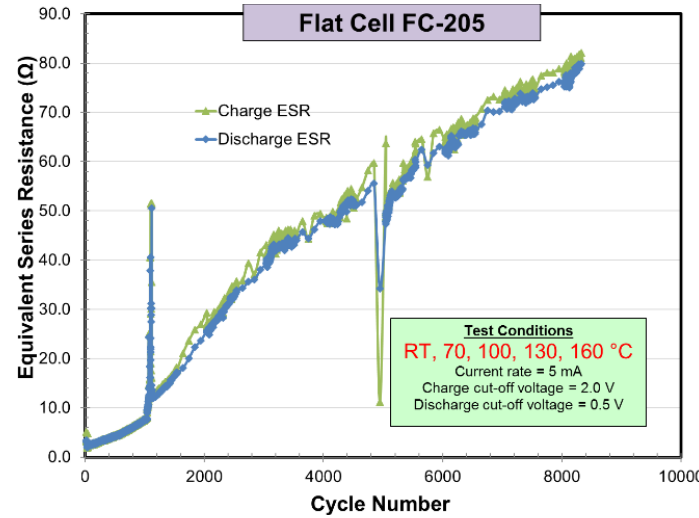




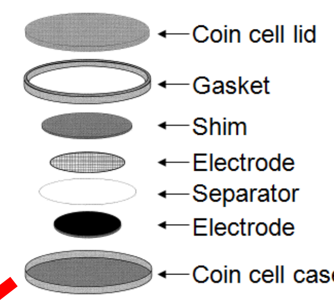
Cyclic voltammetry at 70°C for BMPYR-TFSI ionic liquid electrodes, at scan rates between 10 mV/s and 100 mV/s

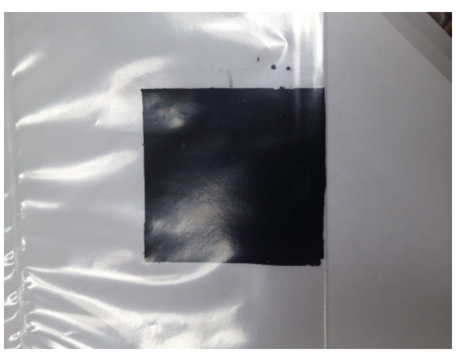
Evaluating Components at High Temperatures In Flat Cells



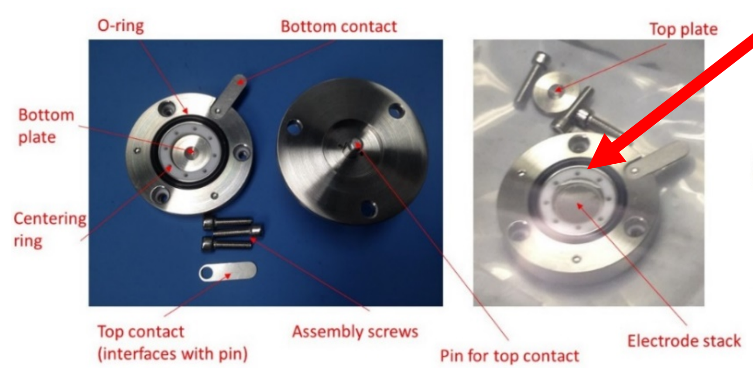


Representative capacitance vs. cycle number and internal resistance data from flat cell testing at a 2V cut-off up to temperature of +160°C.





Spray coated electrode using Teflon-based binder



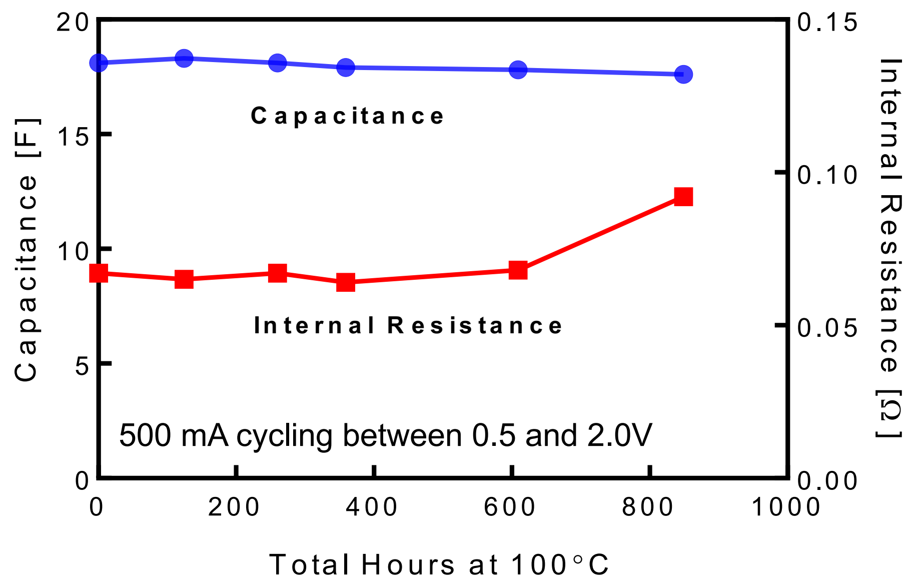
Flat cell assembly

Full Cell Testing at +100ºC

High Temperature Components Used

- Norit high surface carbon electrodes with PTFE binder
- Polyimide separator
- 1-butyl-1-methylpyrrolidinium trifluorosulfonylimide electrolyte

Cells assembled at the Case Western University Electrochemical Capacitor Prototyping Facility

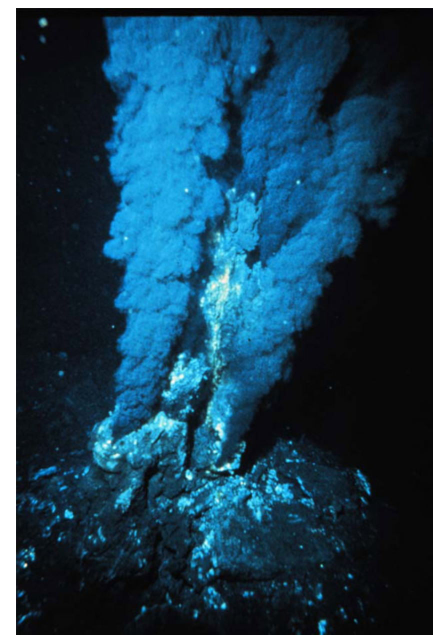


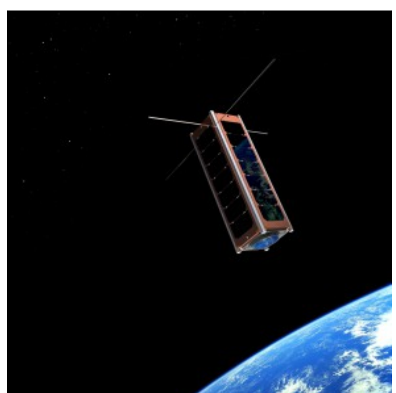
Representative data for cylindrical cell held at 100°C for 849 hours

Summary

- Selection of components is critical in designing supercapacitors for wide temperature operation
- Electrolyte blending is key to extending temperature limit and maintaining salt solubility at low temperatures
- Selection of stable electrode, separator and electrolyte are key for high temperature operation
- Many applications awaiting, on Earth and beyond








Acknowledgements

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