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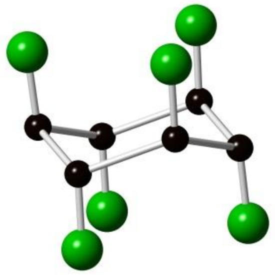
Electrochemical characterization of CF_x material

Ganesan Nagasubramanian, Kyle Fenton
2546 Advanced Power Sources R & D Department
Sandia National Laboratories
Albuquerque, NM 87185
Email: gnagasu@sandia.gov



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Acknowledgement

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National Nuclear Security Administration

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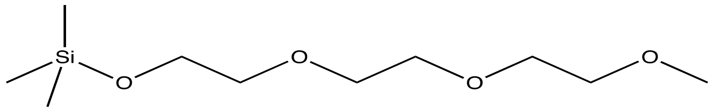
Overall goal of this internally funded work

- Prepare prismatic CF_x cells with electrodes coated at our facility
  - Thermally stable
  - Capable of performing between the temperatures -40º and 60ºC
- Synthesize and evaluate functionalized Si-based nonflammable electrolytes with improved conductivity
- Evaluate performance in these electrolytes

Outline

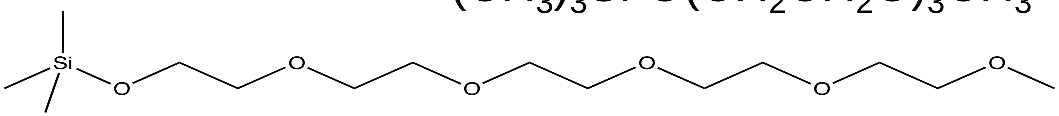
- Test CF_x powder with x≥1 and x~0.9
  - From three different sources
    - Highest theoretical capacity
    - Low self discharge
    - Very long shelf life
    - Operating Voltage ~2.5 V commensurate with modern electronics for operation
- Describe Sandia in-house capability
- Electrolyte studies
  - Nonflammable functionalized siloxane solvents
  - However, initial evaluation of CFx was performed in:
    - Carbonate-based electrolyte; (e.g.) EC:EMC(3:7 w%)/1.2M $LiPF_6$ and Si(PEO)5-1M TFSI
- Electrochemical Studies
  - Discharge coin cells for
    - Capacity, temp performance
  - Impedance studies
- Summary

Silanes synthesized for this study



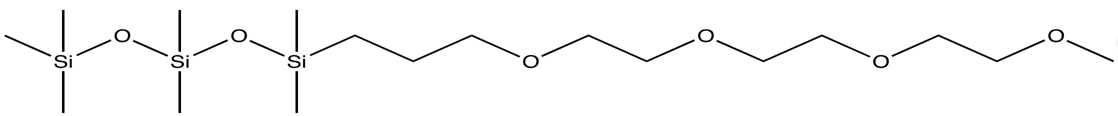
A

$(CH_3)_3Si\text{-}O(CH_2CH_2O)_3CH_3$



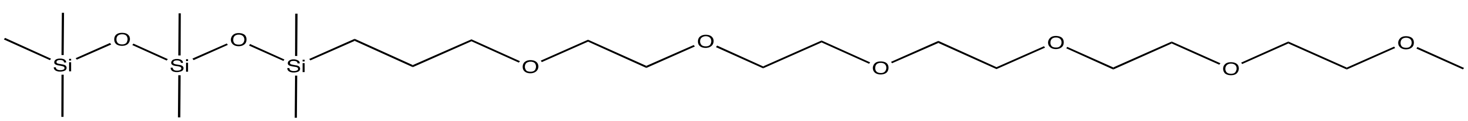
B

$(CH_3)_3Si\text{-}O(CH_2CH_2O)_5CH_3$



C

$(CH_3)_3Si\text{-}O\text{-}(CH_3)_2Si\text{-}O\text{-}(CH_3)_2Si\text{-}CH_2(CH_2CH_2O)_4\text{-}CH_3$



D

$(CH_3)_3Si\text{-}O\text{-}(CH_3)_2Si\text{-}O\text{-}(CH_3)_2Si\text{-}CH_2(CH_2CH_2O)_6\text{-}CH_3$

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CF_x has very high specific capacity and hence long runtime

Chemistry	Voltage (V)	Specific Energy (Whr/kg) Theoretical
Li/CF_x	3.2	2,260

The value of "x" determines the specific capacity which is computed using the formula given below.

$$\frac{xF}{3.6(12 + x19)}$$

Where F= 96,485 Coulombs/equivalent

Value of x	Capacity, mAhr/g
0.9	829
0.95	847
1.00	865
1.05	881
1.10	896

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Materials designation and electrode formulation

- CF_x was purchased from 3 vendors
  - Designated as:
  - Material “A”,
  - Material “B” and
  - Material “C”
- Electrode formulation:
  - CF_x: 94 w%
  - Solvay 5130 PVDF: 3 w%
  - Denka carbon additive: 3 w%

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In-house capability for cell prototyping and solvent synthesis

Facility

Commercial Prototype-Scale Cell Winders and Supporting Cell Fabrication Equipment Located in Two Dry Rooms (1000 sq. ft.)

- **Capability to wind multi format cell types**
  - **18650**
  - **D-size**
  - **prismatic**
- **Prototype 18650 cells to evaluate a variety of battery materials both anodes and cathode**
- **Adapted Li-ion coating technolo form CF_x electrodes**

Solvent Synthesis

- Air and moisture free capabilities
- Battery grade ionic liquids and non-flammable solvents
- Metal ionic liquids
- Versatile scalability

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Examples of Sandia Battery prototyping capabilities

Coater

Winder

For a comprehensive list please refer to:

1) G. Nagasubramanian, Fabrication and testing capabilities for 18650 Li/$(CF_x)_n$ Cells, *International Journal of Electrochemical Science 2 (2007) 913*

2) G. Nagasubramanian and Kyle Fenton, *Electrochim Acta, doi: 10.1016/j.electacta.2012.09.065*

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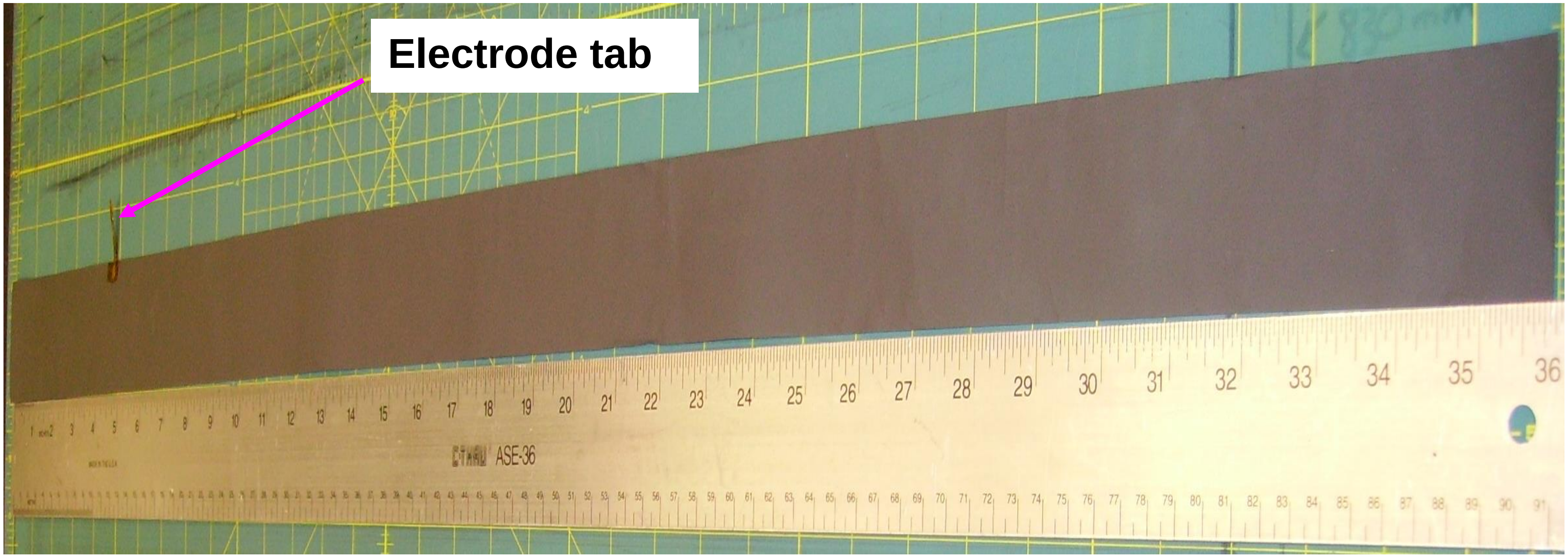
Sandia coated $(CF_x)_n$ electrode



SNL coated $(CF_x)_n$ electrode with tab welded ultrasonically

Electrode Composition: Active: Carbon: PVDF= 94:3:3 (w%).
We adapted Li-ion coating technology to form CF_X electrodes.

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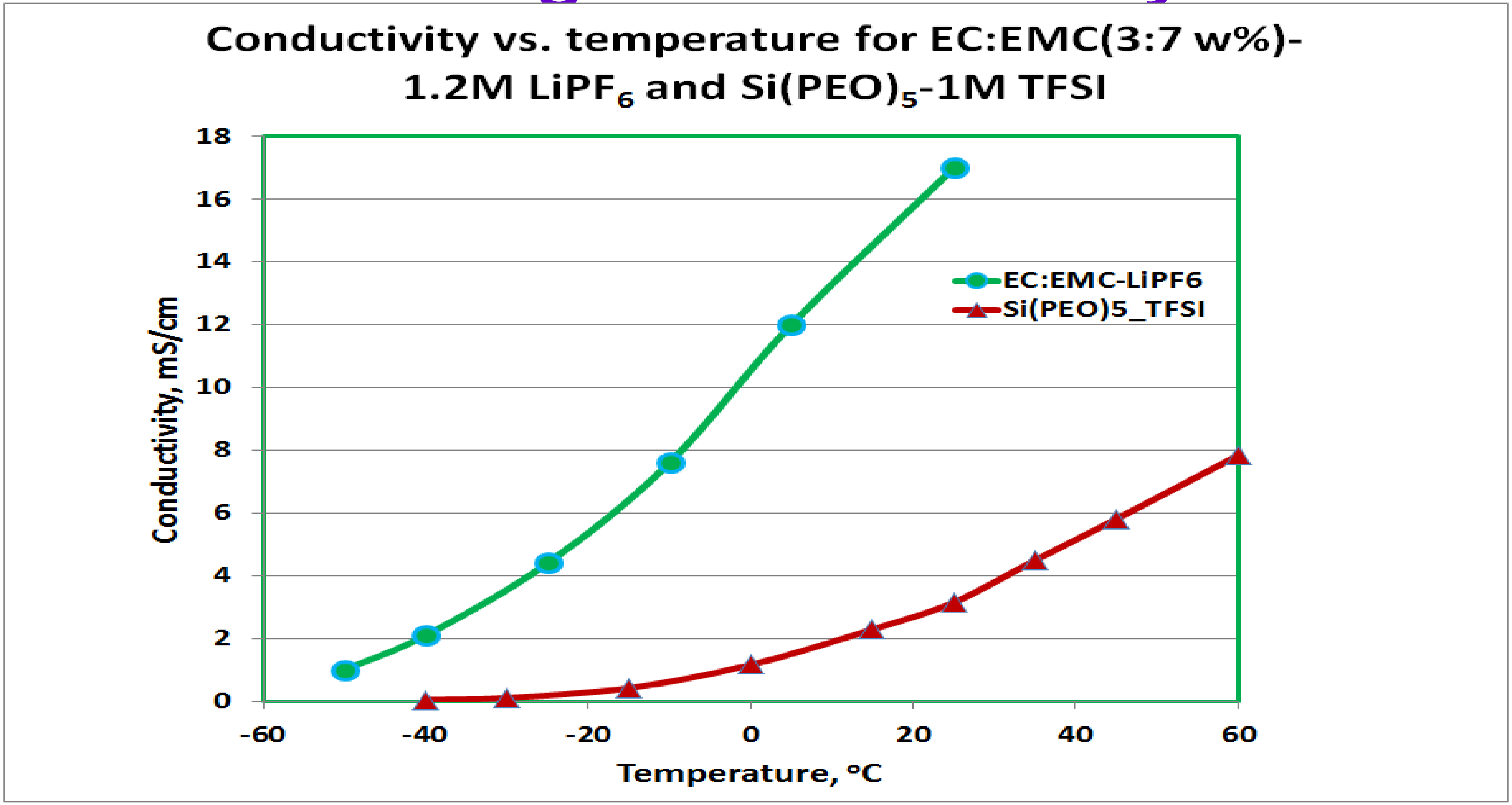
Both electrolytes show high conductivity



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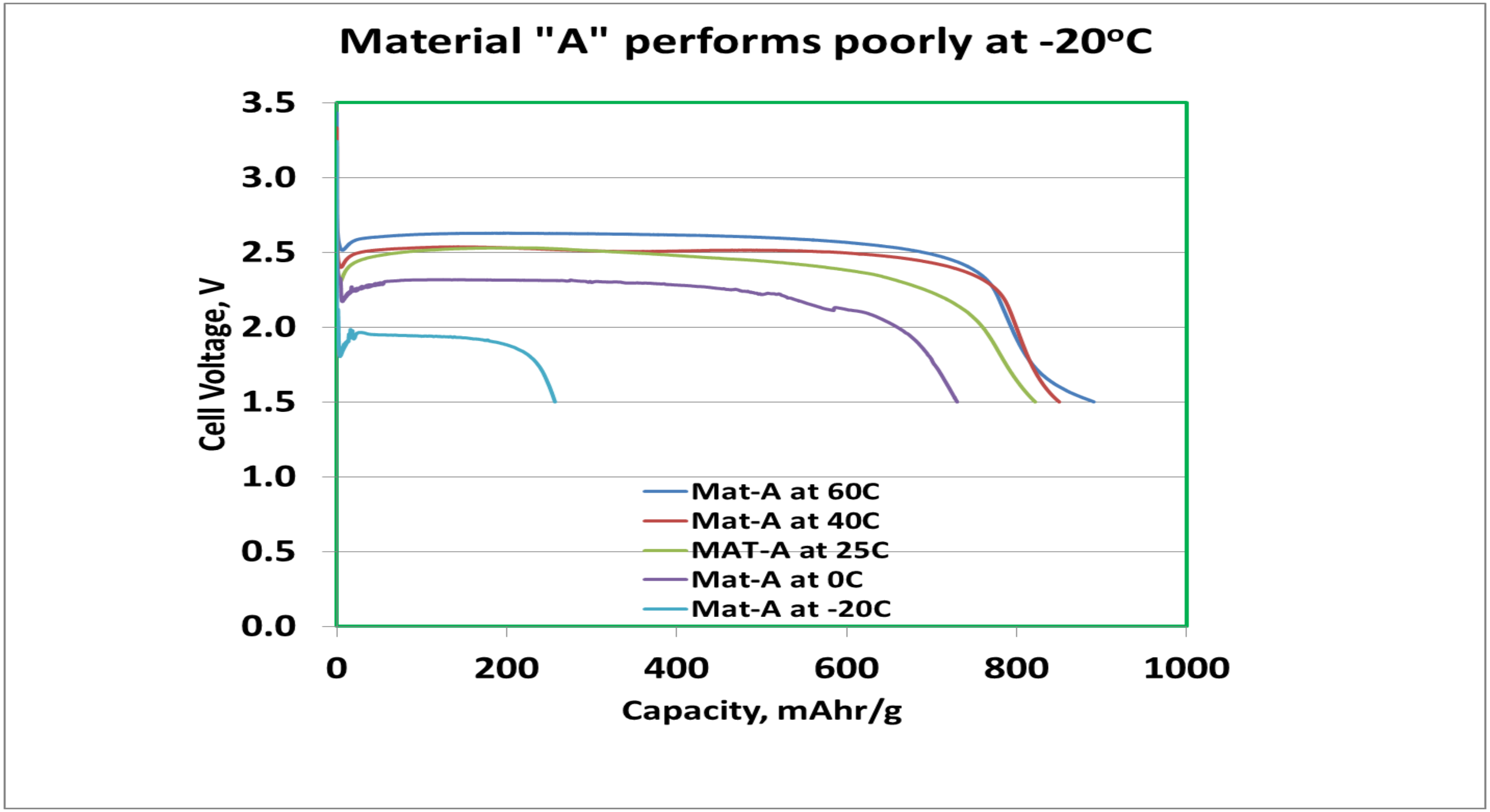
Material “A” performs poorly at -20^{o}C



Discharged at a C/50 rate

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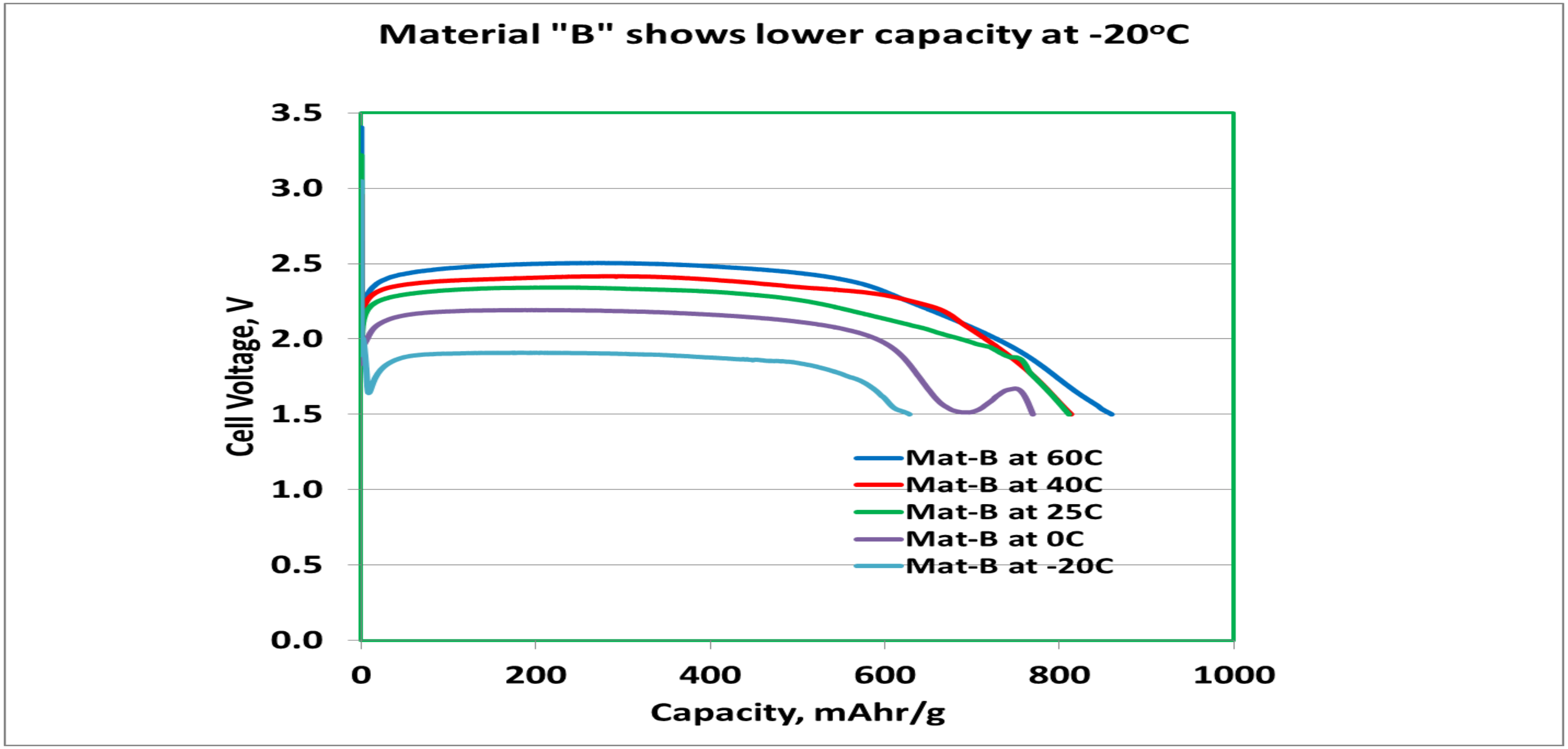
Material “B” shows lower capacity at -20ºC



Discharged at a C/50 rate

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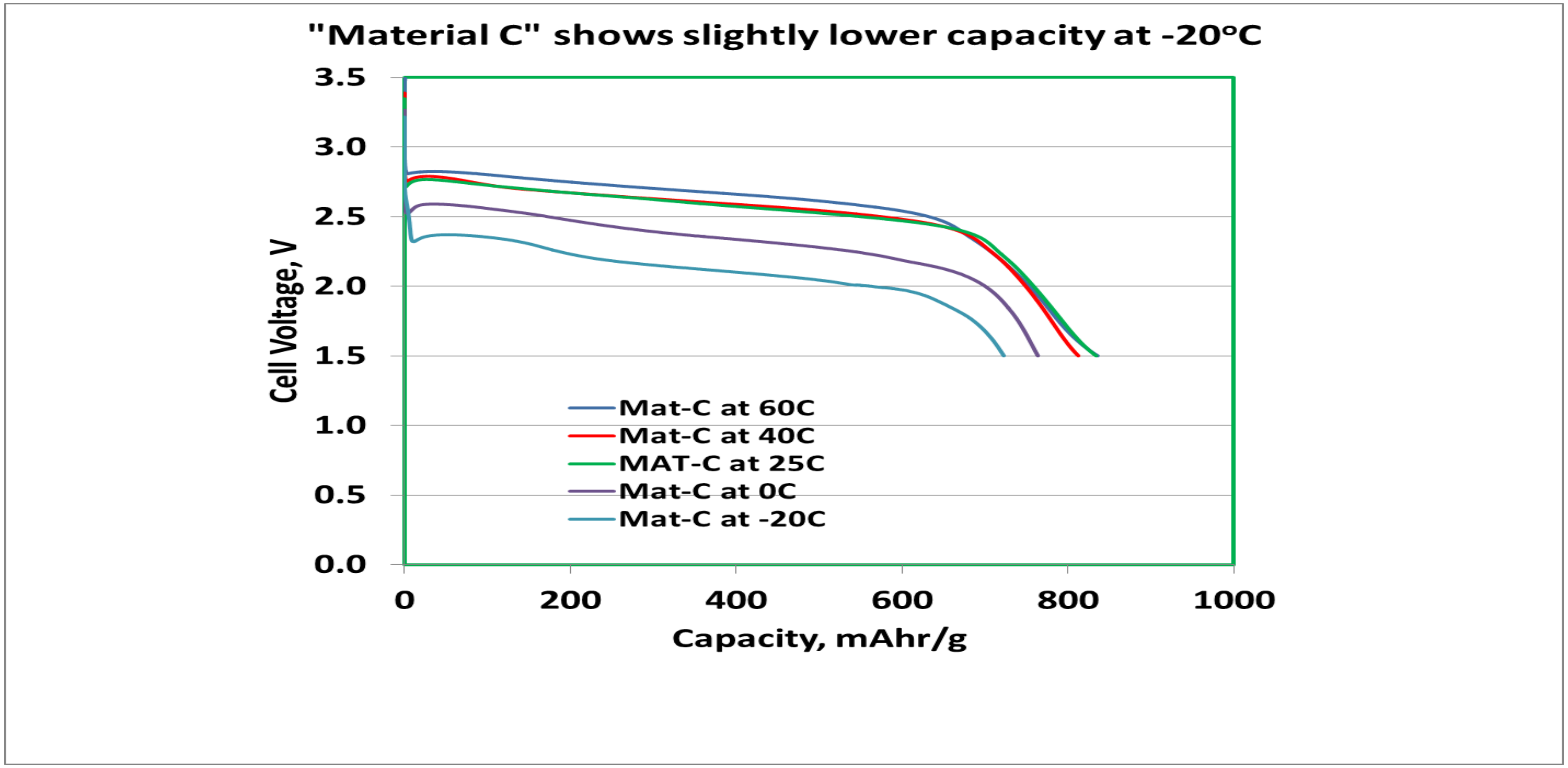
Material "C" shows slightly lower capacity at -20^{o}C



Discharged at a C/50 rate

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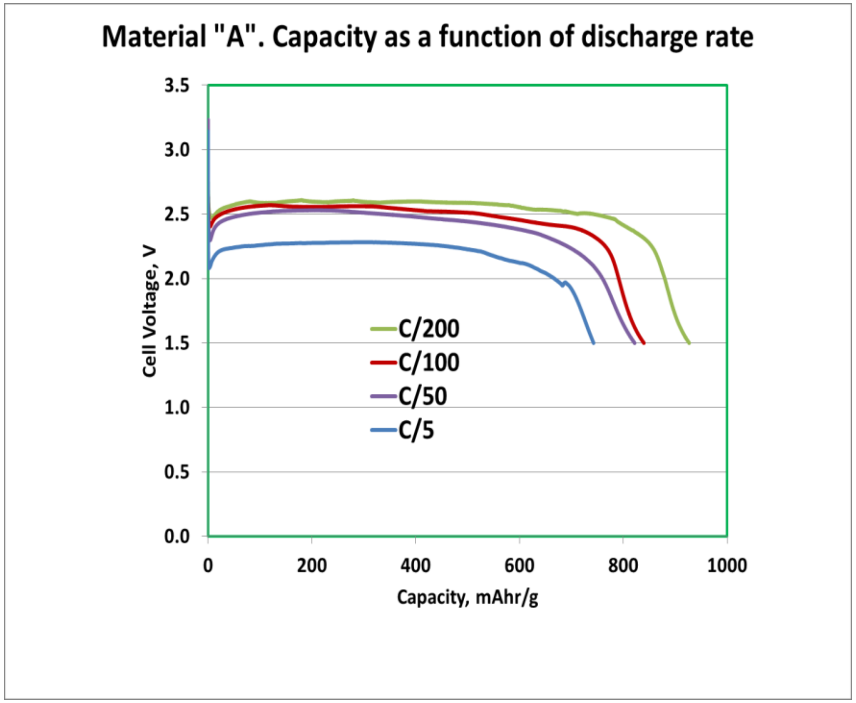
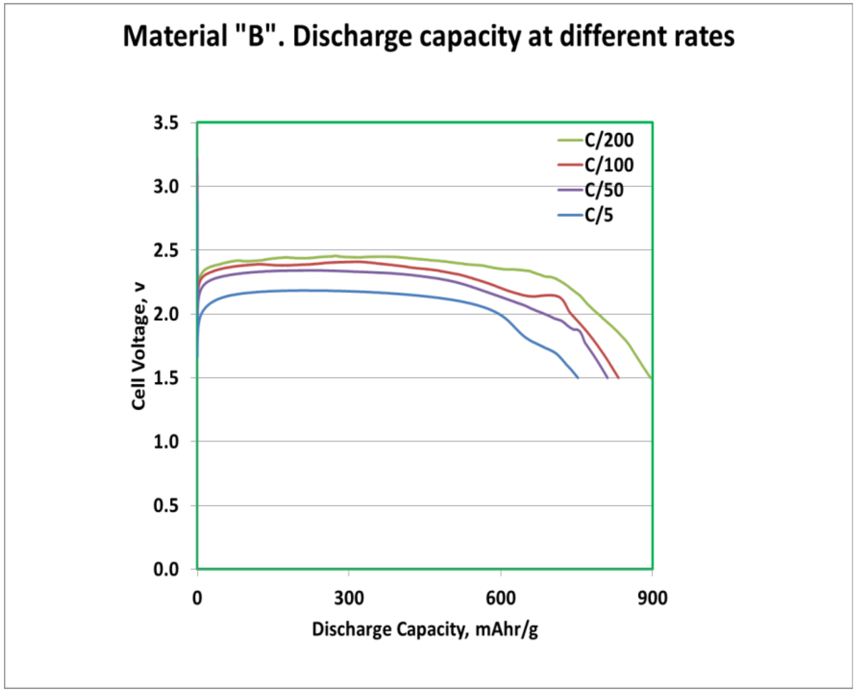
Discharge capacity at different rates

Material-A. Discharge capacity at different rates



Material-B. Discharge capacity at different rates



Tests performed in Carbonate electrolyte

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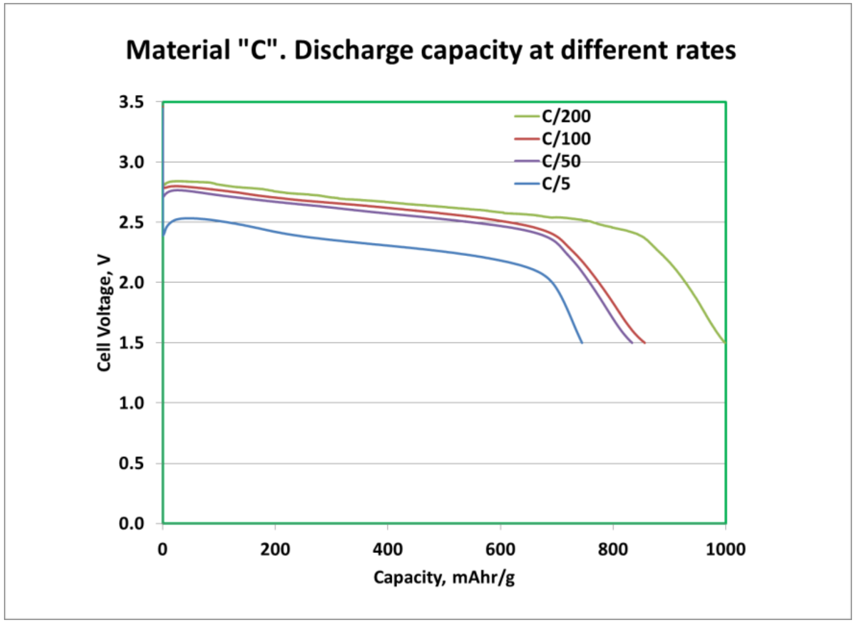
The trend in the material performance is similar

Material-C. Discharge capacity at different rates



Tests performed in Carbonate electrolyte

Observations

- All measurements were made on $CF_{0.9}$ at 25°C in EC:EMC(3:7 w%)-1.2M $LiPF_6$
- C/200 gave the highest capacity followed by C/100 and C/50 and C/5
- At C/5 the voltage drop is higher than the rest

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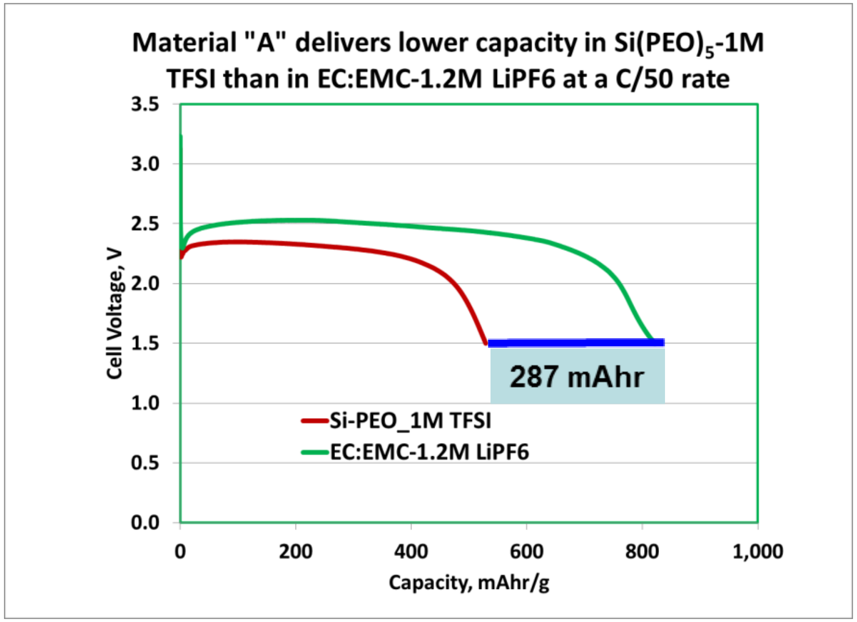
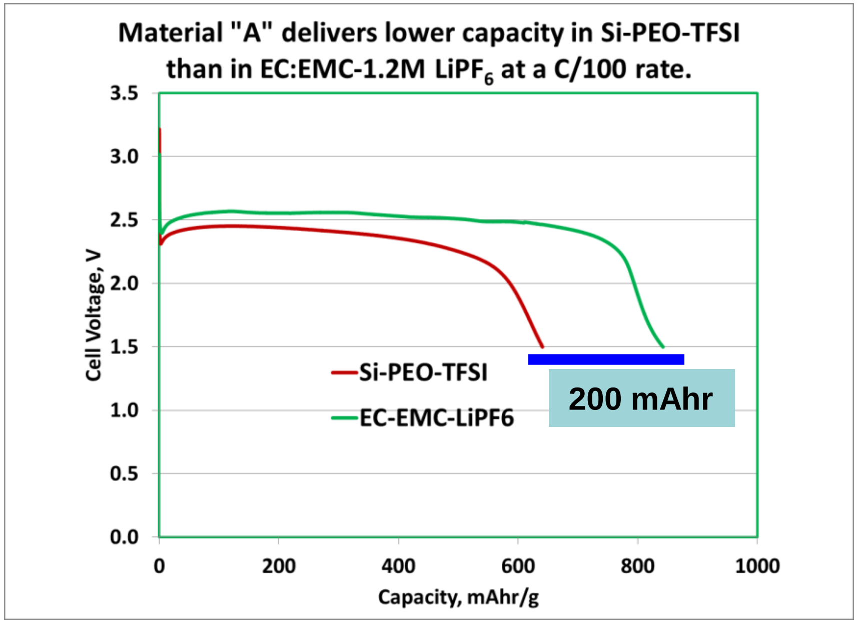
Material "A". Discharge capacity compared in two electrolytes at different rates

C/50 rate	C/100 rate





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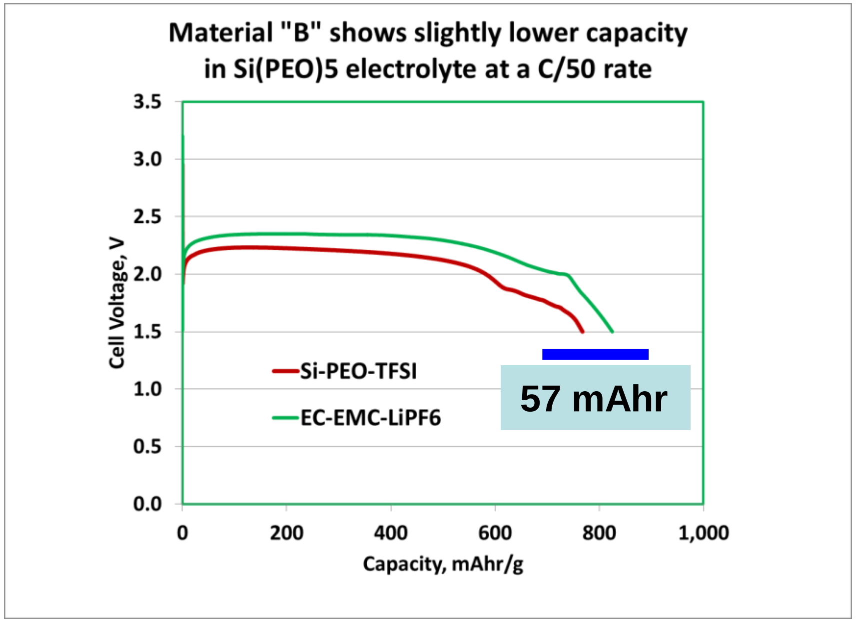
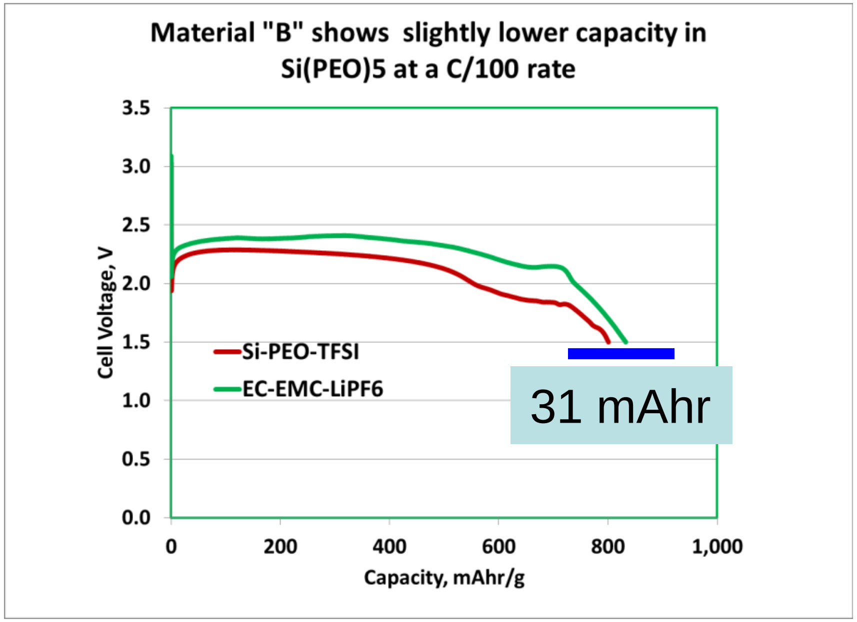
Material “B”. Discharge capacity compared in two electrolytes at different rates

C/50 Rate | **C/100 rate**





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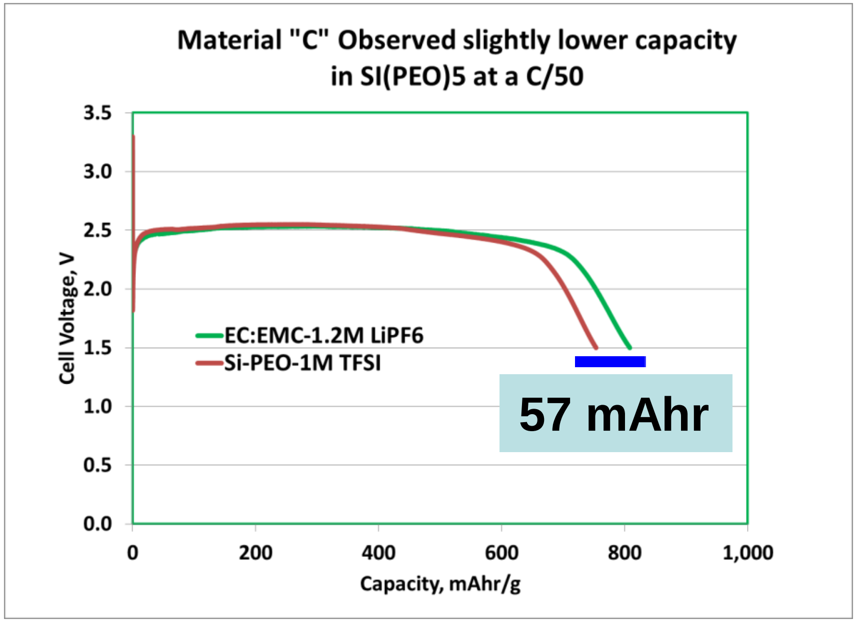
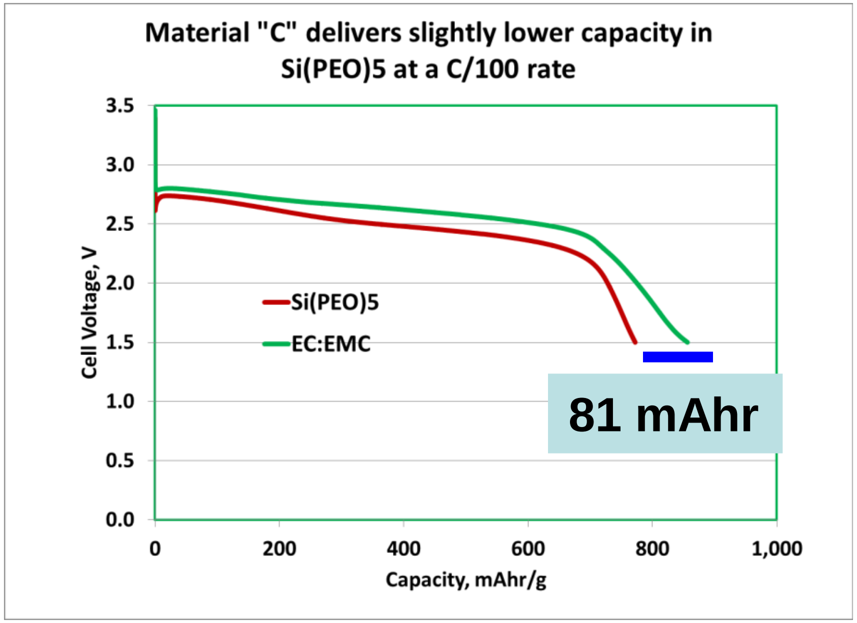
Material "C". Discharge capacity compared in two electrolytes at different rates

C/50 rate

C/100 rate





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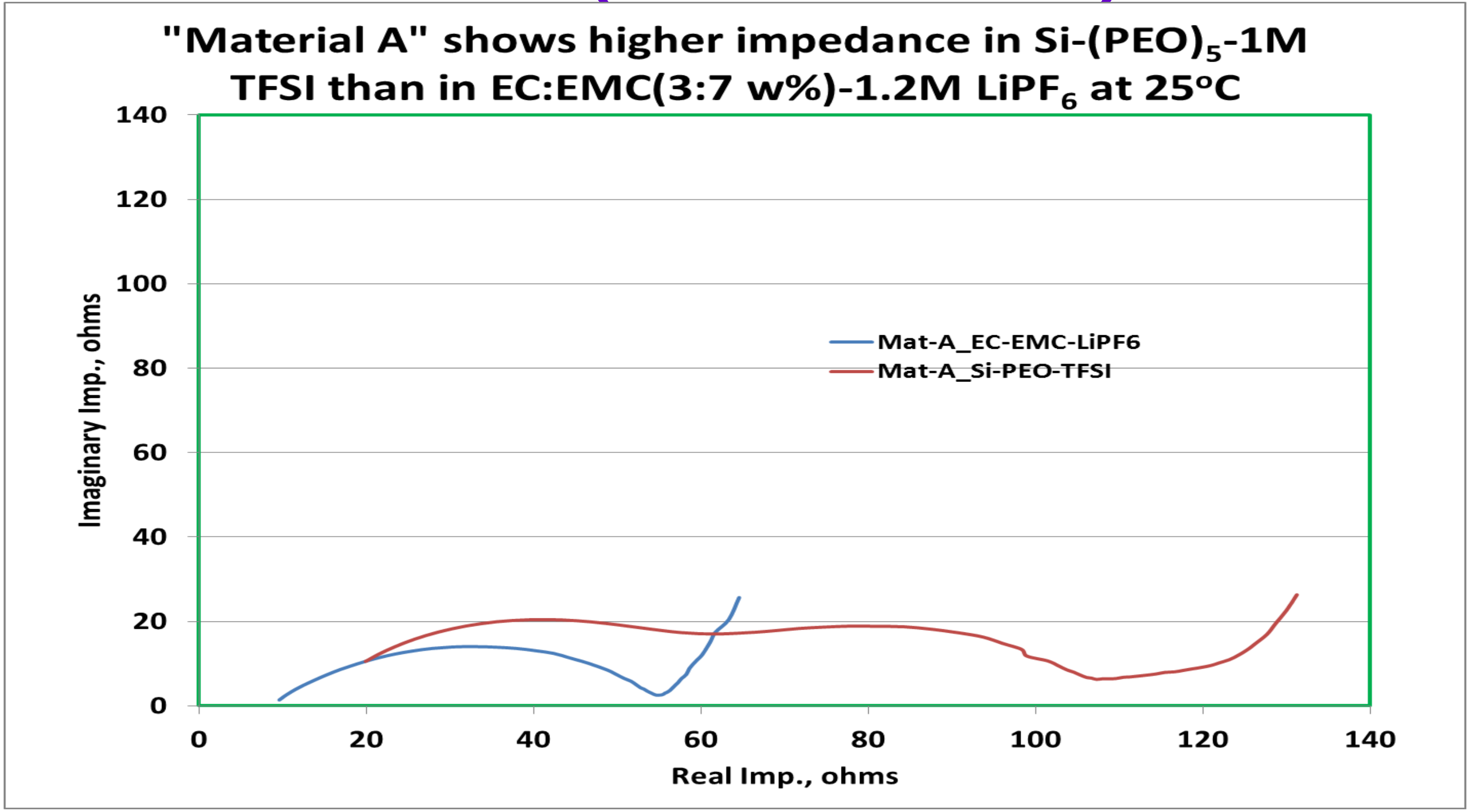
Higher interfacial impedance (Material A)



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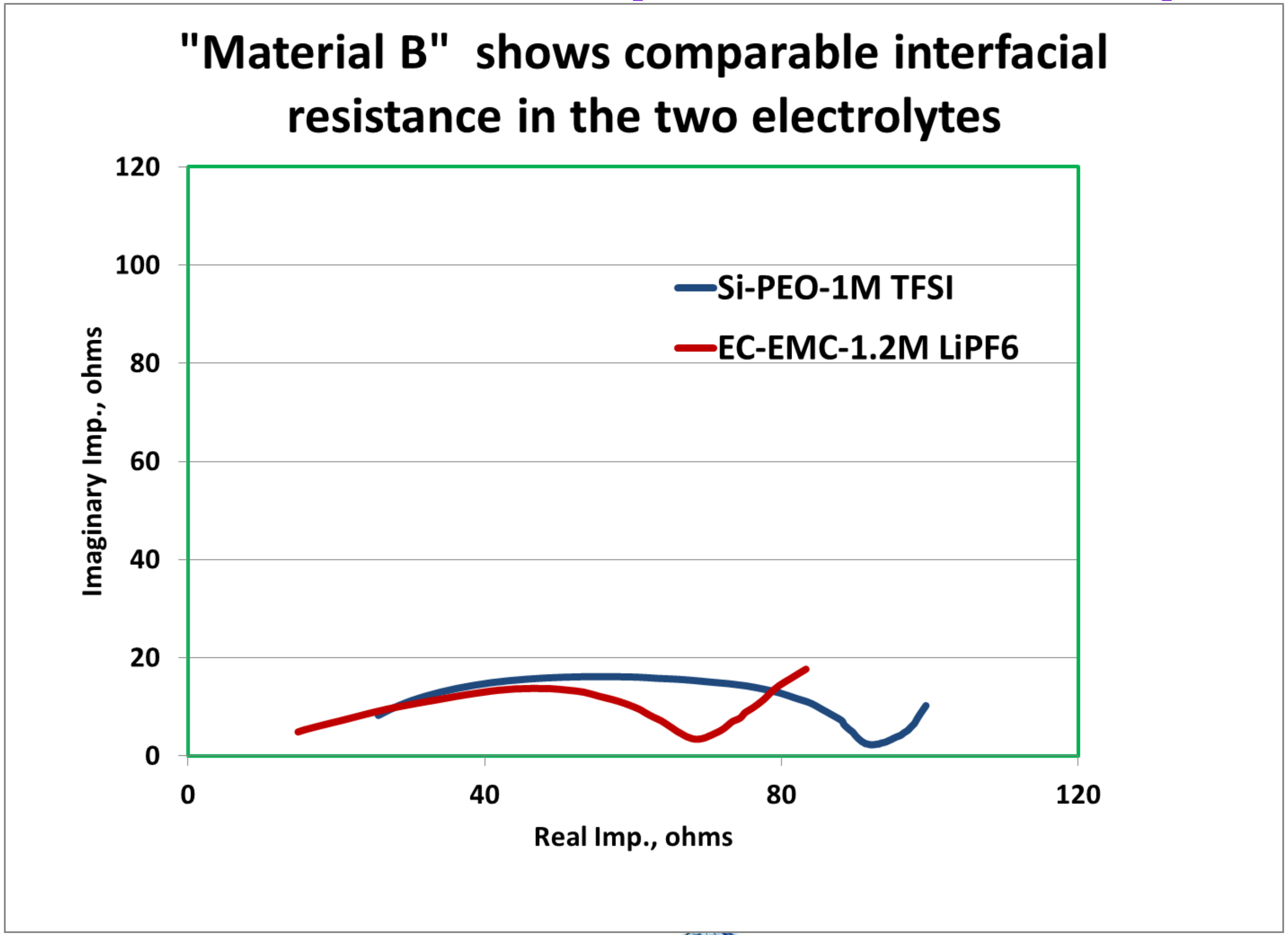
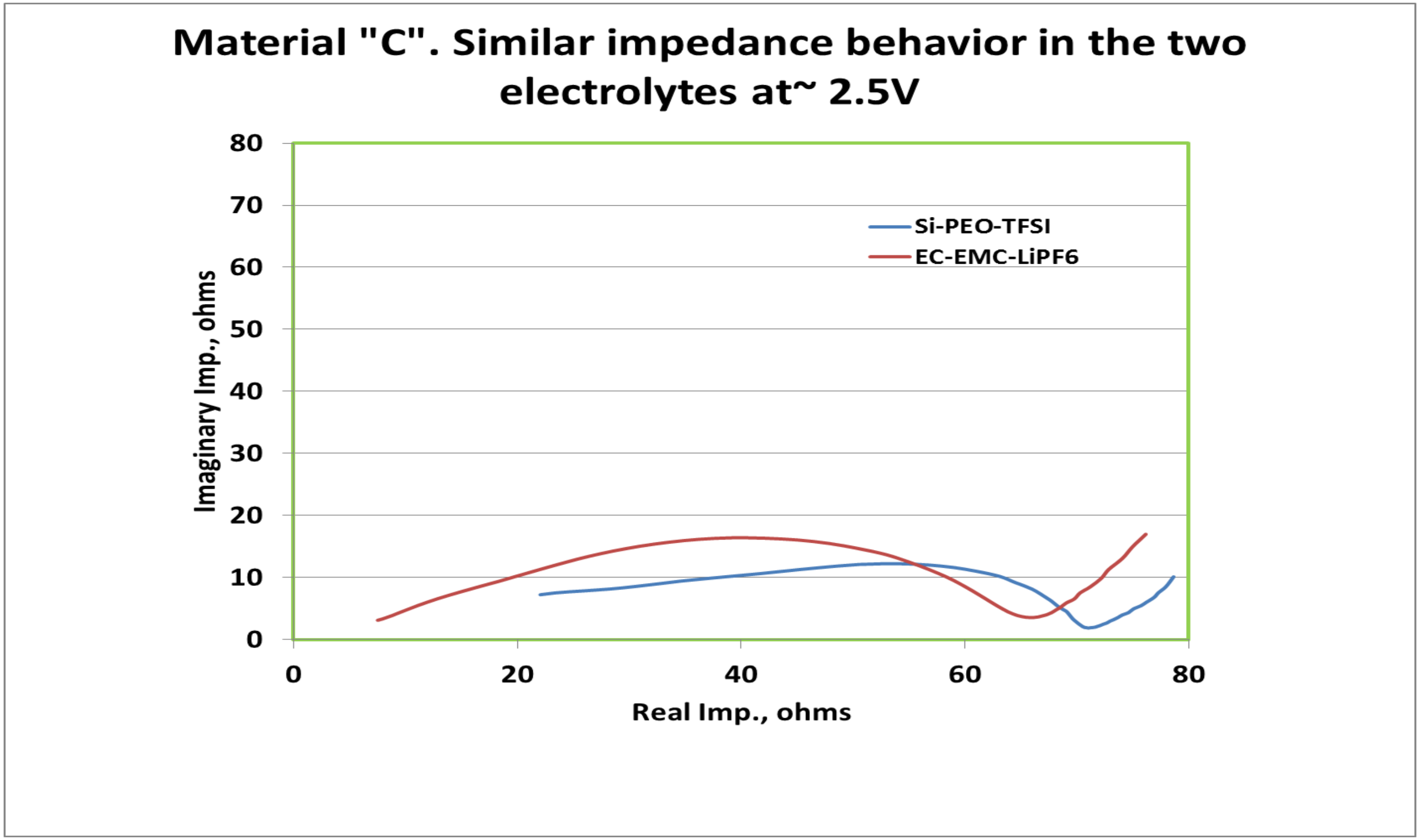
Comparable interfacial resistance (Material B)



Comparable interfacial resistance (Material C)



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Summary

1. Purchased CF_x powder of different compositions from 3 different vendors
2. Electrodes with carbon additive and PVDF binder were prepared
   - Evaluated for electrochemical performance in coin cells in two electrolytes (Carbonate and Siloxane)
   - Capacity at different rates and temperatures
   - Collected impedance to correlate cell performance in electrolytes
3. Cell capacity decreased at higher rates and lower temperature with Material "A" under performing
4. Material "A" delivered lower capacity in the siloxane electrolyte as well
5. Materials "B" and "C" showed virtually similar capacity in the two electrolytes
6. Cell impedance correlates well with delivered capacity