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Innovative Developments in Carbon Cathode Matrix Materials for Li/$SOCl_2$ Reserve Batteries

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Agenda

- Li/$SOCl_2$ Reserve Battery Applications & Characteristics
- Li/$SOCl_2$ Electrochemistry
- Role of Carbon Matrix Material
- Development of New Material
- Mechanical Strength
- Porosity Metrics
- Electrochemical Performance
- Process and Formulation Tradeoffs

Li/SOCl$_2$ Reserve Battery Applications

Lithium oxyhalide battery applications include

- Artillery
- Air delivered Weapons
- Mortar Munitions
- Missiles/Rockets
- Barrier Munitions

Li/$SOCl_2$ Reserve Battery Characteristics

- Long shelf life: > 20 years
- Ability to be fabricated in a variety of configurations
- Large usable temperature range (-60°C to 85°C)
- Open circuit voltage of 3.7 V per cell
- Flat discharge profile
- High energy density
- Moderate rate capability (typical maximum current density of 50 mA/cm2)

Li/$SOCl_2$ Electrochemistry

Lithium: Solid metal anode (where oxidation occurs)

Thionyl Chloride: Liquid cathode serving as its own solvent (catholyte) (where reduction occurs)

Anode Reaction:

$$Li_{(s)} \rightarrow Li^+ + e^-$$

Cathode Reaction (at carbon surface):

$$2SOCl_{2\,(l)} + 4\,e^- \rightarrow SO_2 + 4Cl^- + S$$

Overall reaction:

$$4Li + 2SOCl_2 \rightarrow 4LiCl_{(s)} + S + SO_2$$

Role of Carbon

Overall reaction:

$$\underset{\text{Anode}}{\underset{\nearrow}{4\mathrm{Li}}} + \underset{\text{Cathode}}{\underset{\nwarrow}{2\mathrm{SOCl}_2}} \rightarrow \underbrace{4\mathrm{LiCl}_{(s)} + \mathrm{S} + \mathrm{SO}_2}_{\text{Discharge Products}}$$

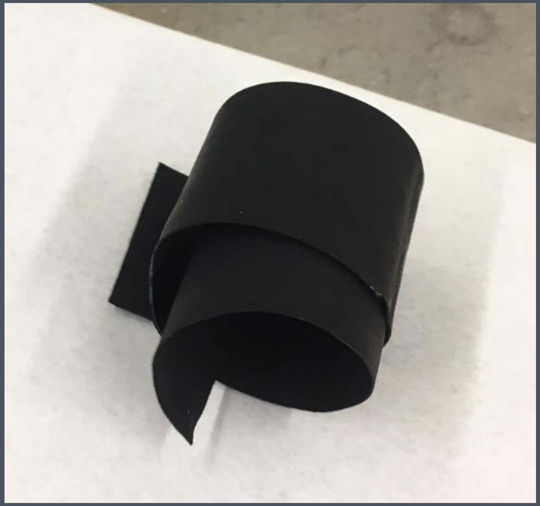
- Carbon supplies energetically favorable deposition sites for the discharge product: LiCl
- Typically referred to as the cathode matrix material even though it does not directly contribute any electrochemical potential or energy to the system
- The carbon presence and specific properties influence the cell’s realized energy and rate capability – it is almost always the limiting reagent
- This occurs due to its role as a facilitator in the discharge reaction at the carbon surface
- Made up of carbon and PTFE. The PTFE acts as a binder.

Relevant Carbon Parameters

Carbon properties which facilitate the maximum amount of deposition sites for the LiCl discharge product, while maximizing mass and charge transfer rates will result in a cell with optimal electrochemical performance

These metrics consist of:

- Porosity
- Pore volume
- Pore diameter
- Tortuosity
- Surface area
- Density
- Conductivity
- Overall Formulation/'Active' Material



Sample of carbon matrix material produced at EAS

Development of New Material

Goals

- Improve electrochemical performance
- Produce production-friendly material in both handling and production capabilities

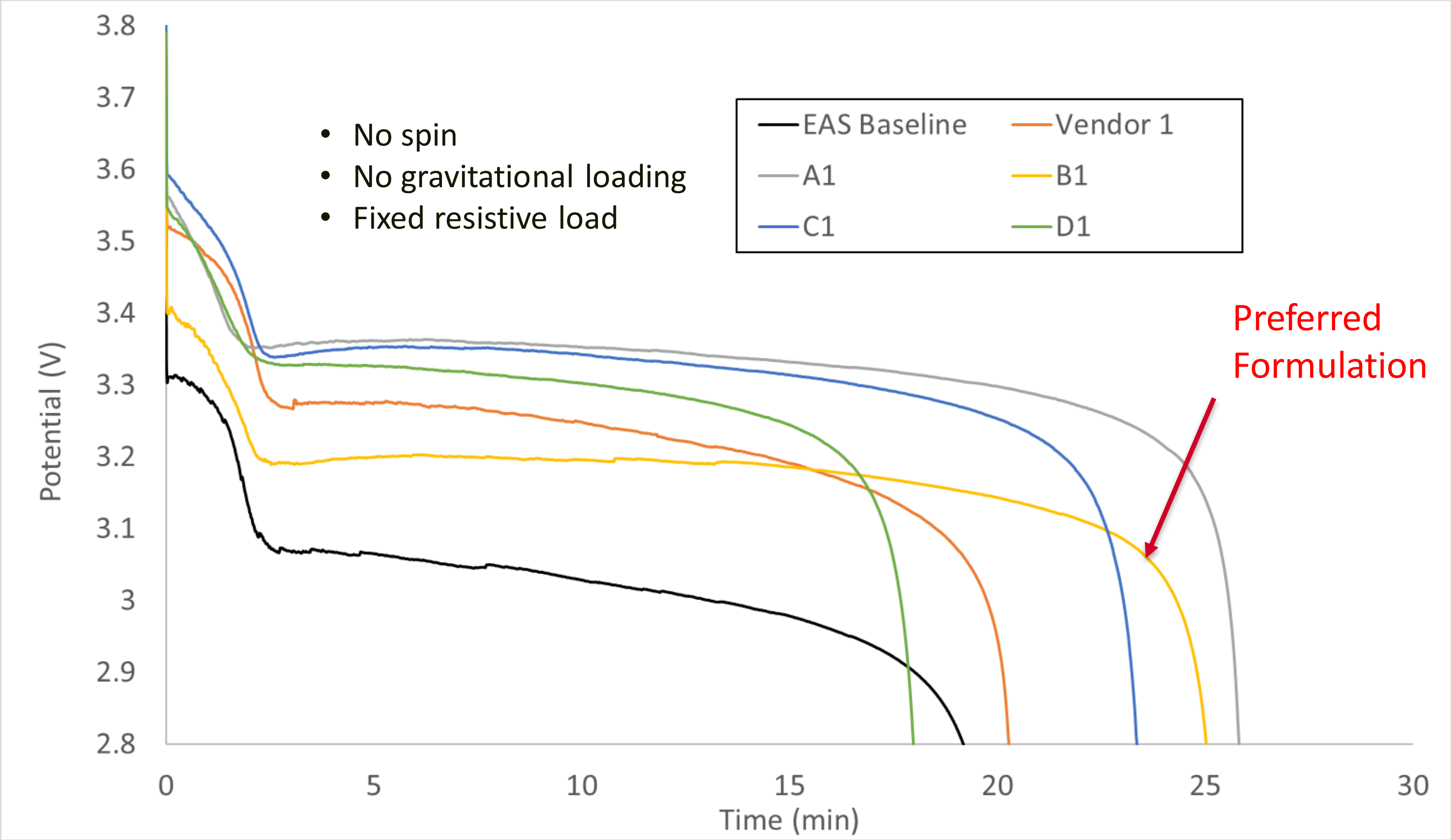
Theory – carbon matrix material consists of high surface area carbon and PTFE. The following can be varied to influence the mechanical and electrochemical performance metrics

- Carbon/PTFE ratio – Developed a process for 4 formulations (A, B, C, D)
- Handling of the material after introduction of the components (Method 1 or 2)

Sample Identification		
Carbon/PTFE Formulation	**Method**	
	1	**2**
A	A1	-
B	B1	B2
C	C1	-
D	D1	-

Electrochemical Evaluation of PTFE Loading In Single Cell Tests

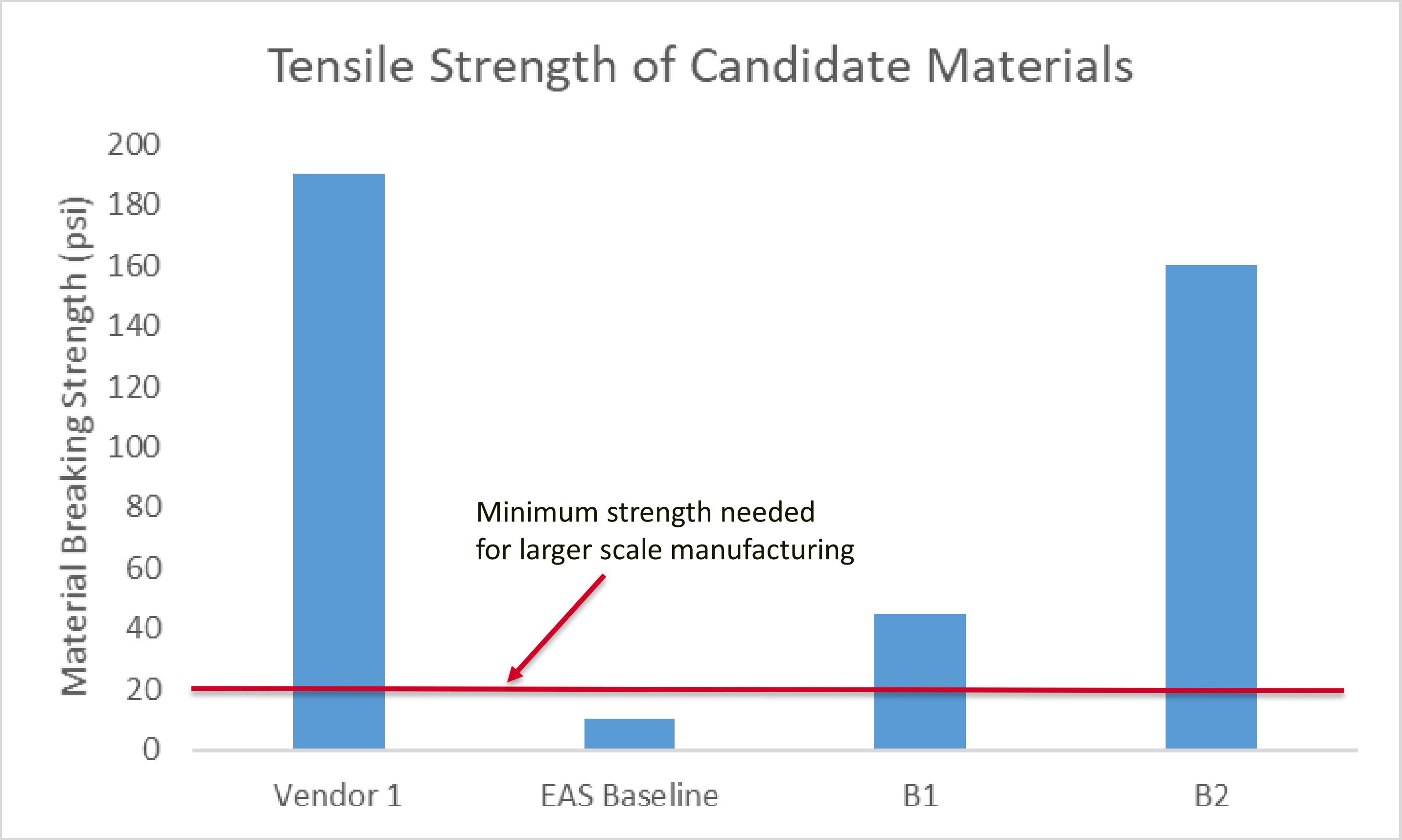
Initial evaluations performed in EAS' G2666B1 device at 63°C showed up to 25% improvement in run time to EAS Baseline and Vendor 1 material. using no spin or gravitational loading.



- No spin
- No gravitational loading
- Fixed resistive load

Preferred Formulation

Mechanical Strength



Minimum strength needed for larger scale manufacturing

- Mechanical strength affects manufacturability, and handling characteristics
- Benefits and drawbacks exist for each material

Porosity Metrics

Matrix Material	Porosity Metric				
	Surface Area (m^2/g)	Porosity (%)	Density (g/mL)	Pore Volume (mL/g)	Avg Pore Diameter (um)
Vendor 1	12	46	0.40	0.19	0.74
EAS Baseline	14	51	0.36	1.41	0.405
EAS B1	62	77	0.44	1.93	0.125
EAS B2	58	62	0.68	0.93	0.065

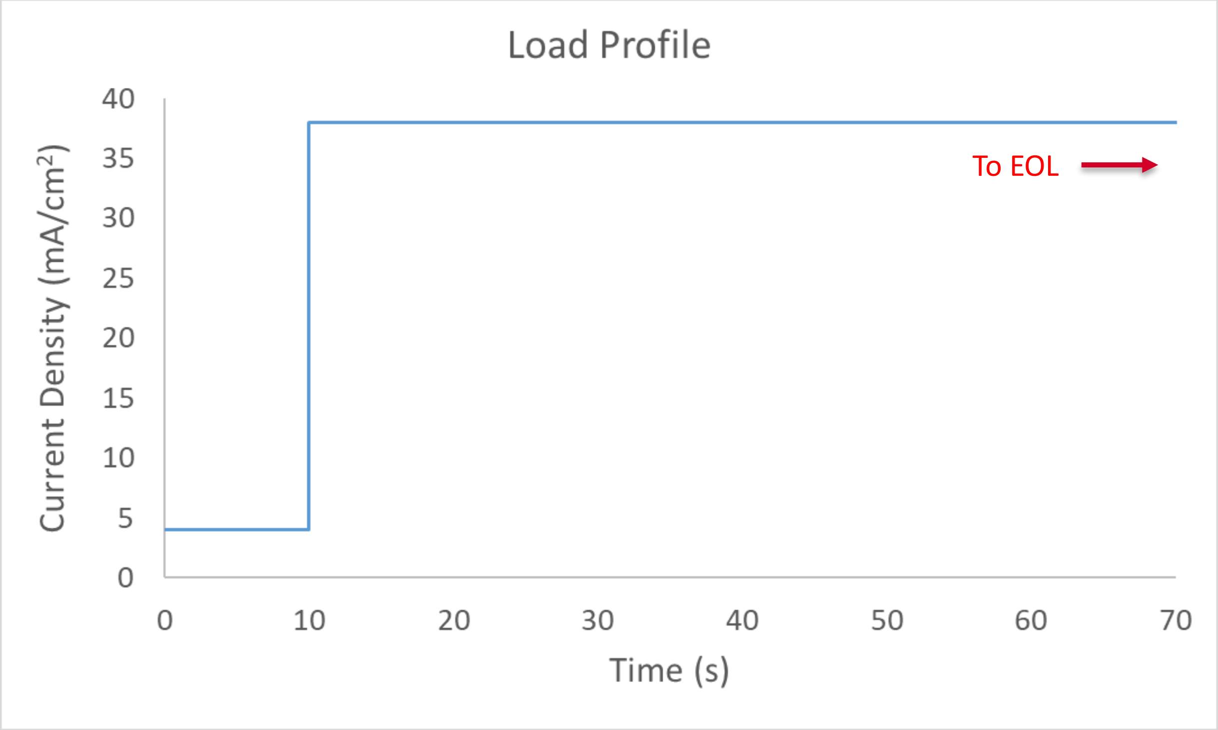
- Newly developed matrix material formulations exhibit significantly more favorable porosity metrics

- As long as mass transfer is not inhibited by small pore diameter or high tortuosity, we expect to see better electrochemical performance in the new formulations

Electrochemical Performance Comparison

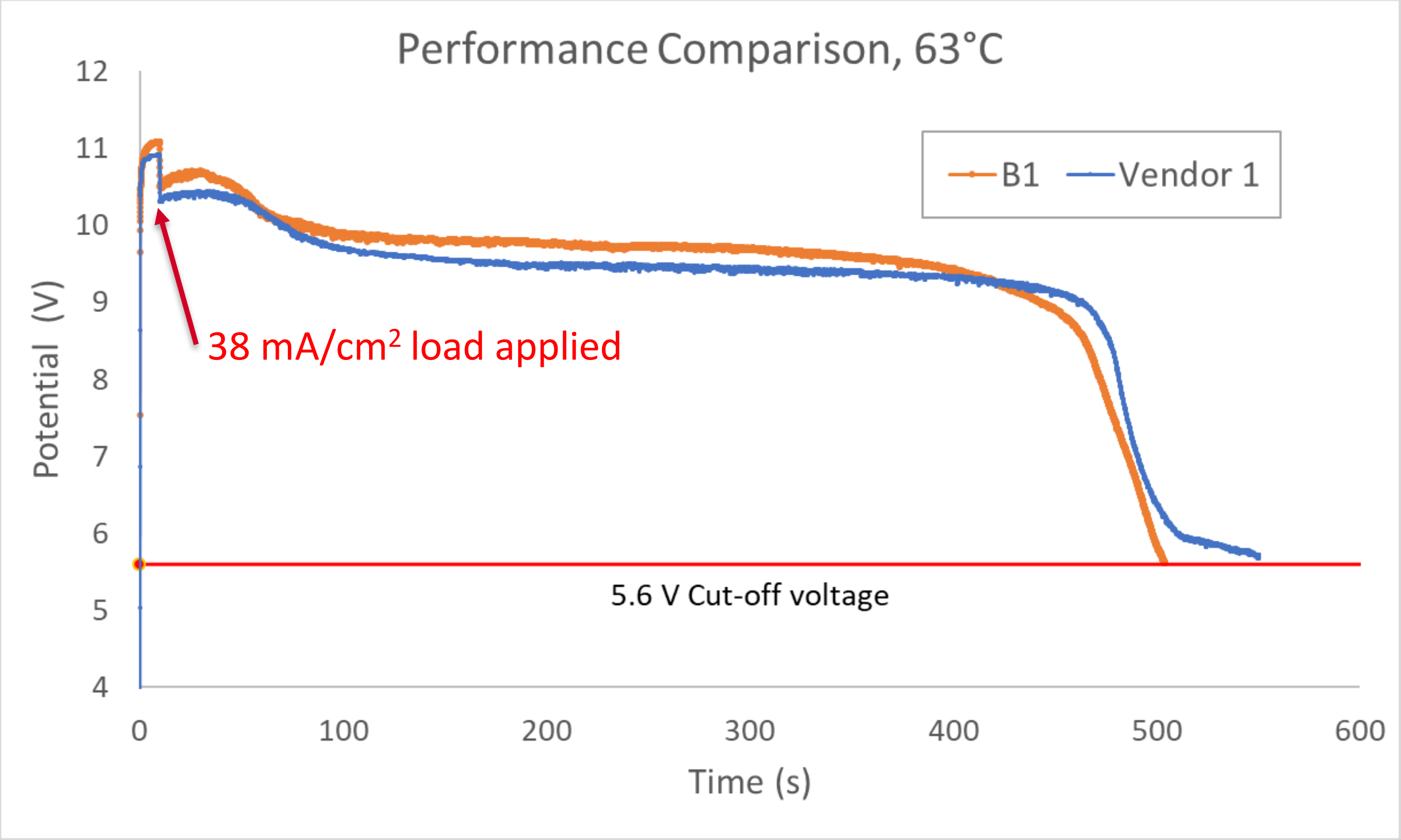
Application-representative environment test setup:

- Built into an existing EAS device with 3S2P configuration
- Tested in a spin-capable airgun at EAS
- Activated via gravitational loading
- Activated into 80 RPS spin
- Discharge rate of 38 mA/cm2



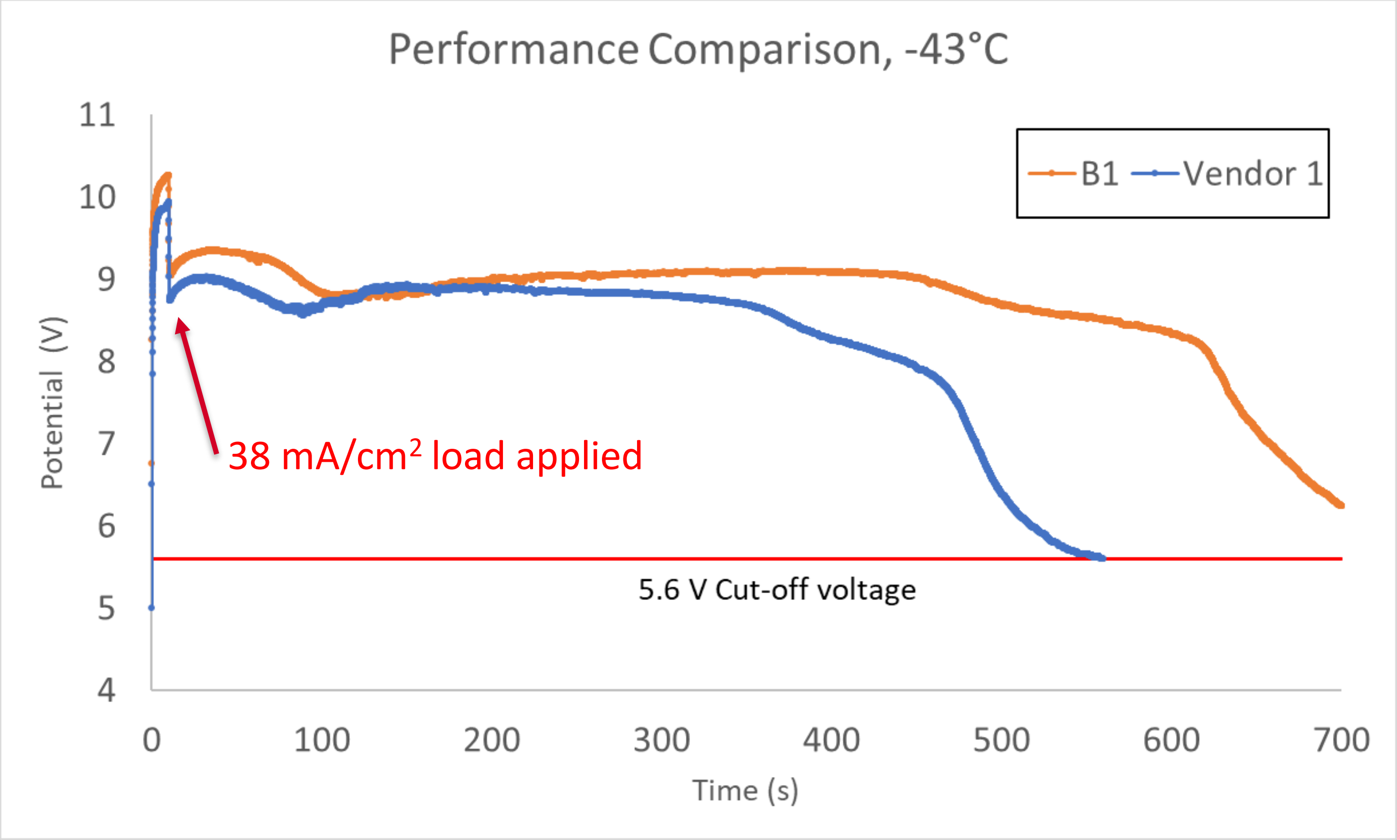
Electrochemical Performance Comparison, 63°C

- Comparable run time seen at 65°C
- New formulation typically runs at slightly higher voltage



Electrochemical Performance Comparison, -43°C

- New formulation runs ~35% longer at -43°C.
- New formulation typically runs at slightly higher voltage



Process and Formulation Tradeoffs

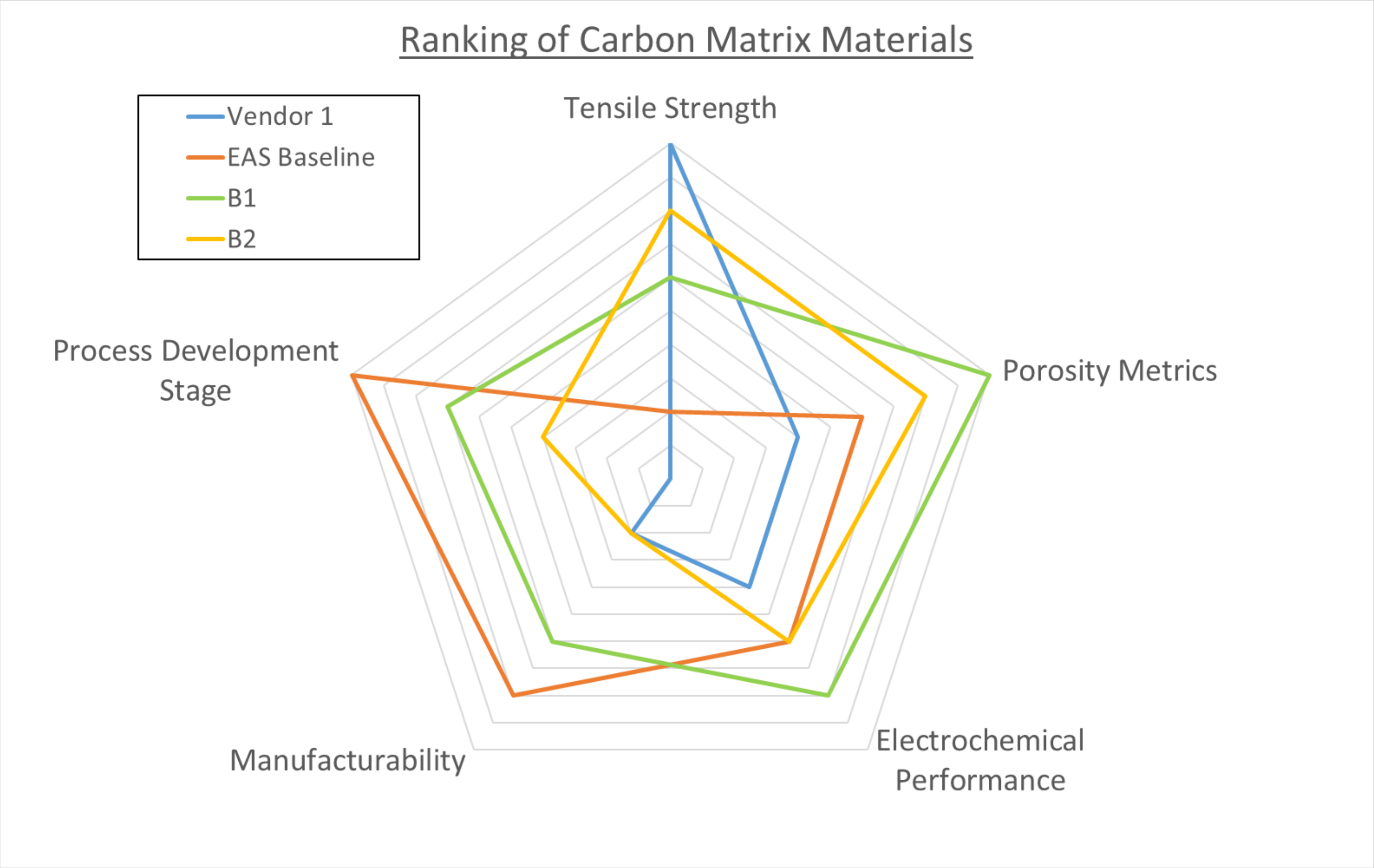
- Vendor 1 material
    - Greatest tensile strength
    - Poor porosity metrics possibly influencing performance.
    - Risky for EAS to rely on a sole source with no control over it

- EAS Baseline
    - Low tensile strength, impacts ability to use at scale
    - Easy and relatively quick to manufacture
    - Serviceable electrochemical performance

- Formulation B1
    - Serviceable tensile strength for scalable production operations
    - Great porosity metrics
    - Great electrochemical performance, especially at cold temperatures

- Formulation B2
    - High tensile strength
    - Good porosity metrics
    - Not very scalable, lots of processing required

Process and Formulation Tradeoffs



Conclusion

- Successfully developed a new carbon cathode matrix material that is compatible with Li/$SOCl_2$ reserve battery chemistry

- Formulation B1 performs better electrochemically than baseline and commercially available material (likely due to porosity metrics), especially at cold temperatures

- The new process is able to create material with sufficient tensile strength to be used in higher-volume production (Formulation B1 and B2) and compete with commercially available material for electrochemical performance and supply chain reliability

- Future work will revolve around further characterization of Formulation B1 and scale up of the manufacturing process