Lithium-ion Batteries with Tri Fluorinated Electrolyte for Low Temperature Space Applications

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Date: 11/17/21

Li-Ion Battery Importance and Challenges

Li-Ion Battery (LIB) Importance

- Highest energy density of viable electrochemical systems
- Low self-discharge and irreversible capacity loss allow to perform for several years
- Low cost to energy storage

Current Challenges

- Instability of **Solid Electrolyte Interphase (SEI)**
- **Dendrite growth** from anode at high rate or long cycle life
- **Kinetic limitations on charging rates**
- **Narrow optimal temperature operating window** between (0°C to 40°C)

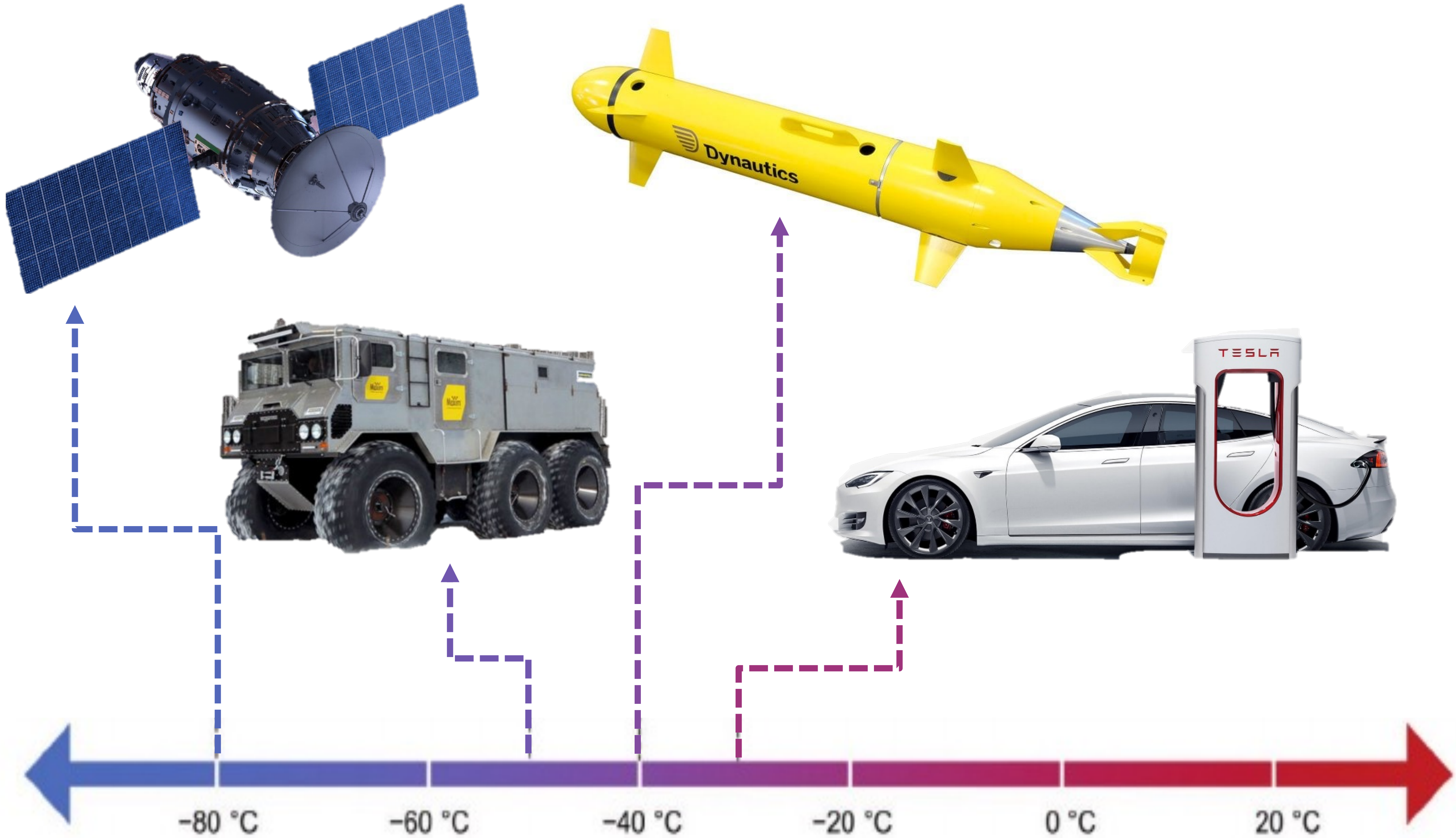
Solid Electrolyte Interphase (SEI)

Dendrite growth at high rate or cycles

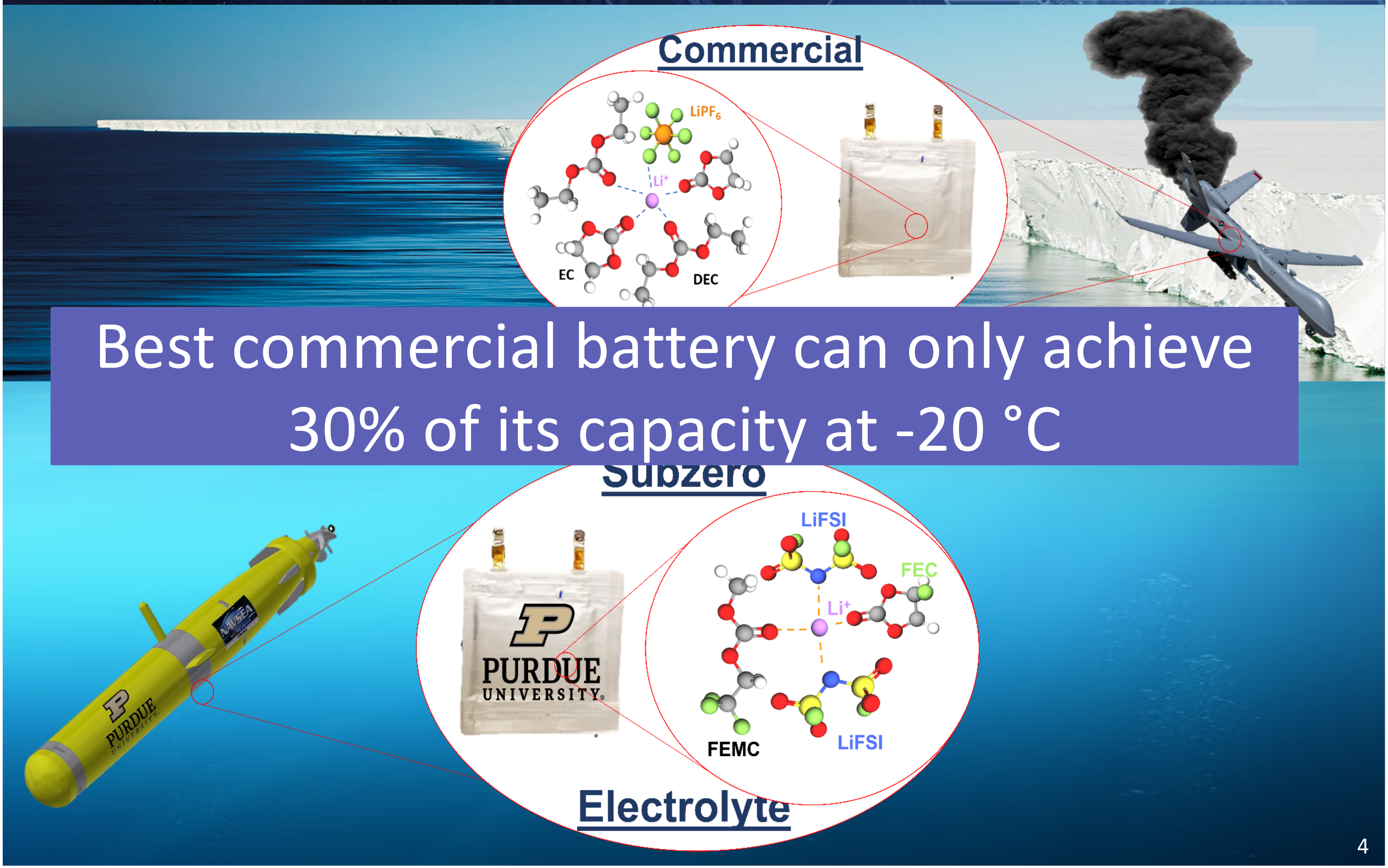
Kinetic limitations for charging speeds

Small optimal temperature operating window

Why do we need low temperature application?



Why do we need low temperature application?



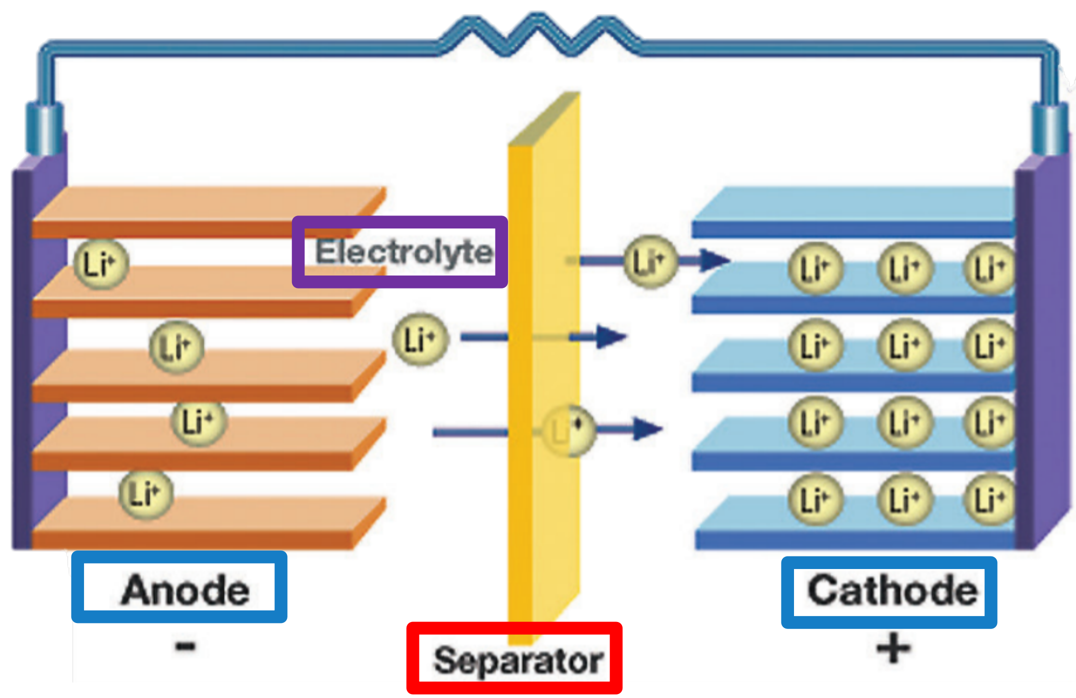
Best commercial battery can only achieve 30% of its capacity at -20 °C

Low Temperature Limitations

Current Problems

1. High resistance for Li ion in electrode
2. Lithium plating due to polarization of anode
3. Reduced Li ion conductivity through electrolyte
4. **Increased charge transfer resistance at interphase**

4 Main Areas of Focus



N Chawla, *Batteries* (2019)

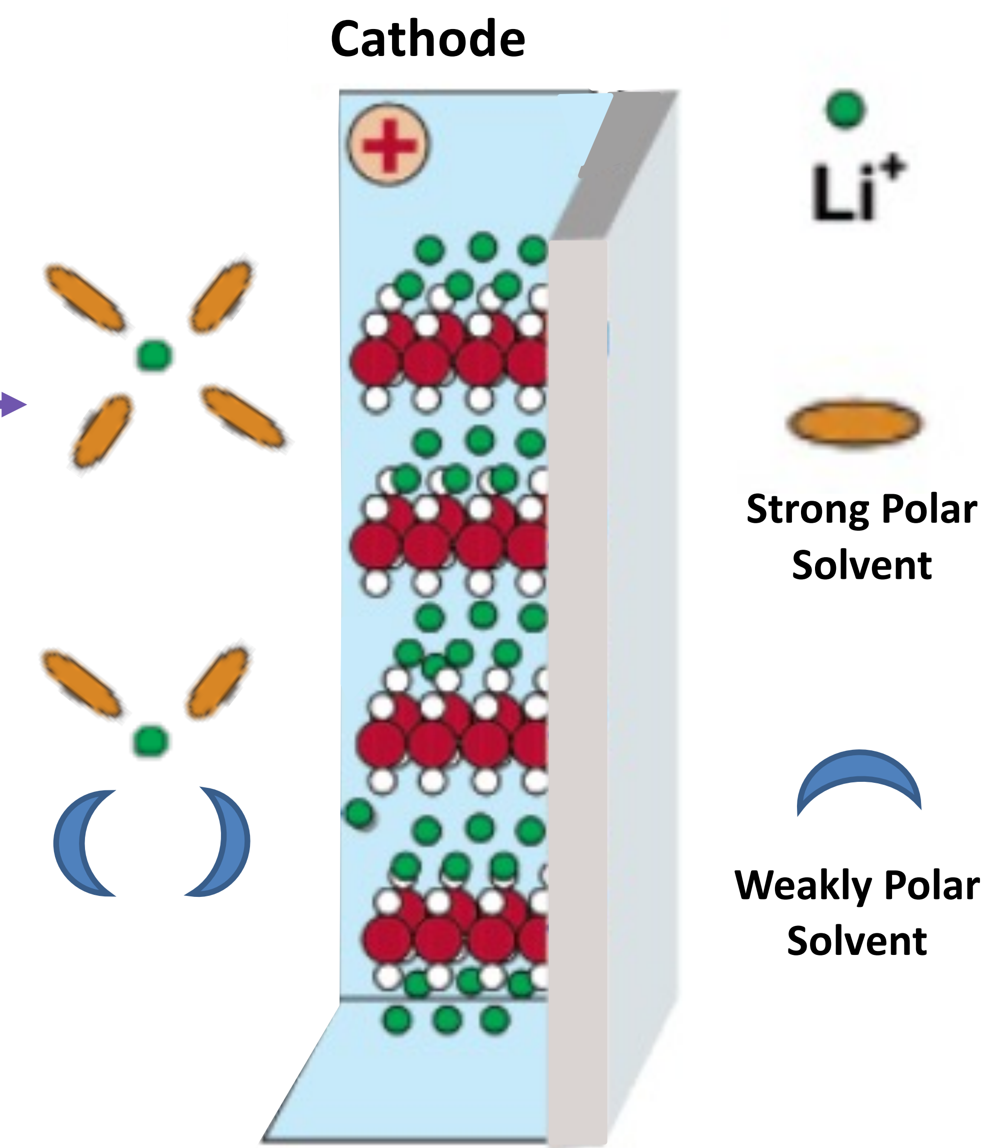
Electrolyte Solvation Mechanism for Reduced Charge Transfer

Typical Carbonate Solvent Shell

- Desolvation shell strongly held together
  - High affinity btw solvent molecule and Li^+

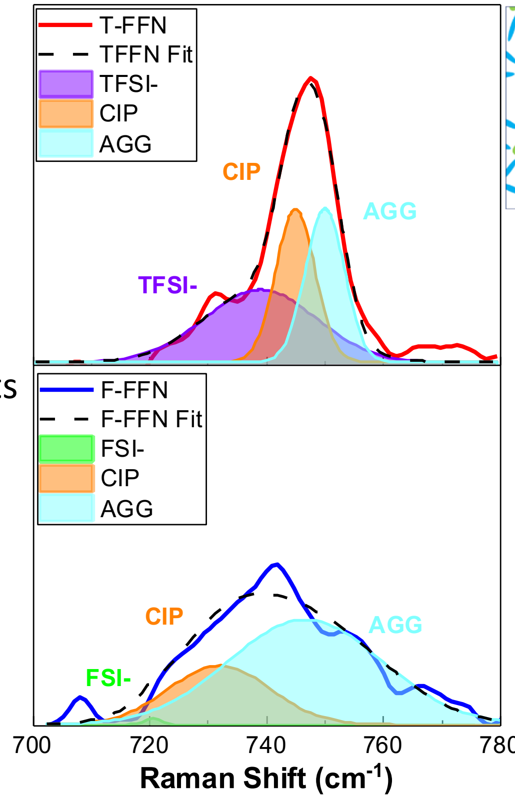
Our Solvent Shell

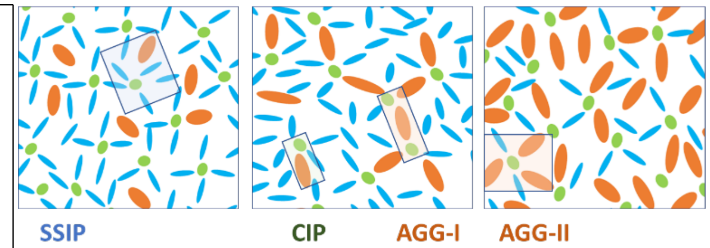
- Desolvation shell weakly held together
  - Diff polarity solvents cause shell to have weaker interaction



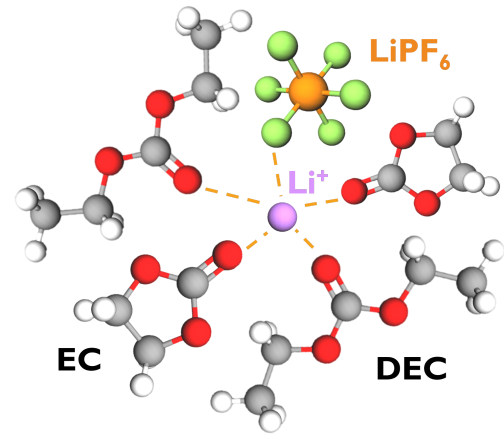
Electrolyte Solvation Shell

- **Solvation Shell**
  - Raman spectra was collected for COM, F-FFN, T-FFN
    - SSIP- Solvent Shared Ion-Pairing
    - CIP- Contact Ion Pair
    - AGG- Aggregates
  - Can fit spectra with known peaks for SSIP, CIP, AGG for each salt to tell relative weights
  - T-FFN
    - TFSI- 45.1% (740 cm^{-1})
    - CIP- 30.4% (745 cm^{-1})
    - AGG- 24.5% (750 cm^{-1})
  - F-FFN
    - FSI- 0.5% (720 cm^{-1})
    - CIP- 27% (732 cm^{-1})
    - AGG- 72.5 (746 cm^{-1})
- **Predicted Solvation Structures**
  - COM- Typical EC/DEC shell with some $LiPF_6$
  - T-FFN – High fraction of free $TFSI^-$ so shell made up of FEC with some FEMC
  - F-FFN- High incorporation of FSI^- with FEC & FEMC weakening interaction forces

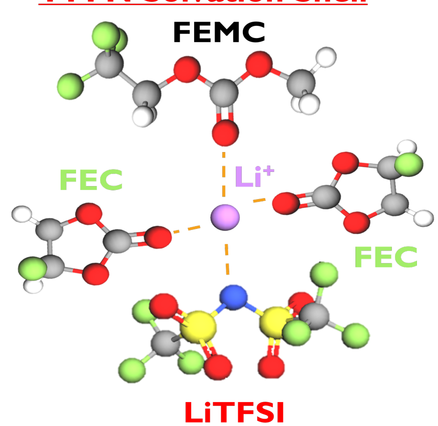




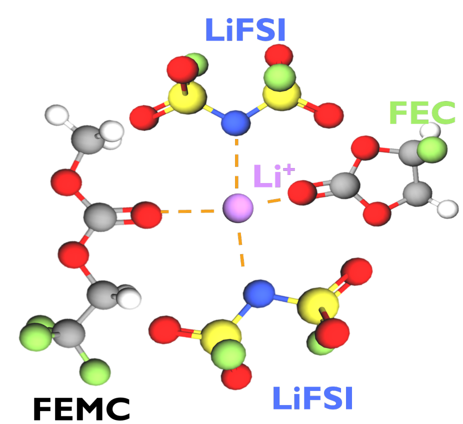
Commercial Solvation Shell



T-FFN Solvation Shell

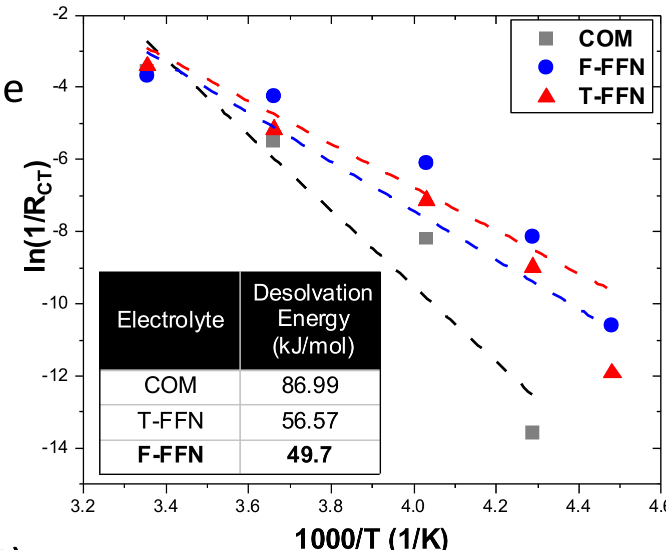


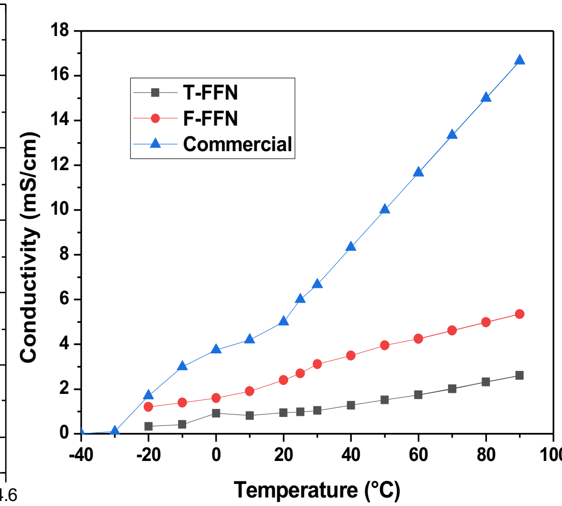
F-FFN Solvation Shell



Electrolyte Characterization

- **Solvation Shell**
  - Desire a less tightly bound together one as at low temperatures this is rate-limiting step
    - Desolvation energy of F-FFN is ~ ½ of the COM
- **Conductivity**
  - At temperatures below -20°C conductivity of Purdue electrolyte (F-FFN) is greater then commercial (COM)
    - Expected due to $LiPF_6$ and high dipole moment carbonates
- **Internal Resistances**
  - R_{CEI} and R_{CT} separate as R_{CT} is more strongly affected by temperature
    - From -40°C to -50°C R_{CEI} increases by factor of 5.5, R_{CT} by factor of 11.42
  - F-FFN has 40% of T-FFN's R_{CT} at -50°C while COM's is larger at -40°C



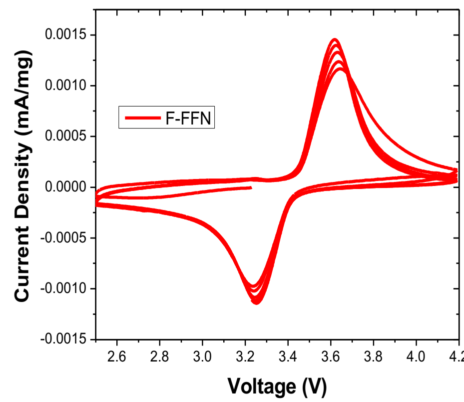


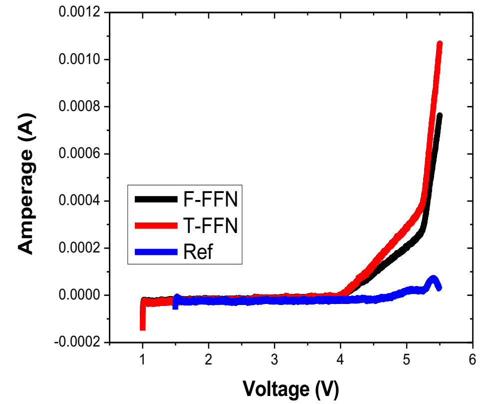
Temp (C)	R_{CEI} F-FFN (Ohm)	R_{CT} F-FFN (Ohm)	R_{CEI} T-FFN (Ohm)	R_{CT} T-FFN (Ohm)	R_{CEI} COM (Ohm)	R_{CT} COM (Ohm)
25	-	40	-	30	-	35
0	-	70	-	175	-	250
-25	-	450	-	1,250	750	3000
-40	330	3,500	600	4,000	500,000	>>
-50	1,800	40,000	4,000	100,000	-	-

Good **Bad**

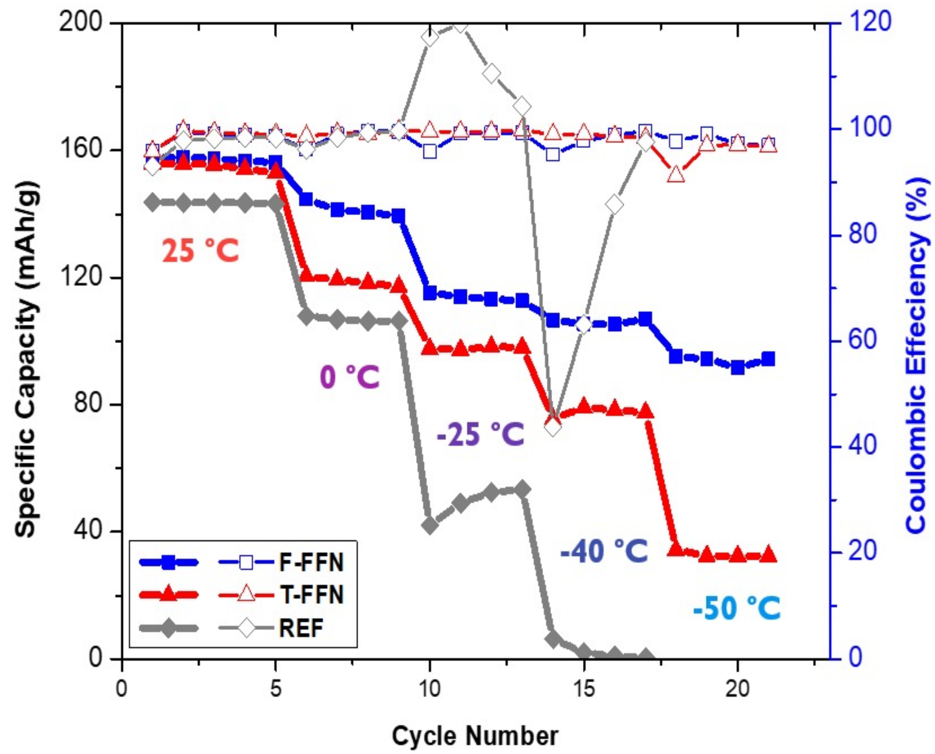
Electrochemical Performance

- **Electrolyte Stability**
  - Cell Configuration:
    - LSV= SS|Celgard|Li
    - CV = Li|Celgard|LFP
  - All electrolytes are stable up to 4.2V with 5 CV cycles of F-FFN [2.5V-4.2V] showing stability





- **Cycling**
  - Cell Configuration: Li|Celgard|LFP
  - COM:
    - At -40 ºC retains 11% capacity
    - 0.5V Polarization
  - T-FFN:
    - At -50 ºC retains 20% capacity
    - 0.35V Polarization
  - F-FFN:
    - At -50 ºC retains 61% capacity
    - 0.15V Polarization



Summary and Future Plans

1. Successfully generated and cycled a LFP|Li half-cell using novel fluorinated electrolyte
   - F-FFN had superior performance to Commercial electrolyte: higher capacity retention, lower polarization, and lower desolvation energy at subzero temps.
2. Determined that LiFSI is the optimal salt for LIB performance within our temperature operating window
   - LiFSI compared to LiTFSI and LiPF6 had better conductivity, capacity retention, desolvation energy
3. Currently testing a full cell coin cell using a Graphite|LFP setup so can be scaled up for real world applications
   - Important to our goal of producing a >200 Wh kg^{-1} pouch cell and to show promise in commercialization and application
4. Build pouch cells and evaluate
   - Will generate pouch cells at BIC before running the necessary electrochemical and thermal tests
5. Demonstrate battery pack's effectiveness at high and low temperatures
   - Combined with thermal and shock testing which is important for designing of proper safety and mitigation strategies.

RECENT PUBLICATIONS, PATENTS, AWARDS

Publications

1. E. Adams, D. Gribble, M. Parekh, T. Adams, V. G. Pol, "Low Temperature Performance Facilitated by a Ternary Fluorinated Electrolyte for Lithium-ion Batteries", *under preparation*
2. C. Jamison, Thomas Adams, V. G. Pol, "Lithium-Ion Battery Testing Capable of Simulating Submarine Climates", *under preparation*

Conference Talks or Presentations

- Pol - "Are Rechargeable Batteries Playing Significant Role in our Lives, Safely?" Workshop on Thin Film Technologies for Sensors and Opto-electronic Applications, Indian Institute of Information Technology, Allahabad, India, July 17, 2021.
- Pol - "Li-metal Batteries: Are they Thermally Safe?", 11th Virtual Battery Safety Summit, June 30, 2021.
- Pol - "Can you Live without me? -Rechargeable Batteries!", International Conference on Fundamental and Applied Sciences, Hazarimal Somani College, Chowpatty, Mumbai, India, March 24, 2021.

Awards

- Pol - Purdue University Outstanding Engineering Teachers, Spring 2021
- Pol - AIChE Excellence in Process (Microwave) Development Research Award (2021)
- Pol - TMS Light Metals, Extraction and Processing division's Energy Best Paper Award, The Minerals, Metals & Materials Society (2021)
- Adams Ethan – Summer 2021 Naval Research Enterprise Internship Program (NREIP) intern, Philadelphia.

Acknowledgments

Thank you all for listening

This work is funded by