Aqueous solid polymer Lithium-ion battery electrolytes: safely enabling high energy batteries with domestically sourced components

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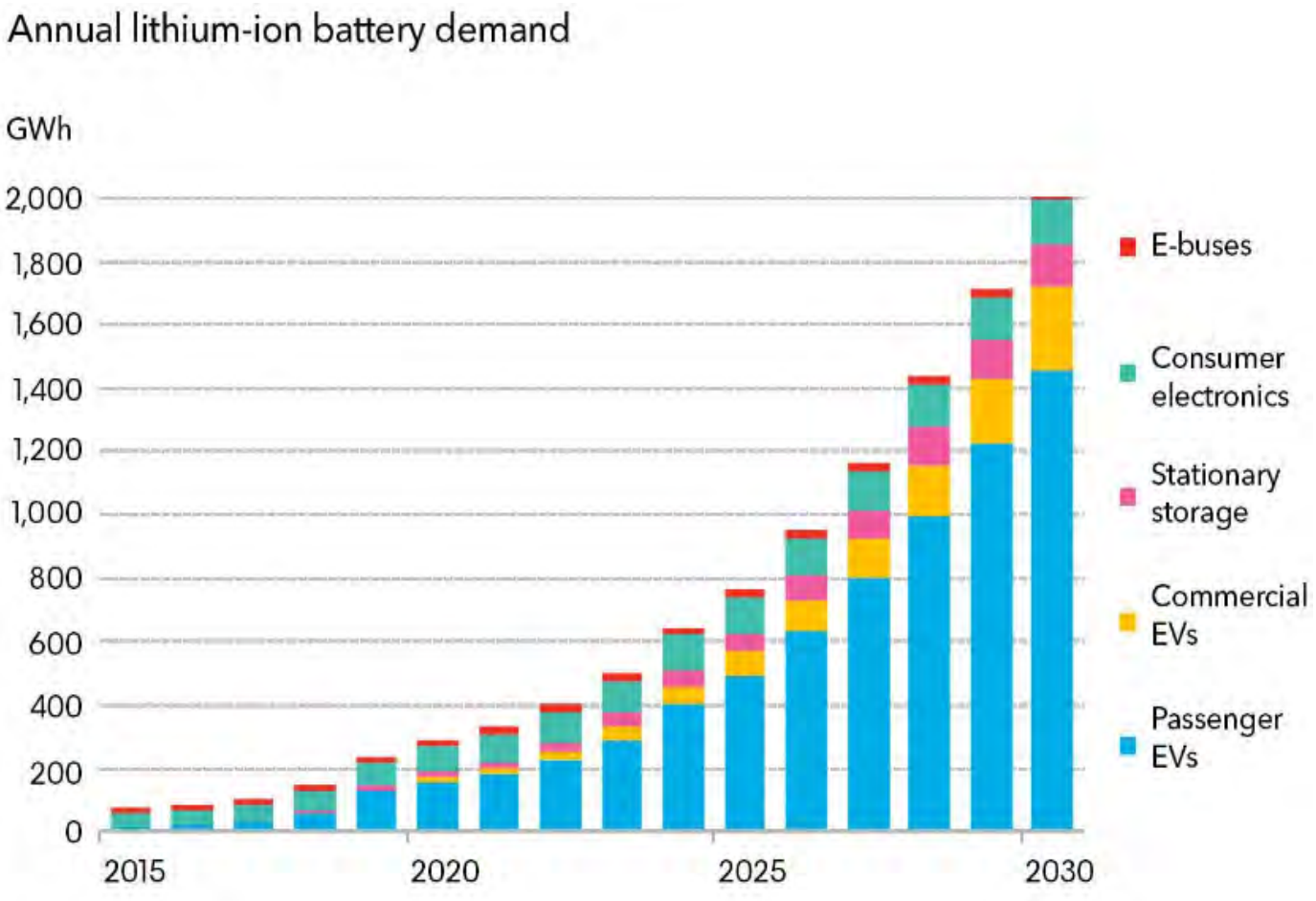
Dr. Arthur Cresce

Li-ion Battery Demand is Rising Exponentially, Driven by EVs

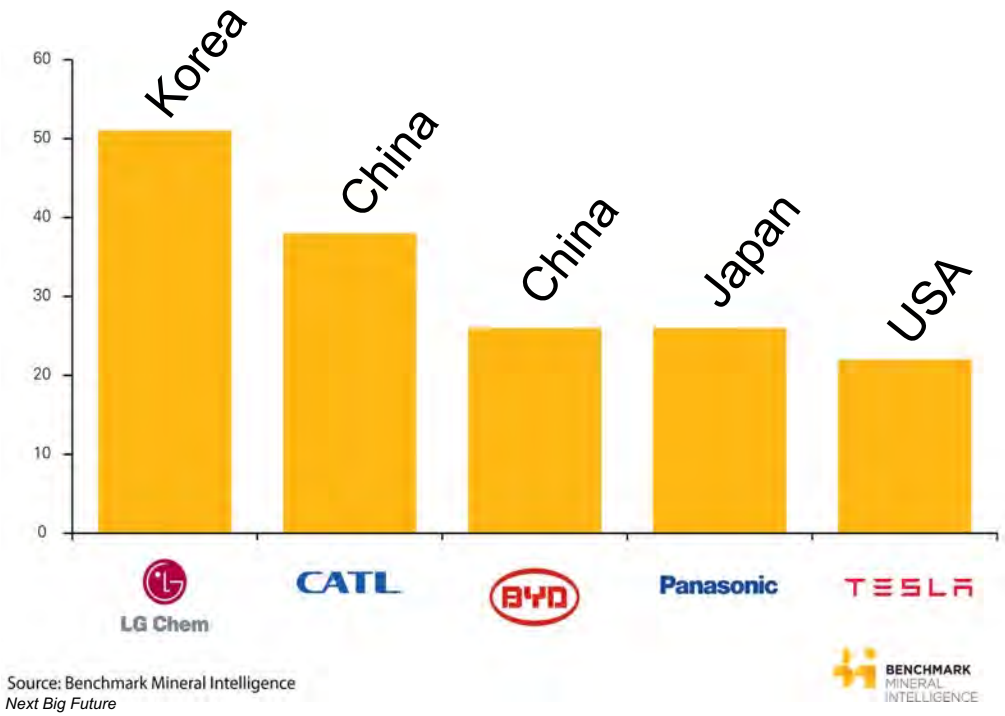


Bloomberg NEF 2019 Electric Vehicle Outlook

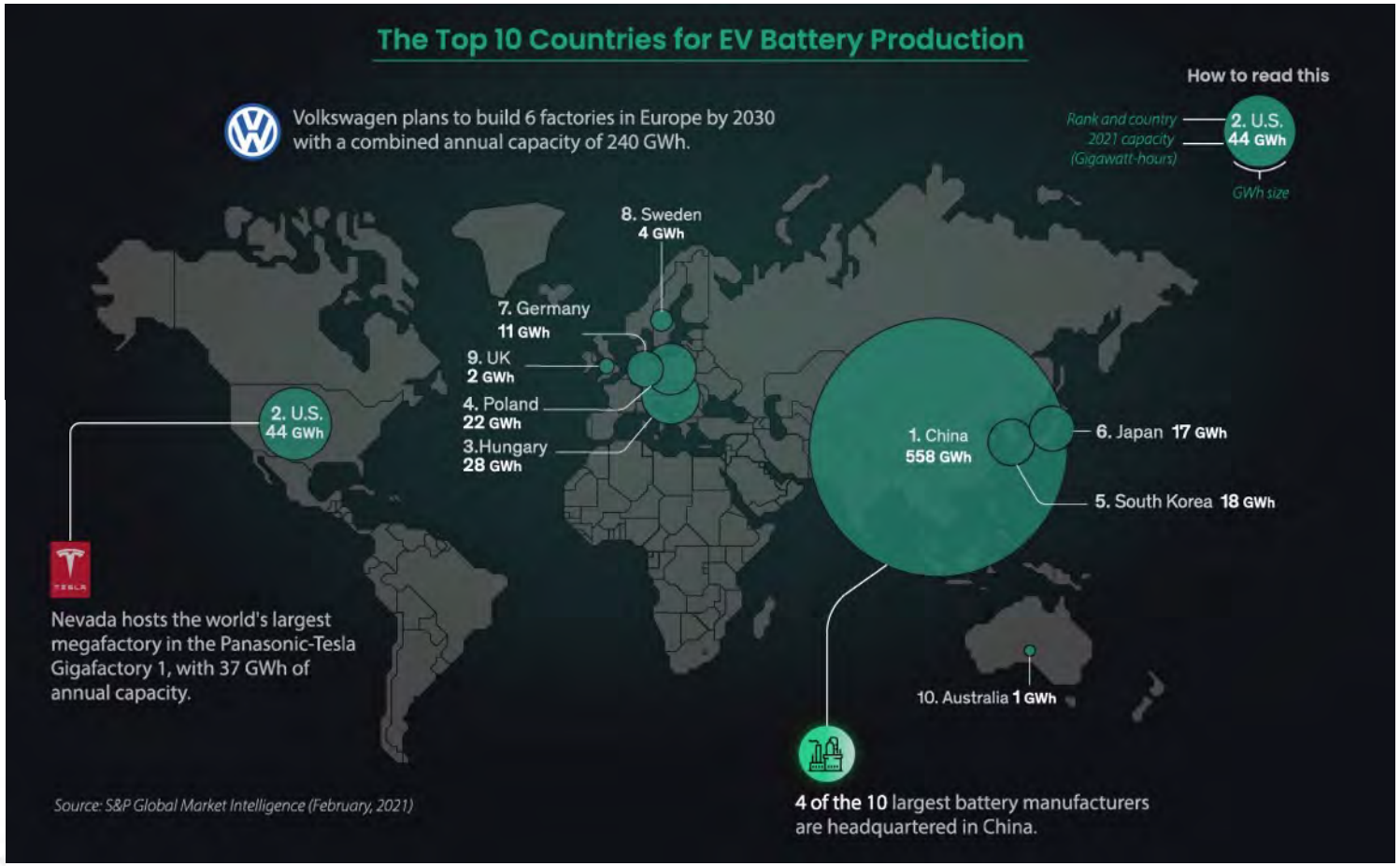
- Lithium-ion battery industry market cap is **$46 billion** (2021)
  - Fairly small compared to large-cap (>$1T) industry sectors
- Demand for lithium-ion batteries grew from **19 GWh** in 2010 to **160 GWh** in 2019
- Demand will continue to accelerate through 2030 with commitments to EVs from manufacturers and worldwide government pollution reduction policies

China Dominates Production in the Current Global EV Battery Manufacturing Landscape

(2019) Top 5 Lithium-ion Battery Producers by Capacity (GWh)

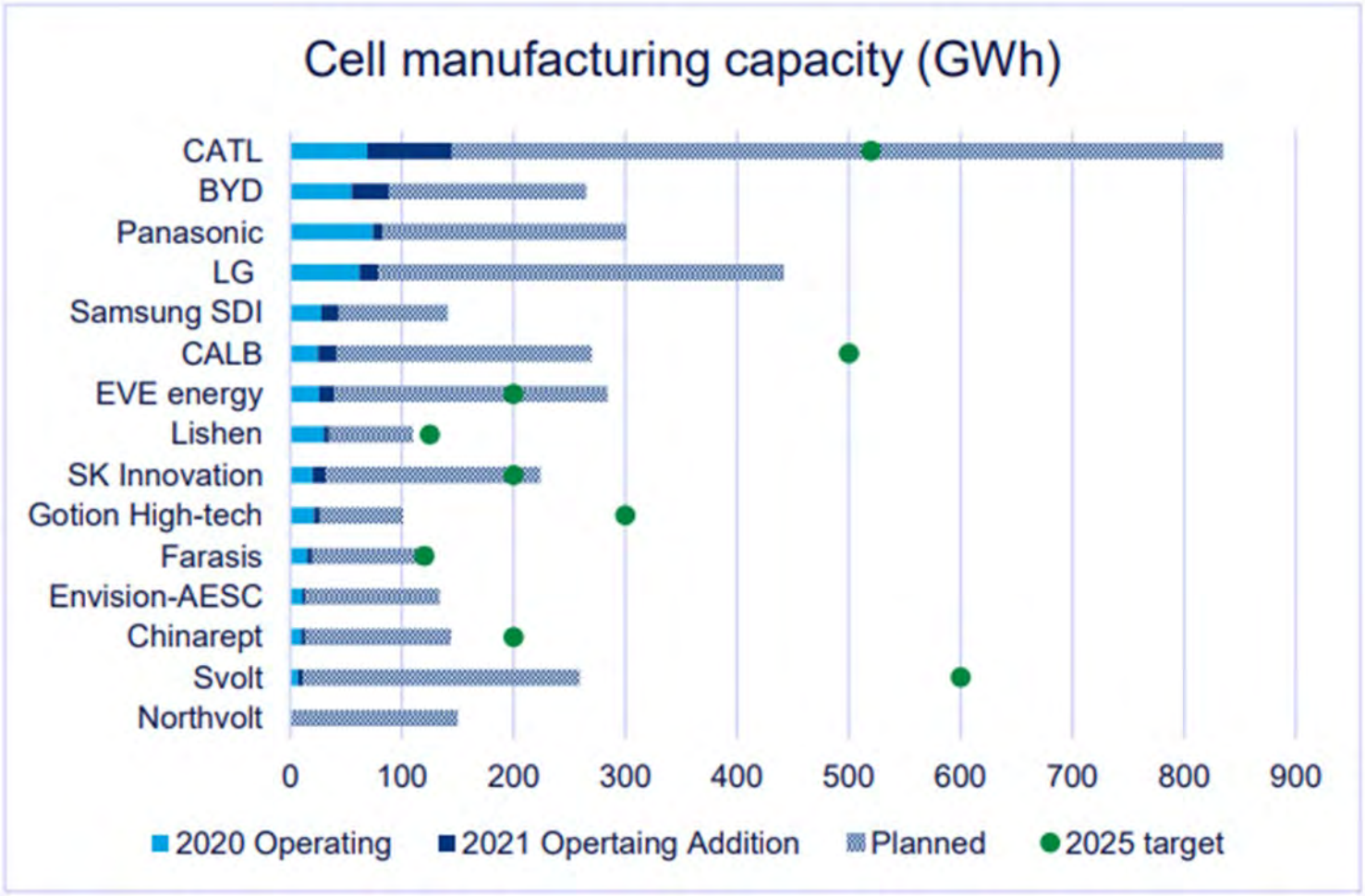


Source: Benchmark Mineral Intelligence
Next Big Future



Visual Capitalist

Worldwide Manufacturers are Rapidly Adding Cell Production Capacity



Wood MacKenzie

By 2025:

- China and Asia/Pacific will account for 69% of global cell production
- Europe will likely overtake North America and account for ~ 20% of global cell production
- North American cell production could jump 2-3x, 10x by 2030 is considered possible

US is Poised to Become a Domestic Battery Manufacturing Powerhouse

Source: BloombergNEF. Note: Shaded areas for manufacturing and/or raw materials indicate that the country has no capacity and comes joint last in the rankings with other countries. Final rankings are an average of the five metrics. The overall ranking for countries in 2026 is shown in the data label but the list is not ordered. The arrow indicates whether the new ranking is higher or lower than in 2021.

- The US has the potential to develop a domestic lithium-ion battery supply chain bolstered by high EV demand
- The US is the #2 EV market after China
- European countries are rapidly increasing demand and production of EVs

Lithium-ion Batteries Have Multiple Modes of Failure

Electrolyte Decomposition

heat generation → thermal runaway

Gas Evolution

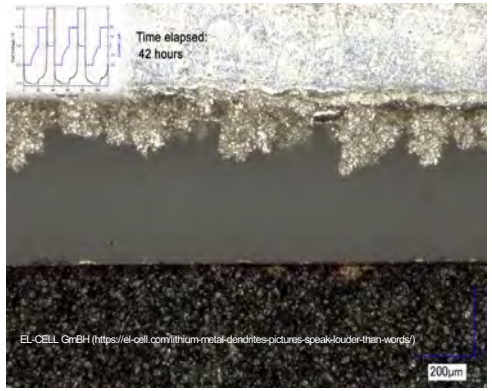
expansion/bloating → rupture

Epec (https://www.epectec.com/batteries/prismatic-pouch-packs.html)

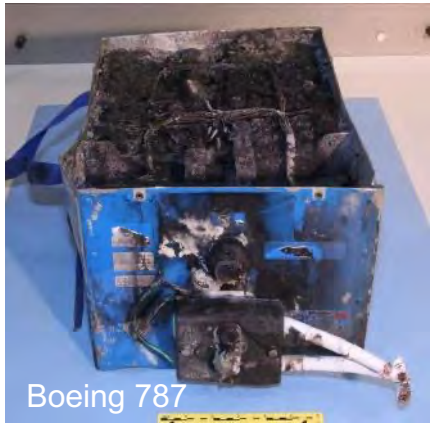
Forbes

Lithium Plating & Dendrite Growth

internal short circuit → Joule heating → thermal runaway



EL-CELL GmbH (https://el-cell.com/lithium-metal-dendrites-pictures-speak-louder-than-words/)



Wall Street Journal

Strategies for safer electrolytes must be explored

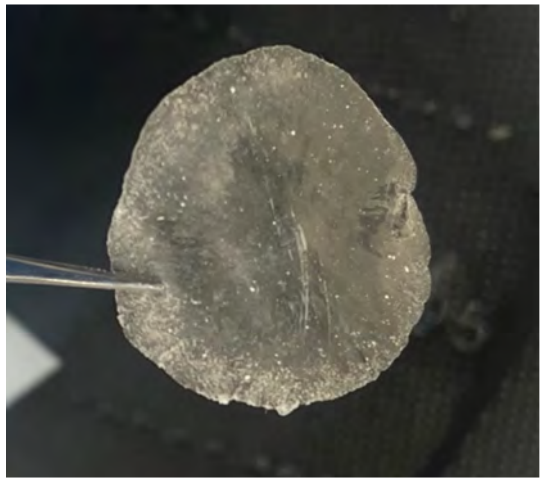
Why are Aqueous-based Solid Polymer and Gel Electrolytes Beneficial?

Aqueous-based Solid Polymer and Gel Electrolytes:

- Nonflammable
- Nontoxic
- Economical (no need for anhydrous salts)
- Simple manufacturing (reduces need for glovebox or dry room)

- Lightweight, flexible, and conforming
- Tunable mechanical properties
- Prevent leaking
- Maintain operation after puncture/cut/mishandle

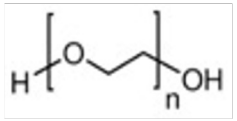
Butane flame held above ASPE: (1900 °C)



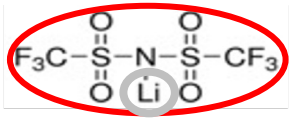
D. Kline, M. Zachariah. (2017)

Water-induced Plasticization of Aqueous-based SPEs (ASPEs)

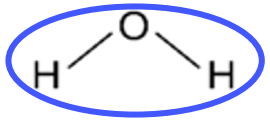
- Water suppresses crystallinity
- Water significantly reduces T_g
  - dry polymer+salt systems (+15°C), pure polymer (-65°C)
- Plasticization effect of water clearly seen through ionic conductivity increase with water content



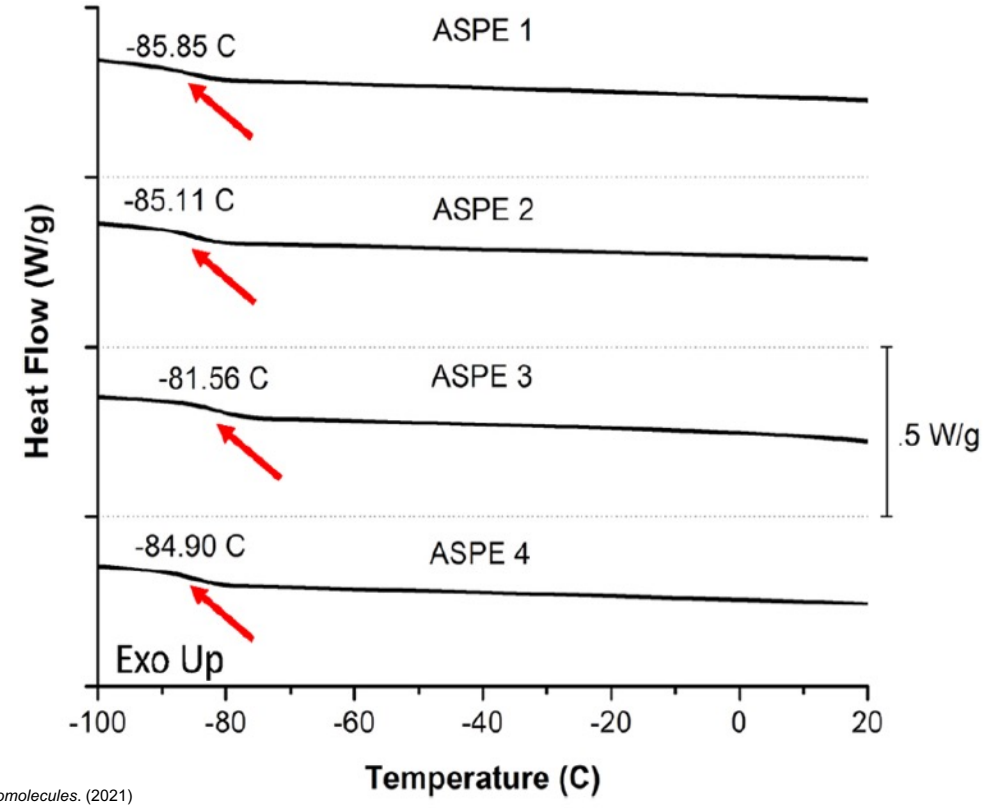
Poly(ethylene oxide)
PEO



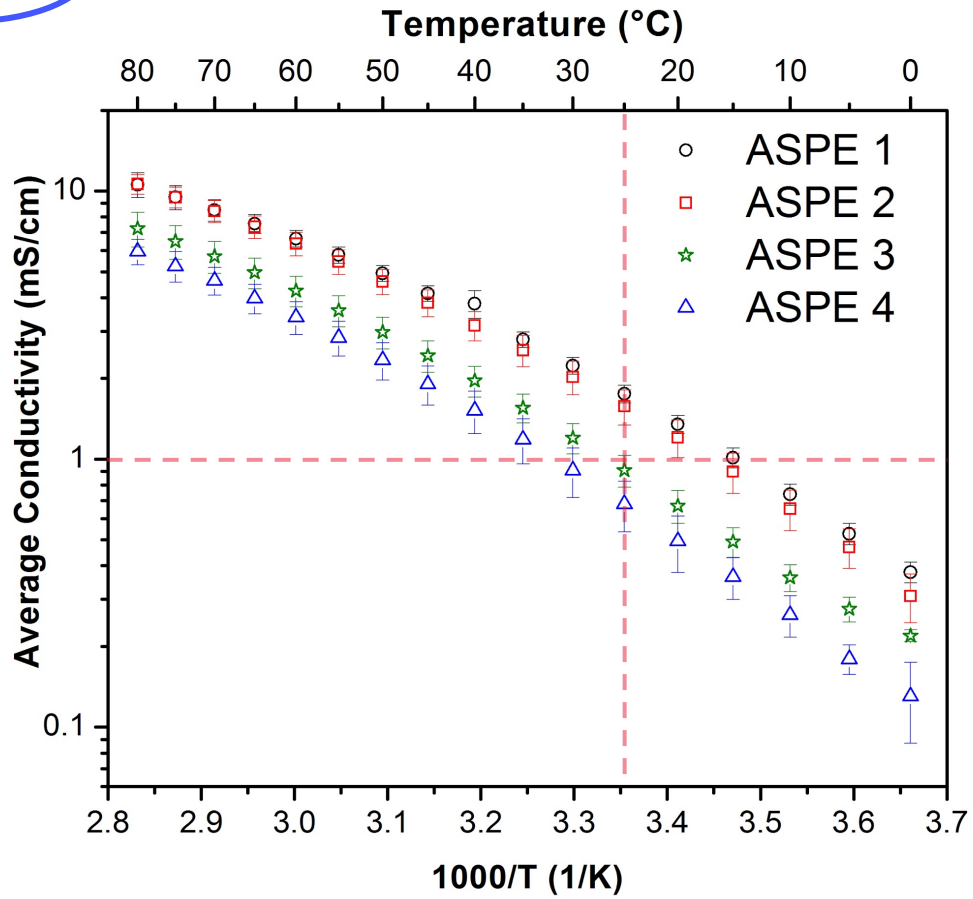
Bis(trifluoromethanesulfonyl)imide lithium salt
Li TFSI



Water
H_2O

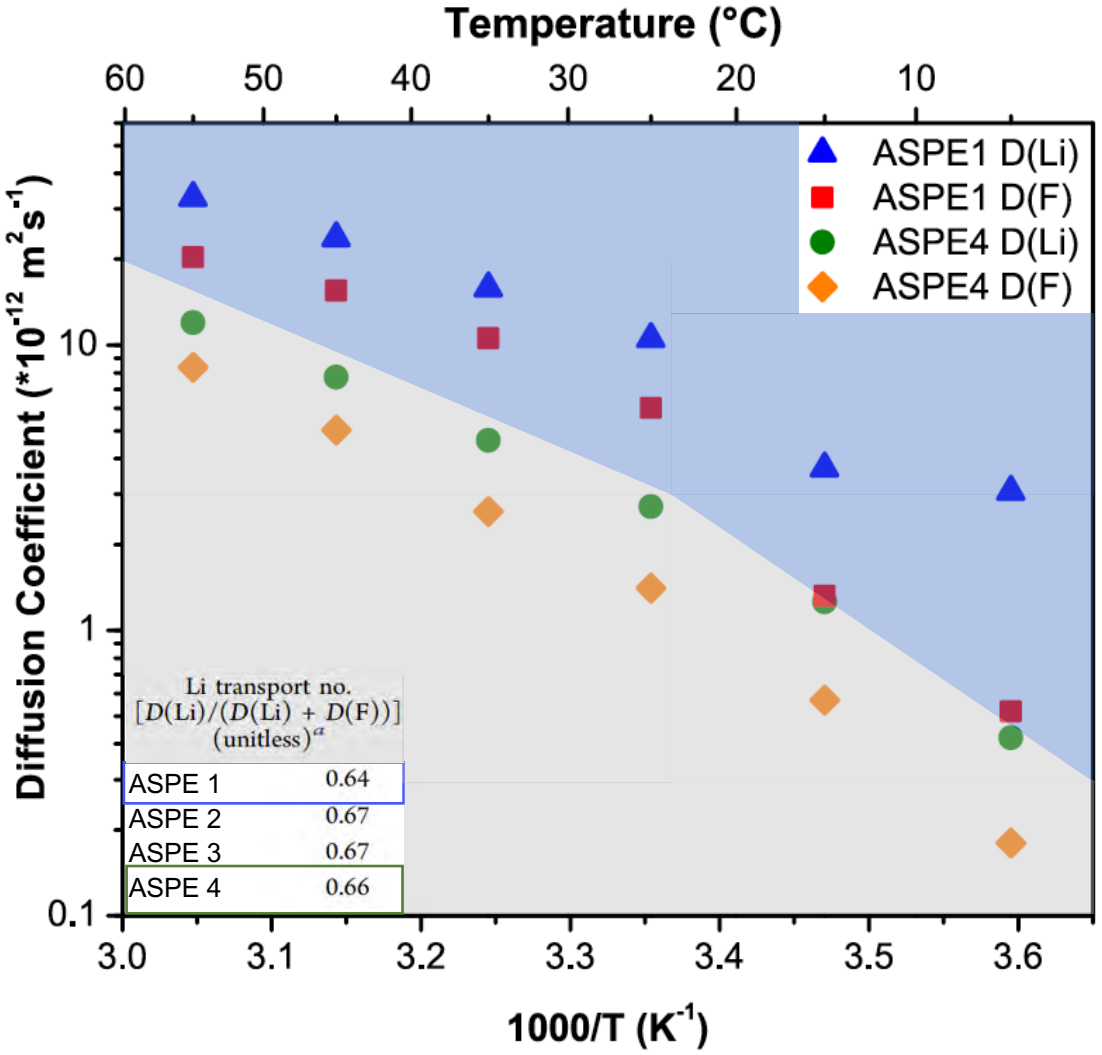


Water Content

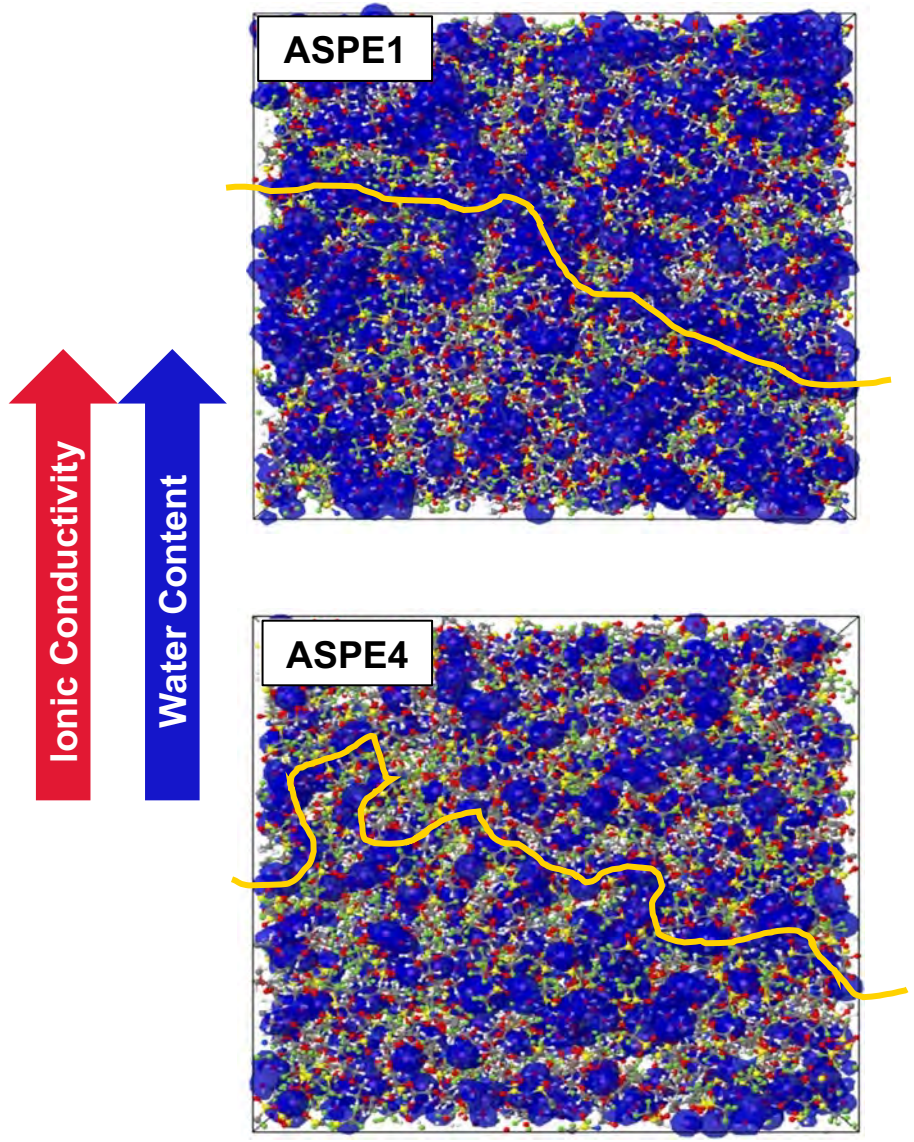


M. Widstrom, *Macromolecules*. (2021)

Water Assists Ionic Transport in ASPEs – Dr. Oleg Borodin, DEVCOM/ARL



Dr. Steve Greenbaum (CUNY)



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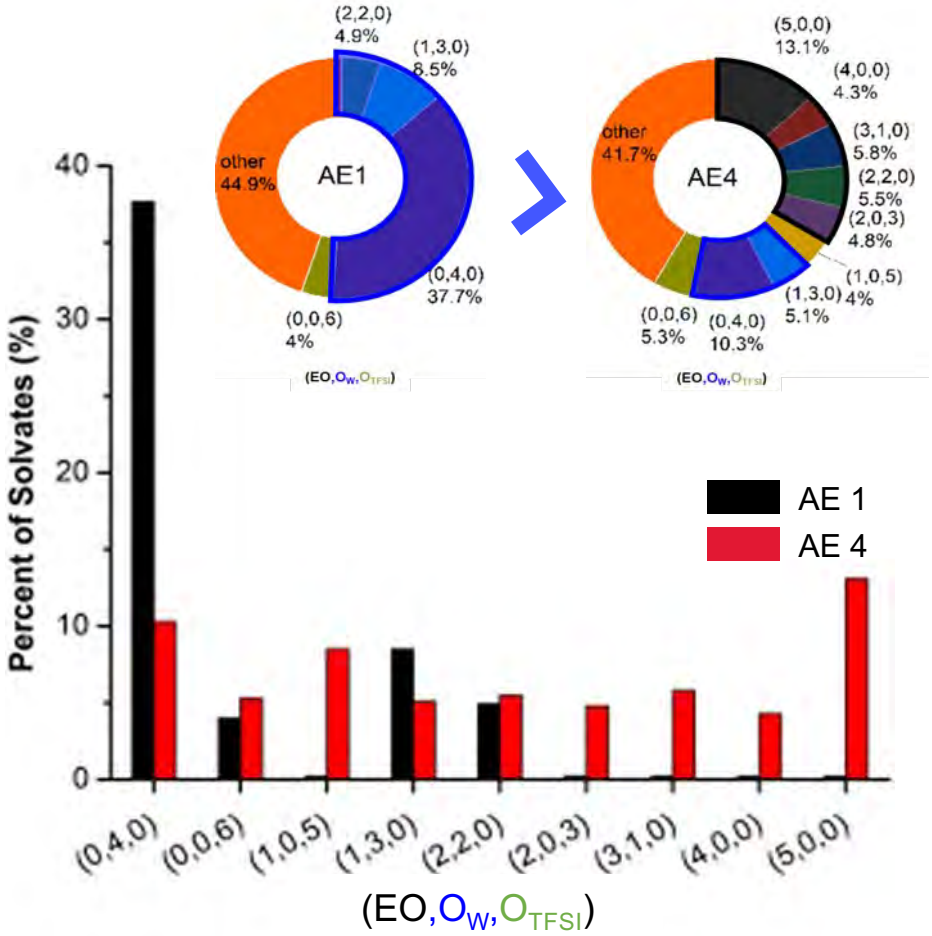
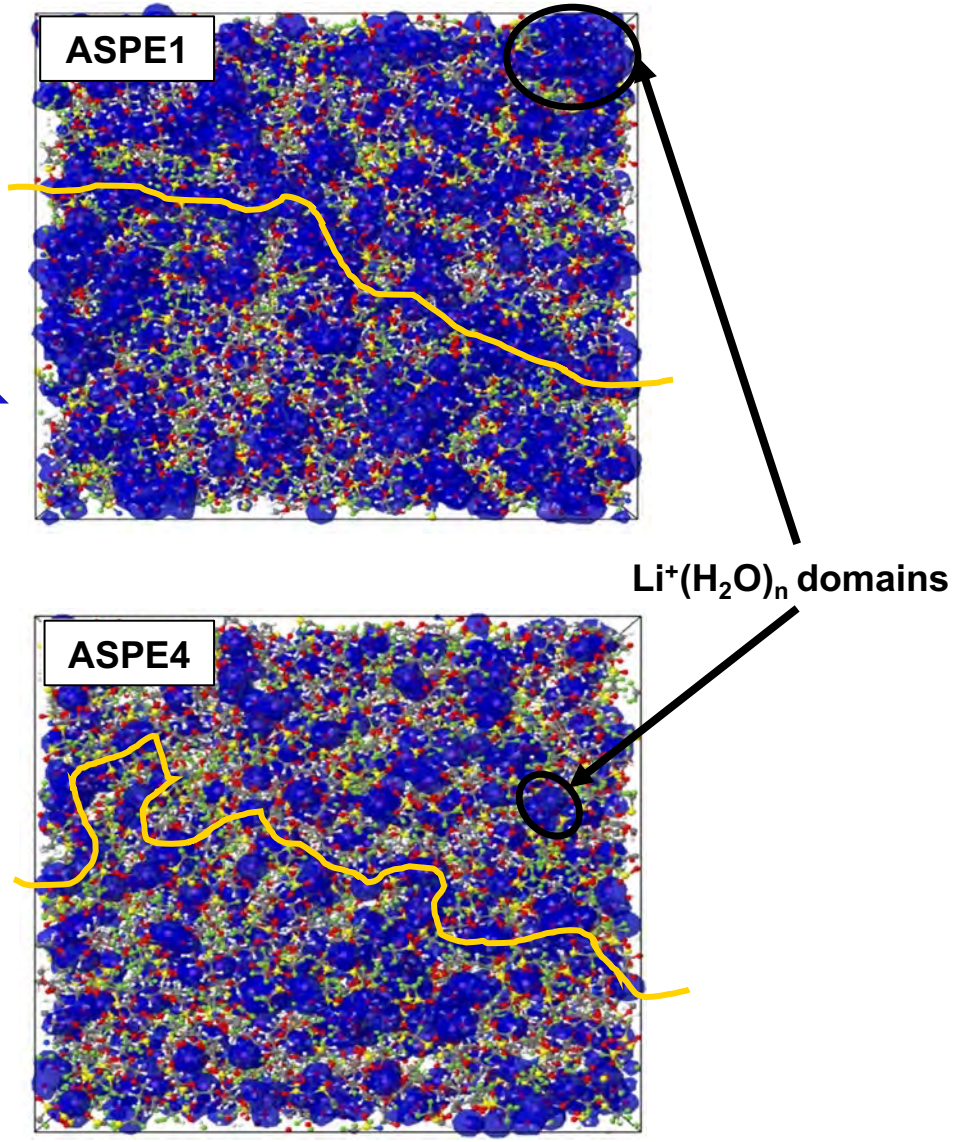


Even small changes in water concentration (5wt%) can shift the solvation structure of Li^+

Tortuosity

Ionic Conductivity

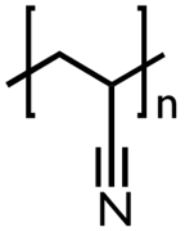
Water Content



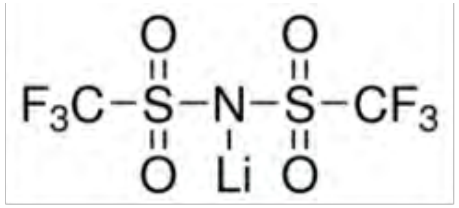
A1: water-assisted transport, A4: PEO-assisted

M. Widstrom, *Macromolecules*. (2021)

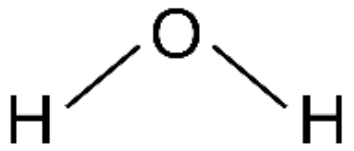
Extending the ESW in ASPEs to Enable Low Voltage Anodes and High Voltage Cathodes



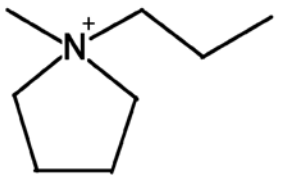
Polyacrylonitrile
PAN

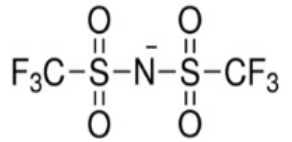


Bis(trifluoromethanesulfonyl)imide lithium salt
Li **TFSI**

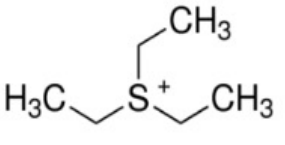


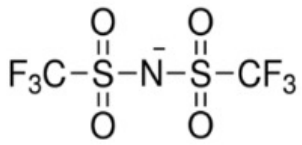
Water
H_2O



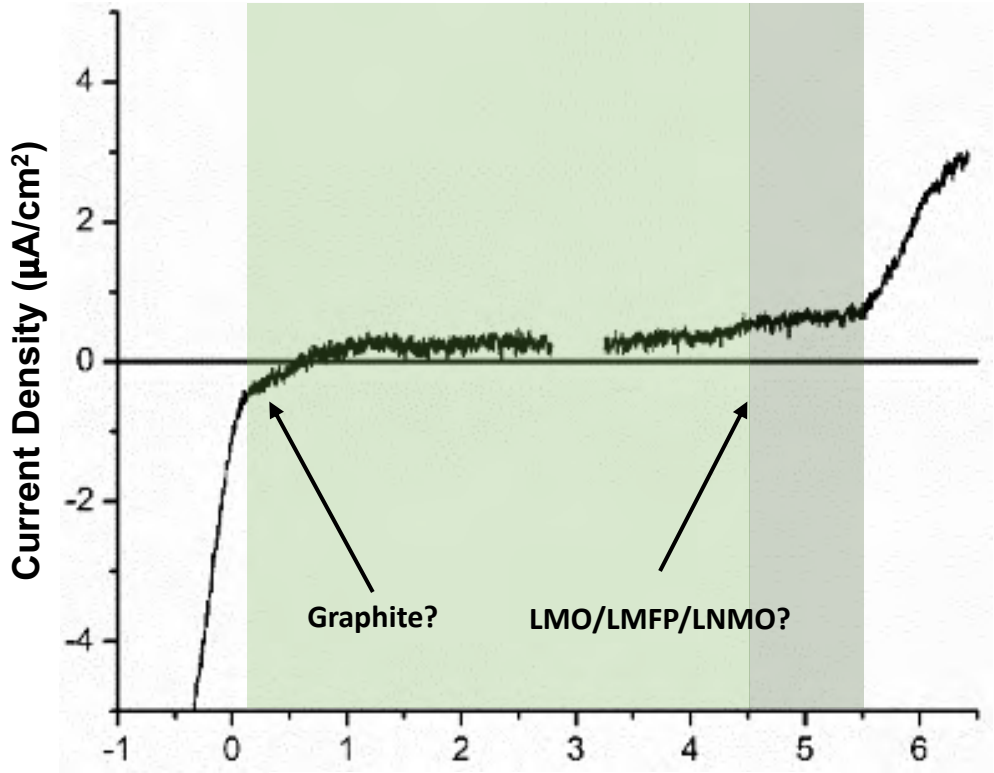


N-methyl-N-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide
$Pyr_{1,3}$ TFSI





Triethylsulfonium bis(trifluoromethylsulfonyl)imide
S_2 TFSI

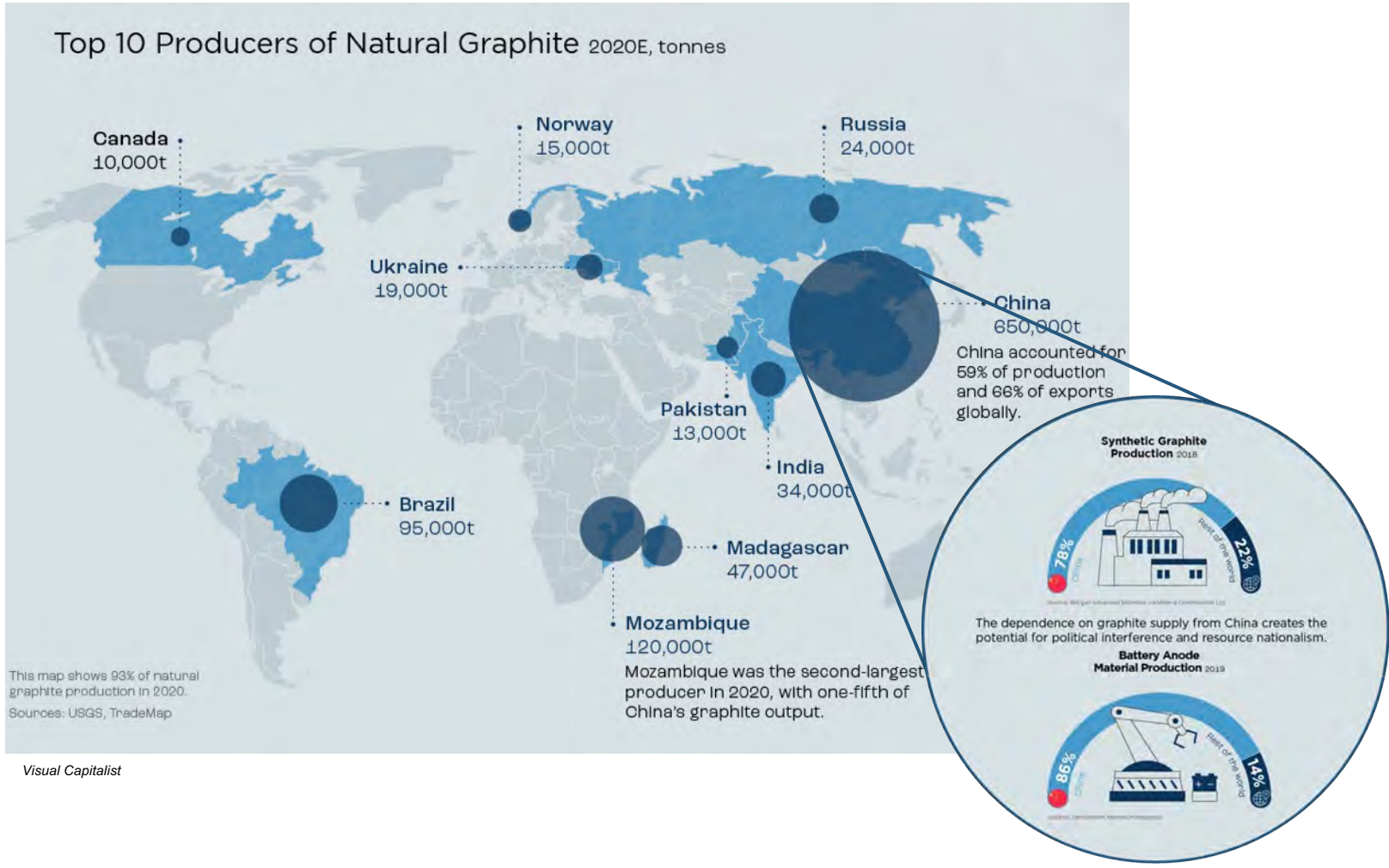


IL Assists in SEI-formation and stability

Graphite: A Critical Mineral

For state-of-the art lithium-ion batteries:

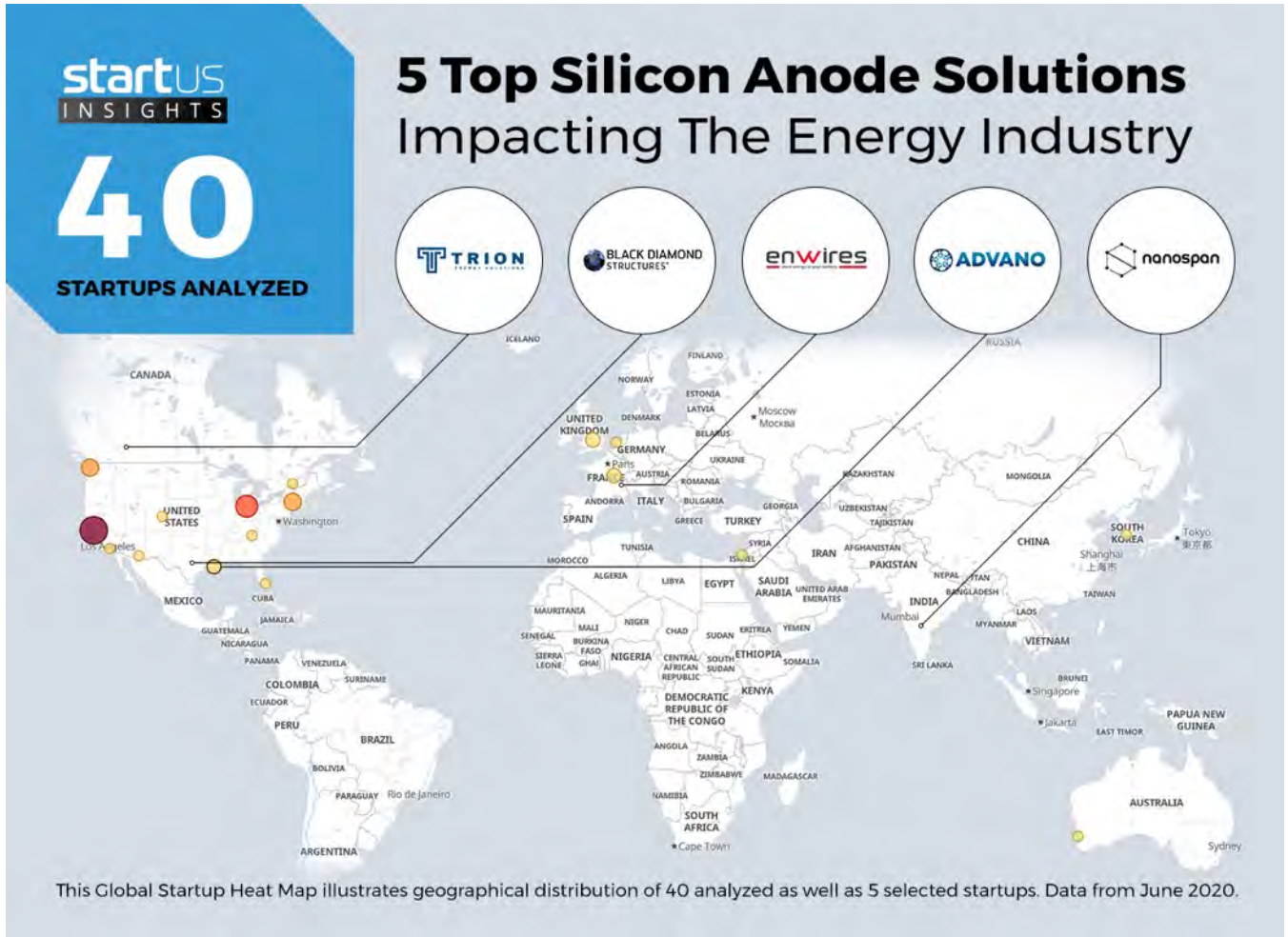
- Graphite is almost exclusively used as the anode in cells intended for EVs and mobile electronics
- China produces/exports much of the world's synthetic and natural graphite
- Alternative anode materials exist, but are produced at a much smaller scale than graphite
  - Silicon
  - Titanate & niobate



Visual Capitalist

Silicon: The Next Step for Lithium-ion Battery Anodes

Distribution of companies producing silicon anode materials is more broadly distributed around the world.



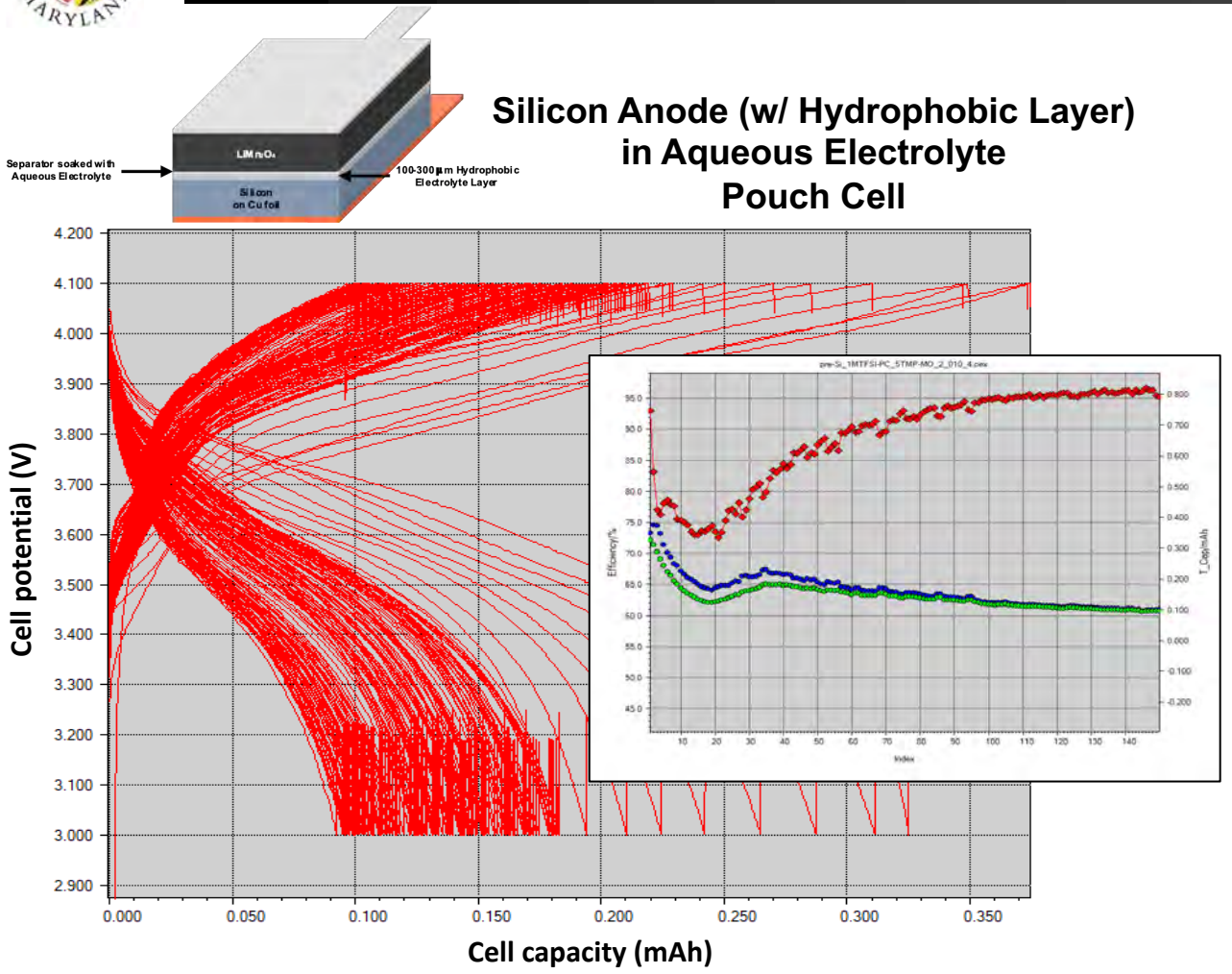
StartUs Insights

Other Notable Suppliers:

- Albemarle Corporation
- Altair Nanotechnologies, Inc.
- Amprius Technologies
- BTR New Energy Material Ltd.
- California Lithium Battery
- Cuberg, Inc.
- Enevate Corporation
- Enovix
- Ganfeng Lithium Co Ltd
- Hitachi Chemical Co. Ltd.
- LeydenJar Technologies BV
- NanoGraf Corporation
- NEXEON LTD.
- OneD Material, LLC
- Paraclete Energy, Inc
- pH Matter LLC
- Poly Plus Battery Co.
- SCT HK
- SES
- Shanshan Technology
- Sila Nanotechnologies Inc.
- T alga Resources Ltd
- Tianqi Lithium Corporation

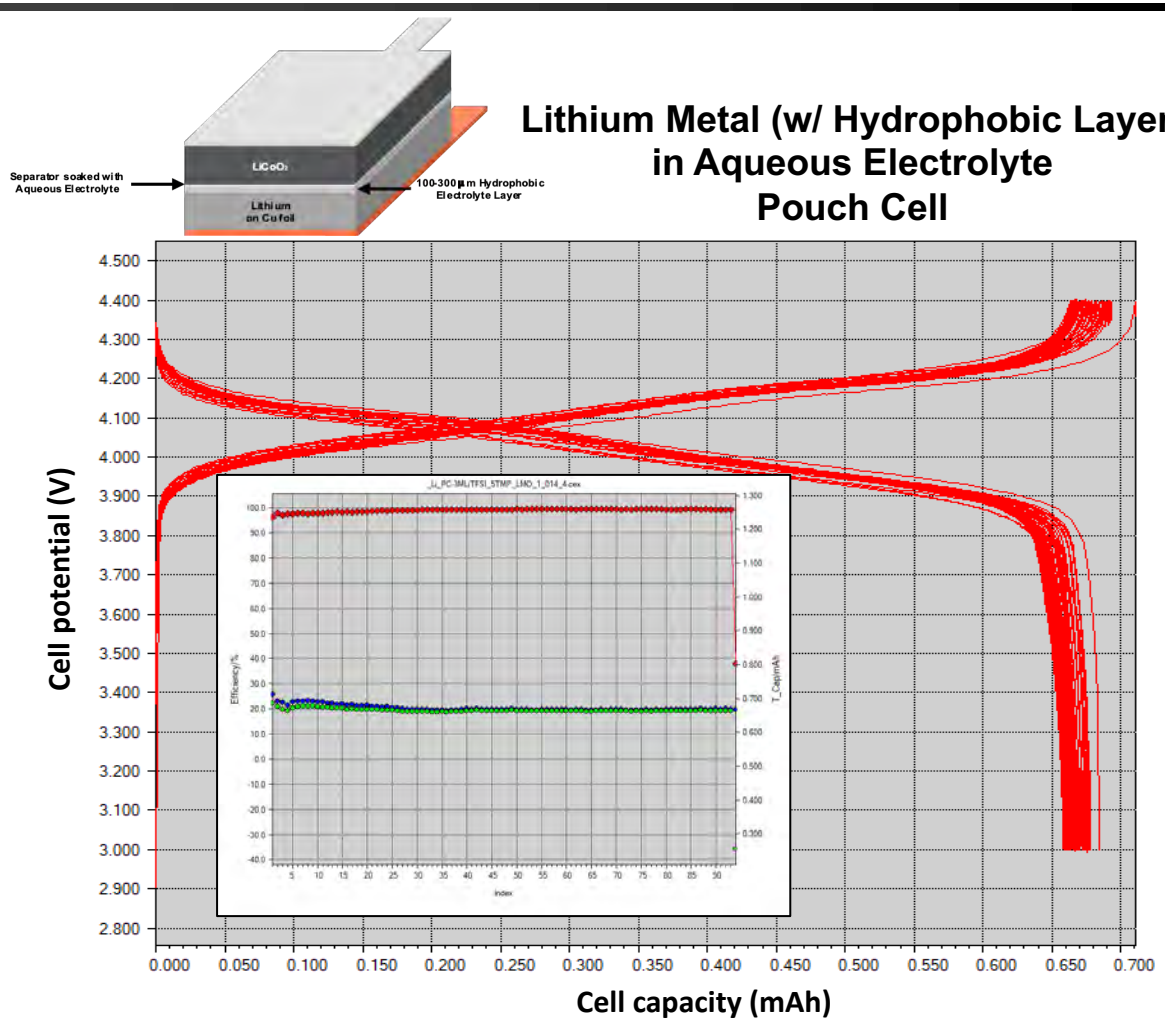
Using Hydrophobic Polymer Protection Layers to Enable

Silicon Anode (w/ Hydrophobic Layer) in Aqueous Electrolyte Pouch Cell



- Cycling can be improved with better sourced Si material, better electrode construction, and better cell construction
- Scalable to higher electrode loadings (>5 mAh/cm^2)
- Pairing with domestically-sourced LFP/LMO/LMFP/LNMO cathodes can achieve high battery energy density

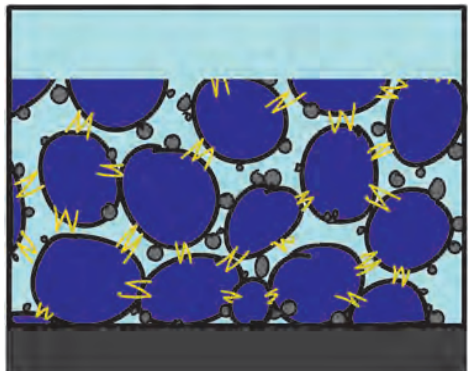
Lithium Metal (w/ Hydrophobic Layer) in Aqueous Electrolyte Pouch Cell



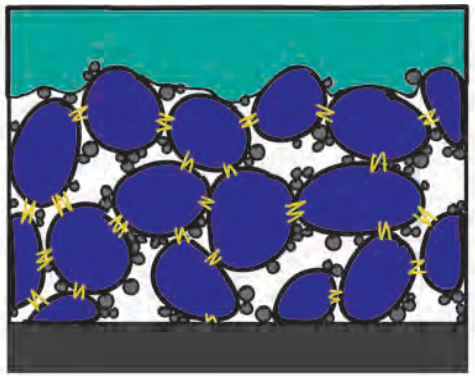
- Good performance for a cell that puts Li metal within 100 microns of a water-containing electrolyte
- 50 µm Li layer on 15 µm Cu foil
- Space to explore thinner Li and anode-free versions

Modifying Electrode Porosity for Better ASPE Compatibility

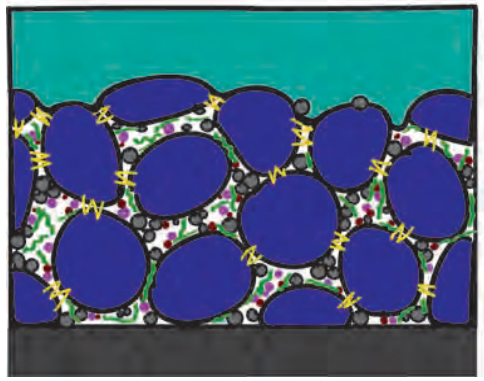
Liquid Electrolyte

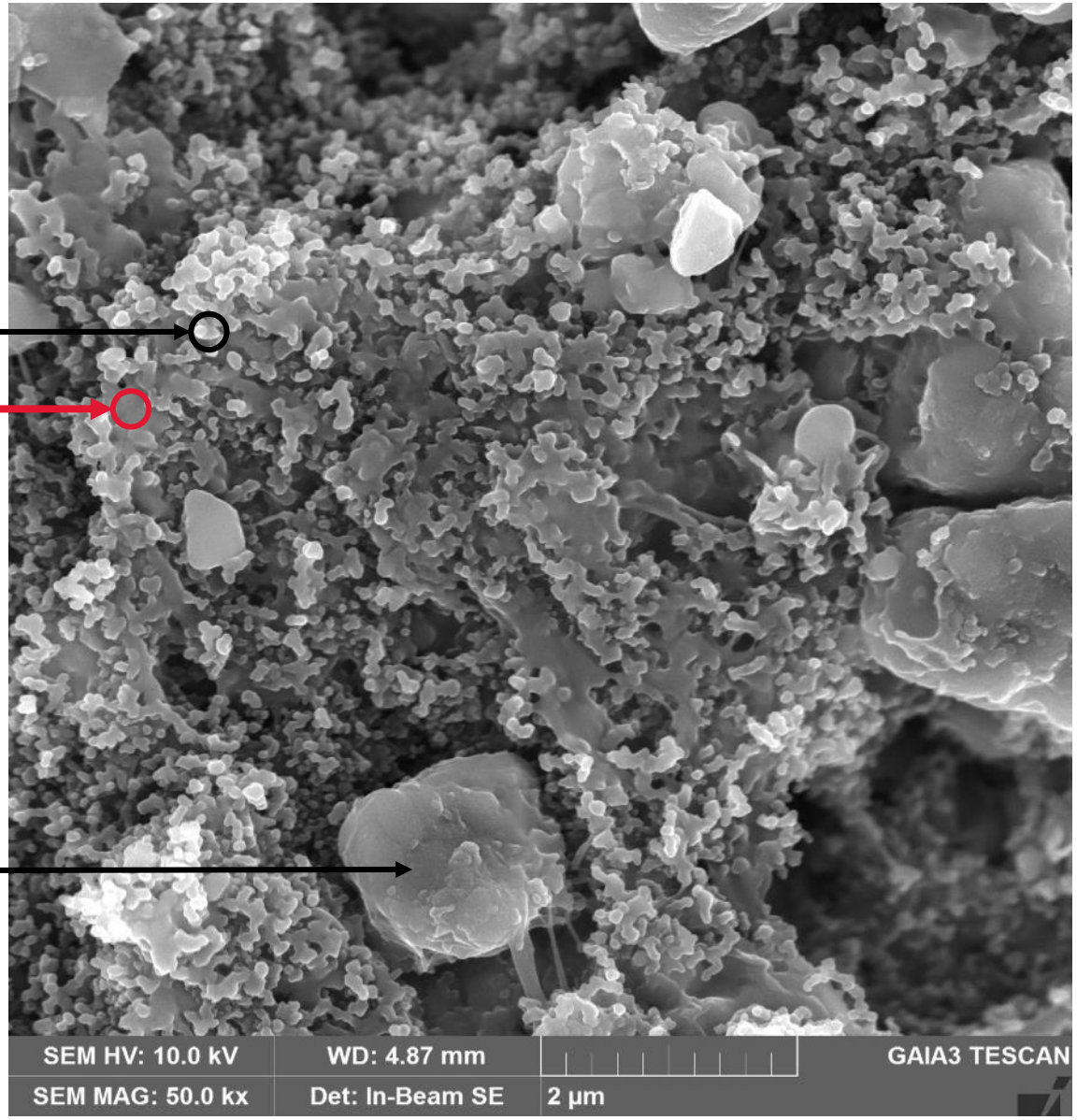


Solid Polymer Electrolyte



SPE w/ Composite Cathode





Conclusions and Takeaways

- Si anodes allow for thin electrodes to be made with high capacity loadings.
- If we can make Si protection layer very compact (<50 µm), then we could hit industrial benchmarks for cell layer thickness and therefore high battery energy density.
  - 200-300 Wh/kg is an early goal. Pairing the Si anode with a protection layer to a highly loaded $LiMn_2O_4$ or $LiFePO_4$ or $Li(Mn,Fe)PO_4$ or $Li(Ni,Mn)_2O_4$.
- Si anodes have Si-OH groups potentially at the surface
  - opportunities to tailor specific polymers or additives to chemically attach to the Si anode surface and become less separated from the Si surface during cycling.
  - The use of Li- Poly(Acrylic Acid) $(CH_2\text{-}CHCO_2H)_n$ binders for Si anodes, instead of Li-PVdF already uses such a technique successfully in practice.
- Those 4 anodes are important in that they use mostly US-sourced materials rather than Co that is mined in the Congo and processed in China. $TiNb_2O_7$ as an anode is another promising US-sourced anode material, it is a low-voltage anode like Lithium titanate (LTO) but has capacity similar to graphite.