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

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

- 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)

1. China
2. U.S.
3. China
4. Germany
5. South Korea
6. Japan
7. Germany
8. Sweden
9. UK
10. Australia

Nevada hosts the world's largest megafactory in the Panasonic-Tesla Gigafactory 1, with 37 GWh of annual capacity.

Source: S&P Global Market Intelligence (February, 2021)

Visual Capitalist
Worldwide Manufacturers are Rapidly Adding Cell Production Capacity

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
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

Lithium Plating & Dendrite Growth
- internal short circuit → Joule heating → thermal runaway

Strategies for safer electrolytes must be explored
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)*
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
Water Assists Ionic Transport in ASPEs – Dr. Oleg Borodin, DEVCOM/ARL

Dr. Steve Greenbaum (CUNY)
Even small changes in water concentration (5wt%) can shift the solvation structure of Li$^+$. A1: water-assisted transport, A4: PEO-assisted
Extending the ESW in ASPEs to Enable Low Voltage Anodes and High Voltage Cathodes

Polyacrylonitrile (PAN)

Bis(trifluoromethanesulfonyl)imide lithium salt (LiTFSI)

Water (H₂O)

N-methyl-N-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr₁,₃TFSI)

Triethylsulfonium bis(trifluoromethylsulfonyl)imide (S₂TFSI)

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

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

- Cycling can be improved with better sourced Si material, better electrode construction, and better cell construction
- Scalable to higher electrode loadings (>5 mAh/cm²)
- Pairing with domestically-sourced LFP/LMO/LMFP/LNMO cathodes can achieve high battery energy density

- 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

SPE w/ Normal Cathode

Carbon
Polymer
IL
Salt
PVdF
LFP

active material
ionic liquid
carbon black
Polymer
PVdF binder
lithium salt
organic liquid electrolyte
current collector
polymer electrolyte

SEM HV: 10.0 kV
WD: 4.87 mm
SEM MAG: 50.0 kx
Det: In-Beam SE
2 μm
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$_2$O$_4$ or LiFePO$_4$ or Li(Mn,Fe)PO$_4$ or Li(Ni,Mn)$_2$O$_4$.
- 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$_2$-CHCO$_2$H)$_n$ 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$_2$O$_7$ 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.