Energy Efficiency &
Renewable Energy

Directions for Energy Storage R&D in the Vehicle Technologies Program

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Scalable Energy Storage Beyond Li-Ion: Materials Perspectives
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Charter and Goals

- **CHARTER**
  - Advance the development of batteries and other electrochemical energy storage devices to enable a large market penetration of hybrid and electric vehicles.
- **TARGET APPLICATIONS**
  - Power-Assist Hybrid Electric Vehicles (HEVs)
  - Plug-in Hybrid Electric Vehicles (PHEVs)
  - Battery Electric Vehicles (EVs)
- **GOALS**
  - **2010 FreedomCAR Goal (Conventional HEVs):**
    - Develop a 25 kW power-assist HEV battery that costs $500.
  - **2014 DOE PHEV Battery Goal:**
    - Develop a PHEV battery that enables a 40-mile all-electric range and costs $3,400.

Energy Storage R&D: Program Structure

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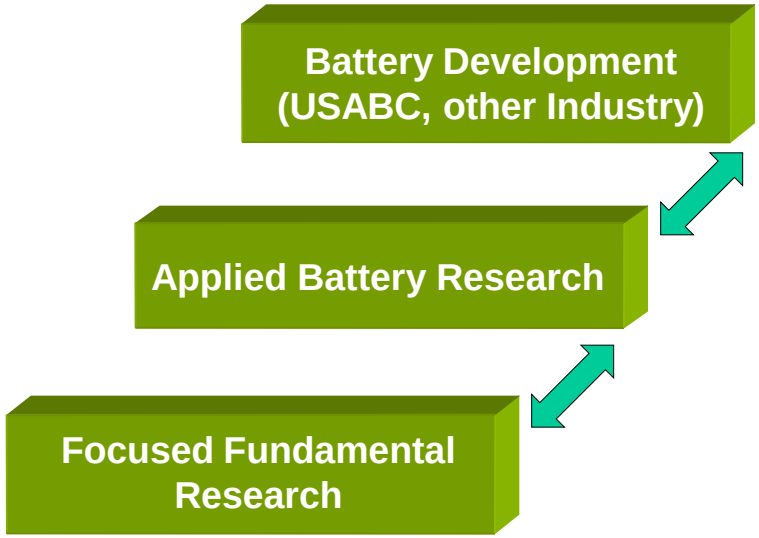

- Develop full prototype battery systems with industry.
- Assist developers of lithium-ion technologies for PHEV applications to overcome market barriers.
- Develop the next generation of battery materials and technologies.

Research effort is coordinated closely with DOE Office of Electricity, ARPA-E, Office of Basic Energy Sciences and NSF

Budget and Focus/Priority

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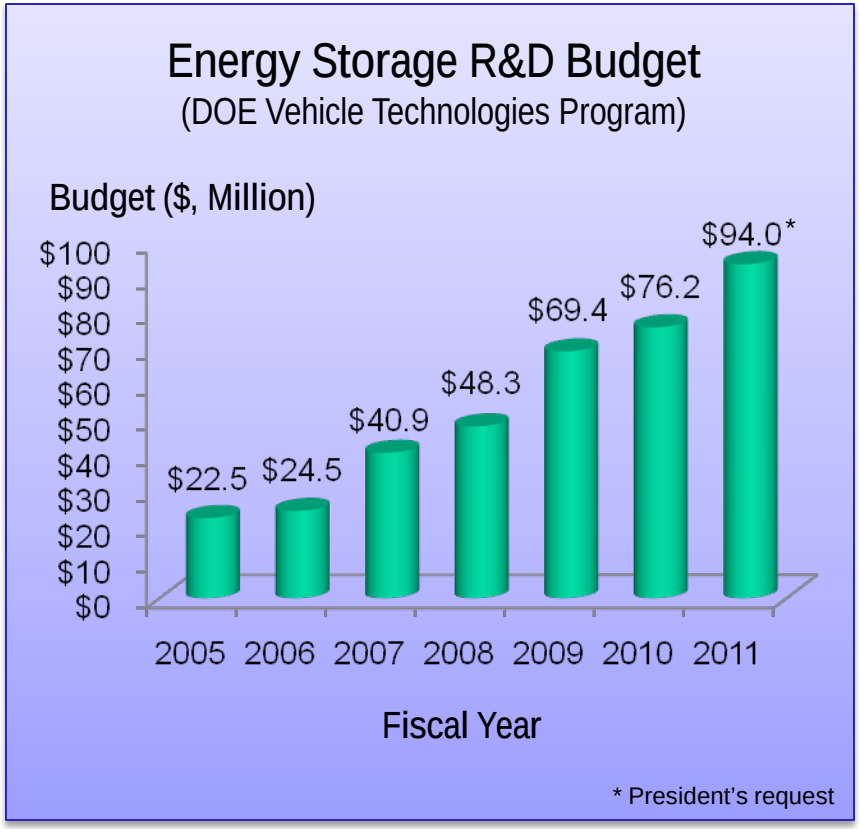
Program focus and priorities have changed over time and the funding profile has changed accordingly.

Year	Focus/Priority
1992 – 1995	EV focus
1995 – 2000	HEV focus (PNGV)
2000 – 2008	Fuel cell vehicles (FreedomCAR Partnership)
2008 - present	PHEVs



Battery Requirements

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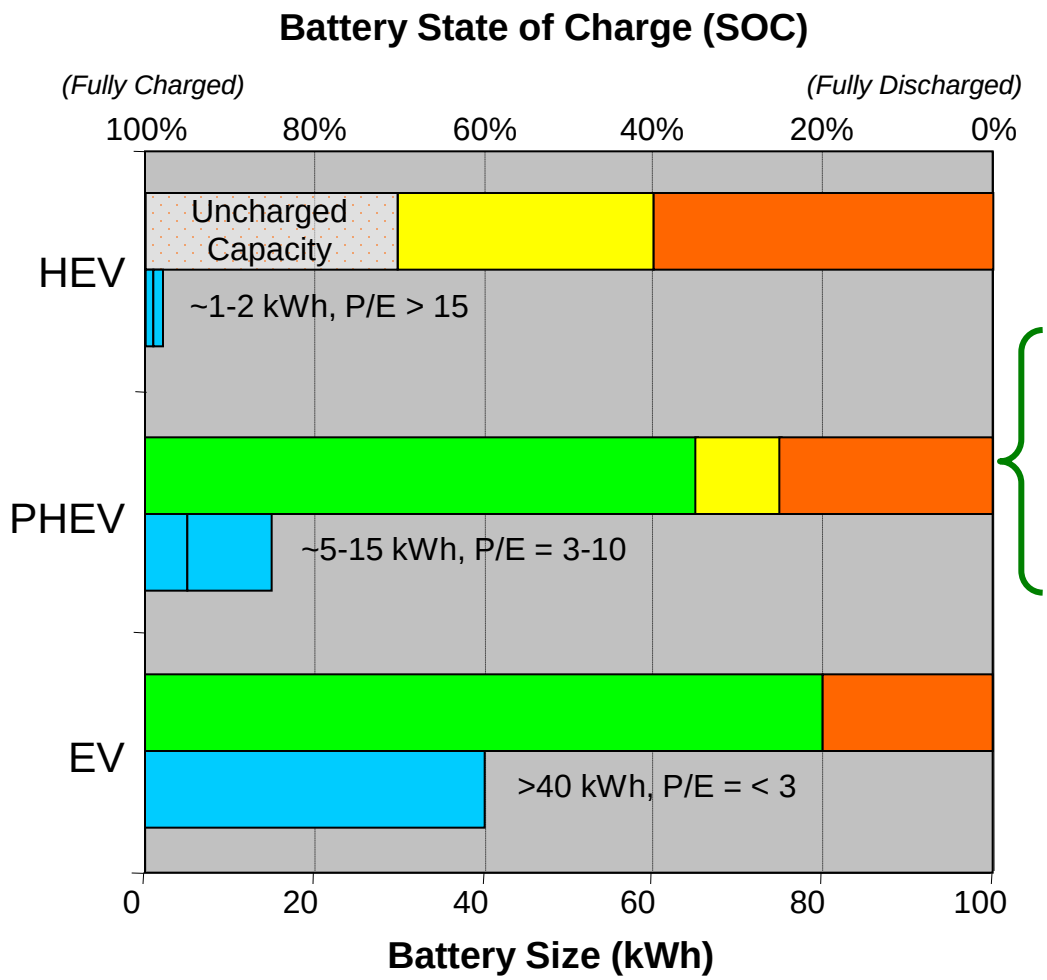

CS only: 300-500 Wh, 25-40 kW (10 sec) @55% SOC, 300,000 cycles

CD-B: Energy scaled for range (10-40 miles), >1,000 deep discharge cycles

CD-E: Required power > 80 kW, energy scaled to > 40-mile range

CS: 300-500 Wh, 25-40 kW (10 sec) @30% SOC, 300,000 cycles

CD only: Energy scaled for 300-mile range, 1,000 deep-discharge cycles

- Charge Depleting (CD-B: blended, E: extended range)
- Charge Sustaining (CS)
- Unused Energy
- Battery Size (kWh)

Current Status of Lithium-ion Technologies

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Chemistry	Anode / Cathode	Ah/kg (Theoretical)	Ah/kg (Observed)	Potential vs. Li/Li^+	Open Circuit Potential
Cobalt Oxide (Sanyo, Samsung, etc.)	LiC_6/ $LiCoO_2$	370/~ 295	~300/160+	100 mV/3.9V	3.9V
Nickelate (Johnson Control/Saft)	LiC_6 / $LiNi_xCo_yAl_z$	370/~ 300	~300/180	100 mV/3.6V	3.8V
Manganese Spinel (LG Chem)	HC/ $LiMn_2O_4$	370/148	~250/~ 120	100 mV/3.9V	3.9V
Iron Phosphate (A123 Systems)	LiC_6/ $LiFePO_4$	370/178	~300/160	100 mV/3.4V	3.4V
Titanate (Enerdel)	$Li_4Ti_5O_{12}$/ $LiMn_2O_4$	233/148	~ 170/~ 120	1.5 V/ 3.10V	2.4V

- For **power** applications, the system limit is **60–65 Wh/kg**
- For **energy** applications, the system limit is **100 Wh/kg**

Status of Cathode Materials

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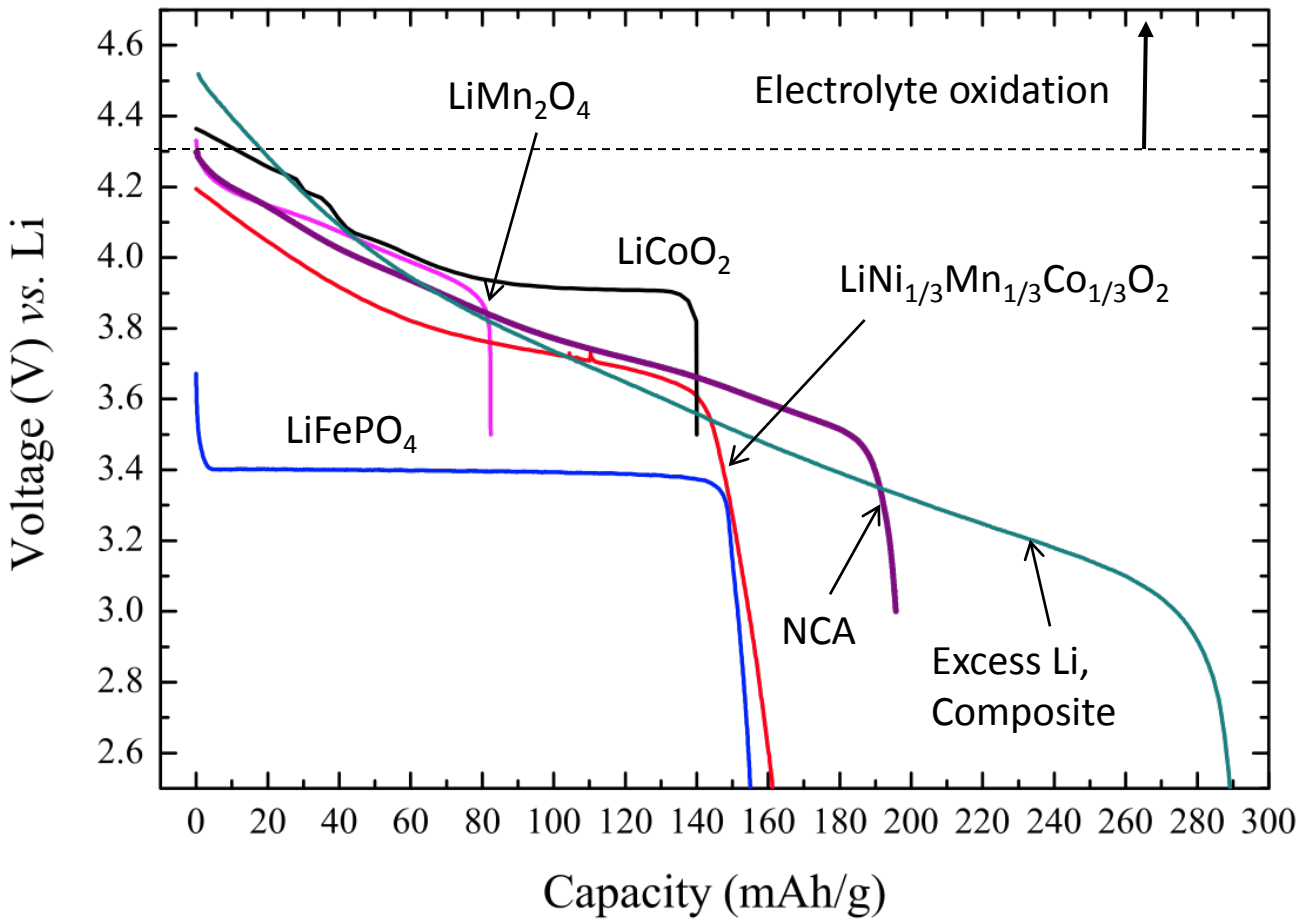
Current lithium-ion batteries are cathode-limited



The Nickelate System

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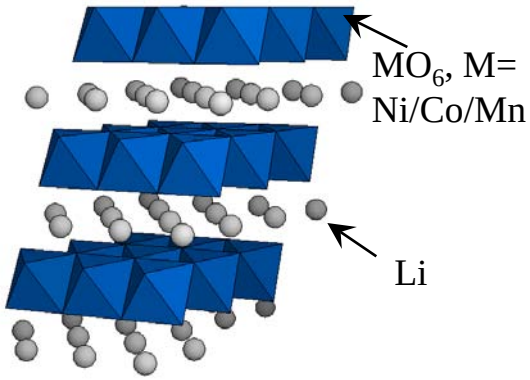

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ / Graphite

- Mature system
- Highest energy of all chemistries available today
- Energy and power satisfactory for PHEV-10 and possibly PHEV-40
- Safety concerns remain because material is prone to thermal runaway

Challenges include safety and cycle life

Approaches

- Move to prismatic designs to improve energy density
- Study the effect on life for deep-discharges

The $LiMn_2O_4$ Spinel System

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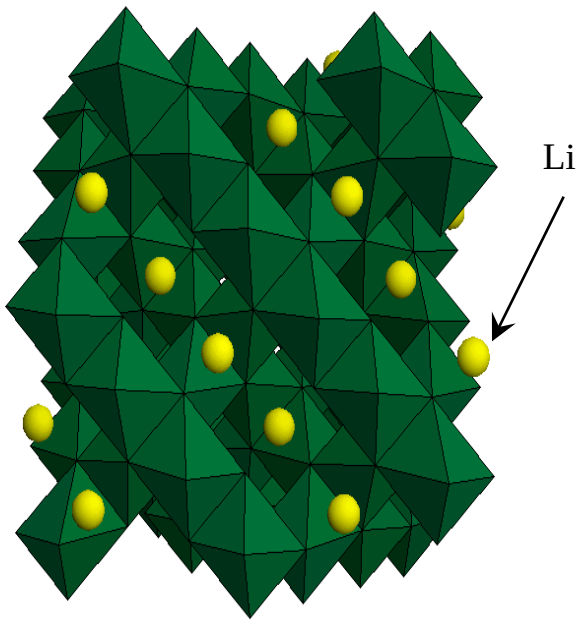

Manganese Spinel / Carbon-based

- Well-studied system that has high power capability and excellent safety, but has low energy
  - Capacity is 110 mAh/g, vs. 180 mAh/g for the nickel-based systems
- Known cycle-life problems due to manganese dissolution, exacerbated at high temperatures
- Could satisfy PHEV-10 energy requirements, but meeting PHEV-40 requirements is difficult

Low energy and poor life are key challenges for use in PHEV-40

Approaches

- Use a mixture of spinel and nickelate to enhance life and increase energy, while maintaining safety
- Move to a graphite-based anode

The Iron Phosphate System

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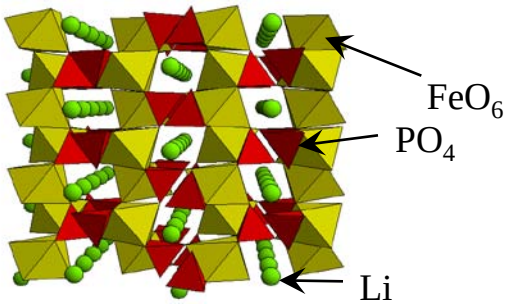
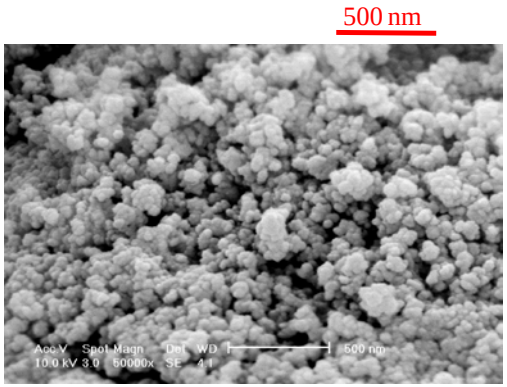
$LiFePO_4$ / Graphite



- Best chemistry in terms of safety characteristics
- Excellent power capability due to nanosize
- Low energy due to low operating voltage (3.4V)
- Cycle life unknown due to limited data
  - Life appears to be related to impurities formed during material synthesis, which could be prevented.
- Flat voltage leads to cell balancing and SOC determination problems



Low energy could impede use in PHEV-40

Approaches

- Move to prismatic designs to increase specific energy and energy density
- Tailor size of nanoparticles to increase tap-density
- Move to alternative phosphate systems that have higher energy, while maintaining safety

The Titanate System

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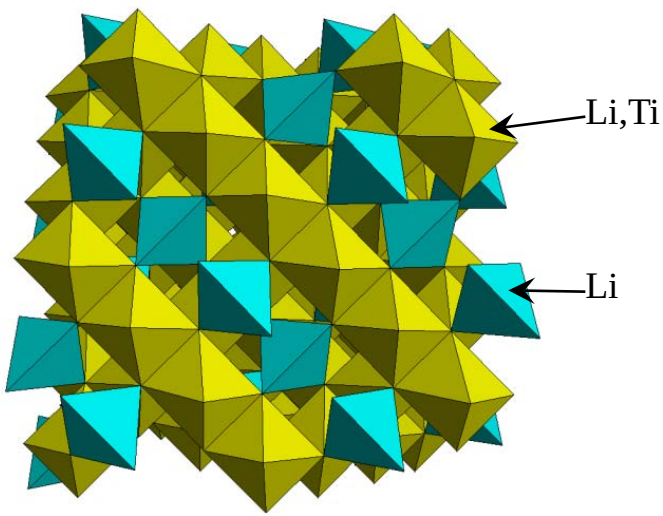

$Li_4Ti_5O_{12}$ Anode-based System

- High anode voltage (1.5V vs. 0.1V for graphite) improves safety
- However, low cell voltage (2.4V) results in significantly lower energy
- Anode capable of fast-charging
  - May compensate for low energy

Chemistry could have difficulty meeting energy requirements for PHEV-40

Approaches

- Couple with high-voltage cathodes to improve energy
  - Require development of high-voltage electrolytes

Accomplishments

- More than a decade of R&D efforts have brought lithium-ion batteries into the auto market.
  - Mercedes/Benz S400 hybrids – nickelate technology
  - Chevy Volt and Nissan Leaf – manganese spinel technology
  - Honda PHEVs and EVs – manganese spinel technology
  - Ford Focus Electric (2011) – manganese spinel technology

- Lithium-ion batteries are also being considered for electric grid stabilization
  - Specifically, lithium iron phosphate and titanate batteries (2 MW/ ~ 250 kWh units) are being demonstrated for use in frequency regulation
  - In the future, lithium-ion batteries are good candidates for small-scale distributed energy storage as well

Advantages of Using Mn-Spinel

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- Despite the lower capacity of Mn-spinel as compared to other cathode materials, there are several advantages that justify this trade-off:
  - Relatively more stable, mature technology, and failure modes are well understood and controlled
  - Mostly Mn-based material → low cost
  - Operating at high voltage → potentially fewer cells
  - High-power performance → good selling point
  - Pouch design offers several advantages:
    - Significant reduction of part count per cell
    - Improved system energy densities (thin and light)
    - Less demand for thermal management
    - Improved safety (tend to fail gracefully)
  - Suppliers (LG-Chem, AESC [Nissan/NEC], Blue Energy) are experienced and deep-pocketed battery manufacturers

Challenges

- Battery life is yet to be demonstrated and cost needs to be reduced by a factor of 3
  - Lack of field demonstration and data
  - Battery capacity is normally oversized for 1st generation vehicles
    - Chevy Volt is designed with a 16 kWh battery for 8 kWh of usable energy
- Performance of advanced batteries still falls short of EV goals set forth in 1992: 200 Wh/kg and 300 Wh/L at $230/kWh
- Development of systems with much higher energy densities, such as lithium-metal polymer and lithium-sulfur, are still elusive

Issues with All Lithium-ion Chemistries

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Durability: Increasing available energy reduces the life for most chemistries. Impact of HEV/PHEV cycles is unknown.

Approaches

- Investigate failure mechanisms and develop methods to mitigate them
- Protect the electrode/electrolyte interface using coatings and additives that form stable surface films
- Develop new and inherently stable electrolytes

Cost: ~$1,000/kWh. Needs to be reduced by a factor of 2–3.

Approaches

- Focus on optimizing cell design and system packaging to improve energy densities
- Recovery Act funding in support of domestic manufacturing of lithium-ion batteries will lead to a more competitive cost

Mid-Term R&D: Advanced Lithium-ion

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Issues

- Advanced Li-rich, layered-cathode (MnO_3/Mn_2O_4) provides capacity up to 220 mAh/g at potentials much greater than 4.3V; however, presently available electrolytes are not stable above 4.3V.
- Sn and Si alloys have capacities in excess of 1,000 mAh/g, but undergo significant volume change with large irreversible capacity loss.

Approaches

- Current research is focused on controlling the volume expansion of these alloys and developing electrolytes/additives and surface coatings to ensure stability above 5V.

Provided these issues are resolved, an advanced lithium-ion battery operating at 150 Wh/kg is possible.

Long-Term R&D: Beyond Li-ion (1)

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- Due to inherent lithium-ion performance limits, next-generation Li-metal anodes and high-capacity cathodes are being investigated.
- Lithium metal as the anode material has a theoretical capacity of 3,862 mAh/g.

Li-metal Anode Issues

- Dendrite formation resulting in loss of lithium and possible safety hazard.
- Solvent reduction resulting in loss of lithium and electrolyte.

Approaches

- Decouple lithium metal from cathode chemistry with ceramic-polymer stabilization layers.
  - Block copolymers and single-ion conducting ceramics are promising barrier layers.

Protection of lithium metal surface from side reactions is critical for batteries beyond Li-ion.

Long-Term R&D: Beyond Li-ion (2)

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- Non-intercalation, low-cost, and high-capacity cathode materials
  - LiV_3O_8: 280 mAh/g, V_2O_5: 441 mAh/g, and others

A thin-film, Li-metal polymer battery may lower production cost

  - Sulfur: 1,675 mAh/g

Sulfur cathode overall reaction: $16Li + S_8 \leftrightarrow 8Li_2S$

Theoretical energy density: 2,550 Wh/kg

Practical energy density: 500 – 650 Wh/kg

Sulfur Cathode Issues

- Dissolution of lithium polysulfides in the electrolyte → high self-discharge
- Insoluble sulfur species such as Li_2S_2 and Li_2S → electrode passivation

Approaches

- Confining the polysulfides in nano-channels can decrease their migration.
- Development of new solvents and additives that can change the solubility of polysulfides.

Long-Term R&D: Beyond Li-ion (3)

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- The "holy-grail" for a low-cost and high-capacity energy storage system is a Li/air battery with theoretical specific energy of ~11,000 Wh/kg (without O_2) and 3,505 Wh/kg (with O_2).
- Overall reaction: $2Li + O_2 \leftrightarrow Li_2O_2$

Air Cathode Issues

- Development of a bifunctional air cathode that reversibly converts oxygen to Li_2O_2 is critical.
- Reaction products may be a mixture of Li_2O_2 and Li_2O that passivates the air electrode and blocks the diffusion of O_2, leading to a low discharge rate.
- Charge process has very large over-voltage, resulting in a system with very poor energy efficiency.
- An oxygen/moisture separation membrane is required for long-term operation in ambient environment.

Revolutionary advances for overcoming the significant issues above will be the subject of future R&D.

Research Focus

- Concentrated search for high-capacity cathode materials including high voltage spinel.
- Develop new solvents and salts that allow for high-voltage electrolytes with stable electrochemical voltage windows up to 5 Volts.
- Develop advanced tin and silicon alloys with low irreversible loss and stable cycle life at capacity under 1,000 mAh/g.
- Initiate a new Integrated Laboratory/Industry Research Program
  - Explore the feasibility of pre-lithiated high capacity anodes.
  - Explore novel ideas to address the dendrite barrier in using lithium metal.

Thank you for your attention!