Keeping up with the increasing demands for electrochemical energy storage

2015
Top of the learning curve: optimize current technology

2020
Frontiers of Li-ion technology: new materials

2030
Frontiers of energy storage: beyond Li-ion technology
Quantifying the demand for energy storage

**Power**: Watts = current · voltage

**Energy**: Watts · time = Watt · hours

**Specific Energy**: Wh/kg

**Energy Density**: Wh/liter
Current and future energy storage tech

- Batteries
  - Wh/kg
  - Wh/kg
- Thermoelectrics
- Lithium
  - Wh/kg
  - Wh/kg
- Beyond Lithium
  - Li-ion
  - Li-sulfur
  - Li-air
  - Na, Mg, ?

Safety

Courtesy S. Whittingham
Is there enough lithium?

Enough Li for:
• $10^{12}$ HEV
• $10^{11}$ PHEV
• $10^{11}$ BEV

Courtesy of Ted Miller
Current Li-ion: Nuts & Bolts


Frontiers of Electrochemical Energy Storage


Frontiers of Li-ion technology: new materials
(> 200km range, <$150/kWh)

Electrode capacity: how much Li/mass (mAh/g)

Graphite anode = \( \sim 330 \text{ mAh/g} \) (theoretical = 372 mAh/g)
Si anode = \( \sim 1000 \text{ mAh/g} \) (theoretical > 4000 mAh/g)

\[ \text{Cui et al. (2012) Nature nanotechnology letters.} \]

+ Si is abundant & cheap
+ Increase in capacity
+ Low voltage

?) Cycle life; 300% volume change
?) Cost of manufacturing nano Si
The Periodic Table of the Elements

Theoretical
Li$_1$MO$_2$ $\sim$ 280 mAh/g

Practical
Li$_{0.5}$MO$_2$ $\sim$ 140 mAh/g
Cathode: maximize Li utilization

Li$_2$MnO$_3$-stabilized Li$_1$MO$_2$: ~ 286 mAh/g

Layered cathodes: Thackeray et al/Argonne National Lab.

+ Doubling of capacity
+ No new elements

? Slow kinetic/power
? Crystallographic stability
? Charged @ > 4.5V: no electrolyte
Impact of new materials

Frontiers of energy storage: beyond Li-ion
(> 400km range, <$150/kWh)

++ Li metal 3375 mAh/g (10X over graphite)
++ Li-Sulfur 2,500 Wh/kg Theoretical
++ Li-O₂ 3,500 Wh/kg Theoretical

Air (O₂), sulfur?
Li-O$_2$ dry (>500 km range, < $150$ kWh)

+++) High Specific Energy
+)
O$_2$ is ubiquitous

?) Must separate O$_2$
?) Kinetics/Power/Hysteresis
?) Li metal anode stability

2030 **Li-Sulfur** (>400 km range, < $150 \text{kWh})

+ High specific energy
+ Cheap, abundant
+ Light
+ 2 Li for every S (Li$_2$S)

?) cycling
?) Sulfur conductivity
?) Li metal anode stability


Beyond Li-ion requires new electrolyte

Beyond Li-ion

Lithium

Air, sulfur?

Solid electrolyte
Sakamoto Group: **Engineering nothing**

**Atomic scale design**

- **Atoms**
  - Å
  - Å-2nm
  - 2-50nm
  - >50nm

**Gas molecules**
- Micro pores facilitate ion transport in ceramic electrolytes

**Solvated ions & proteins**

**Macro scale phenomena**
- Li-ion “lung”: Li-ions move from large linear to small orthogonal capillaries

**Micro pores impede gas transport**

**Meso pores connect molecular-scale phenomena to the macro-scale**

**Meso pores deliver proteins to linear macro pores that guide nerves**
Ceramic electrolyte: Li$_7$La$_3$Zr$_2$O$_{12}$ garnet

**Advantages**

- Li Conductivity similar to liquid electrolytes @ 298K
- First bulk, oxide electrolyte stable against Li
- Stable up to 9 V
- Can be synthesized/processed in ambient air


Xu *et al.* PHYSICAL REVIEW B 85, 052301 (2012).

Towards cycling Li metal anodes

Solid-state, All Ceramic Batteries

+) No organics to degrade
+) Synthesized and fabricated in air
+) Significant reduction in packaging
+) Non-flammable
+) Gets better with increasing temp

?) Interface integrity
?) Kinetics/Power
?) Thermomechanical stresses

Weppner et al. (1999)


Sakamoto group (2011)
Conclusions

1. Energy density (Wh/kg) must increase by ~4X
2. Cost ($kWh) must decrease by ~4X
3. 2020 goal: integrate new materials into current Li-ion
4. 2030 goal: must go beyond Li-ion requiring:
   - Li metal anodes
   - New cathodes
     - Li-O$_2$
     - Li-Sulfur
5. Opportunities
   - New solid and liquid electrolytes
   - Electrode and battery designs
   - Additive manufacturing
   - Predictive analysis
   - Packaging