Advances and Challenges with Rechargeable Lithium-Air Batteries
What do we want from a battery?

<table>
<thead>
<tr>
<th></th>
<th>energy,</th>
<th>power,</th>
<th>cycles,</th>
<th>safety</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-ion</td>
<td>✔️</td>
<td>✔️</td>
<td>1000</td>
<td>✔️</td>
</tr>
<tr>
<td>Li-air</td>
<td>✔️</td>
<td>✔️</td>
<td>&lt; 50</td>
<td>✔️</td>
</tr>
</tbody>
</table>
Source: Li-ion: Volkswagen, Li-air: 2010: PNNL, 2019: Samsung lab prototype, mature Li-air and gasoline: own work
Doing less with more

Lithium air doesn’t need any cobalt, rare or conflict materials.
Outline

• Similarities and differences between Li-ion, Li-air and fuel cells.
• Details of Li-air batteries
• Challenges in bringing Li-air to commercialization
• Successes in bringing this technology closer to market.
Li ion, Li air, fuel cell

Sealed lithium ion battery

Li ions

Discharge

Lithium air battery

Oxygen in air

lithium metal
lithium peroxide

Fuel cell

Fuel

water vapor

Oxygen in air

charge

charger

+ e-

- +

chg

Oxygen released
Rechargeable lithium air batteries - basic science

Li$^+$ + e$^-$ $\leftrightarrow$ Li

O$_2$ + 2 Li$^+$ + 2e$^-$ $\leftrightarrow$ Li$_2$O$_2$

E° 3.6V vs Li$^+$/Li

Oxygen reduction improved with catalyst, cell potential ~2.2V

Oxidize Li$_2$O$_2$ - don’t oxidize anything else.

Electrolyte can be aprotic/organic, solid or both

Li electrode - plate Li, avoid dendrites

Oxygen in air

CO$_2$

H$_2$O

Oxygen comes out

Charge

Discharge
Details of the air electrode: land/sea/air

- Land: porous, conductive electrode with catalyst particles
- Sea: electrolyte to catalyst sites (wet but not flooded)
- Air: gas access to catalyst sites throughout the volume of the electrode

The ideal gas diffusion electrode has a triple point of gas, electronic and ionic access throughout its volume
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• Successes in bringing this technology closer to market.
Air electrode reactions

Discharge

Charge

Graphite catalyzes unwanted side reactions

Adapted from Bruce et. al., dx.doi.org/10.1021/ja310258x
Li-air: historical challenges

• Li metal electrodes are a challenge in any system.
• Fuel cell gas diffusion electrodes? Tried and true.
• Li-air gas diffusion electrodes? Brave new world.
• Exclusion of carbon dioxide and water vapor.
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• **Successes in bringing this technology closer to market.**
Towards a complete device

- fail early, fail often
- cut down on excess cell materials

Pacific Northwest National Laboratory (2010)

Zhang et. al., doi:10.1016/j.jpowsour.2010.01.022

Samsung

Lee et al., High-Energy-Density Li-O₂ Battery at Cell Scale with Folded Cell Structure, Joule (2018), https://doi.org/10.1016/j.joule.2018.11.016

800Wh/L, 1200 Wh/kg
Not so fast!

- Li-air recharge chews up electrodes, solvents, electrolytes
- Some organics, solid electrolytes are OK
- Carbon black, CNTs, graphene electrodes don’t work
- Noble metals, carbides don’t stop side reactions

“It also requires the development of new materials that allow us to leverage desirable reactions and minimize or avoid undesirable ones…”

- Reuben Maciel Filho, director, New Energy Innovation Center, São Paulo, Brazil
Robust carbon

- Doped diamond-like carbon - (DLC)
- unparalleled electrochemical durability
- used for electrochemical generation of ozone and fluorine
- low catalytic activity - stays out of the way

Coulombic's - US Patent 9,831,503
DLC- many types

from J. Robertson, Materials Science and Engineering R 37 (2002) 129-281
DLC inhibits parasitic reactions

Typical recharge range for nonaqueous Li-air

Side reactions—lower is better

Cyclic voltammograms, 1M LiNO₃, TEGDME in dry air, 24C. Scan rate 10 mV/s
In summary

• The pieces for Li-air are coming together

• It’s not easy, but it’s quite possible

• More reasons to be optimistic now than ever
Thank you

Questions?