Development of Li-Air Batteries

Jason Zhang

December 2010

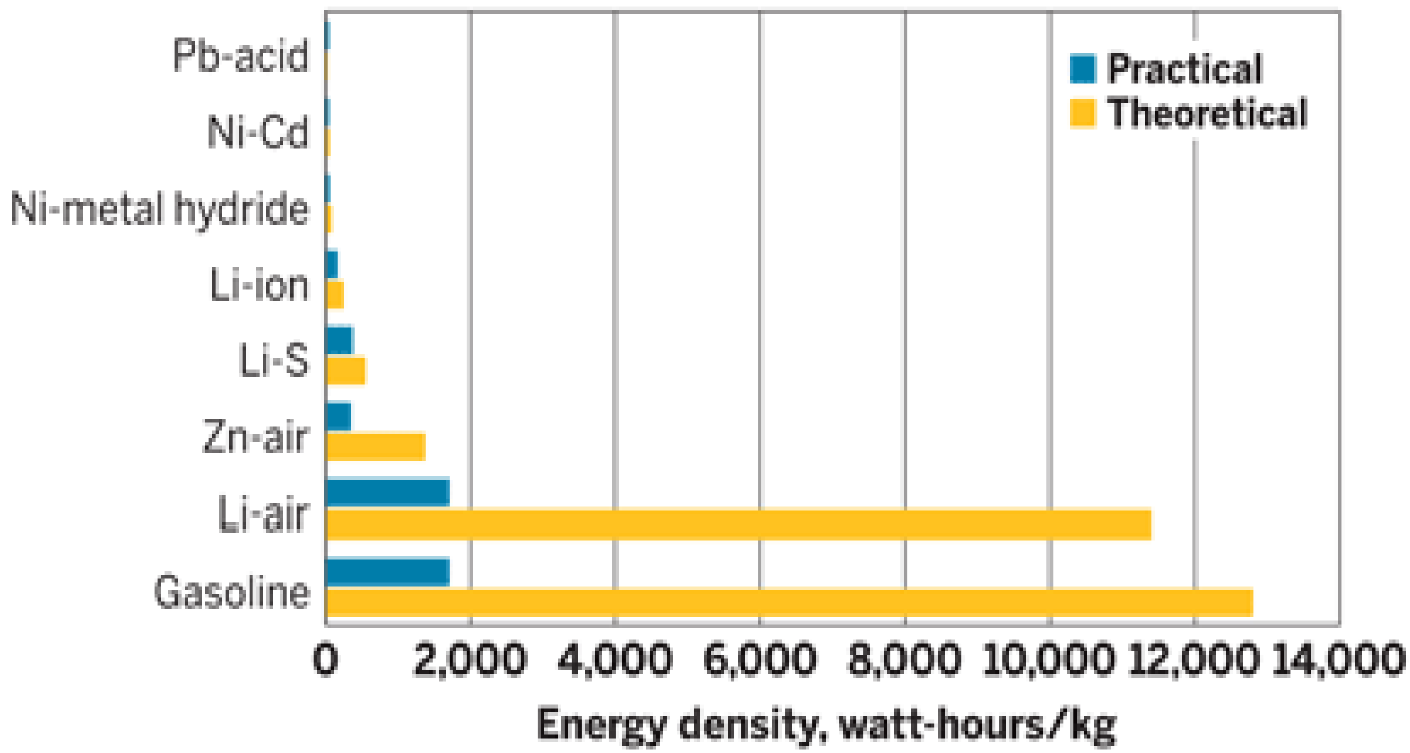
Pacific Northwest
NATIONAL LABORATORY

Outline

1. Advantages and Challenges of Li-air Batteries
2. Development of Primary Li-air Batteries
3. Rechargeable Mechanism in Li-air Batteries
4. Summary

Challenges for Extremely High Energy Batteries:

Li-ion batteries are currently among the most attractive technologies for microelectronic, transportation and defense, but Li-S, and Li-air batteries have the potential to increase the specific energy density by orders of magnitudes



Technologies beyond Li-ion require significant improvement in electrode and electrolyte materials, cell design and fundamental understanding to solve the poor reversibility and reliability, low power and high cost problems.

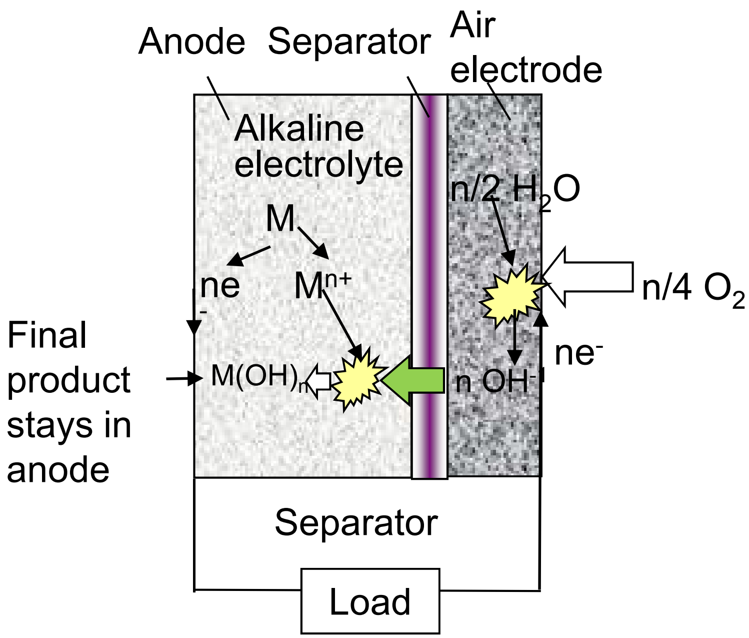
1. Advantages and Challenges of Li-air Batteries

	Nonaqueous Electrolyte Based Li-air Batteries	Aqueous Electrolyte Based Li-air Batteries
Reaction	$2Li + O_2 \rightarrow Li_2O_2$	$4Li + O_2 + 2H_2O \rightarrow 4Li(OH)$
	or $4Li + O2 \rightarrow 2Li_2O$	
Separator	Polymer/glass fiber	LISICON glass
Theoretical specific energy if only Li included (Wh/kg)*	11,238/11,972	~12,000
Theoretical specific energy if Li/carbon/electrolyte are included (Wh/kg)**	3031	1436
Practical specific energy for complete Li-air batteries	?	?

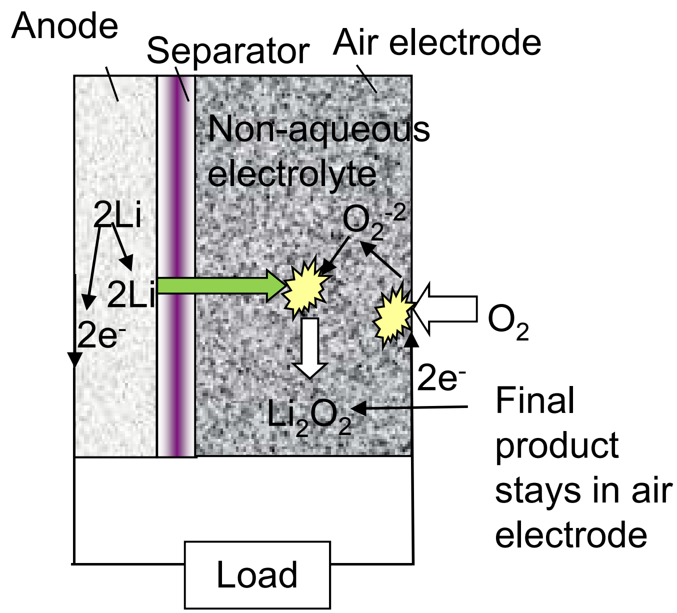
*Abraham, KM and Z Jiang.1996. *Journal of the Electrochemical Society* 143-1, 1 (1996)

** Zheng et al. *Journal of the Electrochemical Society* 155 (6), A432 (2008)

Reaction Processes in Metal-Air Batteries



$M + n/4\ O_2 + n/2\ H_2O \rightarrow M(OH)_n$



$2Li + O_2 \rightarrow Li_2O_2$

(a) Aqueous based electrolyte, where M represents metals (Zn, Al, Mg, Fe, Ca etc.). The reaction products $(M(OH)_n)$ are accumulated in the anode.

(b) Lithium-air battery based on nonaqueous electrolyte. The reaction products $(M(OH)_n)$ are accumulated in the anode.

Challenges in Li-air Batteries

Primary:

1. Improve the specific energy of air electrode
2. Improve the specific energy of full cell.
3. Increase the ambient operation time.
4. Increase the power rate.

Rechargeable:

1. Find stable systems (aqueous or non-aqueous) which are stable in oxygen environment.
2. Understand reversible mechanism of Li-O_2 reaction.
3. Develop an oxygen selective membrane.
4. Prevent Li dendrite growth.

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

2. Development of Primary Li-air Batteries

2.1 Air Electrode Simulation

2.2 Air Electrode Optimization

2.3 Electrolyte Selection

2.4 Li-air Batteries with O_2 Diffusion Membranes

2. Development of Primary Li-air Batteries

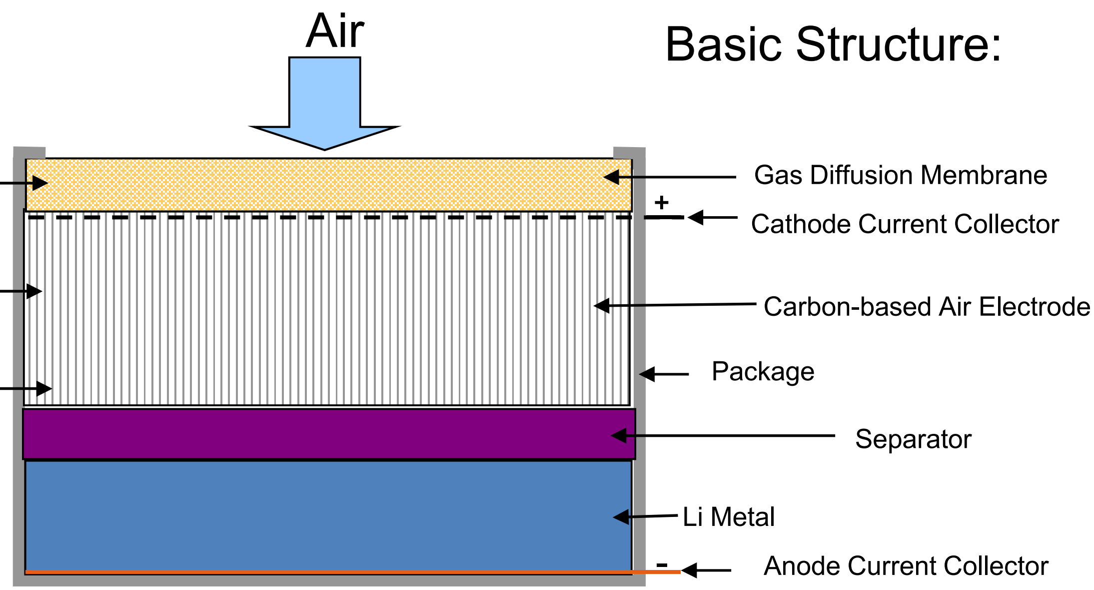
PNNL Approaches:

O_2 Diffusion Membrane/ moisture & electrolyte barrier

Air Stable Electrolyte

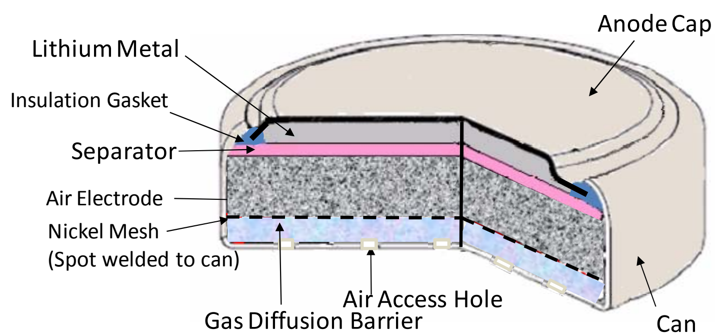
Nanostructured Carbon with High Mesoporous Volume

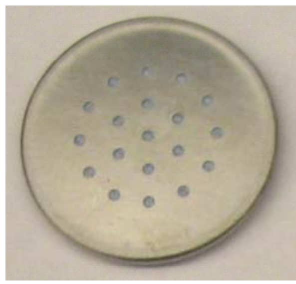
Basic Structure:



Initial cell configuration:
Type 2325 coin cells

Test in dry box (RH ~ 1%)

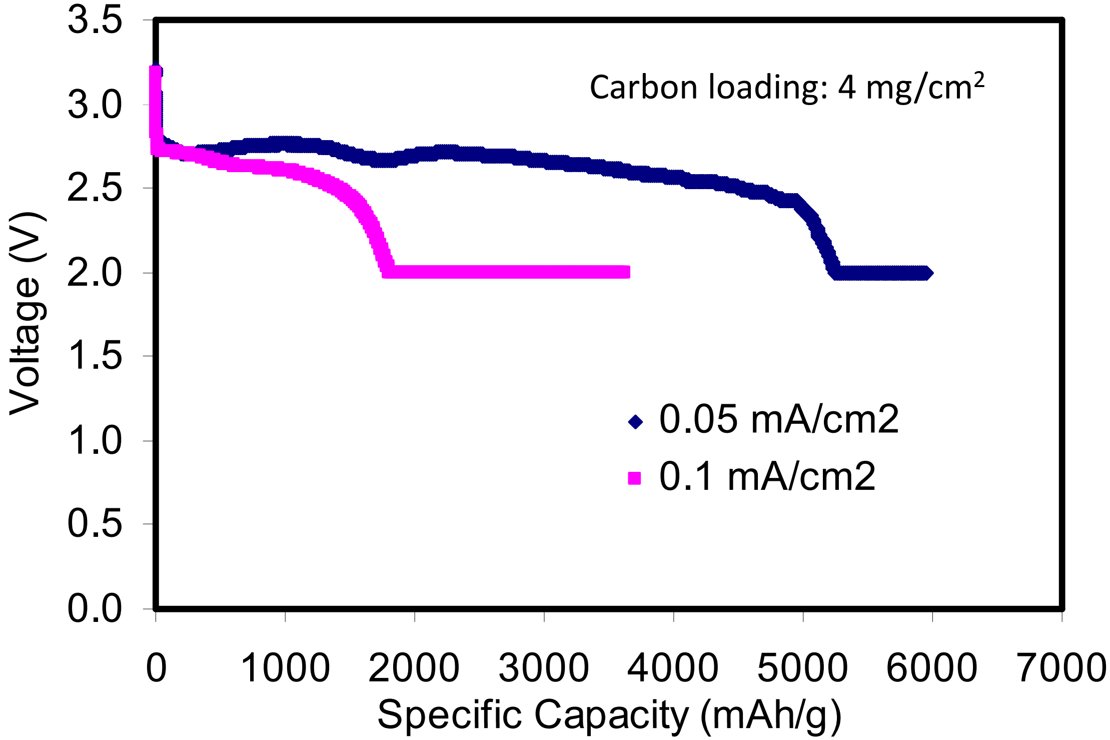




Pacific Northwest
NATIONAL LABORATORY

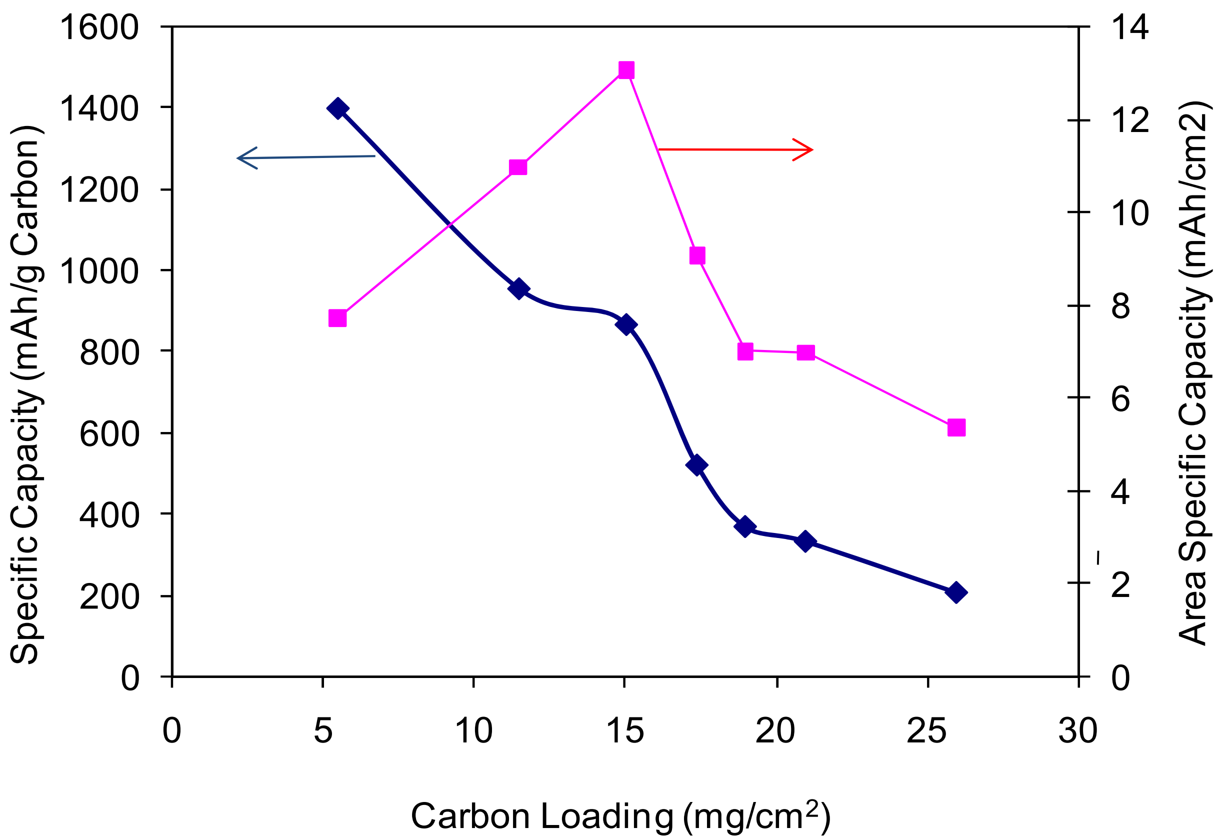
Proudly Operated by **Battelle** *Since 1965*

Performance of Li-air Pouch Cell in Ambient Environment



- ✓ C-PNL based pouch cell is operated in ambient environment.
- ✓ Specific capacity is doubled for C-PNL compared with KB.
- ✓ Rate performance is also improved.

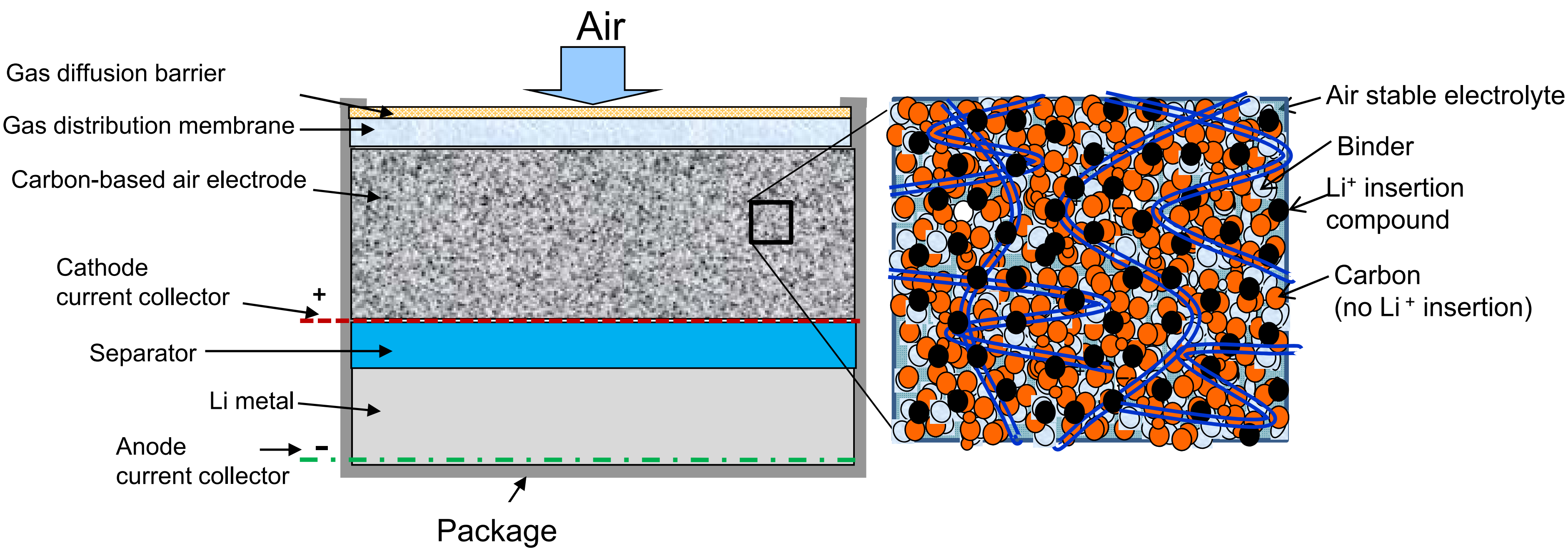
Optimized Area-Specific Capacities



Pacific Northwest NATIONAL LABORATORY

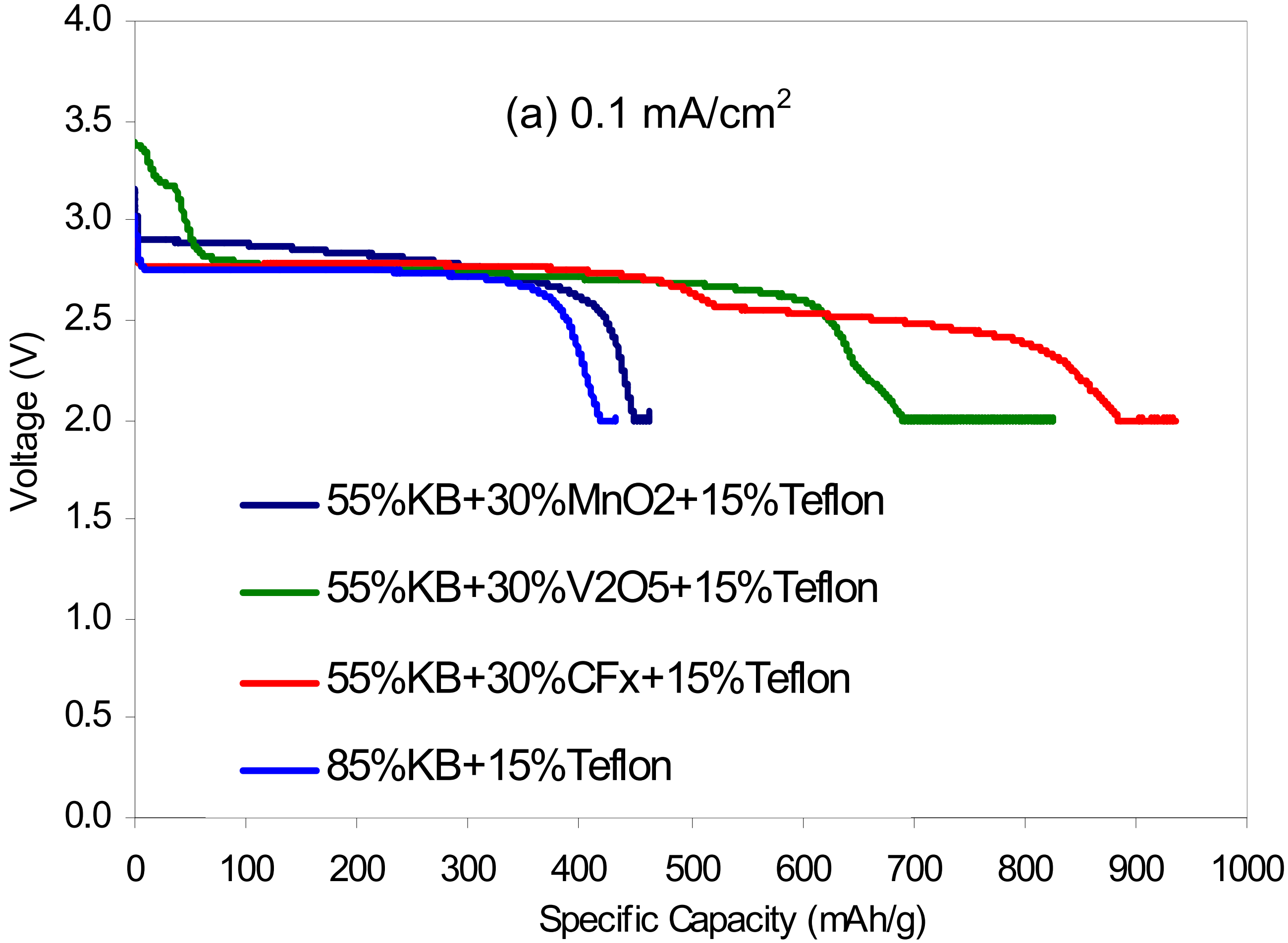
Proudly Operated by **Battelle** *Since 1965*

Hybrid Li-air Battery for High-Rate Operation



- High rate Li^+ insertion compound (< 2.8V) can provide high-rate capability.
- CF_x also reduce electrode blocking.

Comparison of Hybrid Air Electrodes



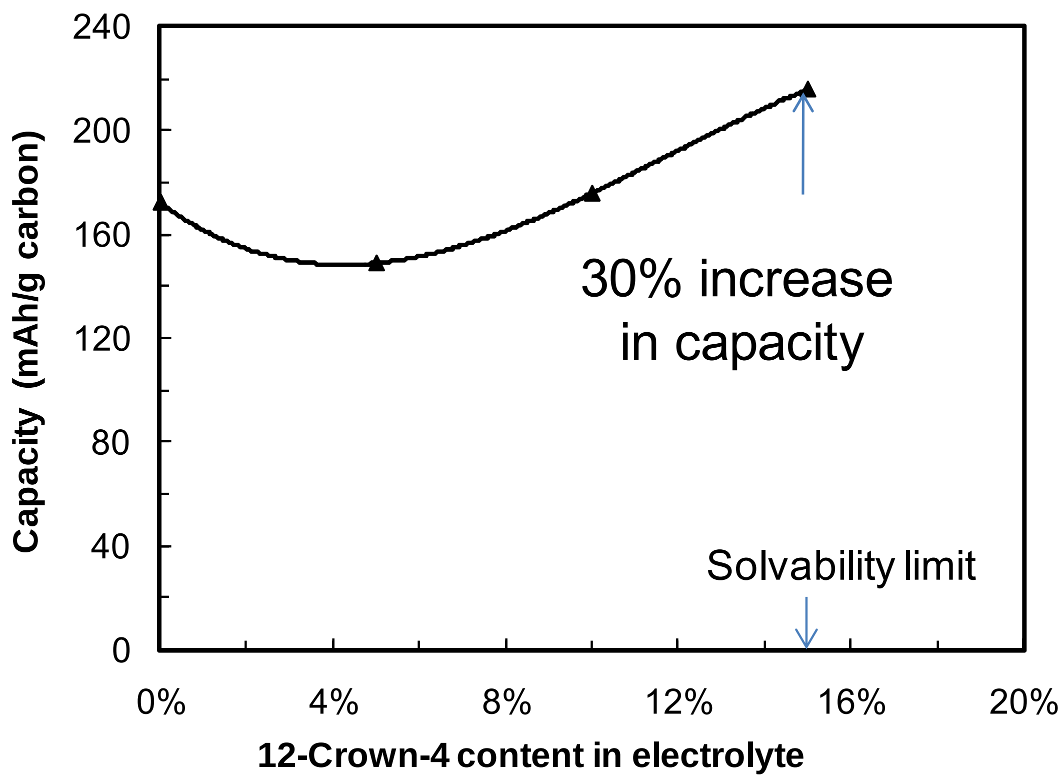
Pacific Northwest NATIONAL LABORATORY

Jie Xiao, Wu Xu, Deyu Wang, and Ji-Guang Zhang, *J. Electrochem. Soc.* 157, A294 (2010).

Proudly Operated by **Battelle** *Since 1965*

Additive Leads to 30% Increase in Capacity

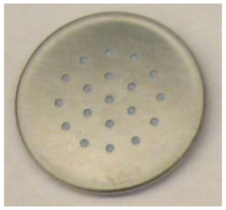
12-crown-4 in 1.0M LiTFSI in PC/EC (1:1 wt)



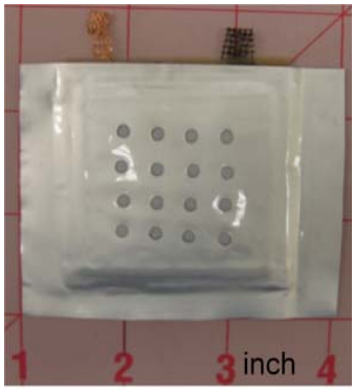
W. Xu, J. Xiao, D. Wang, J. Zhang, and J.-G. Zhang, *Electrochemical and Solid-State Letters,* **13** (4) A48-A51(2010).

Proto-Type Li-air Batteries with O_2 Diffusion Membranes

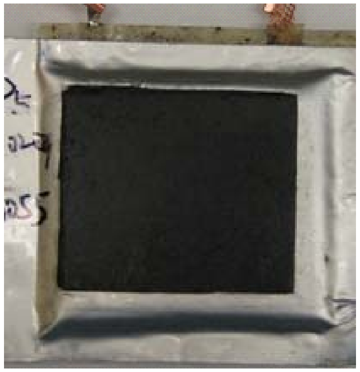
Cell Designs:



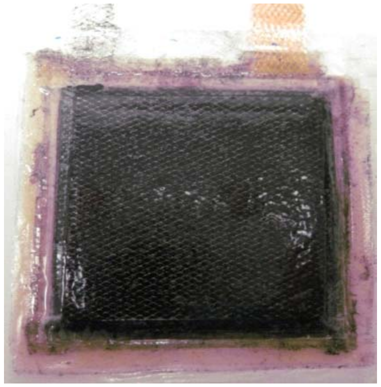
a. G1 cell design. 2325 coin cell. Diameter = 2.3 cm



b. G2 cell design. Single side pouch cell with diffusion holes (4cmx4cm).



c. G3 cell design. Double side pouch cell with low permeability polymer window (4cmx4cm)

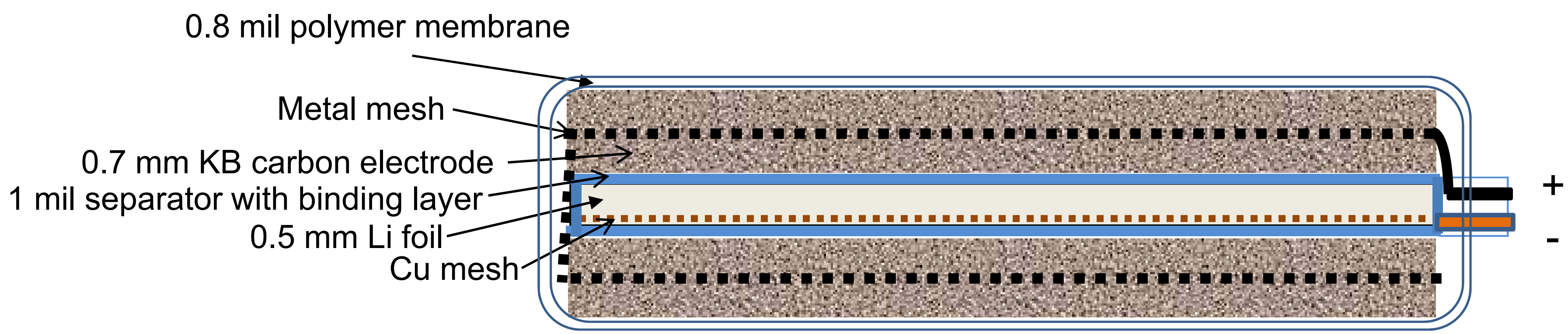


d. G4 cell design. Double side pouch cell with low permeability polymer Window. (4.6cmx4.6cm).

Pacific Northwest
NATIONAL LABORATORY

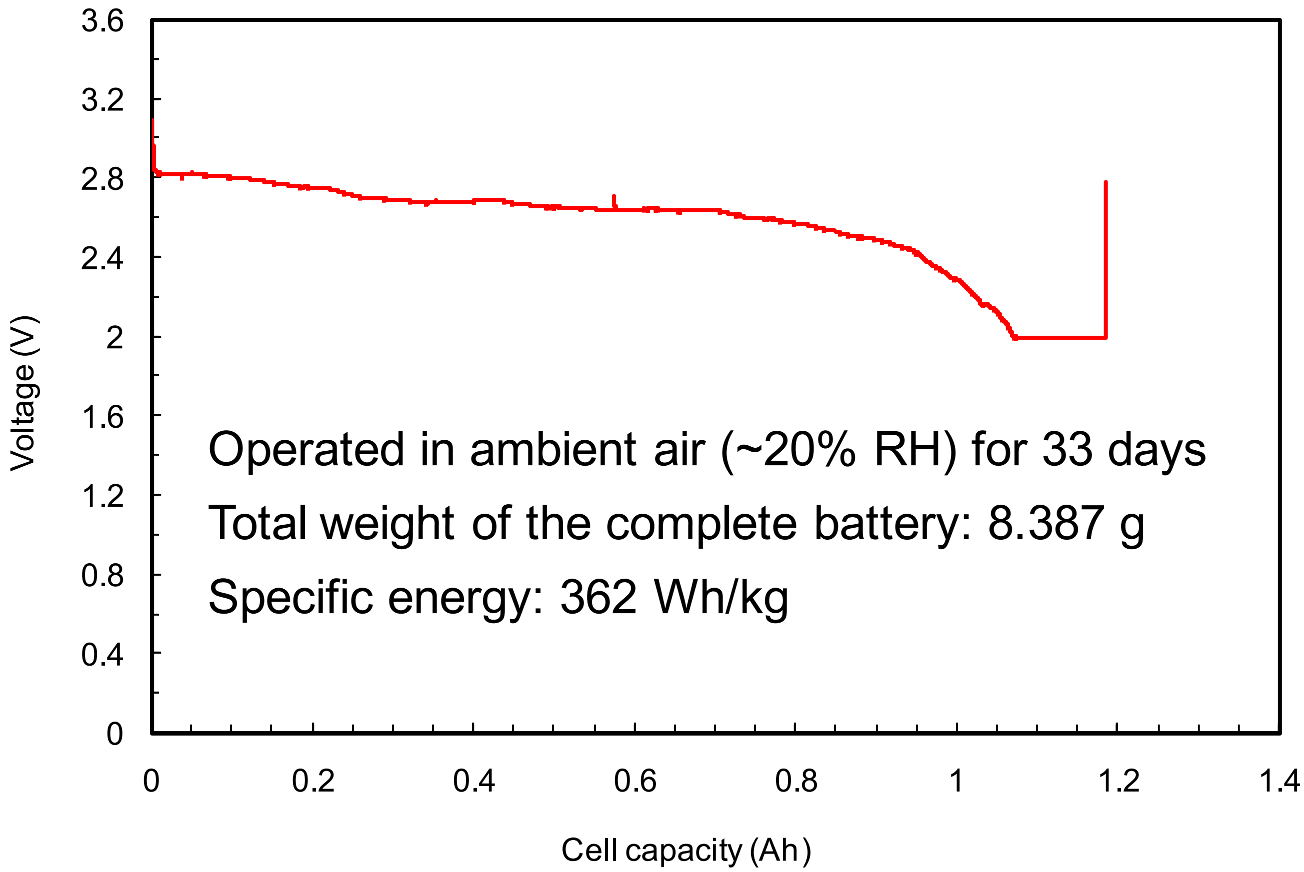
Proudly Operated by **Battelle** *Since 1965*

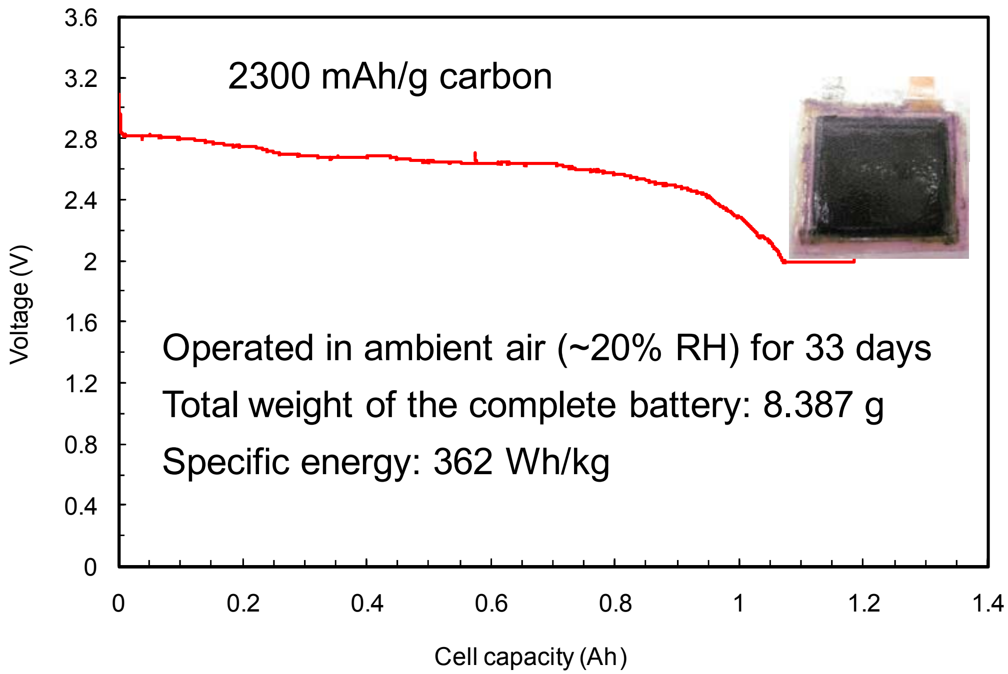
Cell Design with Polymer Diffusion Barrier

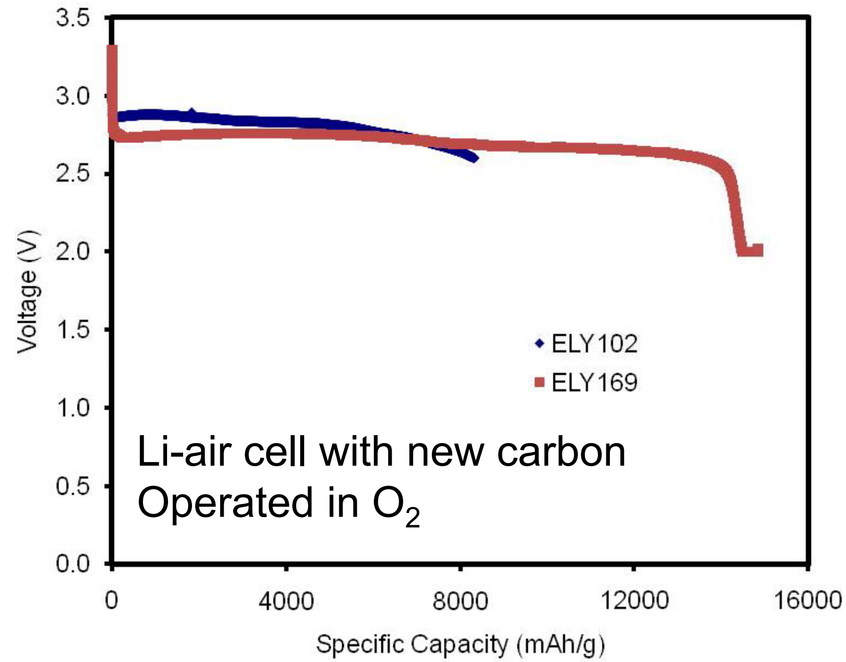


Footprint: 4.6 cm x 4.6 cm; Thickness = 3.8 mm

Discharge Profile of a Li-air Battery with an O_2 Diffusion Membrane







- ✓ Best specific energy for complete Li-air battery operated in ambient
- ✓ New carbon increases capacity to 8000 mAh/g
- ✓ New carbon and new electrolyte further increase the capacity to15,000 mAh/g

4. Summary

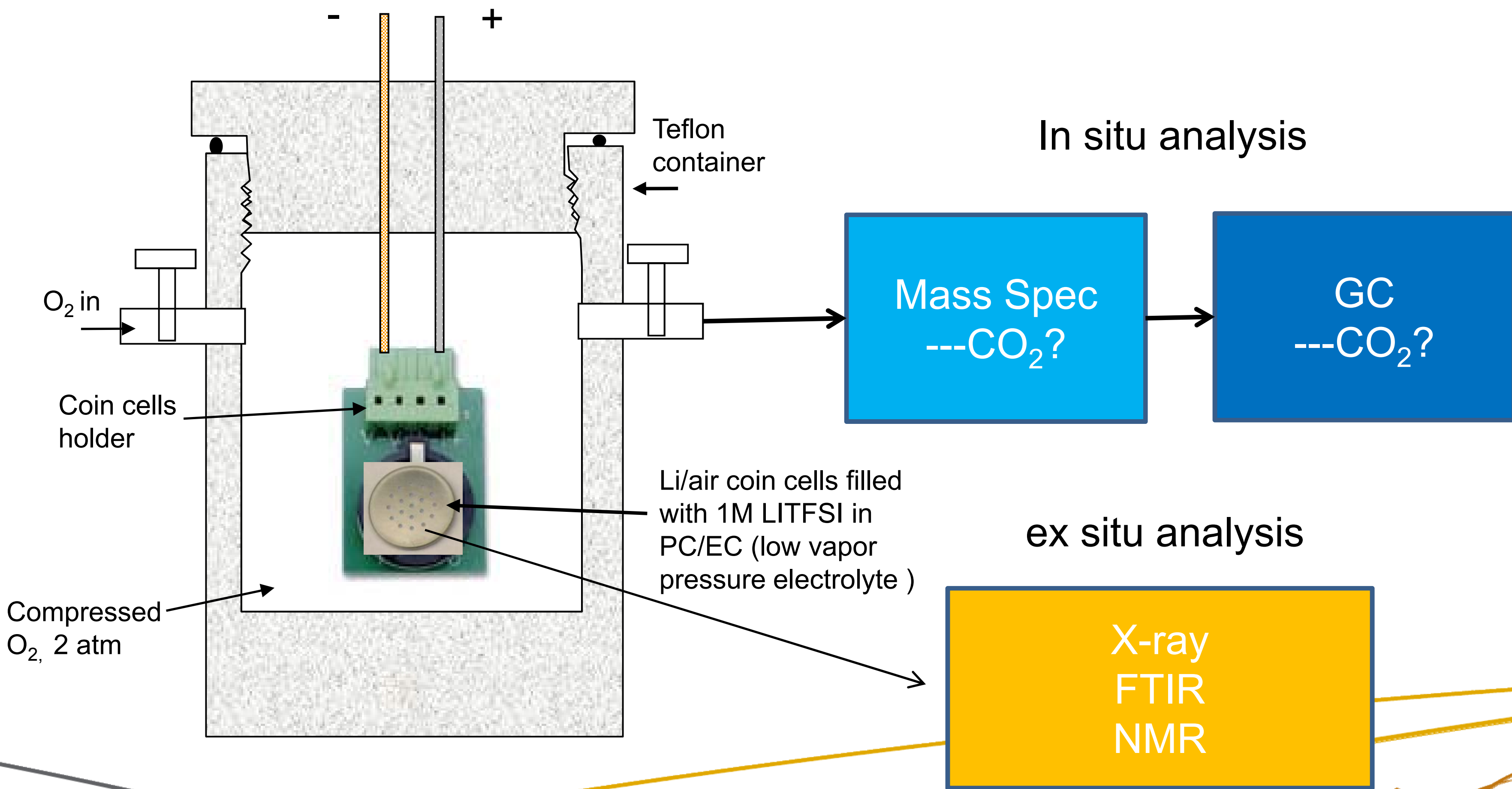
1. Developed an unique package membrane which can also serve as an O_2 diffusion membrane, water barrier, and electrolyte barriers. It enables Li-air batteries to work in ambient air for 33 days.

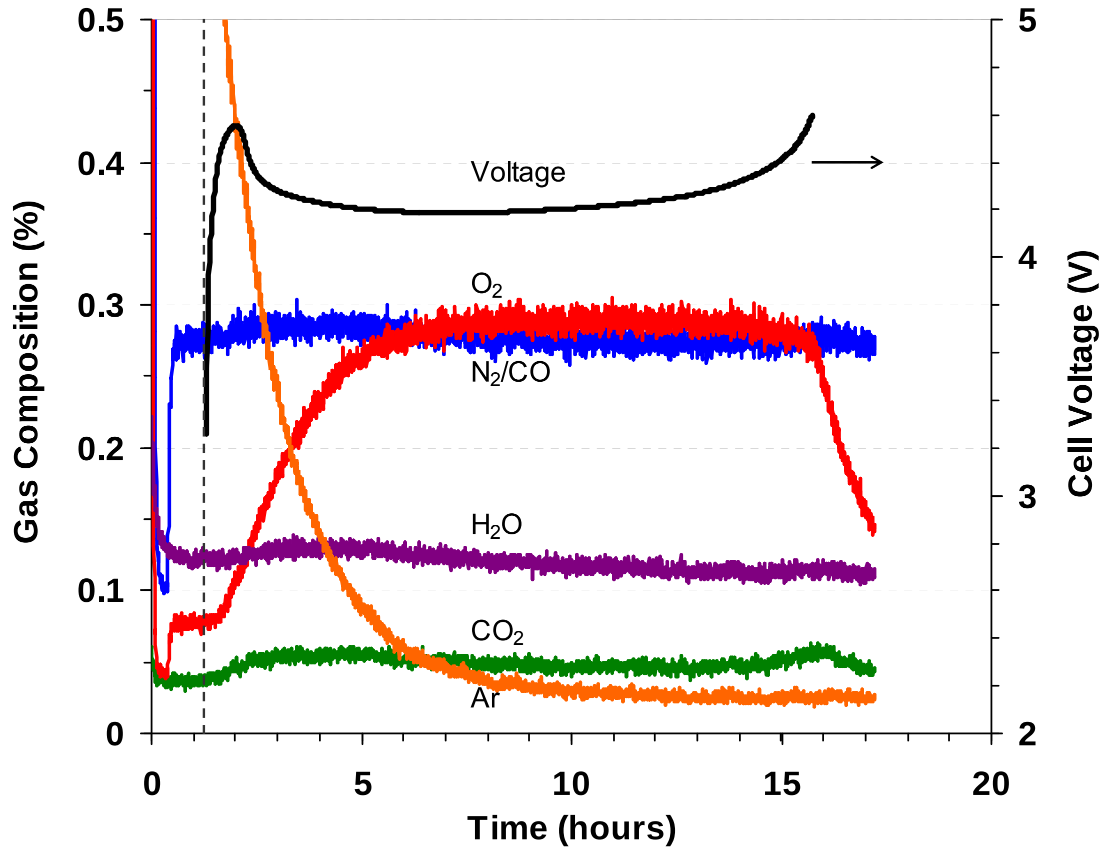
2. Developed Li-air batteries with a specific energy of ~362 Wh/kg for the complete battery.

3. Hybrid air electrode with KB/CF_n can significantly increase the power rate of Li-air batteries.

4. Electrolyte weight dominates battery weight structure. Reducing the electrolyte amount will be the key to further increase the specific energy of Li-air batteries.

2.2 Investigation on the Reaction Products of Li-Air Batteries





85% of Li_2O_2 has been decomposed

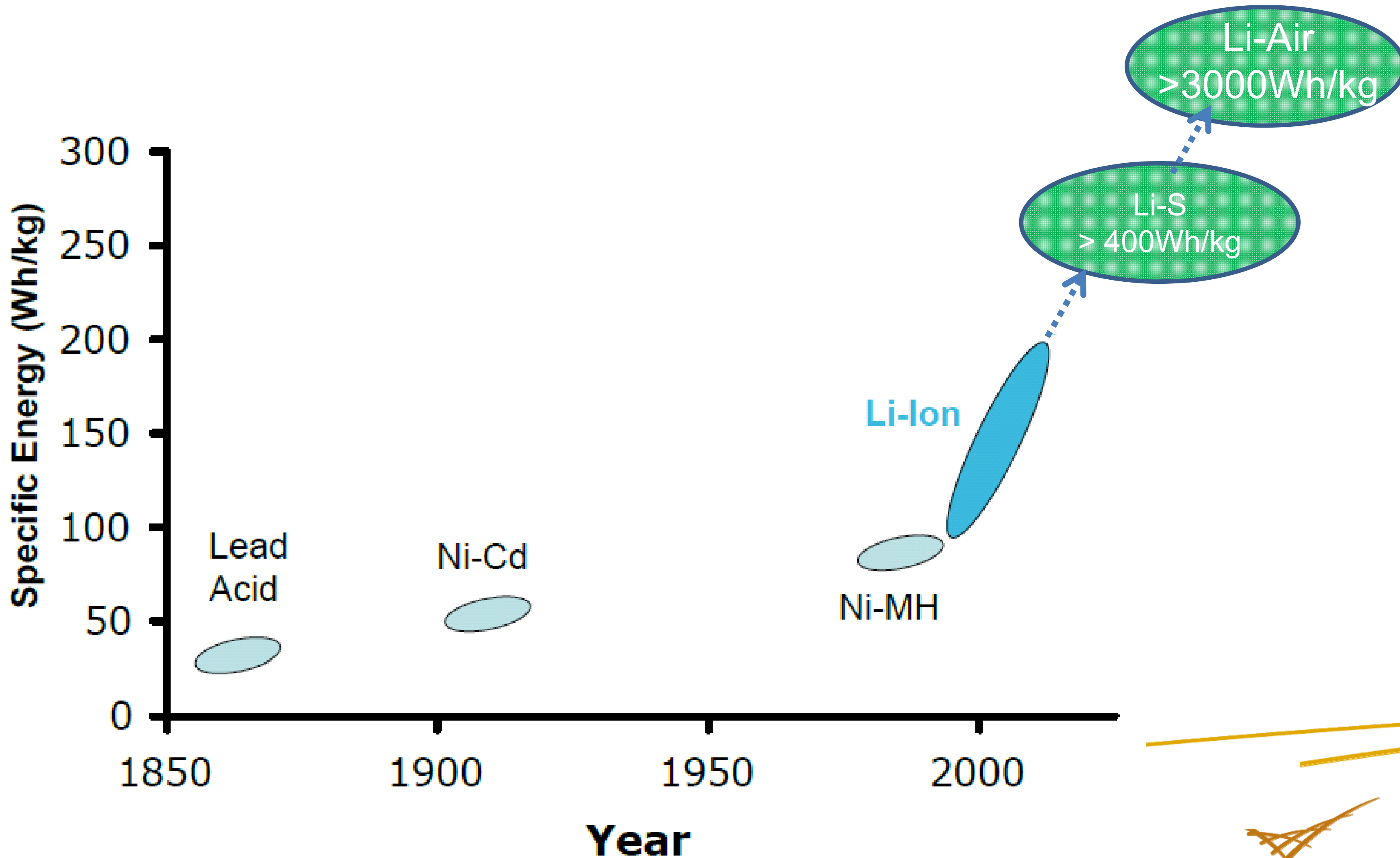
Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Table 1. Electrochemical parameters of metal-oxygen couples

Metal/O_2 Couple	Specific Charge Capacity Based on Metal (Ah/g)	Theoretical Voltage (V)	Practical Voltage (V)	Specific Energy Based on Metal (Wh/kg)	Specific Energy Based on Metal and H_2O (aqueous only) (Wh/kg)	Specific Energy Based on Reaction Products (Wh/kg)
In Nonaqueous Electrolytes						
$Li + \frac{1}{4} O_2 \rightarrow \frac{1}{2} Li_2O$	3.862	2.91	2.80	10,813	10,813	5,023
$Li + \frac{1}{2} O_2 \rightarrow \frac{1}{2} Li_2O_2$	3.862	3.10	3.00	11,586	11,586	3,505
In Aqueous Electrolytes						
$Li + \frac{1}{4} O_2 + \frac{1}{2} H_2O \rightarrow LiOH$[(a)]	3.862	3.45	3.00	11,586	5,044	3,359
$Zn + \frac{1}{2} O_2 \rightarrow ZnO$	0.820	1.65	1.10	902	902	725
$Al + \frac{3}{4} O_2 + 1\frac{1}{2} H_2O \rightarrow Al(OH)_3$	2.980	2.71	1.30	3,874	1,936	1,340
$Mg + \frac{1}{2} O2 + H_2O \rightarrow Mg(OH)_2$	2.205	2.93	1.30	2,867	1,647	1,195
$Fe + \frac{1}{2} O_2 + H_2O \rightarrow Fe(OH)_2$	0.960	1.30	1.00	960	726	597
$Ca + \frac{1}{2} O_2 + H_2O \rightarrow Ca(OH)_2$	1.337	3.12	2.00	2,675	1,846	1,447

(a) In a basic electrolyte with a protected lithium electrode (Visco et al. [5]).



Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*