Challenges and Opportunities in Li-Air Batteries

Jason Zhang

Pacific Northwest National Laboratory
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Outline

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

Practical Li-air Batteries

Li/O_2 Reaction in Different Electrolyte	Theoretical voltage	Theoretical specific energy based on metal	Theoretical specific energy based on reactants (excluding O_2)	Theoretical specific energy based on reaction products	Specific energy based on full reaction
	V	Wh/kg	Wh/kg	Wh/kg	Wh/kg
With precipitation					
$Li + ½ O_2 \leftrightarrow ½ Li_2O_2$	3.10	11972	11972	3622	2790*
$Li + 0.25 O_2 + 1.5 H_2O \leftrightarrow LiOH \cdot H_2O$	3.44	13285	2717	2198	1500
$Li + 0.25O_2 + HCl \leftrightarrow LiCl + 0.5H_2O$	4.27	16491	2637	2227	1607
With no precipitation					
$Li + 0.25 O_2 + 11.14 H_2O \leftrightarrow LiOH + 10.64H_2O$*	3.44	13285	444	428	444
$Li + 0.25O_2 + HCl + 2.29H_2O \leftrightarrow LiCl + 2.79H_2O$*	4.27	16491	1352	1236	1353

*J. P. Zheng et al, *J. Electrochem. Soc.*, 158 (1), A43- A46 (2011).

2. Development of Primary Li-air Batteries

- Air Electrode Optimization
- Electrolyte Selection
- Li-air Batteries with O_2 Diffusion Membranes
- **Graphene Based High Capacity Air Electrode**

Design of Primary Li-air Batteries

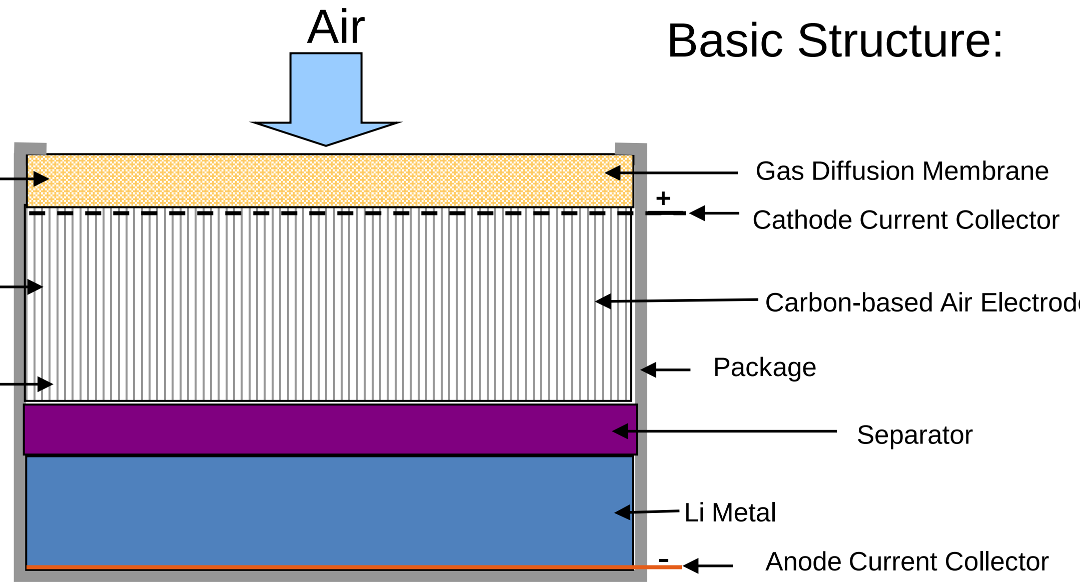
PNNL Approaches:

O_2 Diffusion Membrane/ moisture & electrolyte barrier

Air-Stable Electrolyte

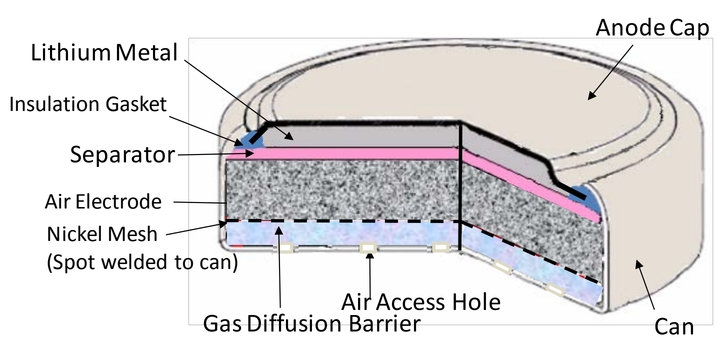
Nanostructured Carbon with High Mesoporous Volume

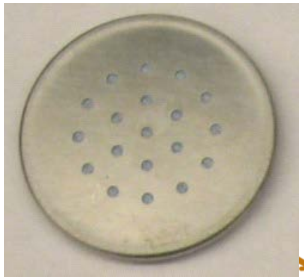
Basic Structure:



Initial cell configuration:
Type 2325 coin cells

Test in dry box (RH ~ 1%)





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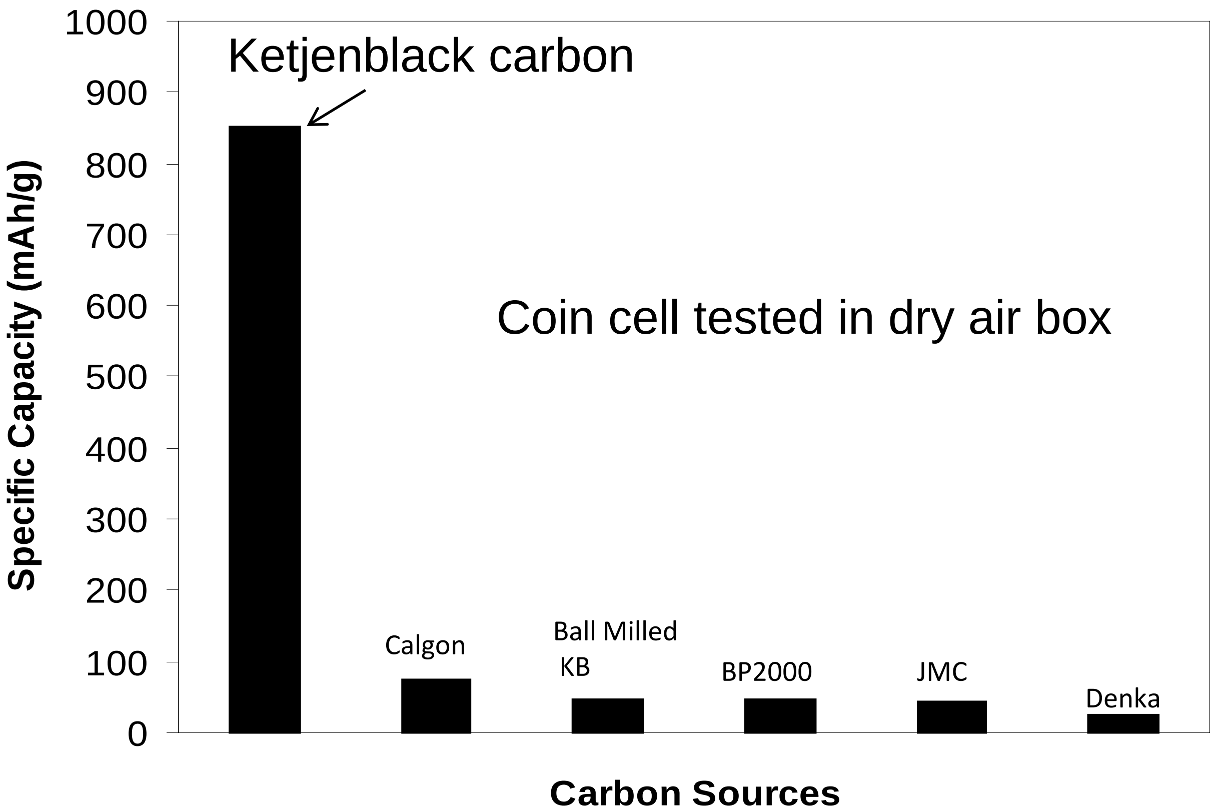
Air Electrode Optimization

Comparison of Carbon Sources



The specific capacity increases with increasing mesopore volume of the carbon used in the air electrode.

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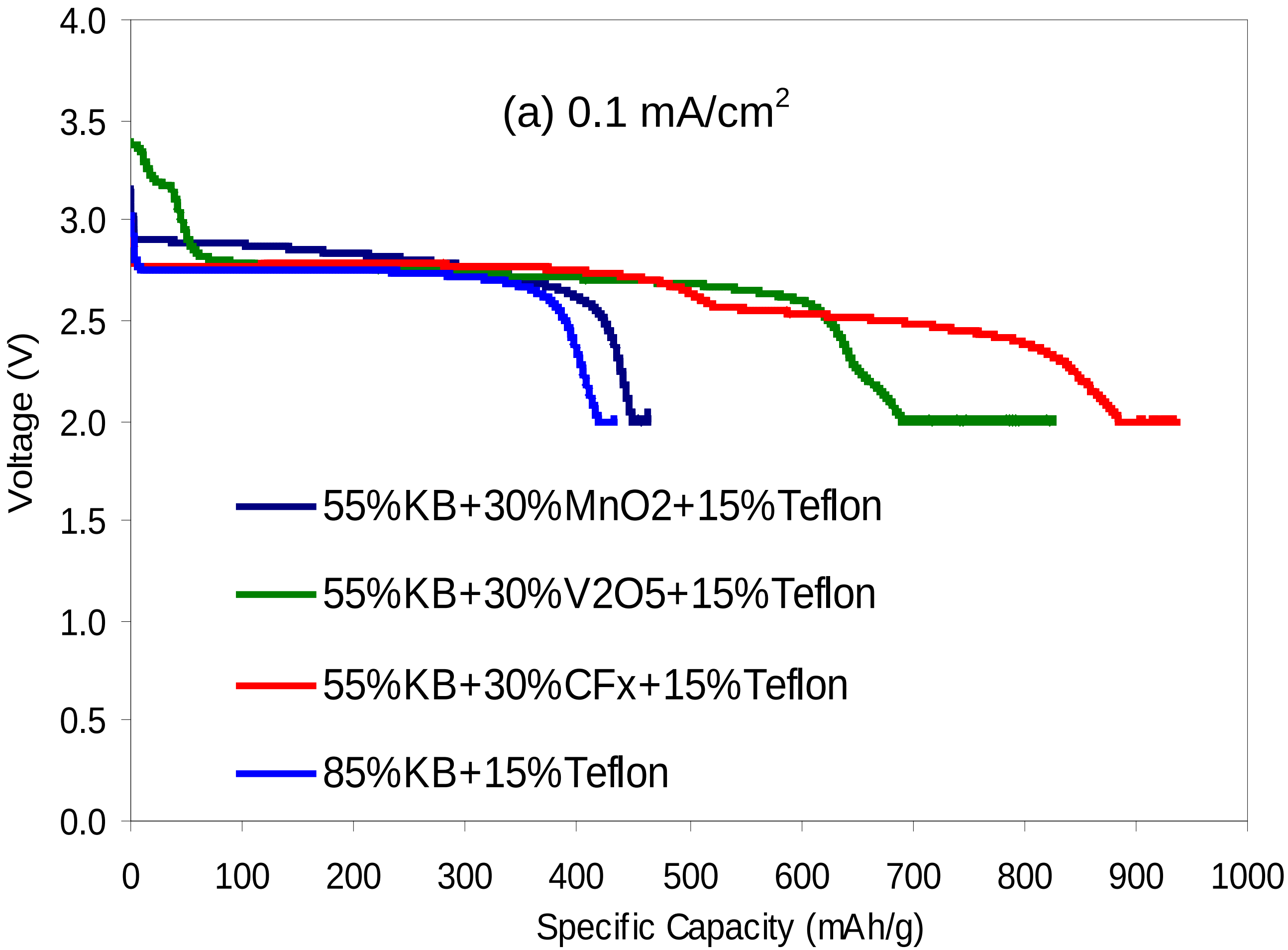
Comparison of Hybrid Air Electrodes



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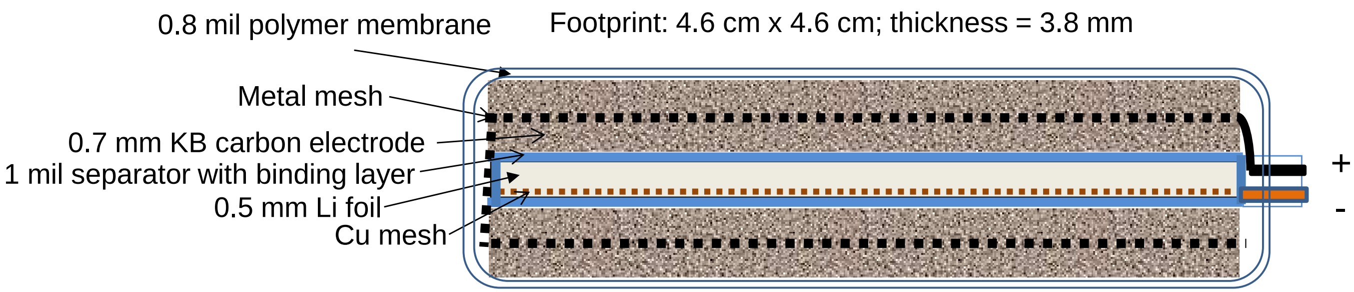
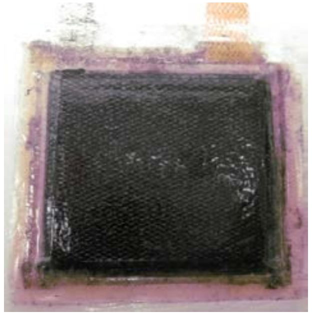
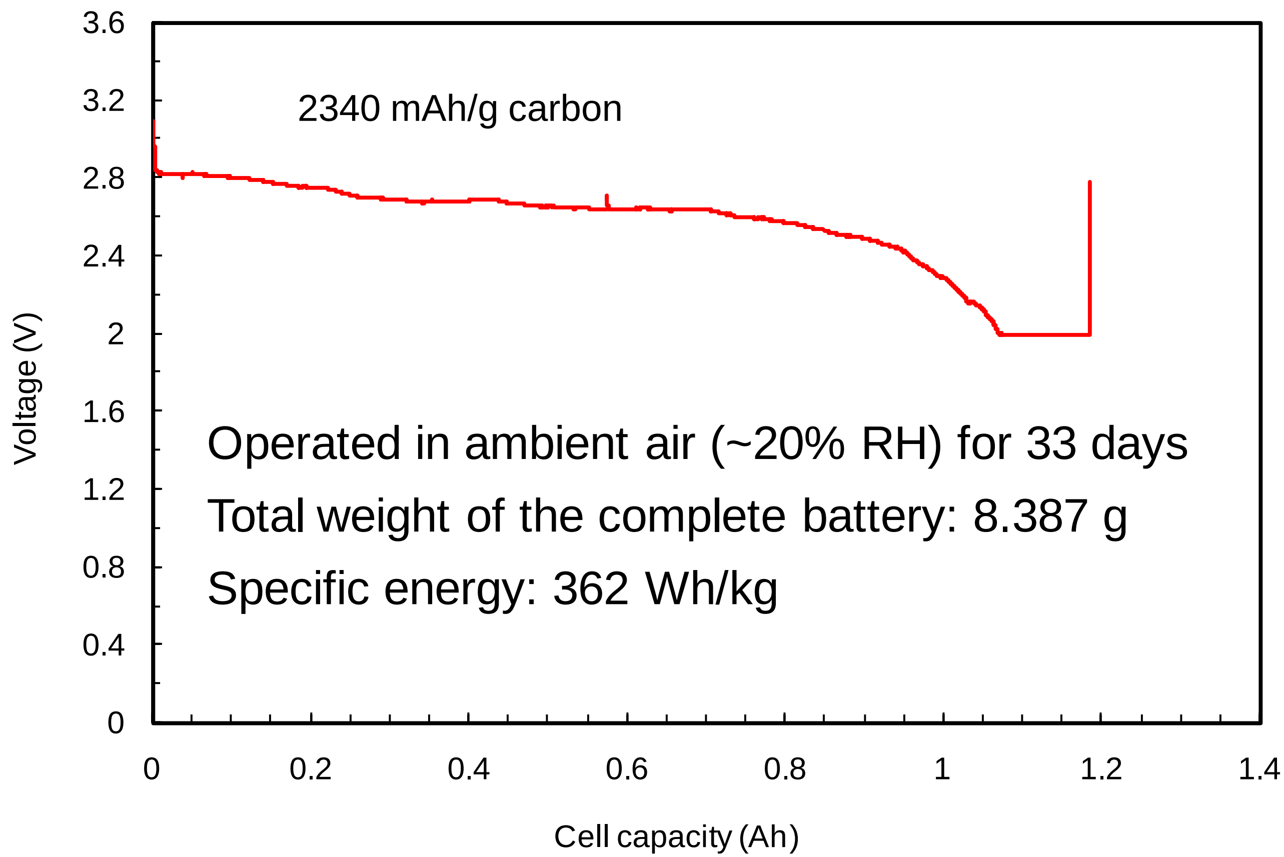
Jie Xiao, Wu Xu, Deyu Wang, and Ji-Guang Zhang, *J. Electrochem. Soc*. 157, A294 (2010).

Performance of Li-air Batteries







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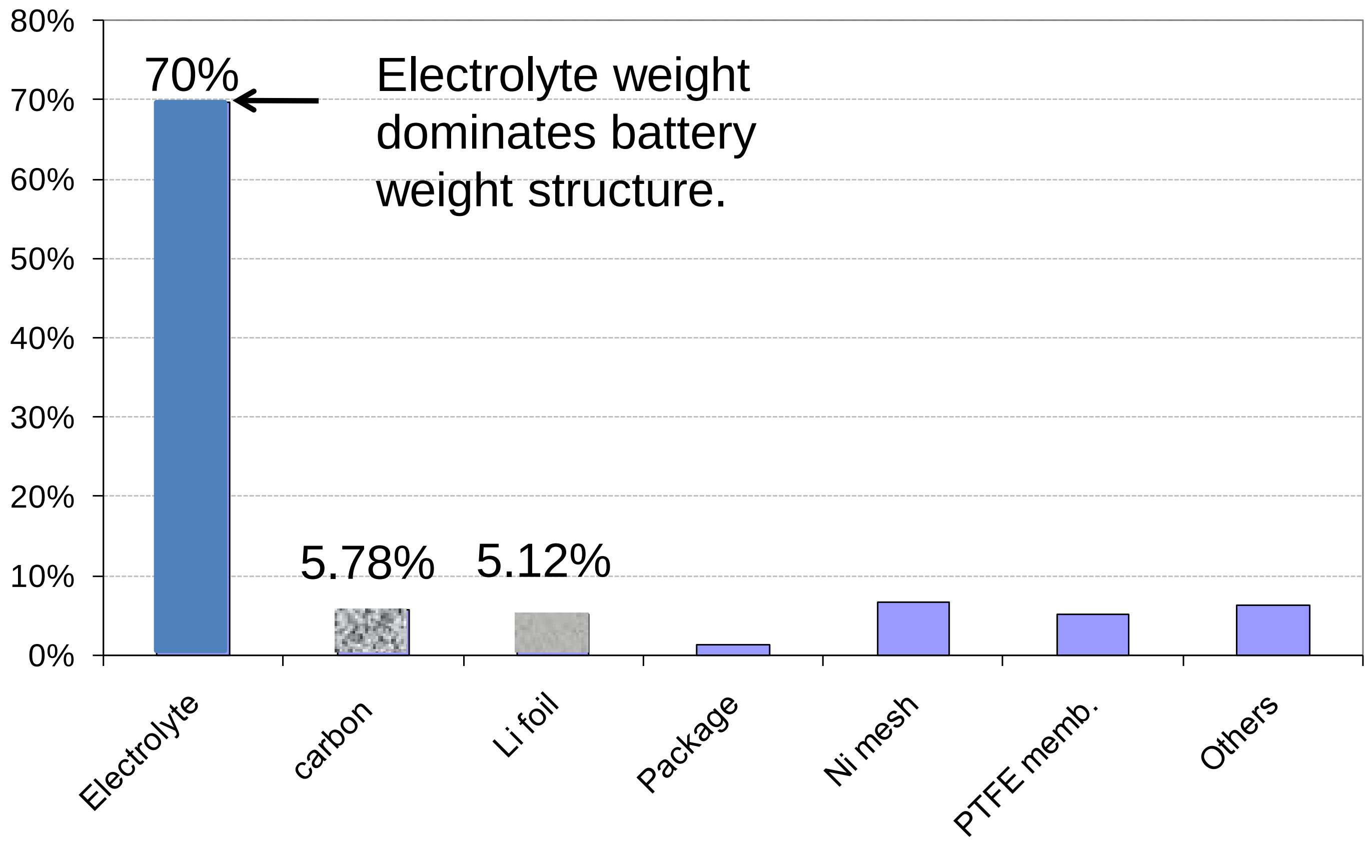
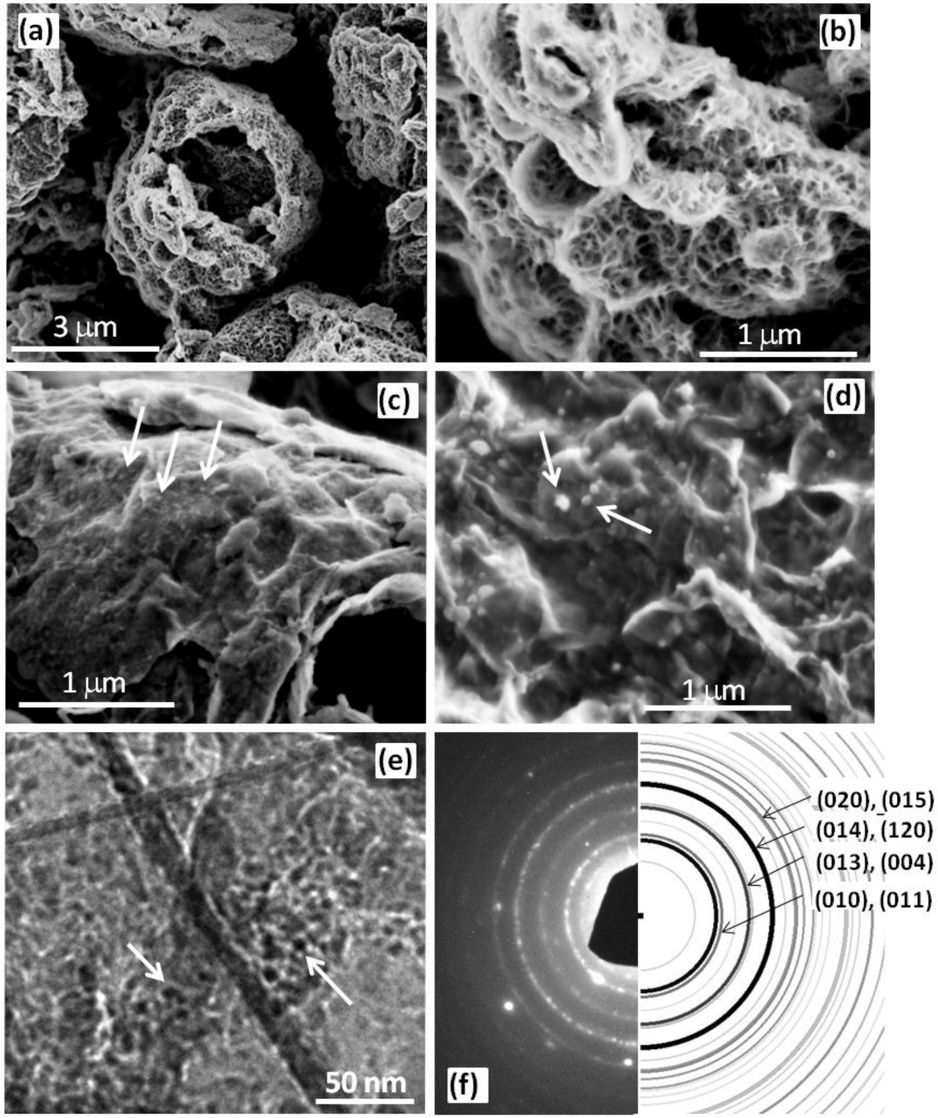
Weight Distribution of a Practical Li-air Battery



- New challenge in practical Li-air batteries: high-performance carbon (Ketjen black) expends more than 80% after soaked with electrolyte and absorbs much more electrolyte than previous prediction.

Hierarchically Porous Graphene as a Lithium-Air Battery Electrode



a and **b**, SEM images of as-prepared graphene-based air electrodes

c and d, Discharged air electrode using FGS with C/O = 14 and C/O = 100, respectively.

e, TEM image of discharged air electrode.

f, Selected area electron diffraction pattern (SAED) of the particles: Li_2O_2.

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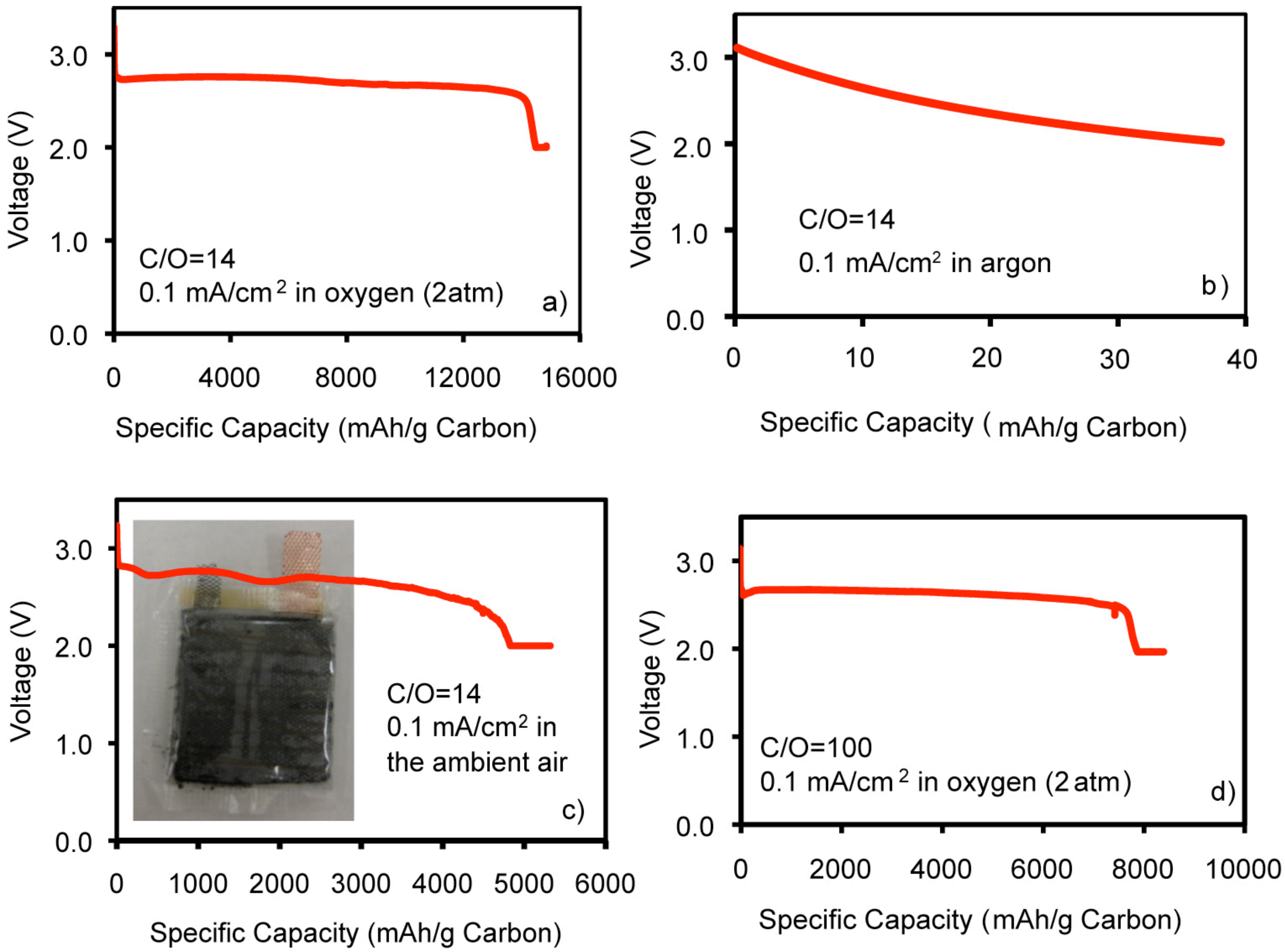
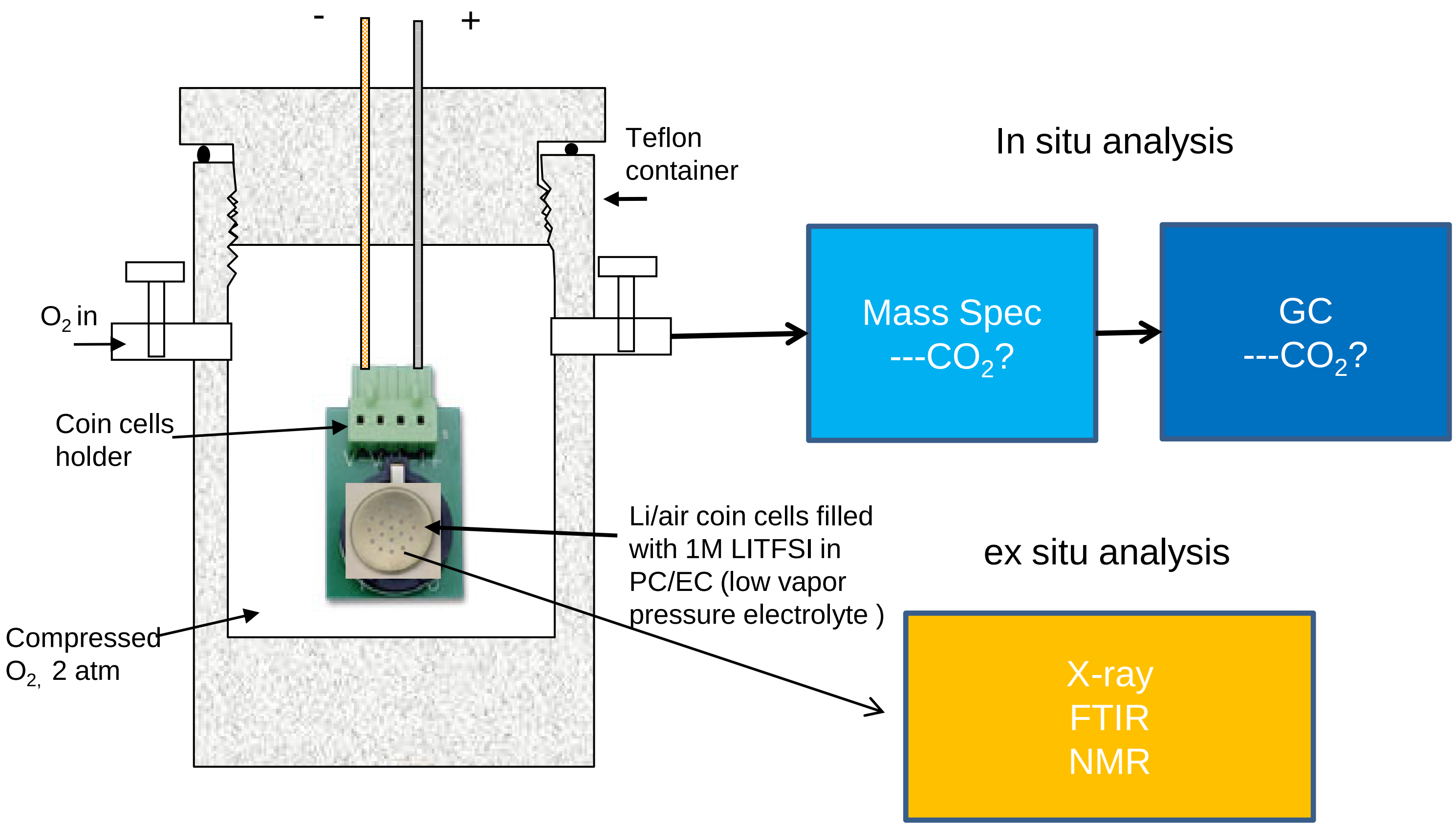
Graphene as a Lithium-Air Battery Electrode

➢ Record Capacity of 15,000 mAh/g



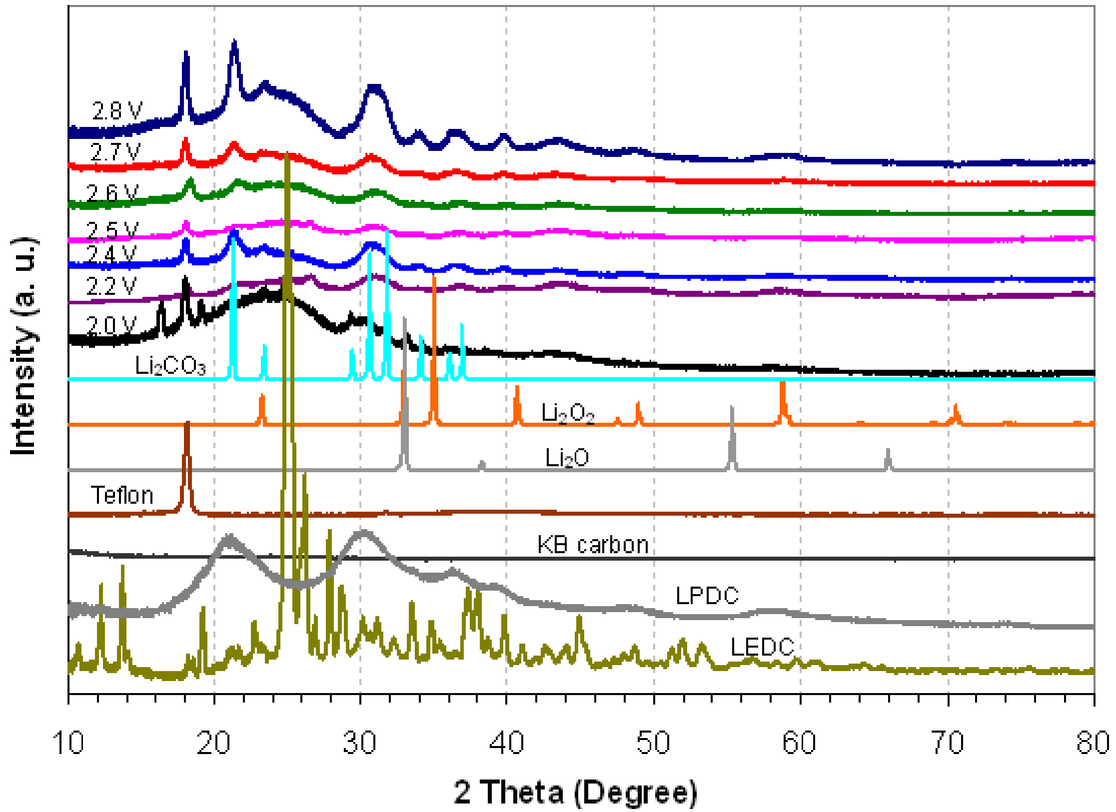
3. Rechargeable Mechanism in Li-air Batteries

$$2Li + O_2 \xleftrightarrow{?} Li_2O_2$$



<u>Developed unique characterization tools</u>

Carbonate Based Electrolytes Decomposes During Li-O_2 Reduction Process



XRD patterns of the air electrodes discharged at different DOD, with comparisons of the standard chemicals of KB carbon, Teflon, Li_2CO_3, LEDC, LPDC, Li_2O_2 and Li_2O.

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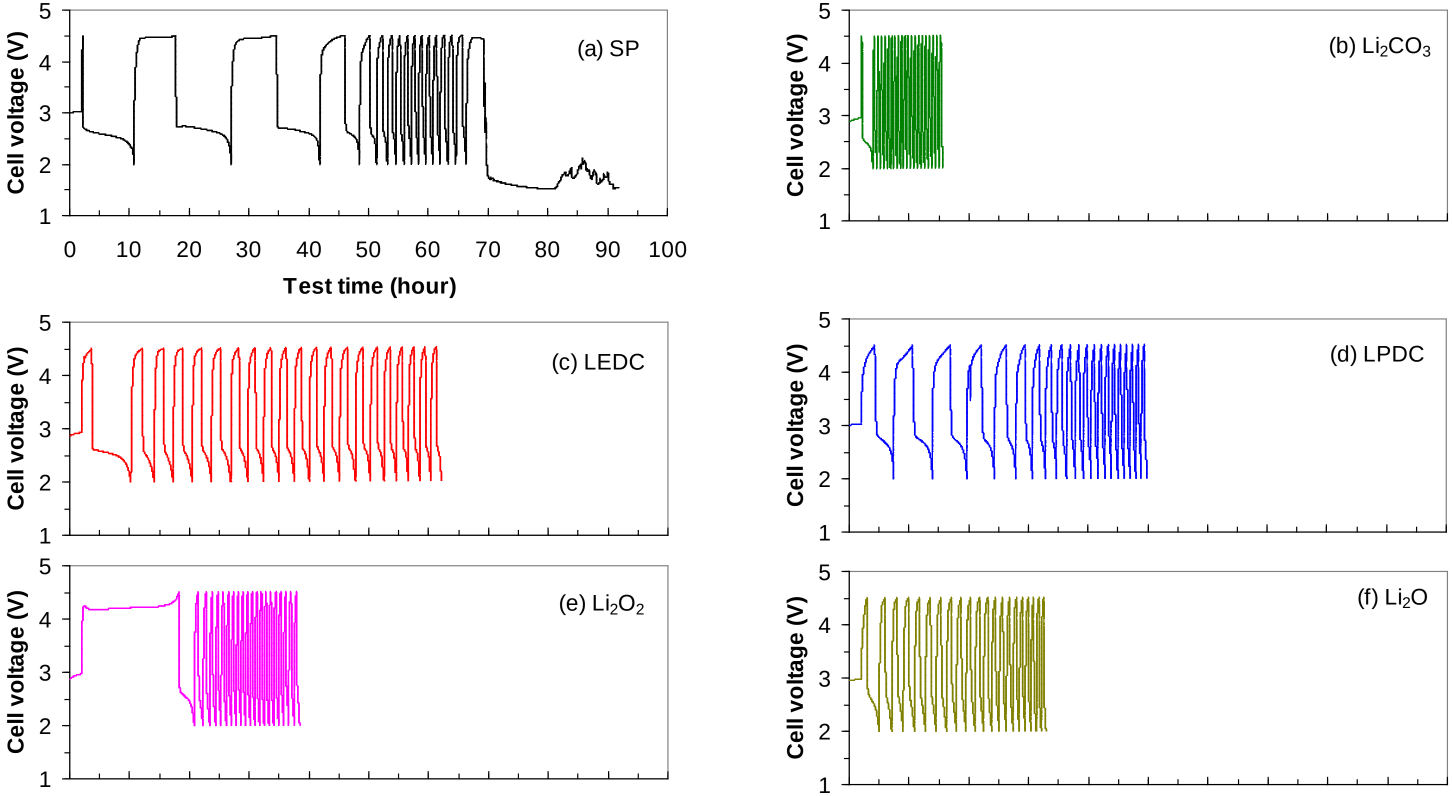
Rechargeability of Related Compounds

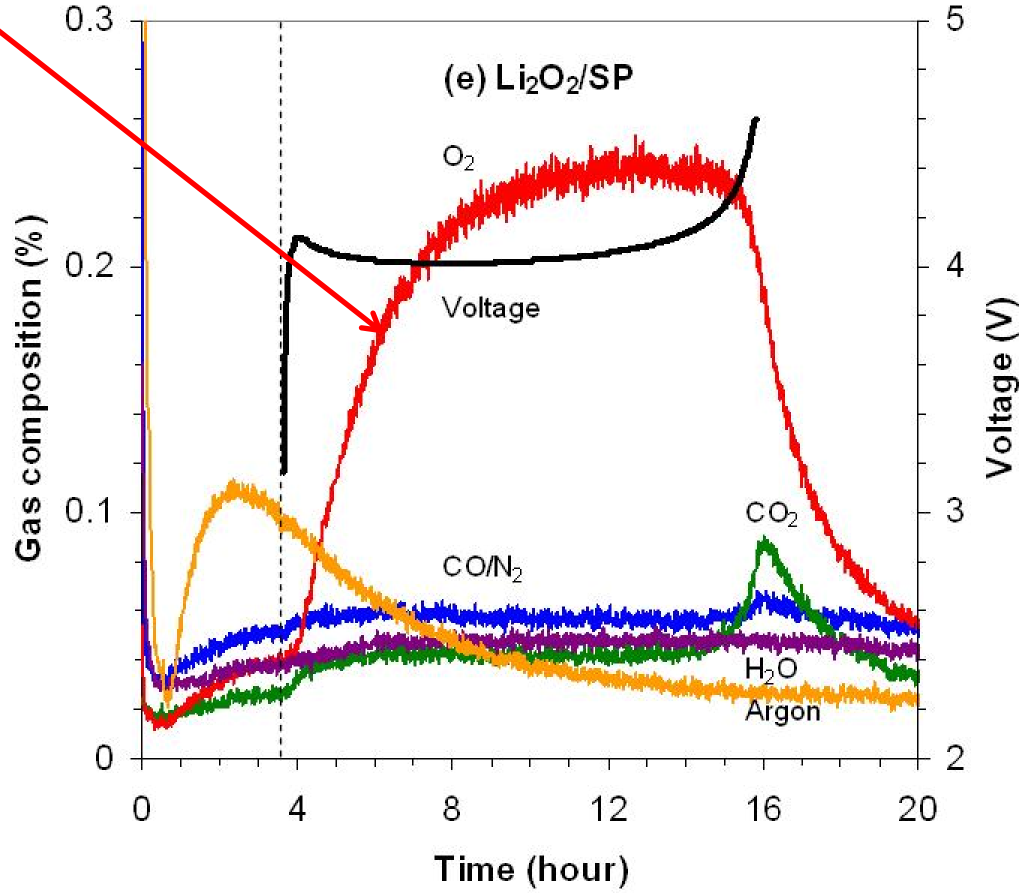


- Li_2O_2: highly oxidizable (>93%)
- Lithium alkylcarbonates (LEDC and LPDC) are oxidizable (~42-69%) and is responsible for apparent recharge-ability reported before.
- Li_2O and Li_2CO_3: Not rechargeable

Is Li-O_2 Battery Rechargeable?

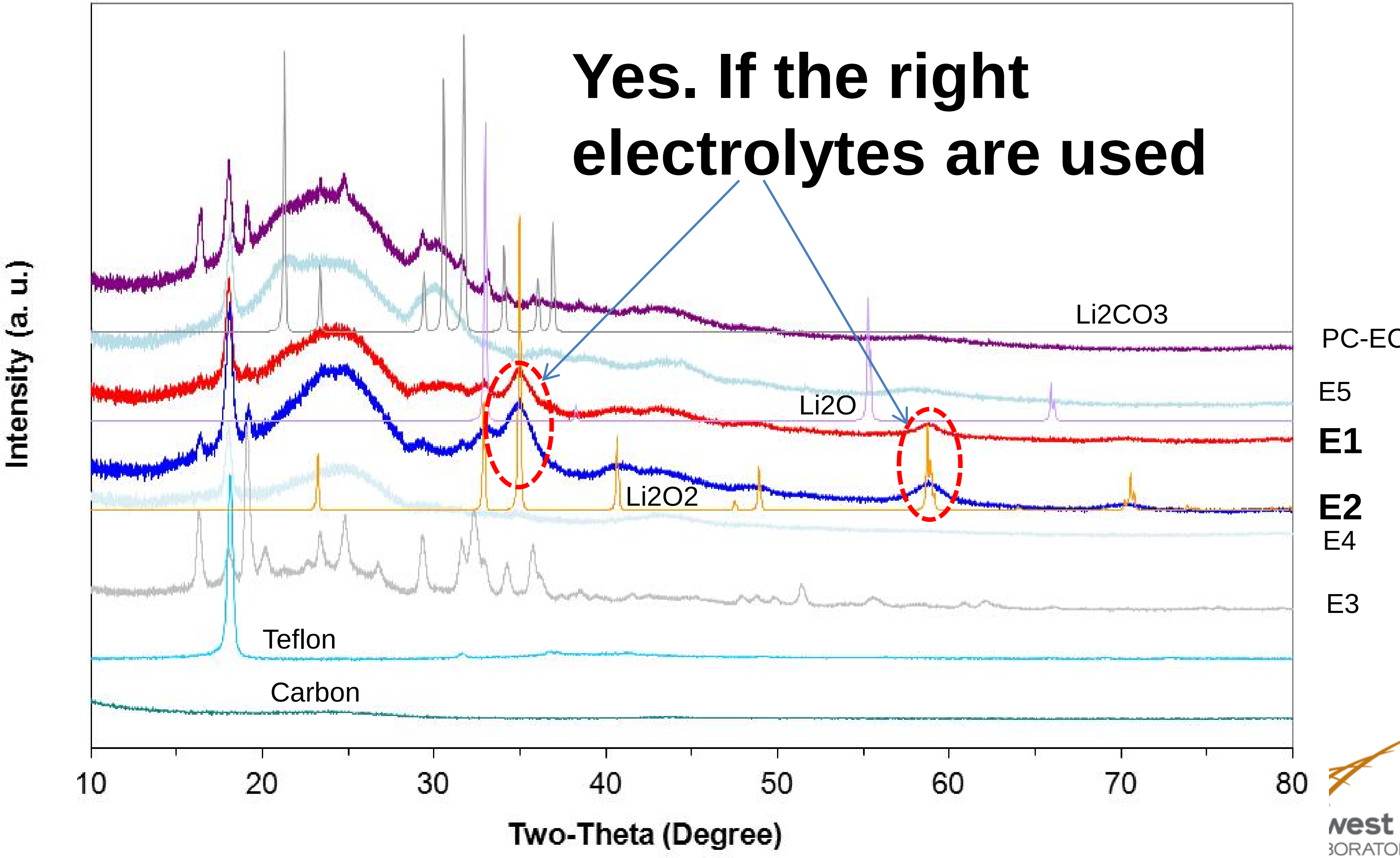
$$2Li + O_2 \xleftarrow{?} Li_2O_2$$

Yes. > 93% of Li_2O_2 has been decomposed and led to O_2 release



Can Li-O_2 Battery Produce Li_2O_2 During Discharge?

$$2Li + O_2 \xrightarrow{?} Li_2O_2$$



Progress Summary

1. Developed primary Li-air batteries to operate in ambient air for 33 days with a specific energy of ~362 Wh/kg for the complete battery.

2. Developed ultra-high capacity air electrode (~15,000 mAh/g) for next generation Li-air batteries.

3. Discovered reaction mechanism in Li-air batteries using carbonate based electrolyte

4. Developed new electrolyte which enables rechargeable reaction in Li-air batteries.

4. Challenges and Opportunities

- Improve the power rate.
- Develop a stable electrolyte.
- Improve the reversibility (bifunctional catalyst)
- Develop an oxygen selective membrane.
- Prevent Li dendrite growth.
- Improve cell design to increase practical specific energy.

Acknowledgments

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