Stable Operation of Li-Air Batteries

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Richland, Washington, U.S.A.

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Outline

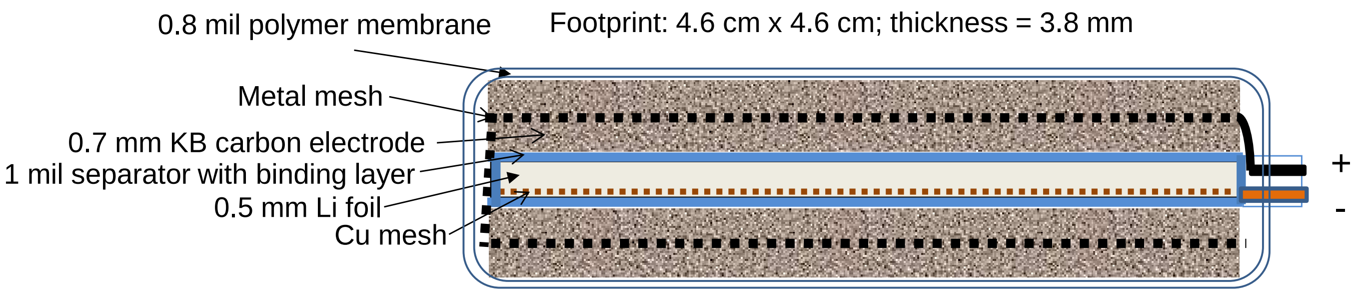
1. Development of High Capacity Primary Li-air Batteries
2. Stability of Li-air Batteries Using Aqueous Electrolyte & NASICON Glass
3. Stability of Li-air Batteries Using Non-Aqueous Electrolyte

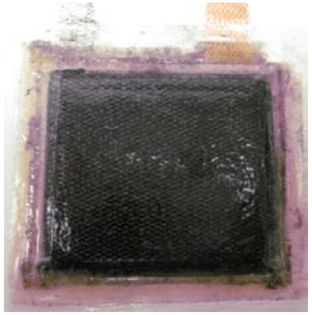
   3.1 Reaction Products During Discharge Process

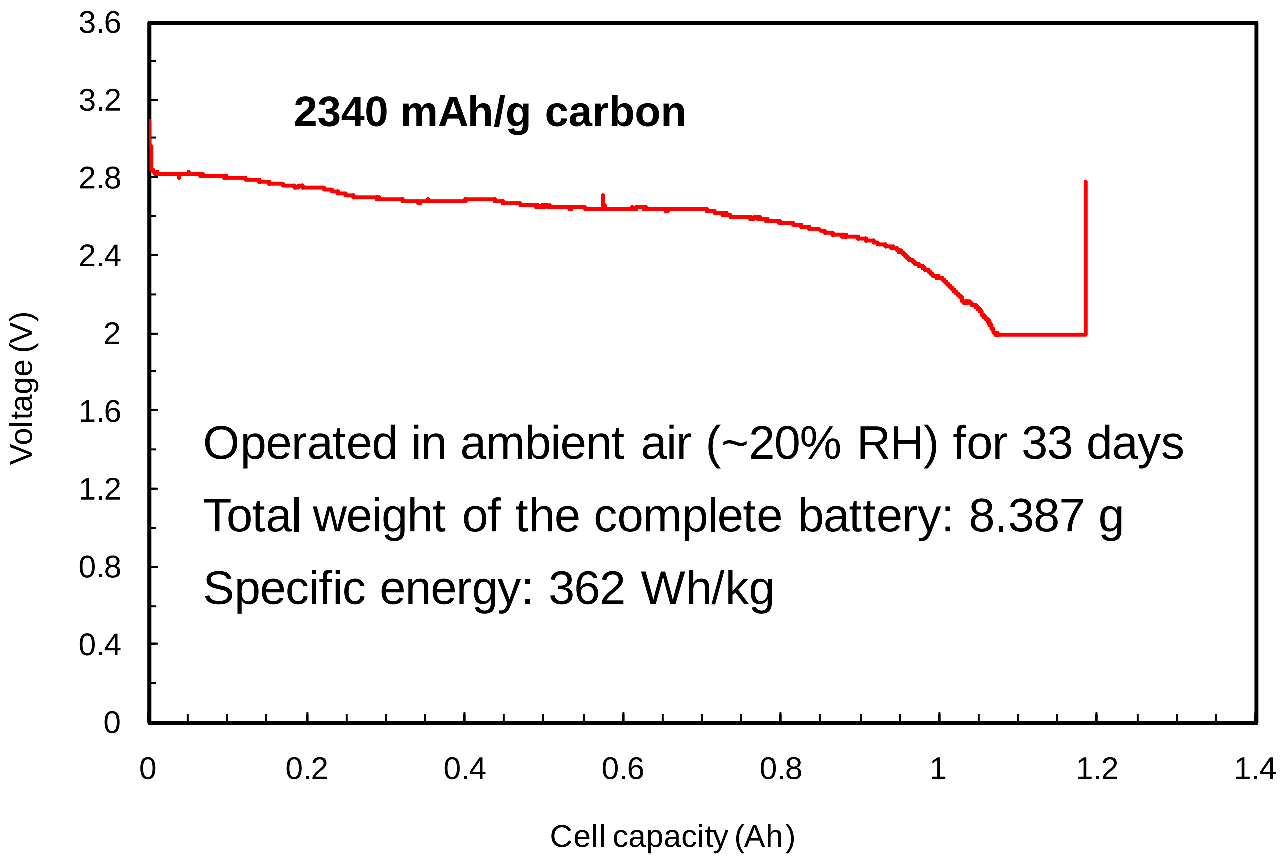
   3.2 Reaction Products During Charge Process

4. Summary

1. Development of High Capacity Primary Li-air Batteries







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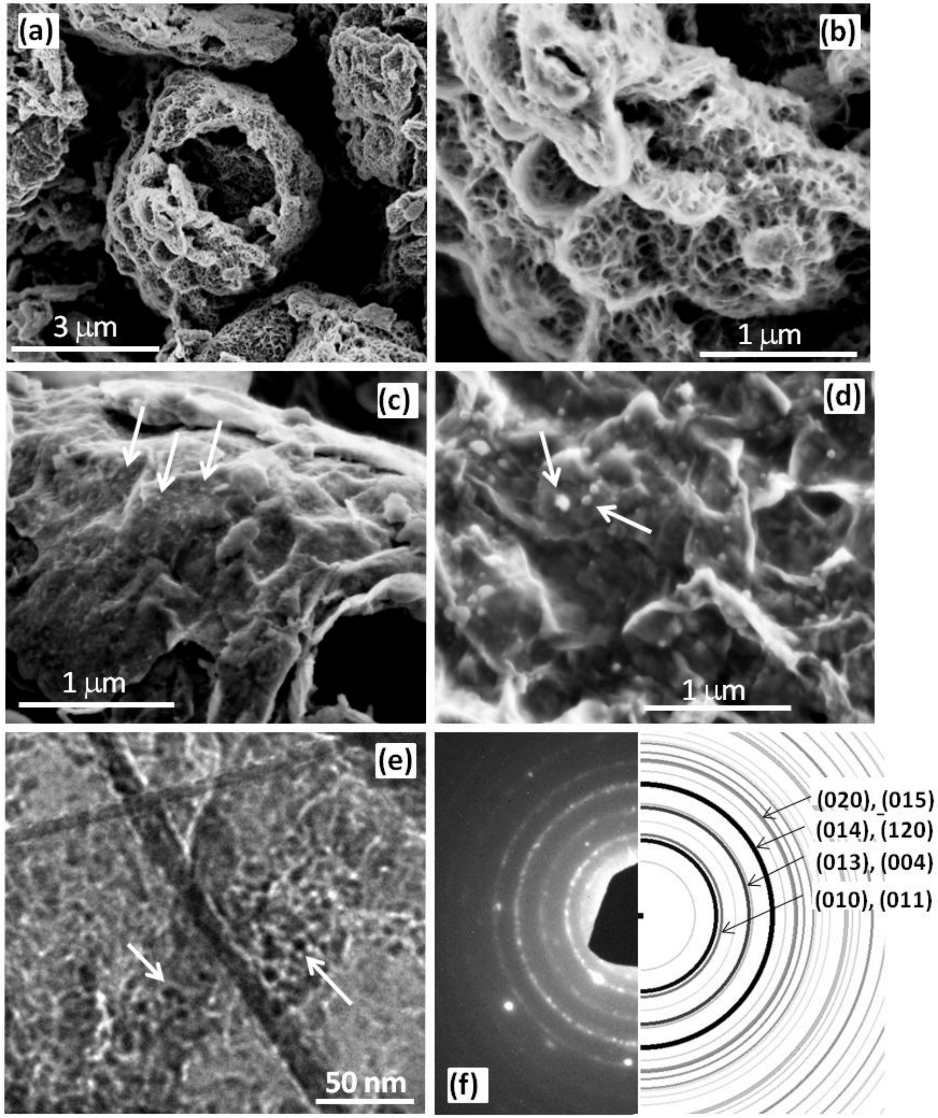
Hierarchically Porous Graphene as a Lithium-Air Battery Electrode



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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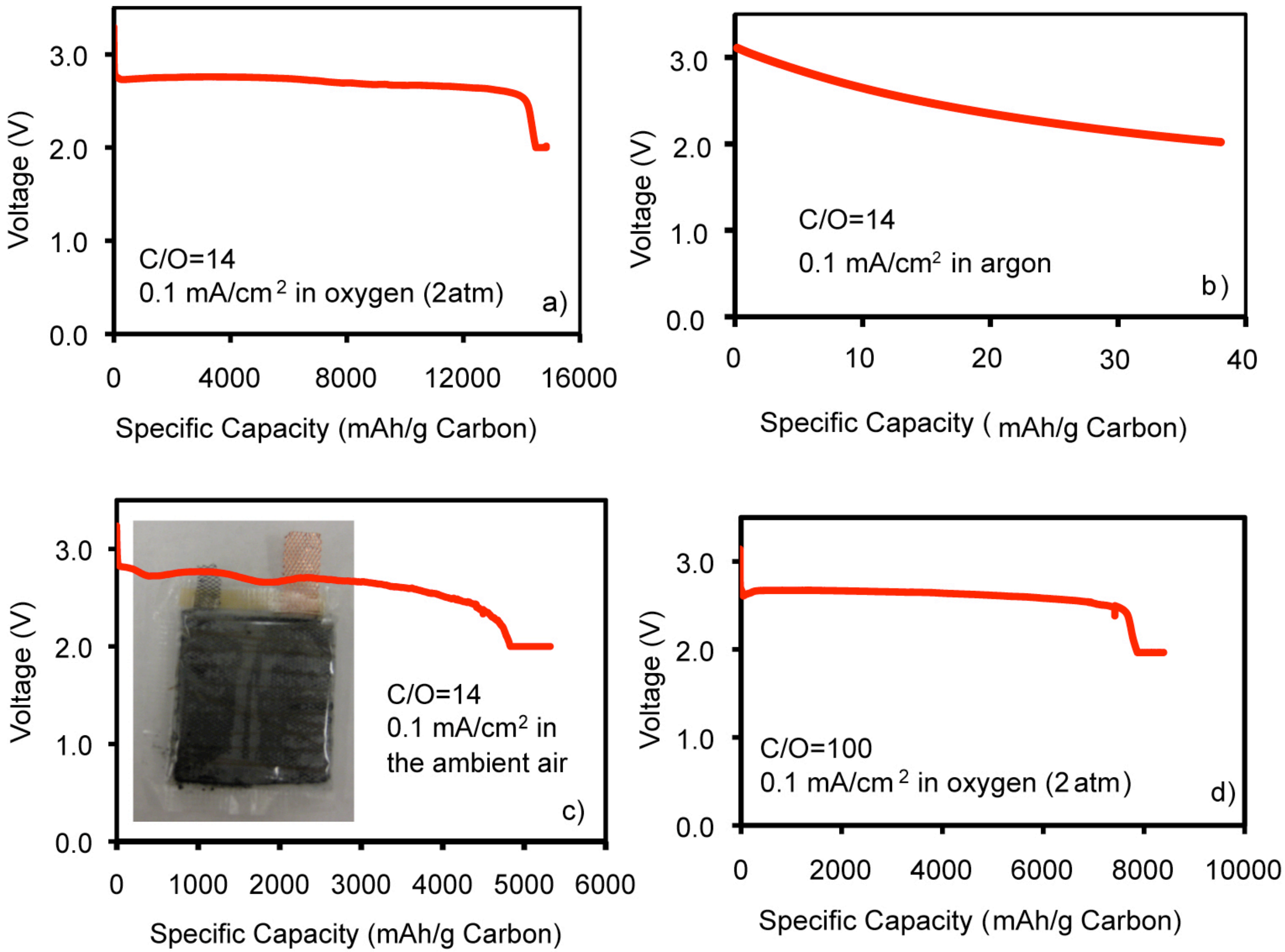
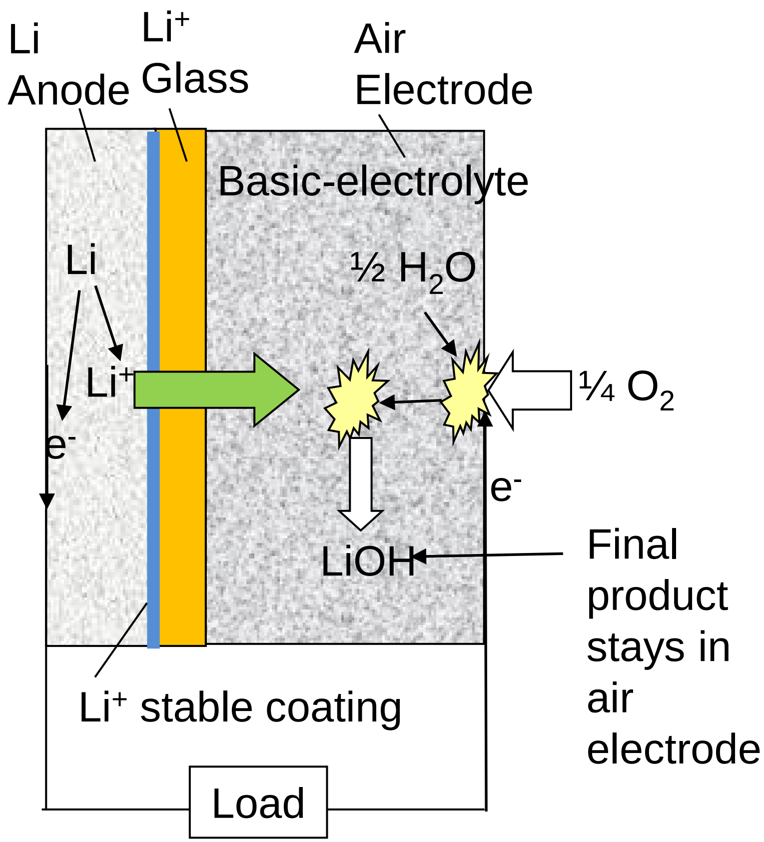
Jie et al, to be published

Graphene as a Lithium-Air Battery Electrode
➢ Record Capacity of 15,000 mAh/g



2. Stability of Li-air Batteries Using Aqueous Electrolyte & NASICON Glass

In Aqueous Electrolyte



$Li + ½ O_2 + ½ H_2O \leftrightarrow LiOH$

Challenges:
Stable glass electrolyte at strong acid and alkaline environment

- Chemical stability
- Electrochemical stability
- Single ion conductivity

Advantages and Challenges in 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/electrolyte/carbon)					
$Li + ½ O_2 \leftrightarrow ½ Li_2O_2$	3.10	11972	11972	3622	2790**
$Li + 0.25 O_2 + 1.5 H_2O \leftrightarrow LiOH \cdot H_2O$	3.4-3.86*	~12000	2717	2198	1500
$Li + 0.25O_2 + HCl \leftrightarrow LiCl + 0.5H_2O$	3.86-4.44*	~12000	2637	2227	1607
With no precipitation (Li & electrolyte)					
$Li + 0.25 O_2 + 11.14 H_2O \leftrightarrow LiOH + 10.64H_2O$	3.4-3.86*	~12000	444	428	444
$Li + 0.25O_2 + HCl + 2.29H_2O \leftrightarrow LiCl + 2.79H_2O$	3.86-4.44*	~12000	1352	1236	1353

* Voltage is a function of pH value: $V = 4.268 – 0.059$ pH

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

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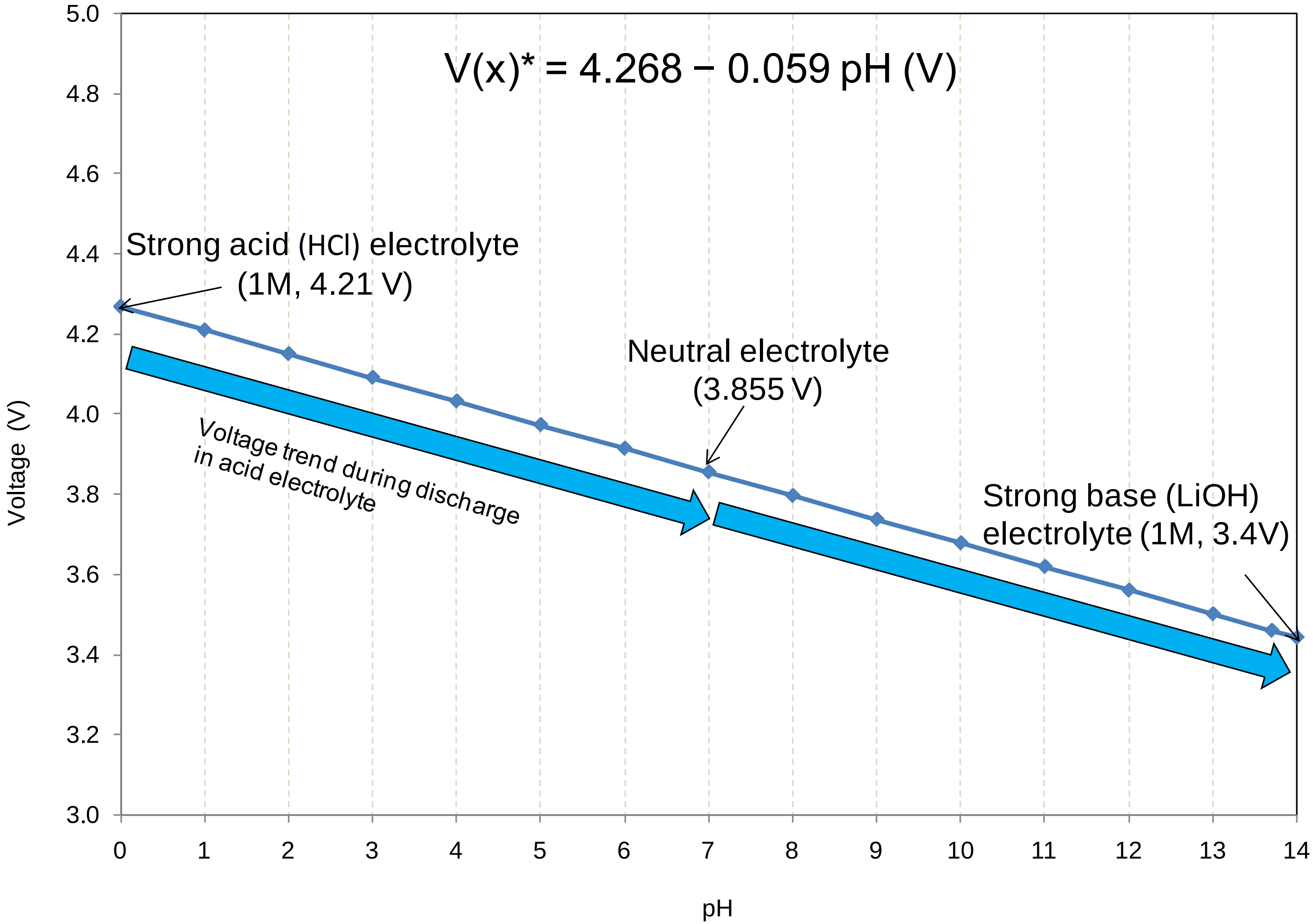
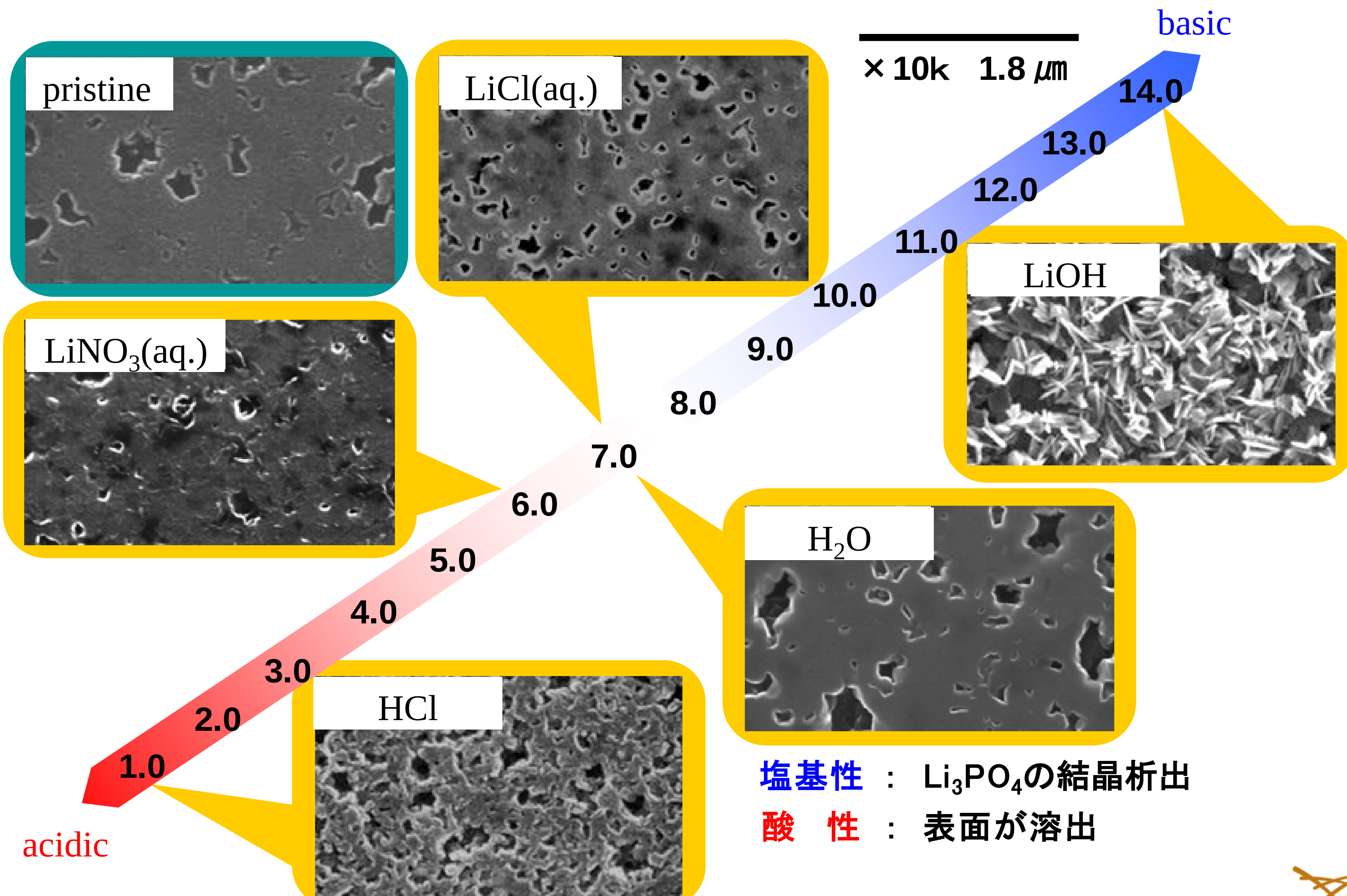
Voltage in Li-Air Batteries Strongly Depends on pH Value of Aqueous Electrolyte



*Xia et al, NATURE CHEMISTRY, VOL 2, SEPTEMBER , 760 (2010)

Stability of LTAP Glass vs. pH

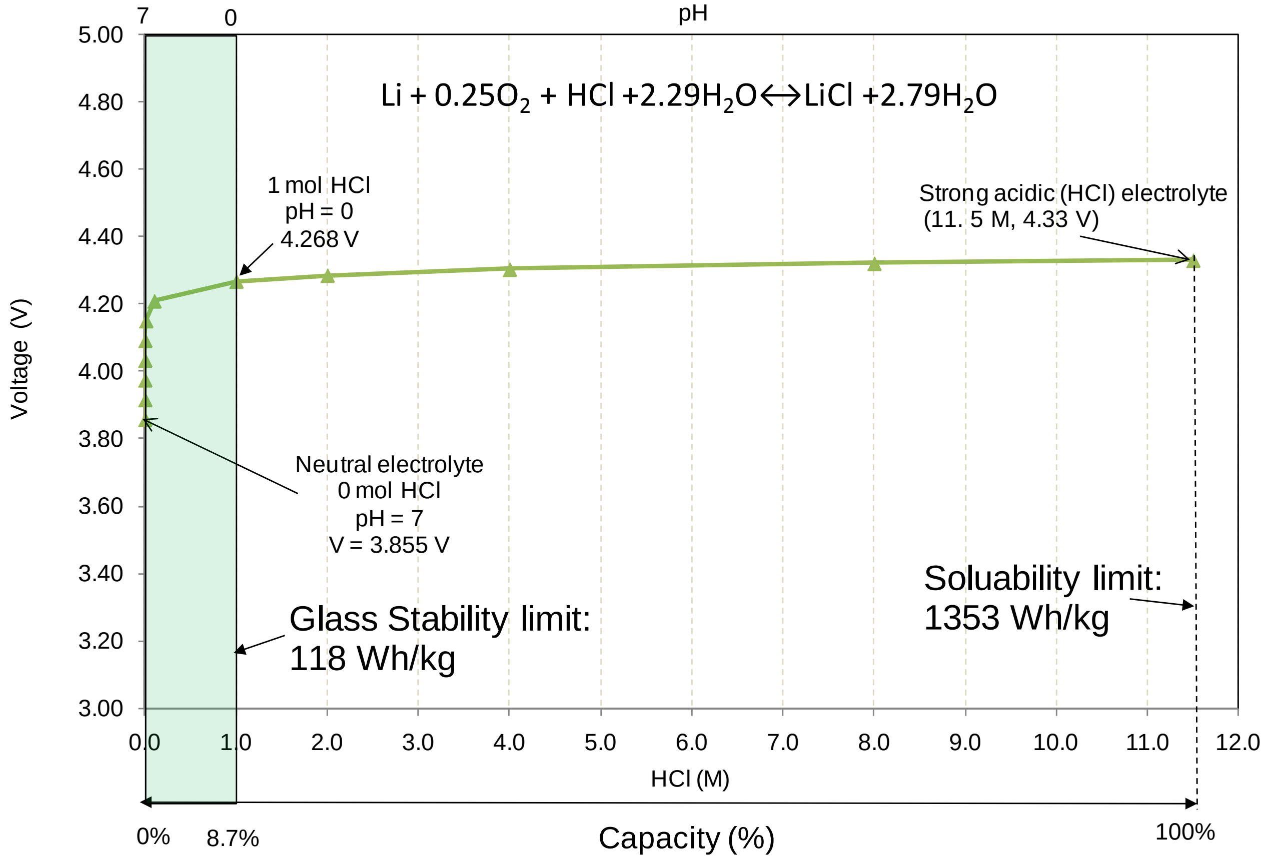


塩基性 ： Li_3PO_4の結晶析出

酸　性 ： 表面が溶出

Yamamoto et al, presentation in Symposium on Energy Storage Beyond Lithium Ion, ORNL, Oct, 2010
https://www.ornl.gov/ccsd_registrations/battery/presentations/Session6-840-Yamamoto.pdf

Limitation of Li-air Batteries in Acid Electrolyte



➢ To utilize the full capacity of acid electrolyte based Li-air batteries, pH value of the electrolyte has to be limited to be larger than 4.

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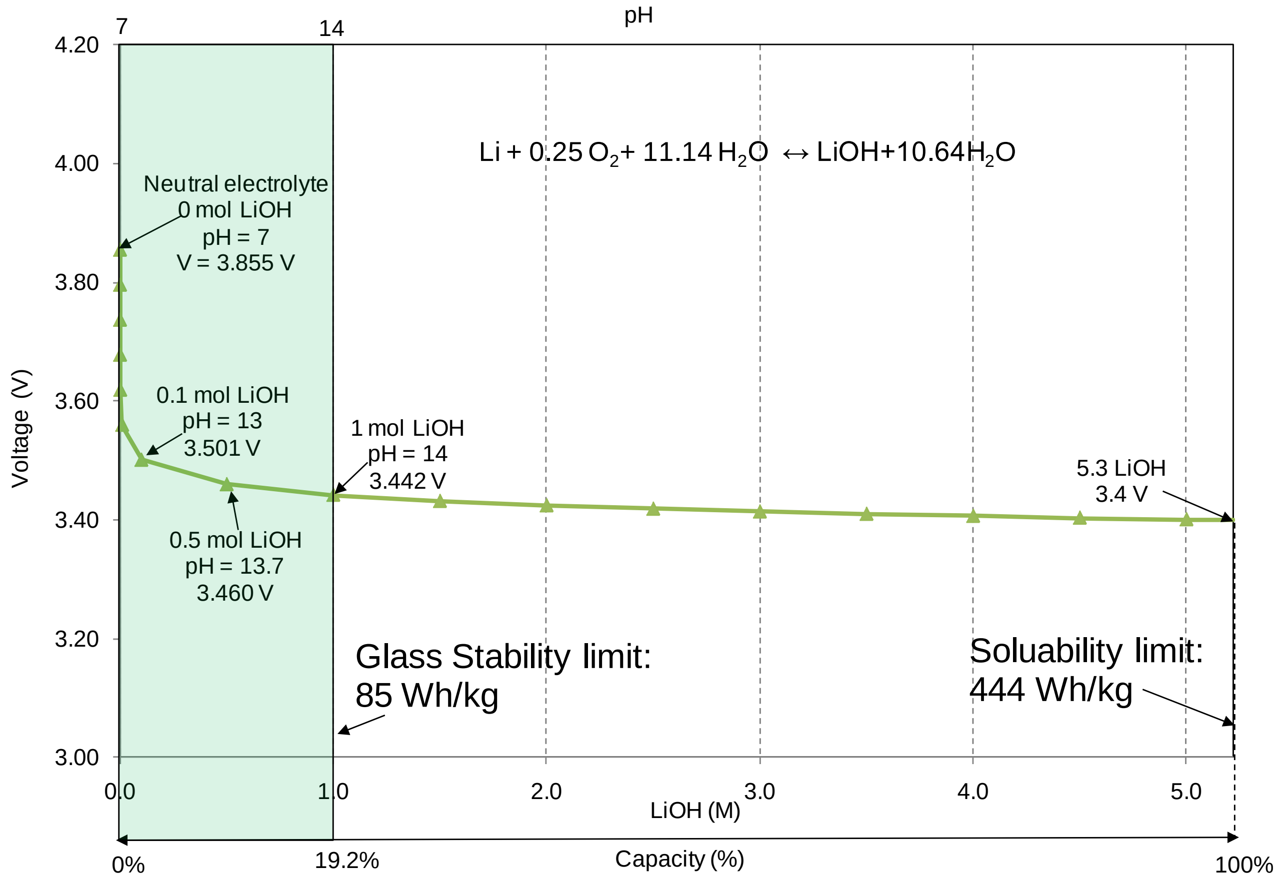
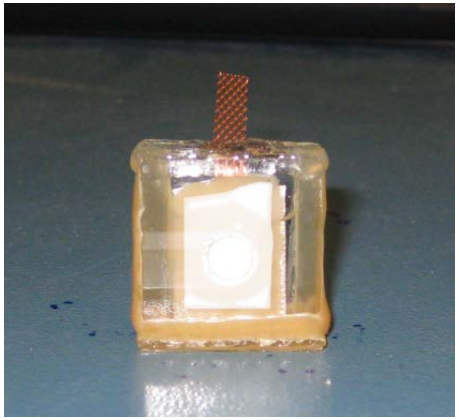
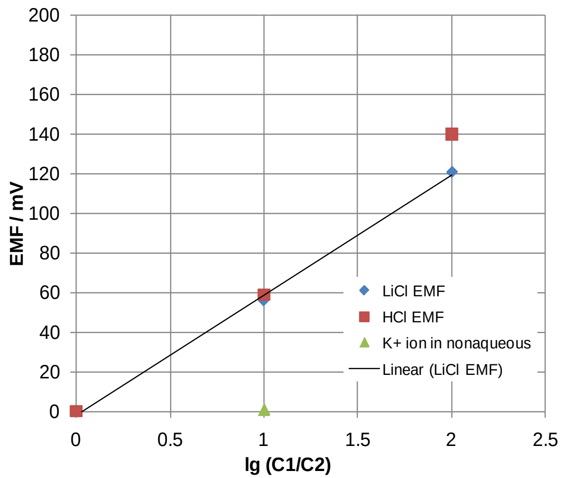
Limitation of Li-air Batteries in Alkaline Electrolyte



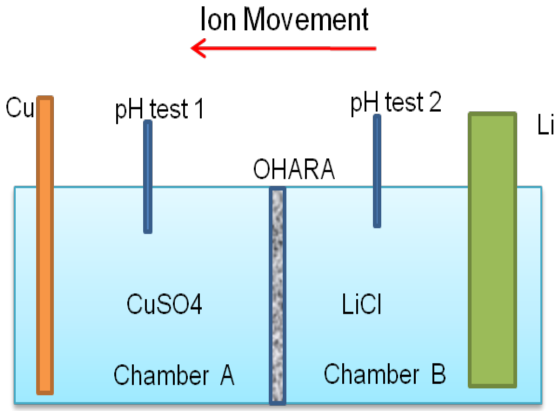
➢ To utilize the full capacity of alkaline electrolyte based Li-air batteries, pH value of the electrolyte has to be limited to be less than 10.

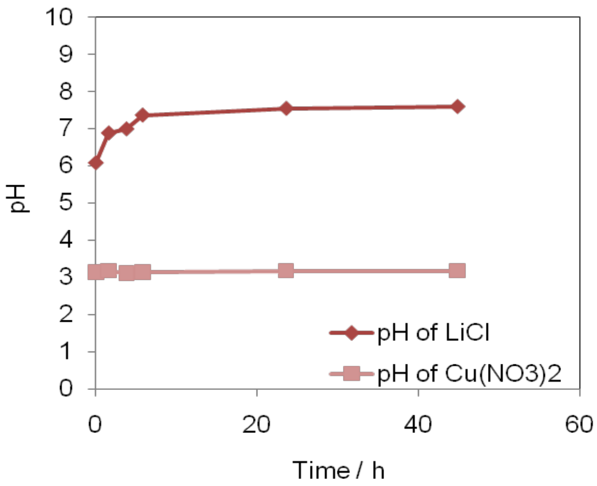
Electrochemical Stability of NASICON Glass in Aqueous Electrolytes





- ➢NASICON solid electrolyte cannot distinguish between H^+ ions and Li^+ ions, at least on the interface.





- ➢Both Li^+ and H^+ ion in chamber B participate in the electrochemical process. Increase of pH value in chamber B may indicate the reaction of H^+ with glass electrolyte.

- ➢See Dr. Fei Ding's poster for more details

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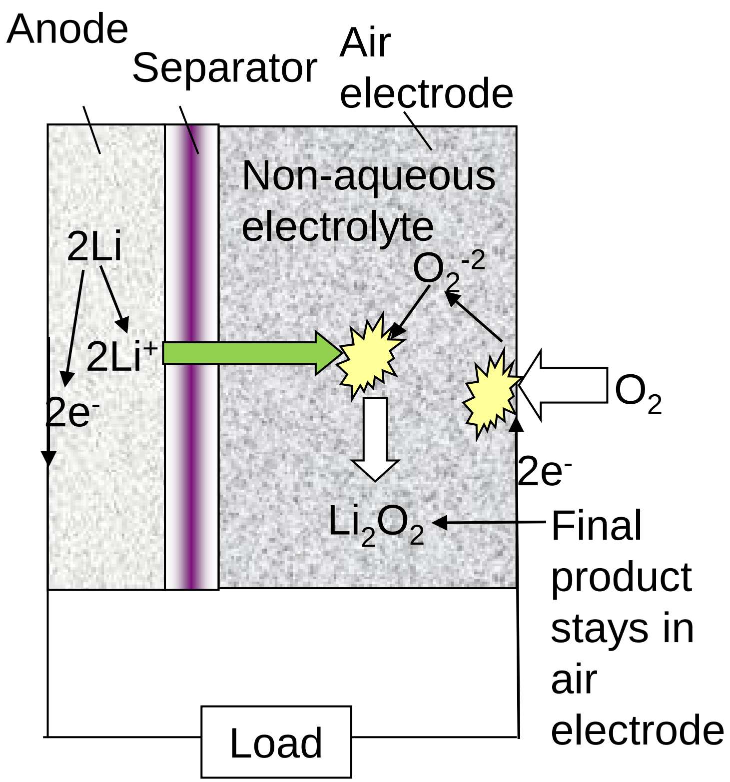
3. Stability of Li-air Batteries Using Non-Aqueous Electrolyte



$2Li + O_2 \longleftrightarrow Li_2O_2$ $E^0 = 3.1V$

Schematic of reaction processes in metal-air batteries.

Challenges:
Stable non-aqueous electrolyte in oxygen rich environment

a. $2Li + O_2 \xrightarrow[\text{electrolyte}]{\text{In non-aqueous}} Li_2O_2$

b. $2Li + O_2 \xleftarrow[\text{electrolyte}]{\text{In non-aqueous}} Li_2O_2$

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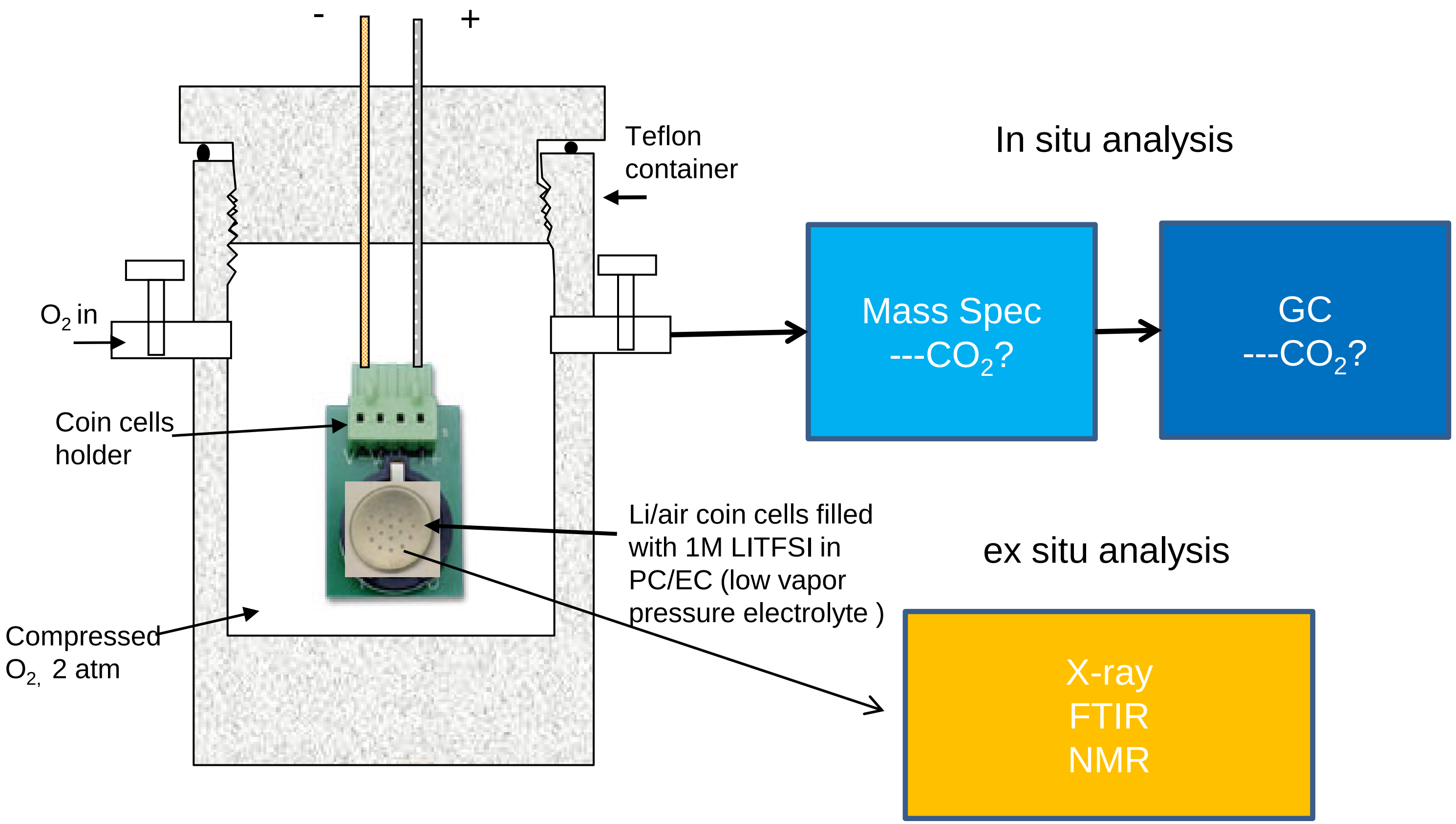
Investigation on the Reaction Products in Li-O_2 Batteries

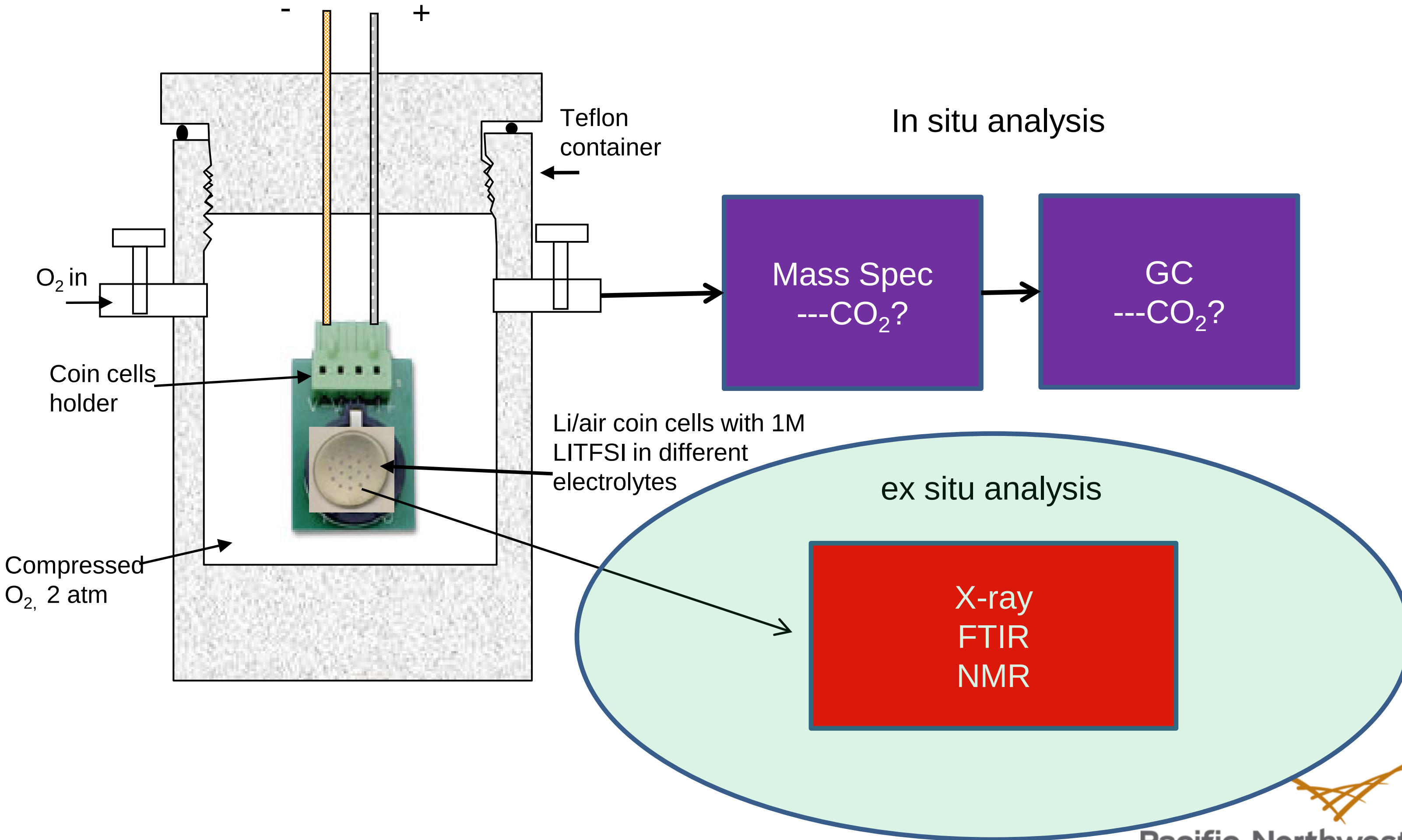
$$2Li + O_2 \xleftrightarrow{?} Li_2O_2$$



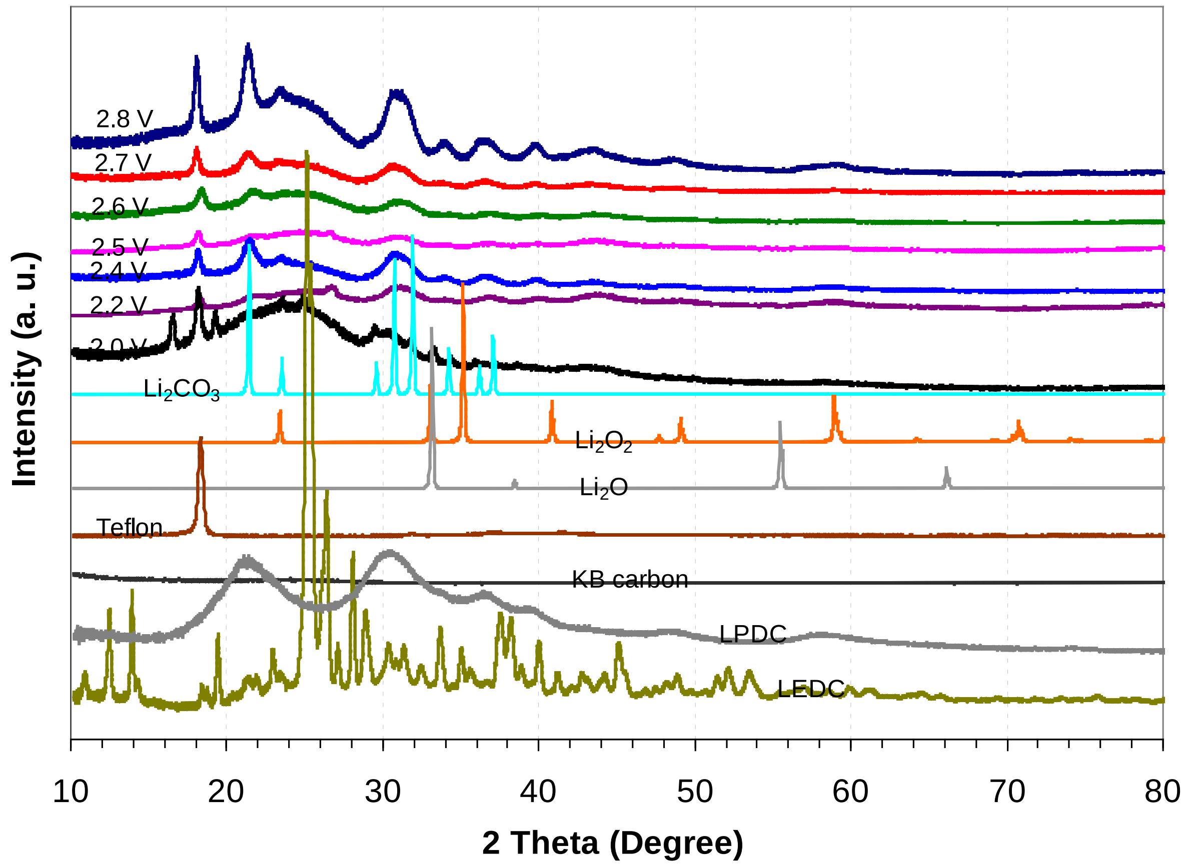
Developed unique characterization tools

3.1. Reaction Products During Discharge Process

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



Li_2O_2 Was Not Observed in the Discharge Products When Carbonate Solvents Was Used



- For all DODs (from 2.8 V to 2.0 V), nearly no Li_2O_2 and Li_2O were detected.
- Lithium alkylcarbonates (LPDC and LEDC) and Li_2CO_3 are identified to be the primary discharge products.

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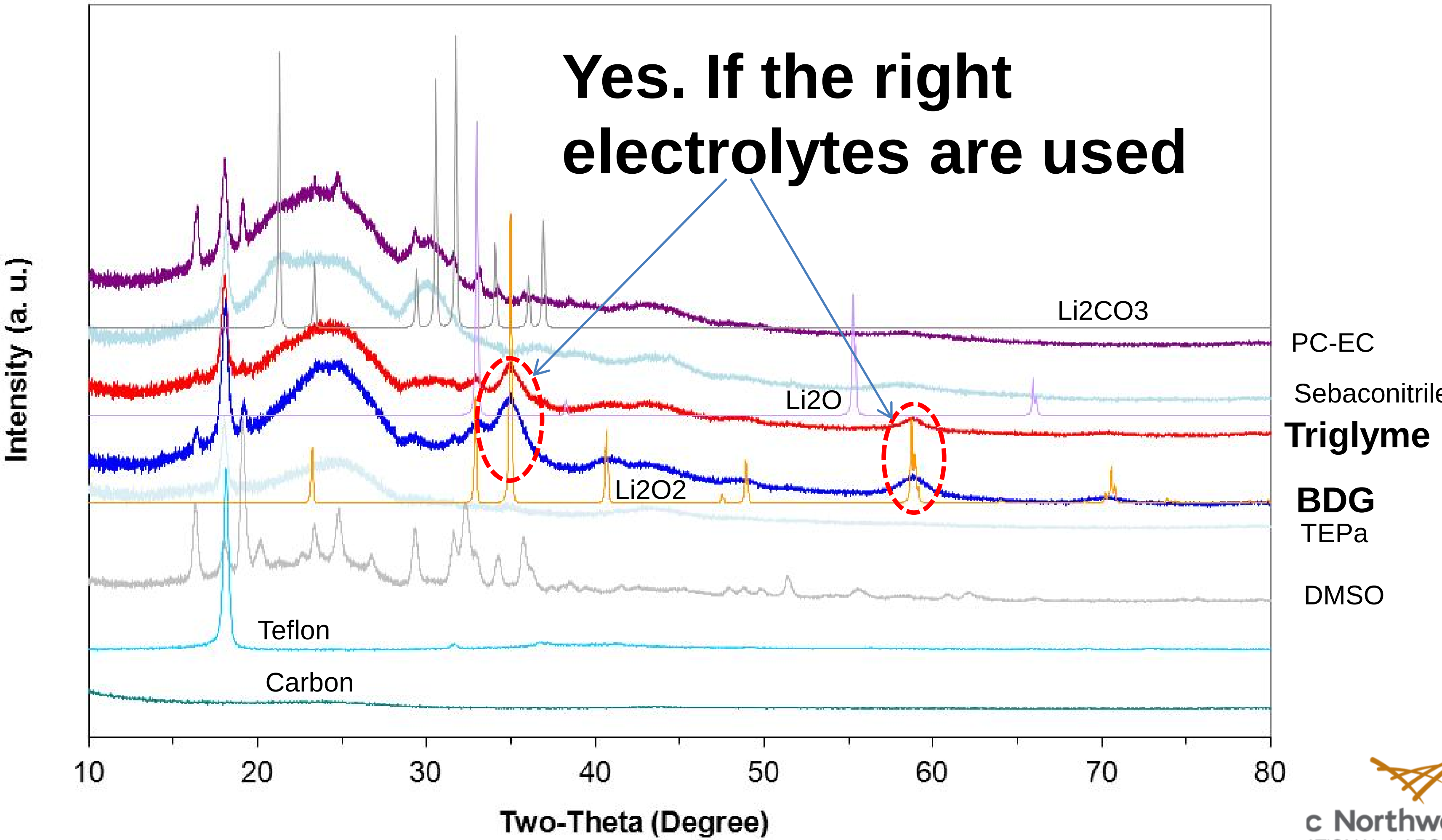
Ether Based Electrolytes Can Lead to the Formation of Li_2O_2 During Discharge

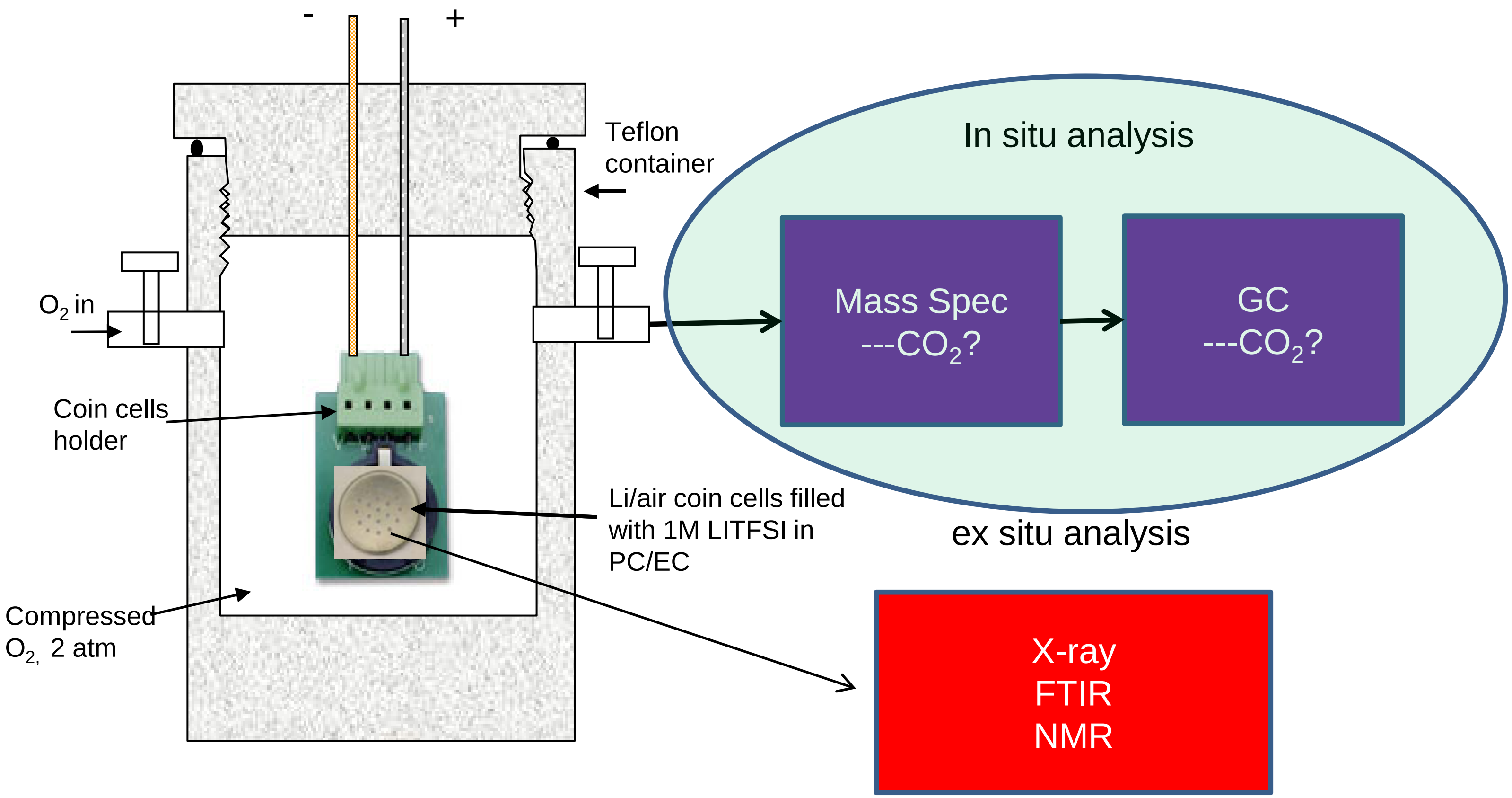
$$2Li + O_2 \longrightarrow Li_2O_2$$



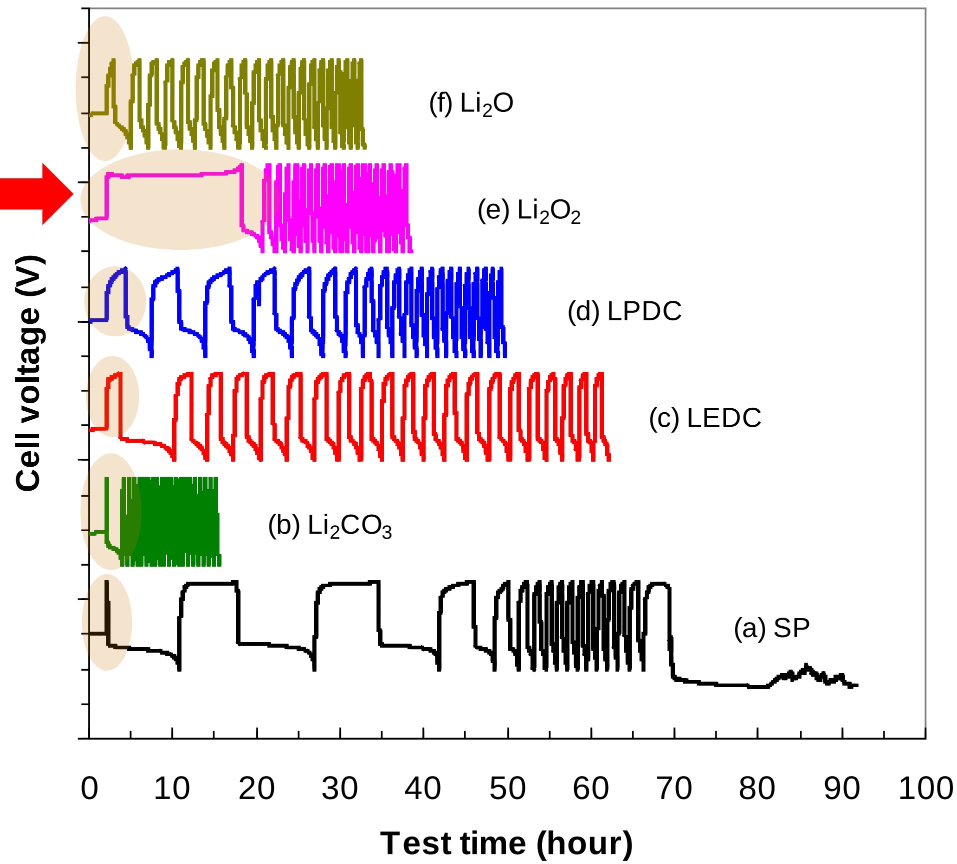
➤See Dr. Wu Xu's poster for more details

3.2 Reaction Products During Charge Process

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



What Can be Charged?



<u>First cycle charge</u> capacities:

a) SP: 4.1 mAh/g
b) Li_2CO_3 : 4.8 mAh/g
c) LEDC: 99.6 mAh/g (331 mAh/g, 30.1%)
d) LPDC: 153.3 mAh/g (308 mAh/g, 49.8%)
e) <u>Li_2O_2 : 1078.6 mAh/g (1165 mAh/g, 92.5%)</u>
a) Li_2O: 63.3 mAh/g

- **<u>Li_2O_2: Highly chargeable (>92%)</u>**
- LEDC and LPDC: Partially chargeable (~42-69%) and is responsible for apparent recharge-ability reported before.
- Li_2O, SP, and LiC_2O_3: Not chargeable

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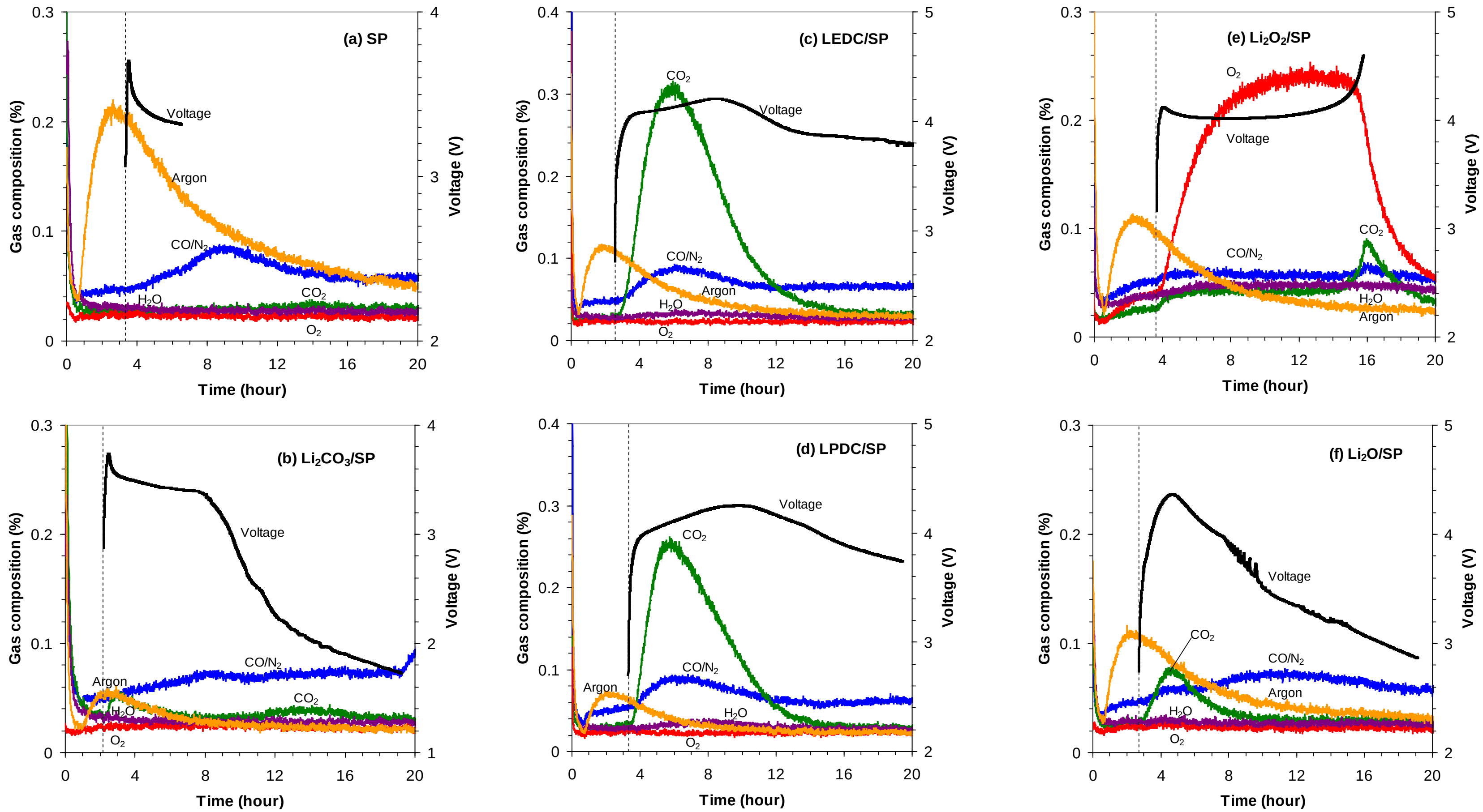
What Are the Charge Products?
(GC/MS Analysis)



a) SP – mainly CO with minor CO_2
b) Li_2CO_3 – small amount of CO_2 and CO
c) LEDC – large amount of CO_2
d) LPDC – large amount of CO_2
e) <u>Li_2O_2 – mainly O_2 with minor CO_2</u>
f) Li_2O – some CO_2 and CO. It cannot be oxidized.

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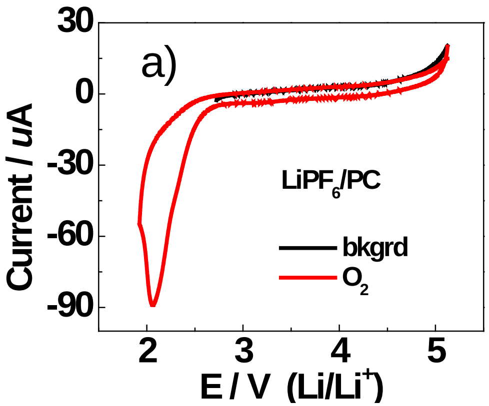
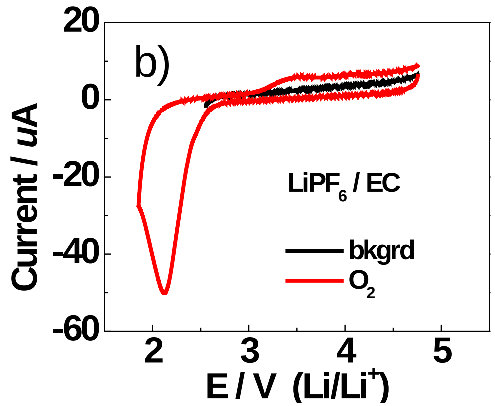
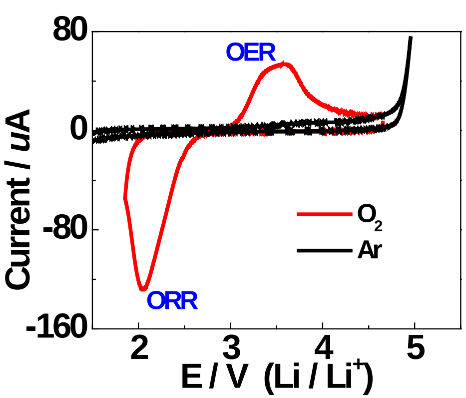
Charge Efficiency in Different Non-Aqueous Electrolytes in Oxygen-Rich Environment

Cyclic voltammograms (100 mV/s) on glass carbon in O_2 and Ar saturated $LiPF_6$ in different non-aqueous solvent

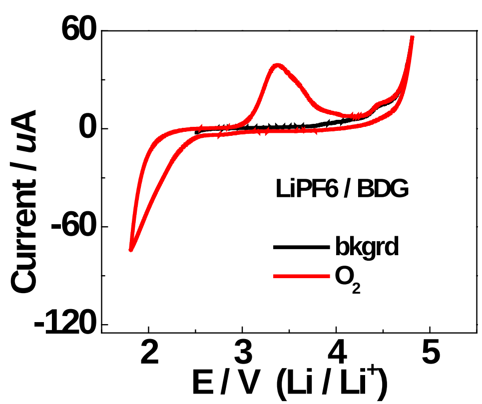




- ➢No OER peak for $LiPF_6$/PC solution indicates that all the ORR products react with PC which leads to the products that can not be oxidized/recharged within the potential range.



DME (0.1M):
Q_{OER}/Q_{ORR} = 97.5%



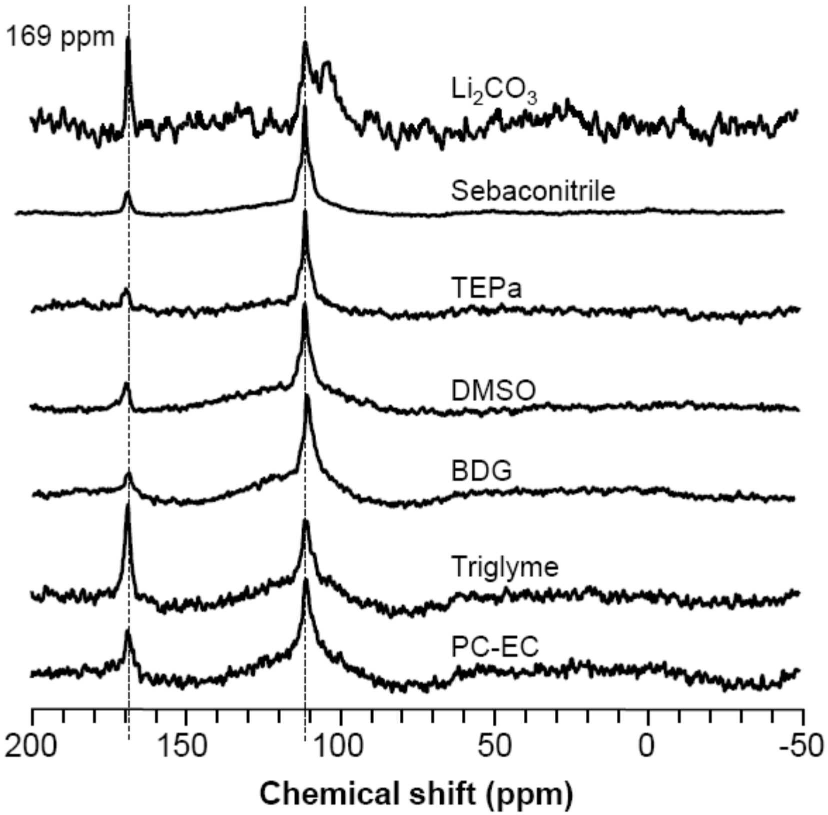
Butyl Diglycol Ether (1.0M)
Q_{OER}/Q_{ORR} = 96.7%

- ➢Large Q_{OER}/Q_{ORR} ratio for $LiPF_6$/ether solution indicates that most ORR products can be oxidized/recharged within the potential range.

- ➢See Dr. Yuyan Shao's poster for more details

What Are the Source of Limited Efficiency?

--NMR Investigation on Discharged Electrodes

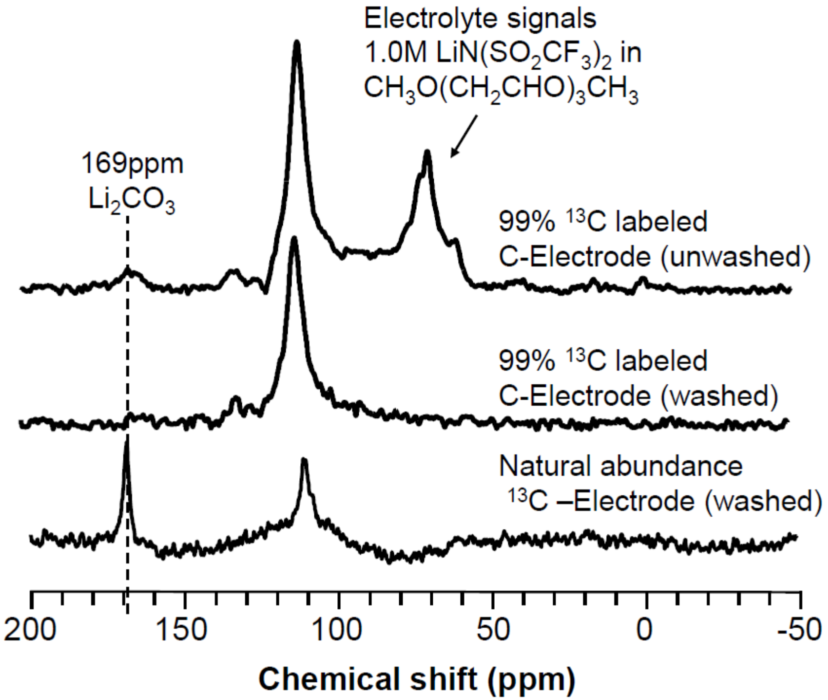


The characteristic peak of carbon for Li_2CO_3 is located at 169 ppm and the peak at 112 ppm is ascribed for Kel-F signal from the two end plugs inside the MAS rotor.

- ➢ Li_2CO_3 is still found in all electrodes discharged in all different electrolytes.
- ➢ The formation of Li_2CO_3 during discharge process of a Li-air battery will limit the cycle life of the batteries.
- ❖ **Where is Li_2CO_3 from – carbon electrode or electrolyte?**

Li_2CO_3 Comes From the Electrolyte
--^{13}C-MAS NMR Study

- ^{13}C-labeled air electrode was prepared and discharged in the same electrolyte.
- If Li_2CO_3 comes from the carbon electrode, the ^{13}C-MAS NMR signal corresponding to Li_2CO_3 would increase by nearly 90 folds using 99% ^{13}C labeling since the natural abundance of ^{13}C is only 1.1% without isotope enrichment.



- ➢ The signal of Li_2CO_3 in the ^{13}C-labeled carbon electrode is not larger, but even less, than the corresponding signal in the natural abundance carbon electrode.
  $\Rightarrow$ This result unambiguously reveals that the Li_2CO_3 is originated not from the carbon electrode but from the electrolyte.
- ➢ Oxygen and/or superoxide radical anions may oxidize the alkyl groups (CH_3 or CH_2) or ether bond (C–O) into the carbonate groups that in turn form Li_2CO_3.

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See Dr. Jian Zhi Hu's poster for more details

4. Summary

1. Graphene based air electrode exhibits very high capacity (~15,000 mAh/g) due to its dual pore structure and defect activity.
2. Specific energy of Li-air batteries with aqueous electrolyte is strongly limited by the operational pH window of NASICON glass. Electrolyte additives and other approaches which can stabilize pH value of electrolyte is critical for long term operation of aqueous based Li-air batteries.
3. In carbonate electrolytes, the majority of the discharge products in Li-air batteries are lithium alkylcarbonates and Li_2CO_3. Apparent rechargeability is due to oxidation of Lithium alkylcarbonates which release CO_2 and CO. This process is not sustainable.
4. Li_2O_2 can be formed during discharge process when ether based electrolytes were used, Li_2CO_3 was still observed and need to be minimized.
5. Electrolyte is the key for rechargeable, long term operation of Li-air batteries.

Acknowledgments

Technical Team:

Wu Xu, Jie Xiao, V. Viswanathan, Jianzhi Hu, Vijayakumar Murugesan, Silas A. Towne, Phillip Koech, Donghai Mei, Fei Ding, Zimin Nie, Yuyan Shao, Jian Zhang, Dehong Hu, Deyu Wang, Jun Liu, and Gordon L. Graff

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