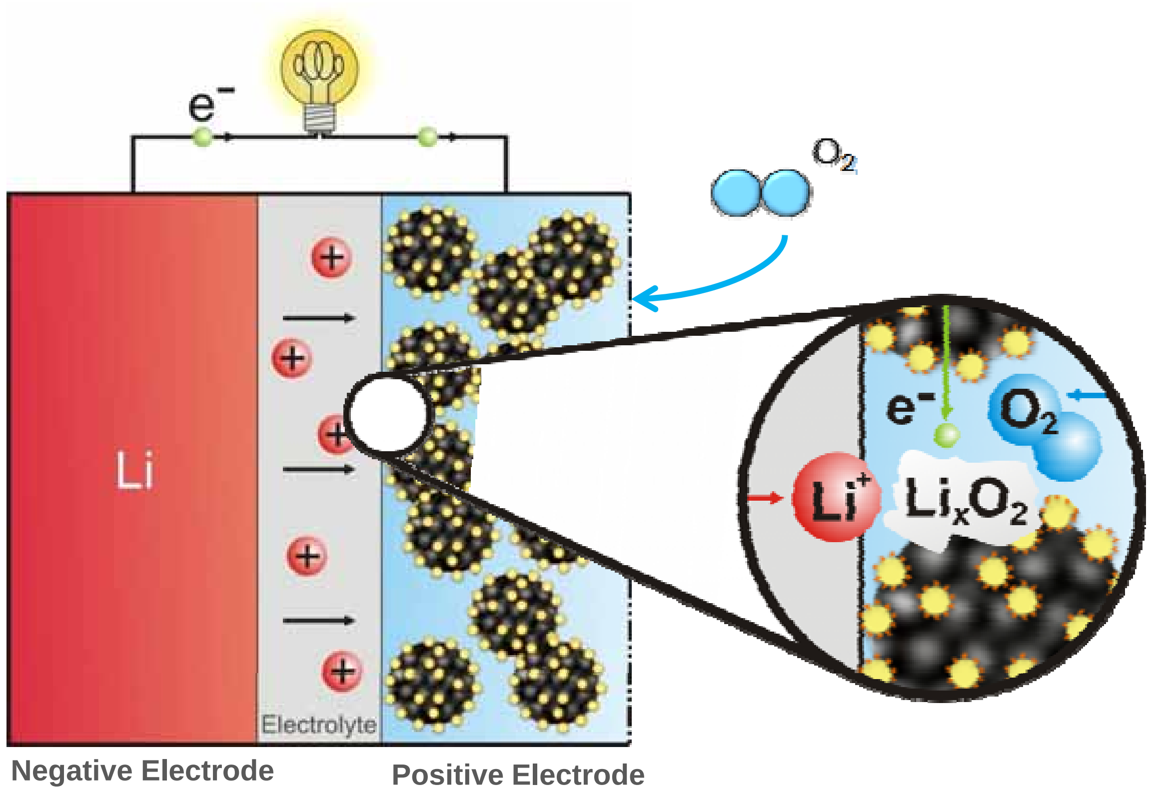
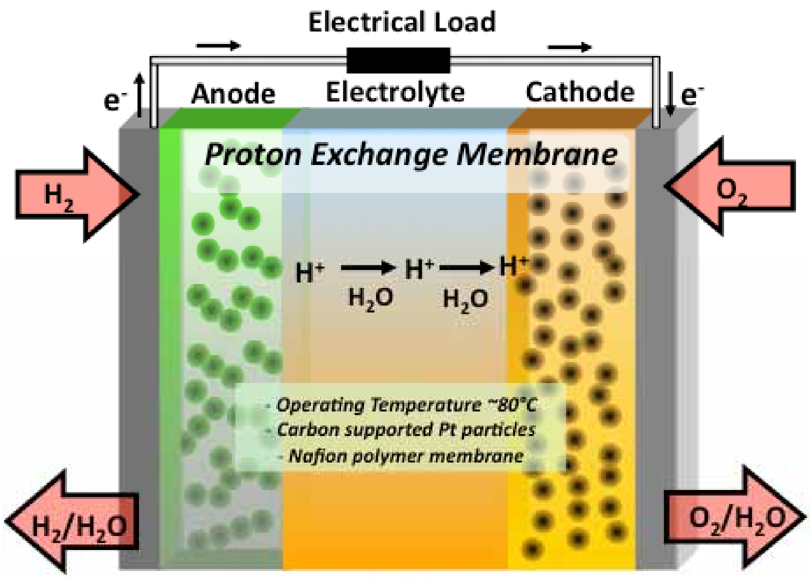
O_2 Electrocatalysis for Rechargeable Li-Air Batteries



Y.C. Lu, H.A. Gasteiger, R. McGuire, Z.C. Xu, K. Hamad-Schifferli, Jonathon Harding, Y. Shao-Horn
MIT, Cambridge, MA 02139, USA

Electrocatalysis in Fuel Cells + Li-Air Batteries

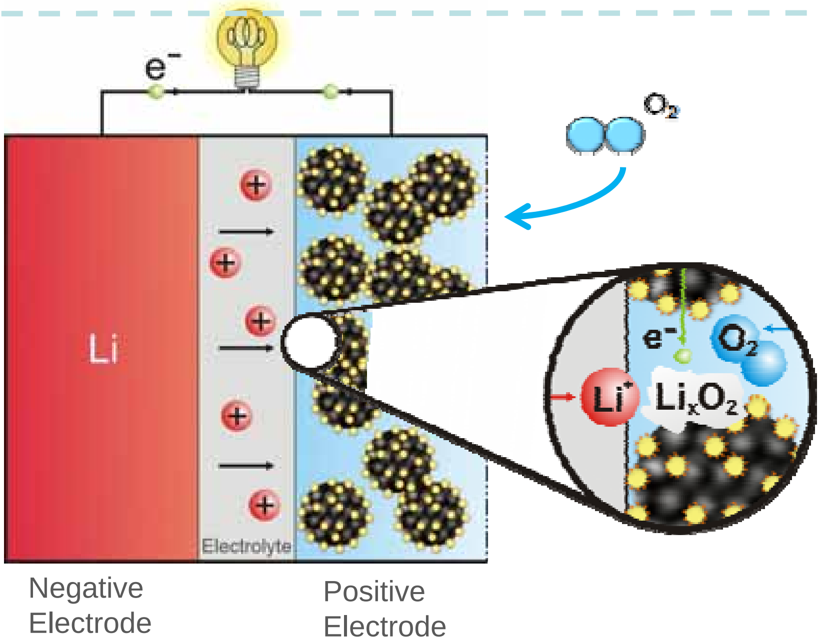


$$1/2O_2 + 2\,H^+ + 2\,e^- \Rightarrow (H_2O)$$
$$2\,H_2 \Rightarrow 2\,H^+ + 2\,e^-$$

$$H_2 + 1/2O_2 \Rightarrow (H_2O)\ 1.2\ V$$

$E_{rev\text{-}ORR}$ = ~4.3 V vs. Li (acid)

$E_{rev\text{-}ORR}$ = ~3.5 V vs. Li (alkaline)



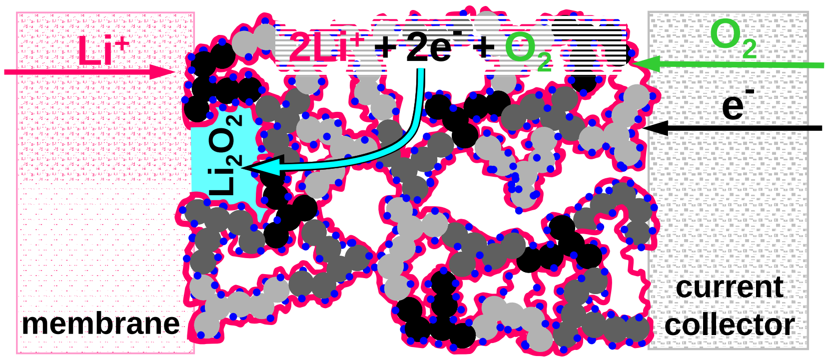
$$1/2O_2 + 2\,Li^+ + 2\,e^- \Rightarrow (Li_2O)_{solid}$$
$$2\,Li \Rightarrow 2\,Li^+ + 2\,e^-$$

$$2\,Li + 1/2O_2 \Rightarrow (Li_2O)_{solid}\ \sim 2.9\ V$$

$E_{rev\text{-}ORR}$ = ~2.9 V vs. Li

Electrochemical Energy Lab

~5-fold in energy density vs. Li-Ion batteries



assumptions:

0.36 g_{carbon}/cm^3 [*)], 15% ε_{carbon}, 25% $\varepsilon_{electrolyte}$, 60% ε_{Li2Ox}

	Li_2O_2	Li_2O	$LiCoO_2$
Q_s wrt. C [mAh/g_{carbon}]	4600	6000	
Q_s wrt. C+Li_2O_x [$mAh/g_{(C+Li2Ox)}$]	**900**	**1350**	**160**
average discharge voltage [V]	2.75	2.75	3.9
E_s wrt. C+Li_2O_x [$Wh/kg_{(C+Li2Ox)}$]	**2450**	**3700**	**620**

*) W. Gu, D.R. Baker, Y. Liu, H.A. Gasteiger; in: *Handbook of Fuel Cells* (eds.: W. Vielstich et al.); Wiley (2009): *vol. 6*, p 631

Li-Air

Estimated gravimetric energy

~ 3000 $Wh/kg_{Li2Ox\text{-}cathode}$

Projecting on the cell level – 1/3

~ 1000 $Wh/kg_{Li\text{-}air\ cell}$

Li-Ion ($LiCoO_2$)

Estimated gravimetric energy

~ 620 $Wh/kg_{LiCoO2\text{-}cathode}$

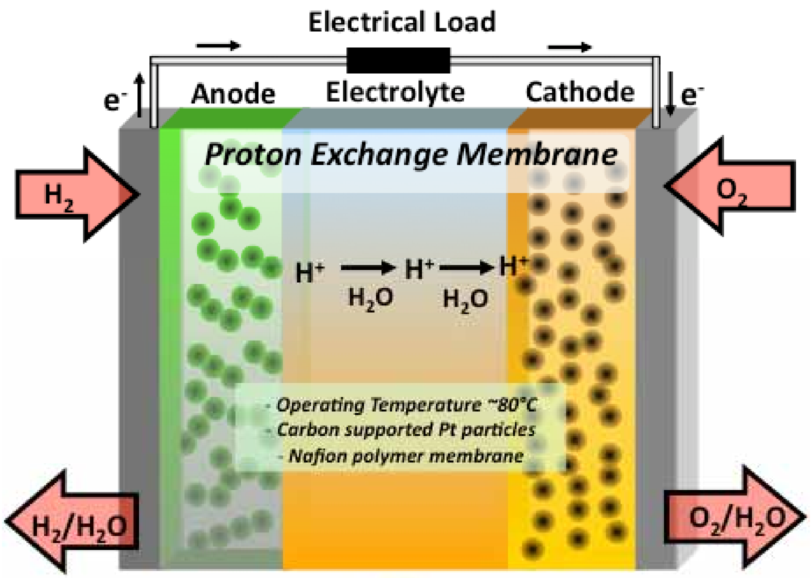
Projecting on the cell level – 1/3

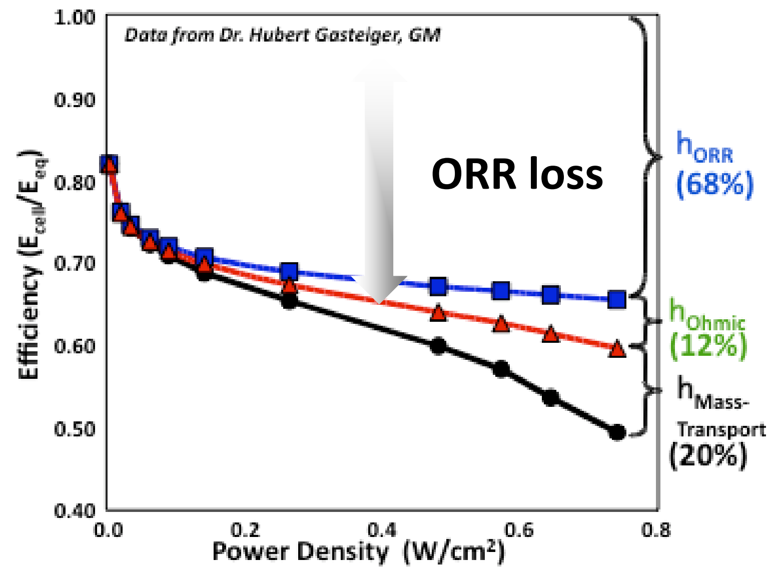
~ 210 $Wh/kg_{LiCoO2\ cell}$

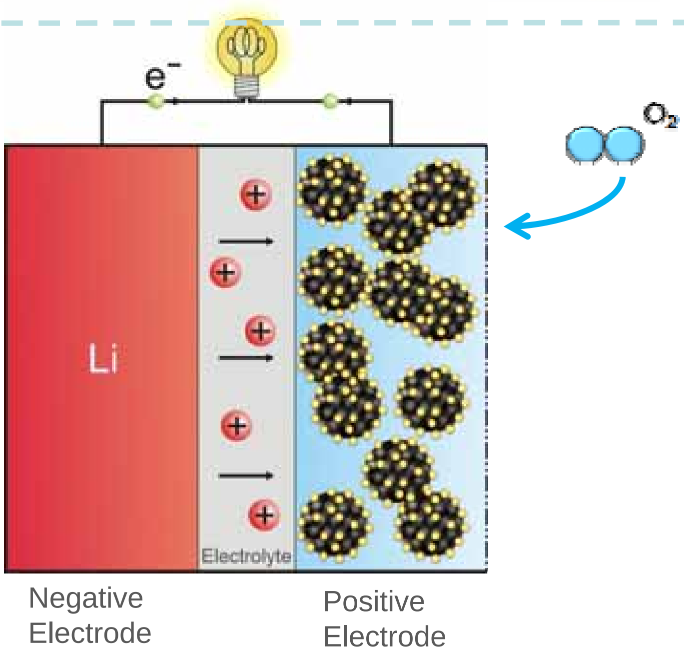
Electrochemical Energy Lab

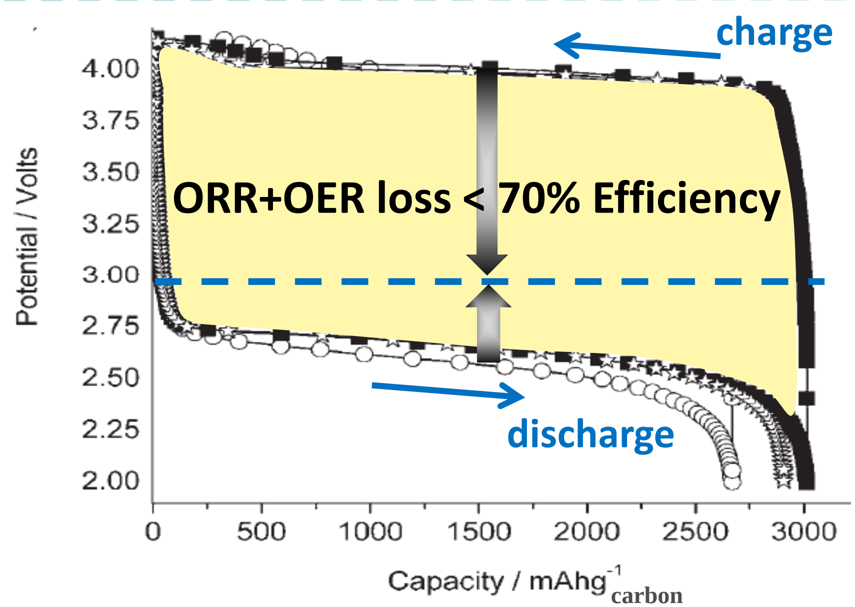
Yi-Chun Lu, Hubert A. Gasteiger, Michael C. Parent, Vazrik Chiloyan, and Yang Shao-Horn,, *Electrochem. Solid State Lett.* 13(6), A69-A72 (2010)

Electrocatalysis in Fuel Cells + Li-Air Batteries









Electrochemical Energy Lab

A. Débart et al, *Angew. Chem. Int. Ed. 47* (2008) 4521

Challenges for Rechargeable Li-Air Batteries ?

- Poor reaction kinetics
  - Poor round-trip efficiencies (<70%)
  - Low rate capability (0.01 mA/cm^2 - 0.1 mA/cm^2)
- Cycle life (10-100 cycles)
- Non-volatile electrolytes
- Engineering challenges
  - No exposure to moisture
  - Safety issues -> Li metal

Poor reaction kinetics - Achieved Lab Performance vs. Practical Viable

Full automotive power require **100 kW**

Fuel Cells
- $1 W/cm^2_{geo}$
- $10\ m^2$

Li-Ion
- $30 mW/cm^2_{geo}$
- $300\ m^2$

Li-Air
- $0.3 mW/cm^2_{geo}$ ($\sim 0.1 mA/cm^2$)
- $30000\ m^2$

~ **2 orders** of magnitude higher in power density is required for Li-air

→ Highly active **catalyst** to facilitate the kinetics is critical !

Wagner et al, JPCL, 2010, (1), 2204

Challenges – No proper method to access the intrinsic activity

Catalyst	Discharge voltage (V)	Capacity of cycle 1 ($mA\,h\,g^{-1}$)	Capacity of cycle 10 ($mA\,h\,g^{-1}$)
Pt	2.55	470	60
$La_{0.8}Sr_{0.2}MnO_3$	2.6	750	40
Fe_2O_3	2.6	2700	75
Fe_2O_3-carbon loaded	2.6	2500	75
NiO	2.6	1600	600
Fe_3O_4	2.6	1200	800
Co_3O_4	2.6	2000	1300
CuO	2.6	900	600
$CoFe_2O_4$	2.6	1200	800

No effect of catalyst on $E_{discharge}$ implies:

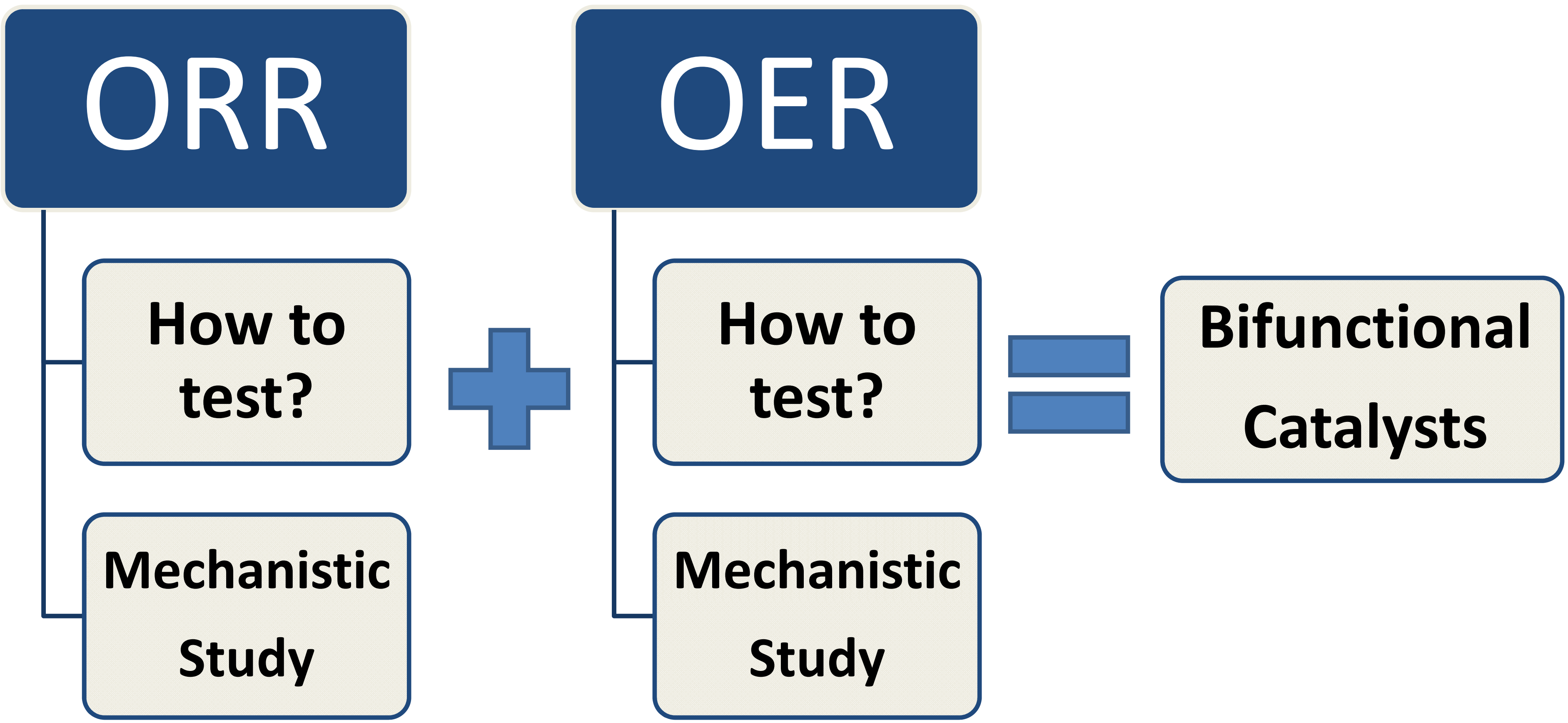
- reaction insensitive to catalyst ?

- catalyst surface blocked by Li_2O_x ?

- high activity of carbon (60-75%wt.) ?

Methods for quantifying intrinsic activity are needed.

A. Débart et al, *J. Power Sources 174* (2007) 1177

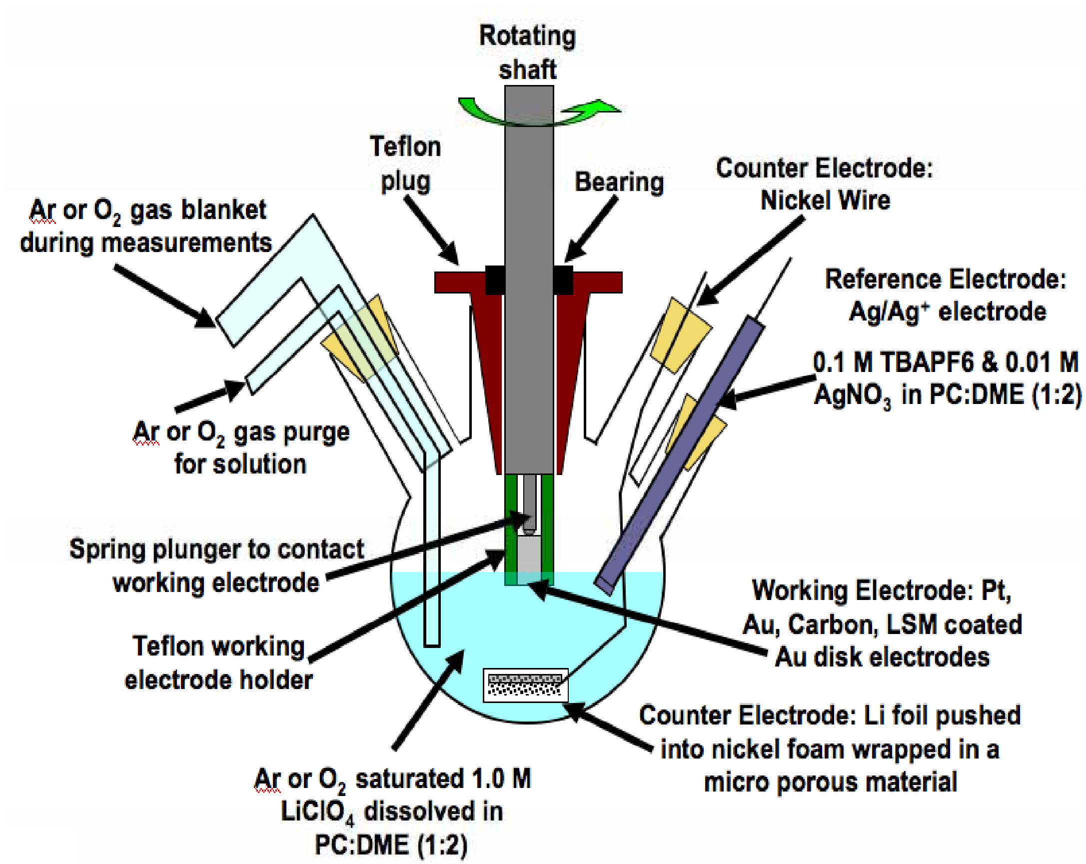

ORR
How to test?
Mechanistic Study
OER
How to test?
Mechanistic Study
Bifunctional Catalysts

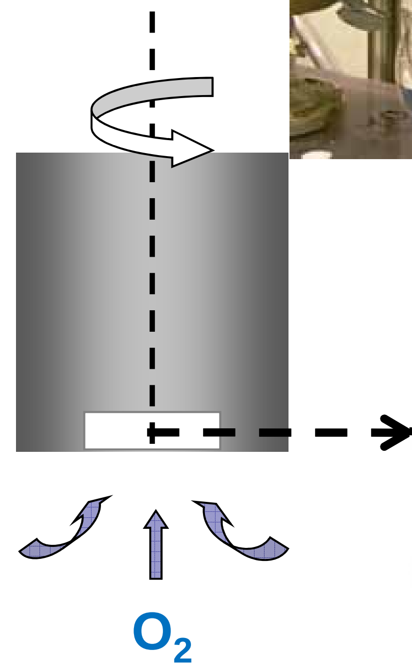
ORR

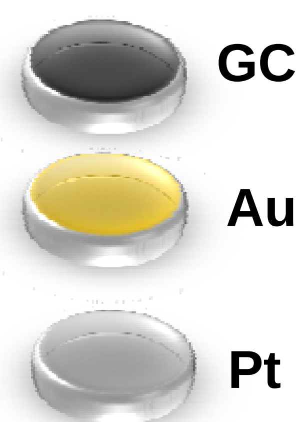
How to test?

Model Surfaces → High surface area catalyst

Rotating Disk Electrode → decouple mass transport loss → probe the intrinsic catalytic activity

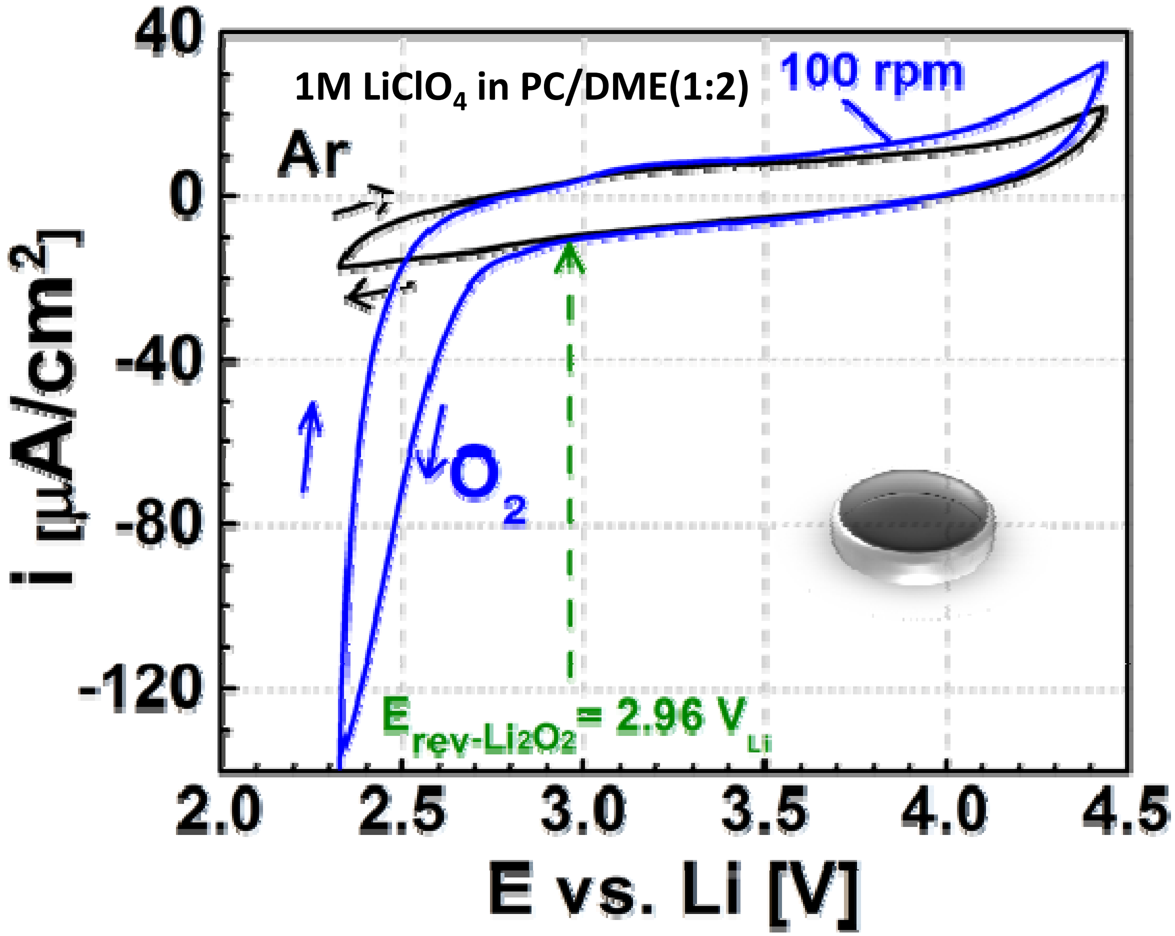






Yi-Chun Lu, Hubert A Gasteiger, Ethan Crumlin, Robert McGuire, and Yang Shao-Horn, , *J. Electrochem. Soc. 157(9) A1016* (2010)

ORR kinetics on Glassy Carbon



• The observed cathodic current is due to dissolved oxygen

• ORR: 4 $\mu A/cm^2_{GCE}$ at 2.7 V >> ~0.2 $\mu A/cm^2_{carbon}$ required at the cell level

Yi-Chun Lu, Hubert A Gasteiger, Ethan Crumlin, Robert McGuire, and Yang Shao-Horn, , *J. Electrochem. Soc. 157(9) A1016* (2010)

Hypothesis – carbon is active enough to dominate

Catalyst	Discharge voltage (V)	Capacity of cycle 1 ($mA\,h\,g^{-1}$)	Capacity of cycle 10 ($mA\,h\,g^{-1}$)
Pt	2.55	470	60
$La_{0.8}Sr_{0.2}MnO_3$	2.6	750	40
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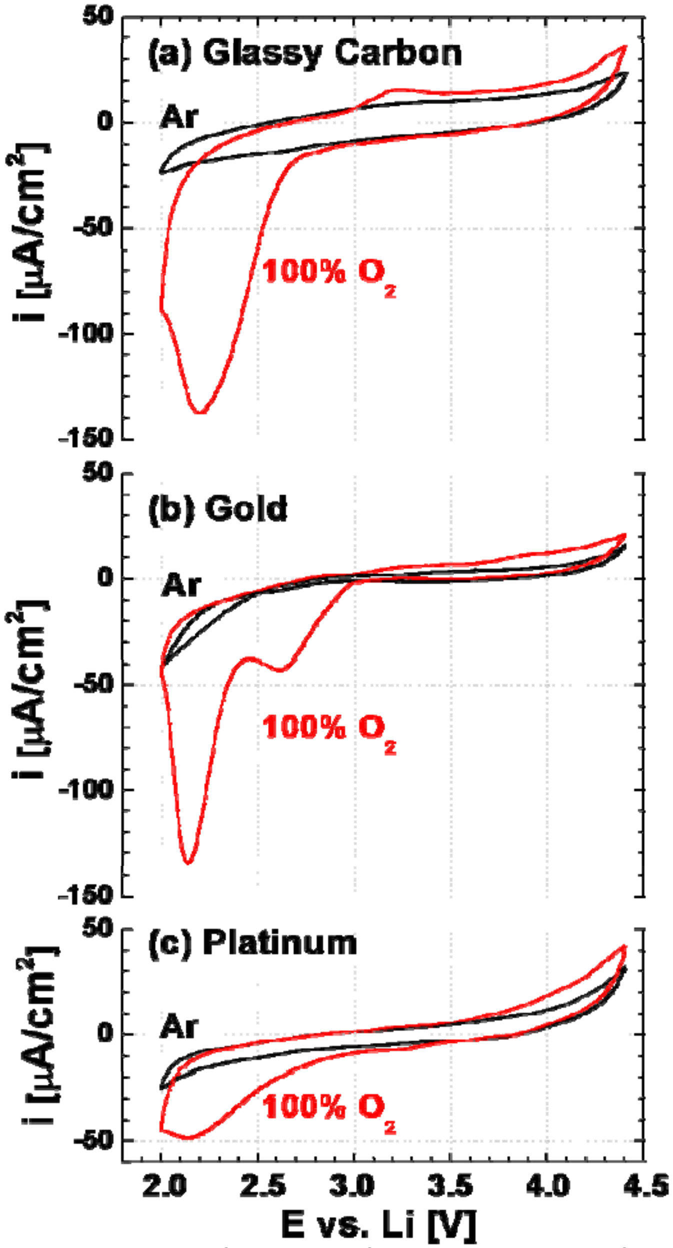
CuO	2.6	900	600
$CoFe_2O_4$	2.6	1200	800

RDE helps to decouple the contribution from carbon.

A. Débart et al, *J. Power Sources 174* (2007) 1177

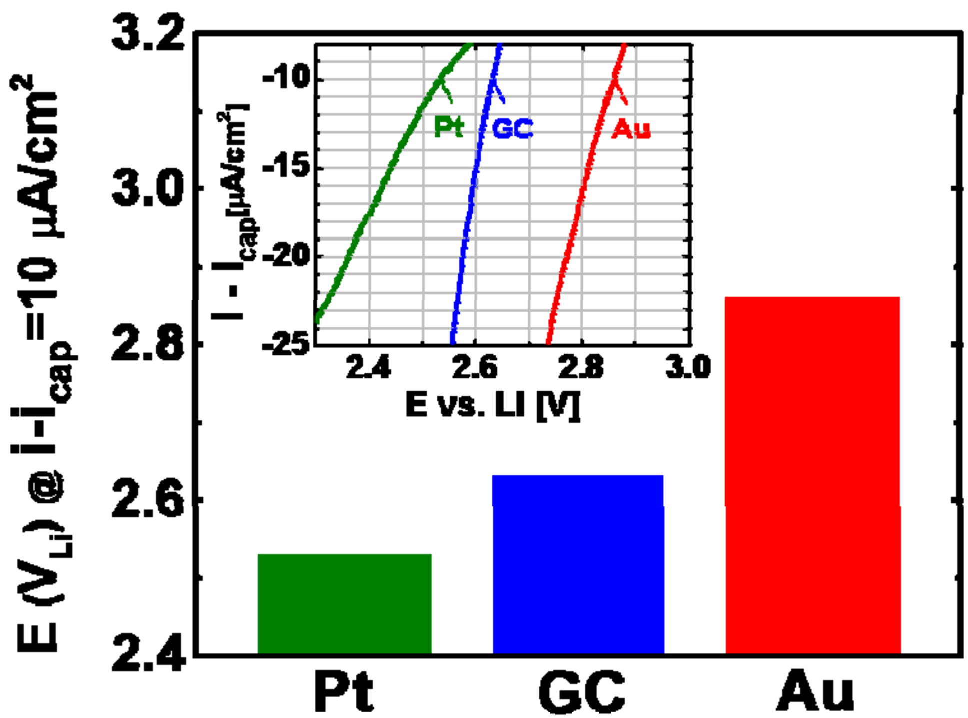
ORR activity comparison on model surfaces



Air electrode characteristics and requirements:

- 100 $m^2/g_{catalyst}$ BET area
- 1 $mg_{catalyst}/cm^2_{cell}$
- 10 mA/cm^2_{cell} as i_{target}

=> 10 $\mu A/cm^2_{disk}$



Au >> GC > Pt

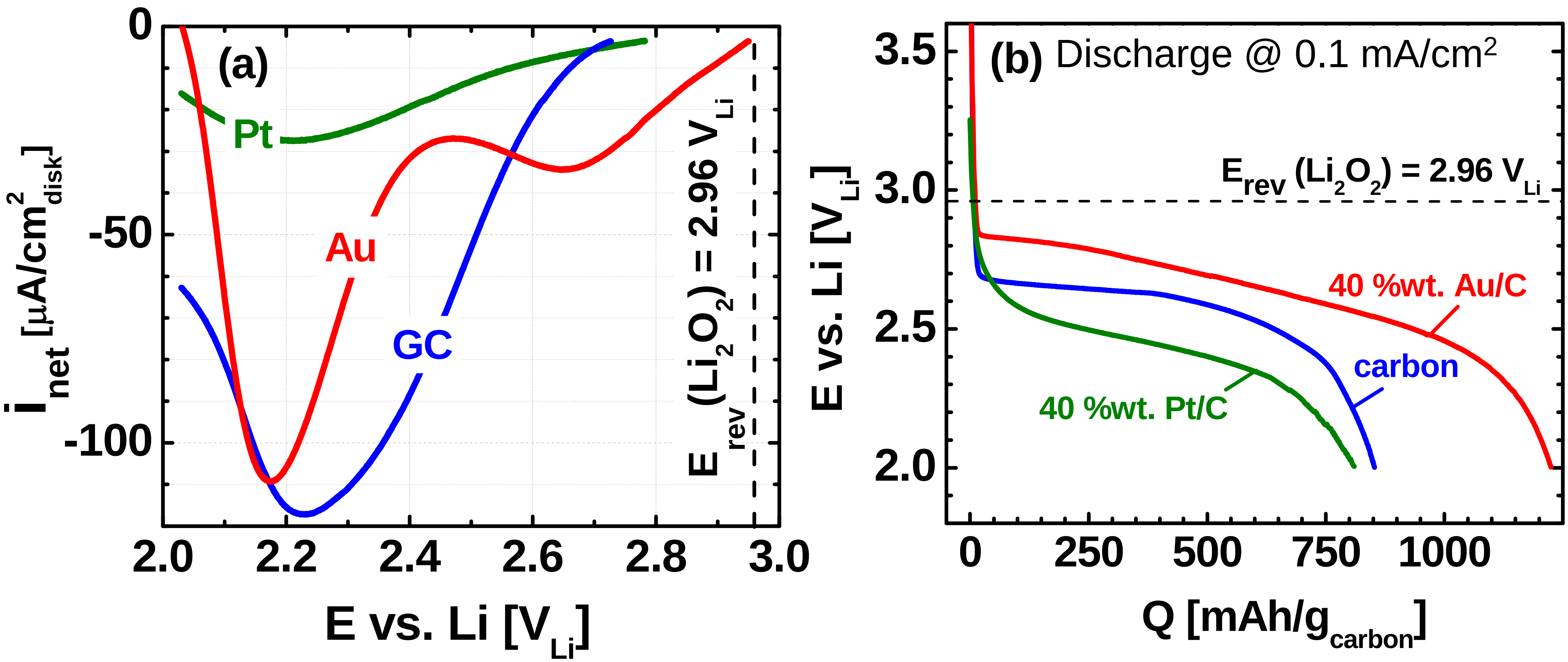
Yi-Chun Lu, Hubert A Gasteiger, Ethan Crumlin, Robert McGuire, and Yang Shao-Horn, , *J. Electrochem. Soc. 157(9) A1016* (2010)

ORR

How to test?

Model Surfaces → High surface area catalyst

Translate model surface trends to practical batteries

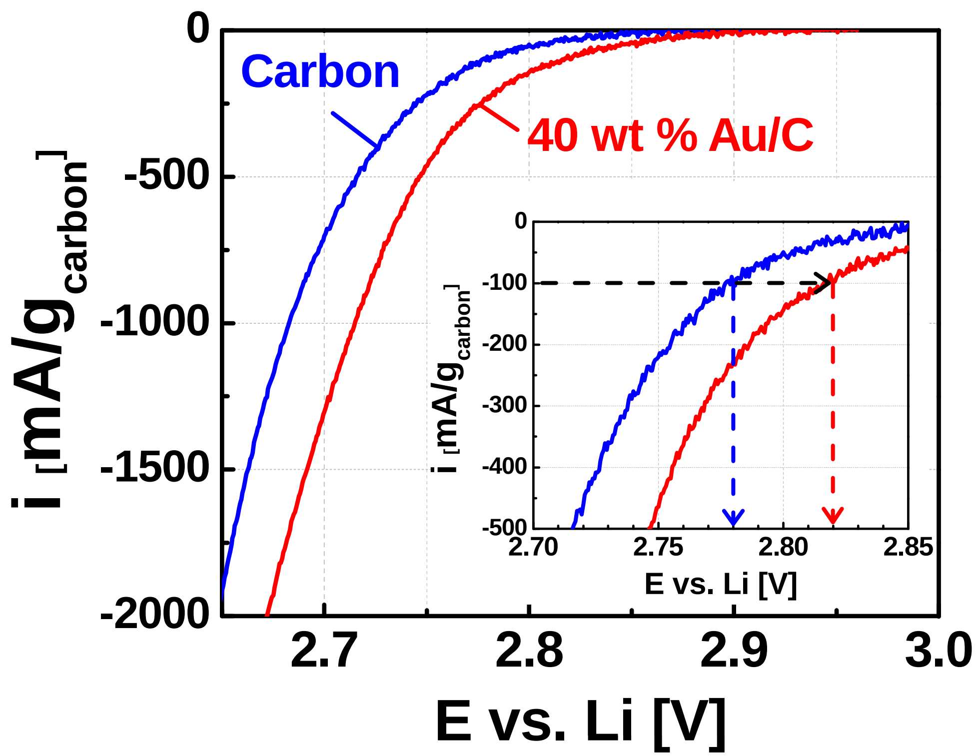


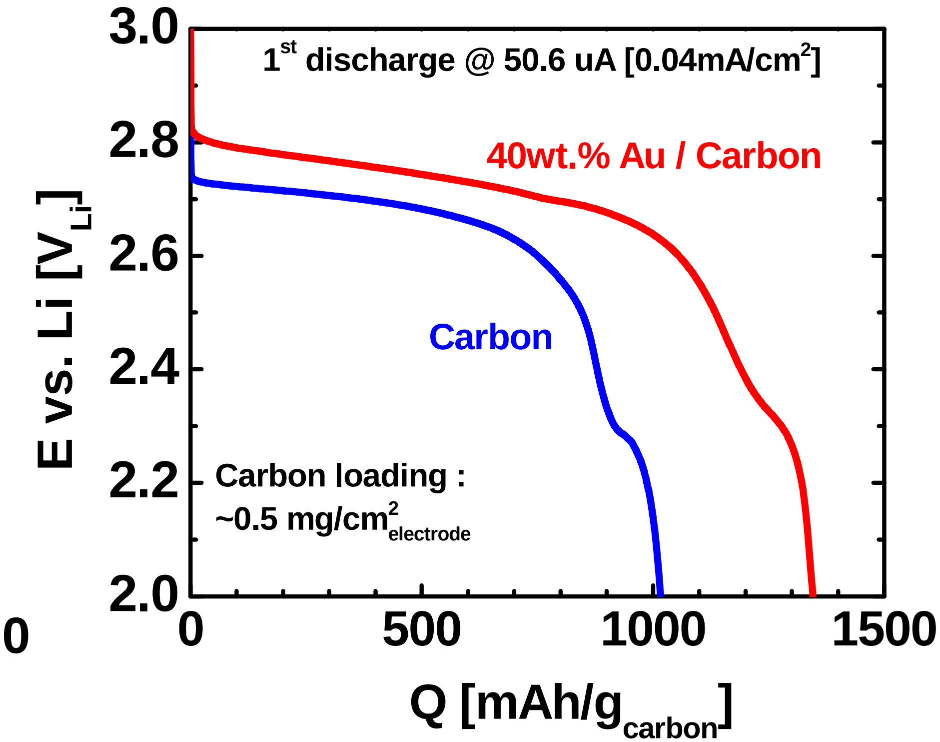
❖Getting precious metal disks is not easy and expensive.

❖Making air electrodes is tricky.

What are alternative ways to evaluate NPs?

RDE Measurements of Thin-Film Catalyst NPs





✓Provide a convenient way of catalyst screening.

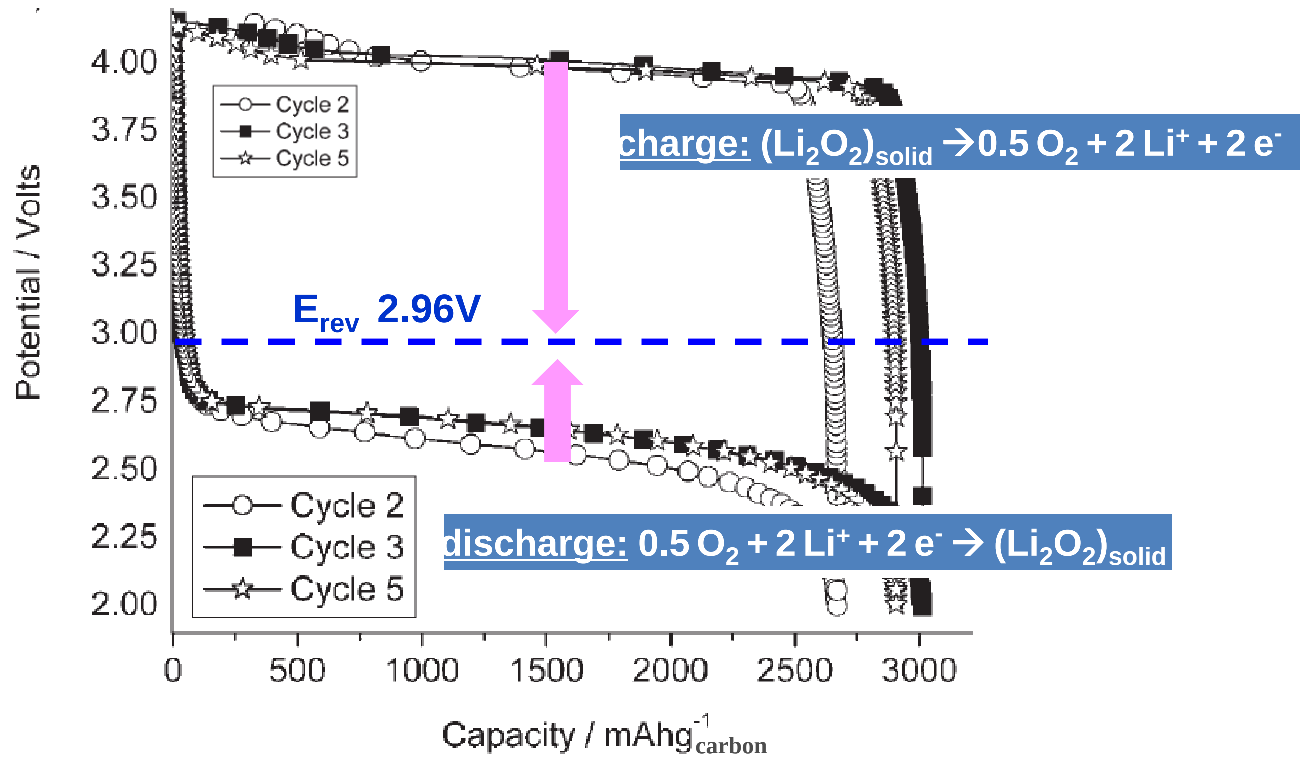
=> To implement the technique to study activity trends

Yi-Chun Lu, Hubert A Gasteiger, and Yang Shao-Horn, , Manuscript in preparation (2010)

OER

How to test?

Challenges – Low efficiency & Power



A. Débart, A.J. Paterson, J. Bao, P.G. Bruce; *Angew. Chem. Int. Ed. 47* (2008) 4521

Low efficiency$_{round\text{-}trip}$ ~ 67.5% (2.7/4.0V)

@ low rates of ~ 0.04 mA/cm^2 (70 mA/g)

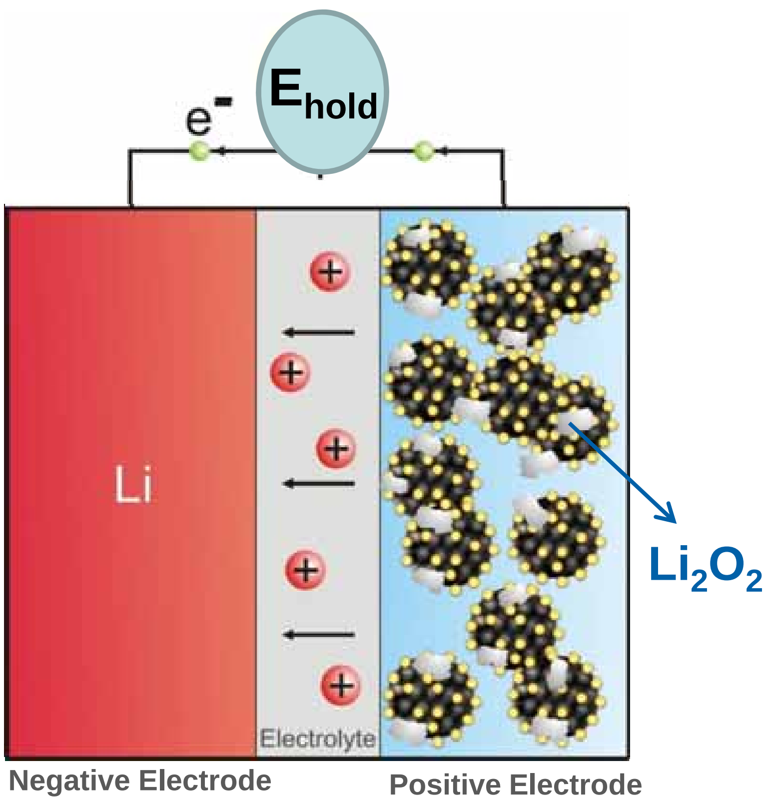
Bifunctional catalysts are needed.

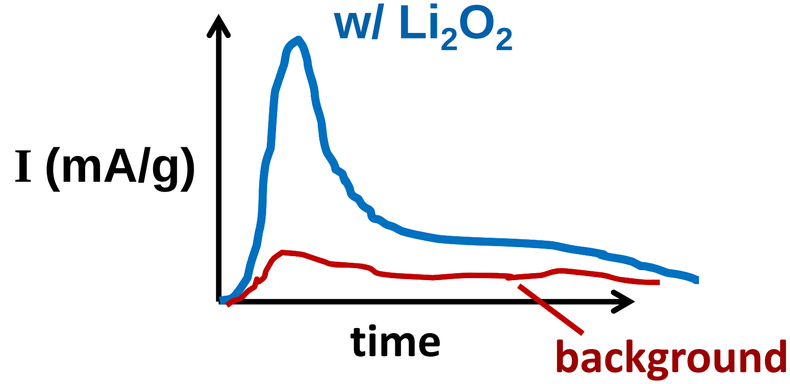
How about RDE for OER ?

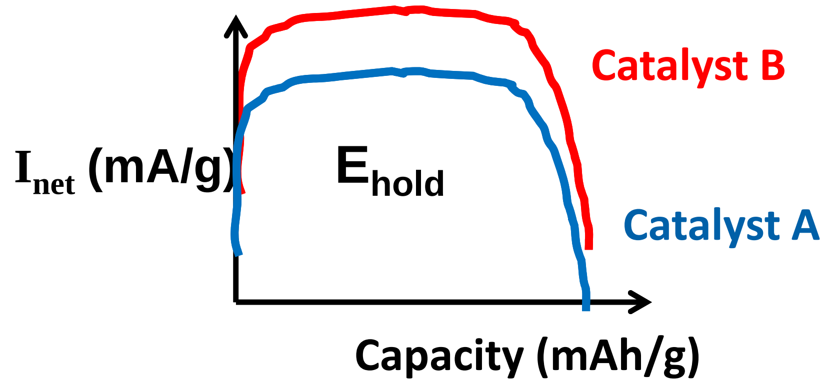
In sufficient Li_2O_2/Li_2O solubility in aprotic solvent -> RDE become very complicated

Understanding OER activity to reduce polarization on charge

Li_2O_2- filled cell



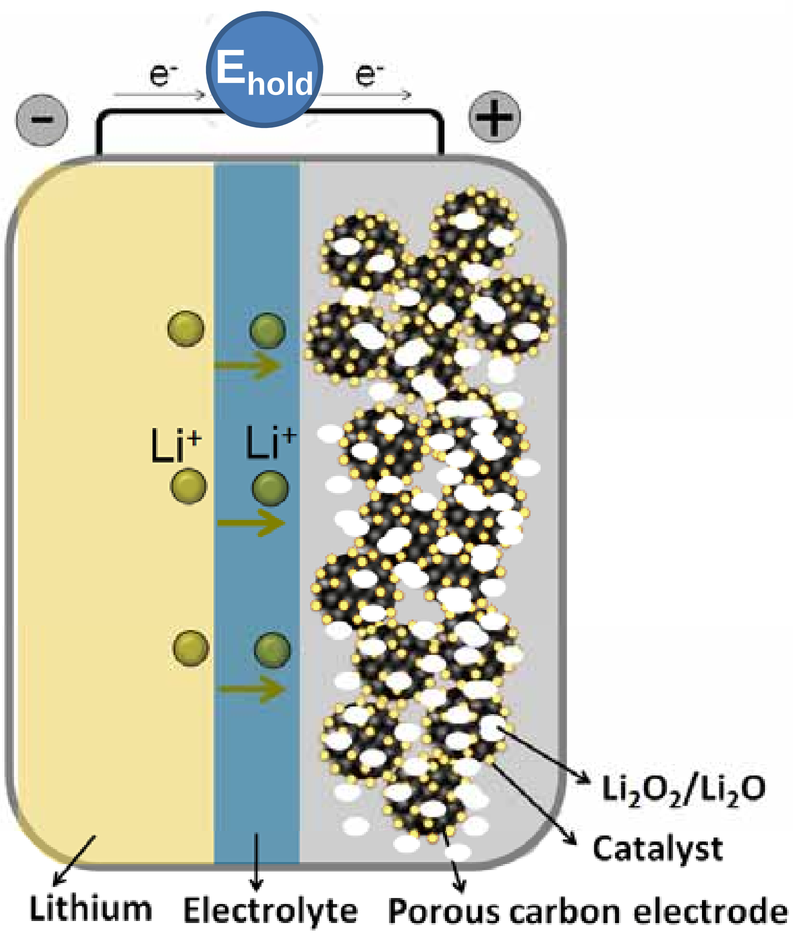


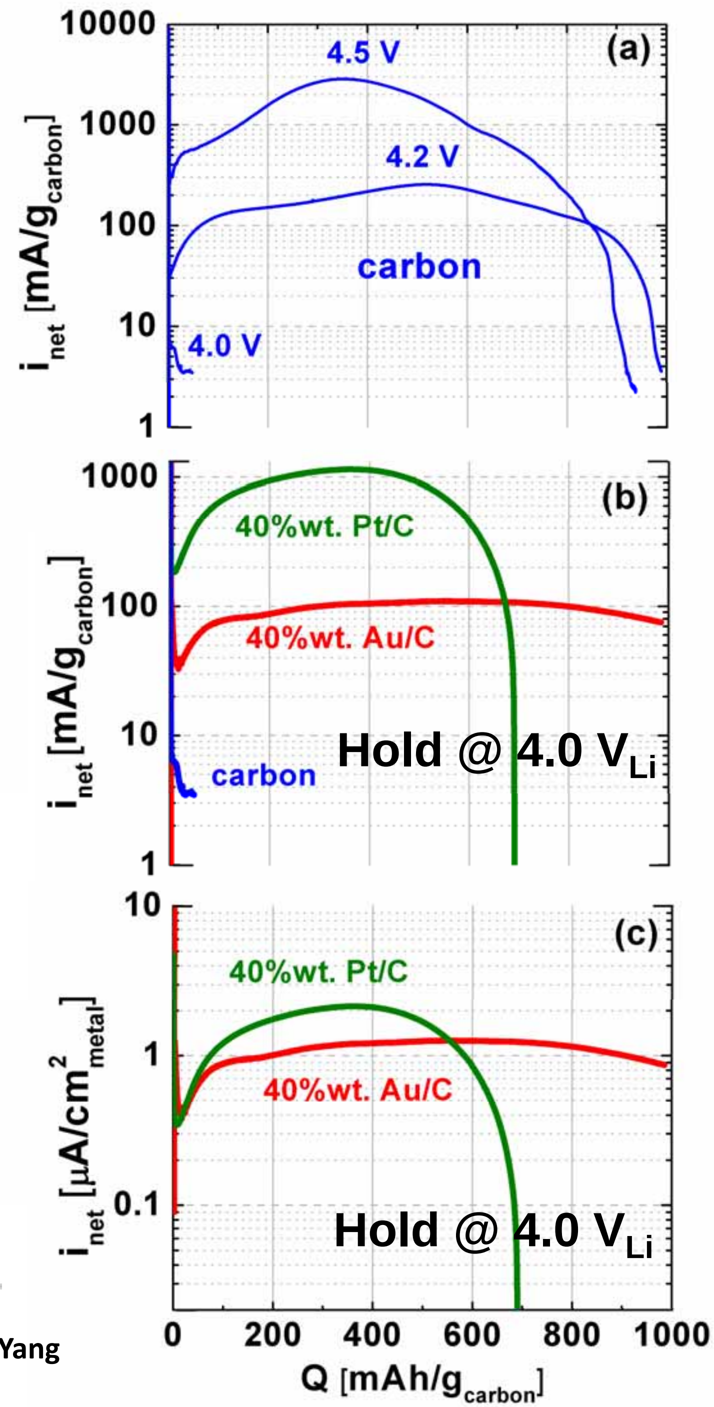


Yi-Chun Lu, Hubert A. Gasteiger, Michael C. Parent, Vazrik Chiloyan, and Yang Shao-Horn,, *Electrochem. Solid State Lett.* 13(6), A69-A72 (2010)

OER activity – Li_2O_2: Pt >> Au > C ?

Li_2O_2- filled cell

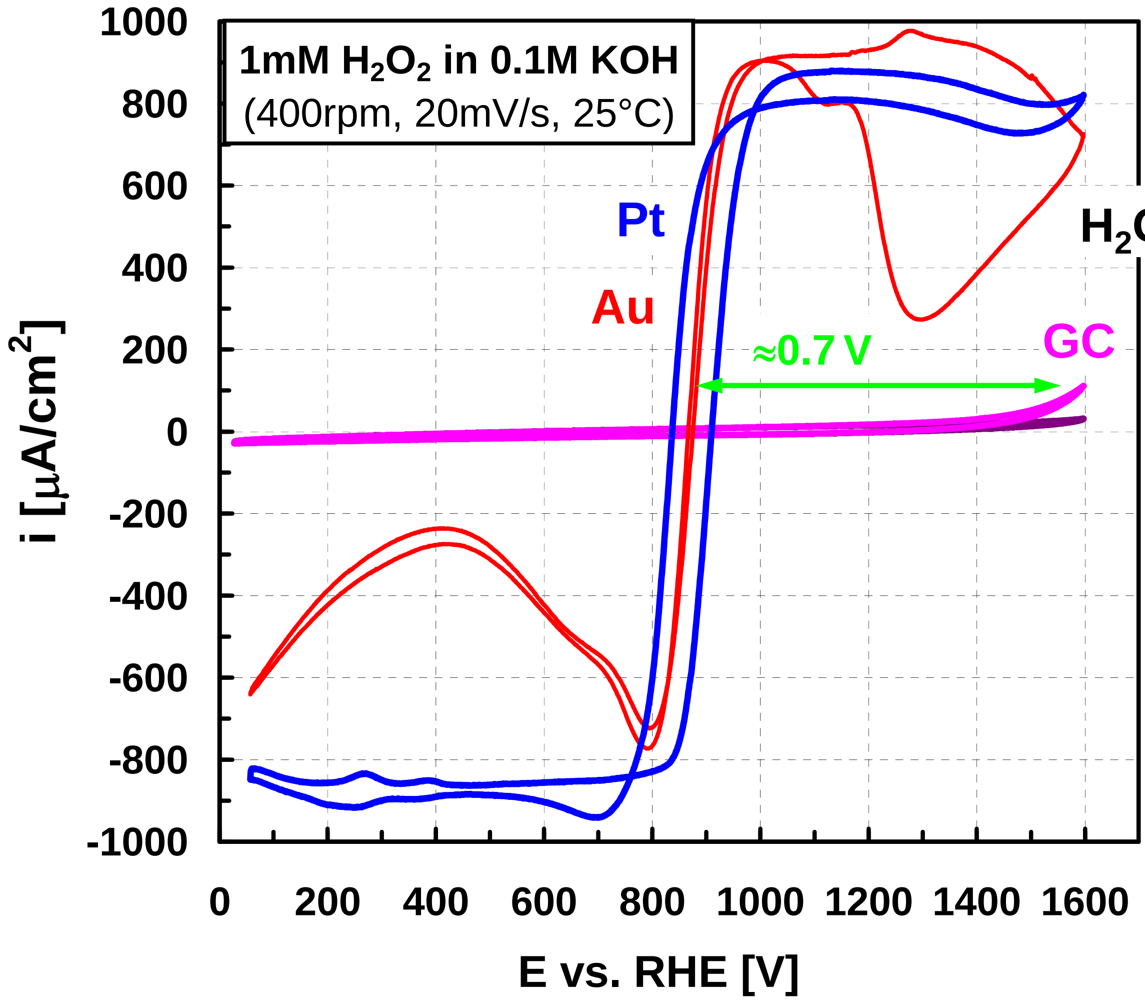




Yi-Chun Lu, Hubert A. Gasteiger, Michael C. Parent, Vazrik Chiloyan, and Yang Shao-Horn,, *Electrochem. Solid State Lett.* 13(6), A69-A72 (2010)

H_2O_2 Decomposition in Aqueous Electrolyte

- **intrinsic OER activity on flat model electrodes (Au, Pt, glassy carbon)**

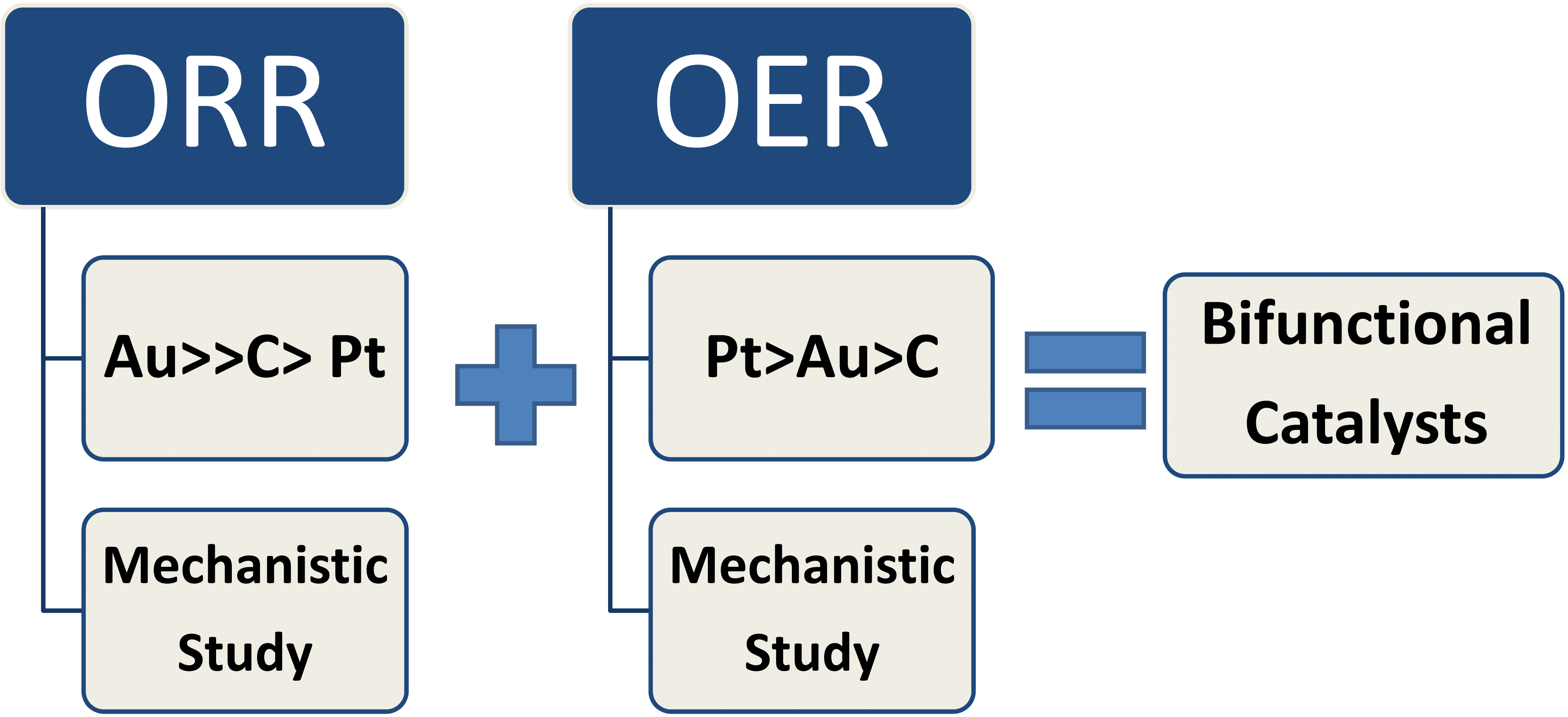


$H_2O_2 \rightarrow 0.5\,O_2 + 2\,H^+ + 2\,e^-$; E_0=0.69V

($H_2O_2 + 2H^+ + 2e^- \rightarrow 2\,H_2O$)

same H_2O_2 OER activity of Pt and Au; much lower activity for C

consistent with Li_2O_2 decomposition in Li-Air cathodes


ORR
Au>>C> Pt
Mechanistic Study
OER
Pt>Au>C
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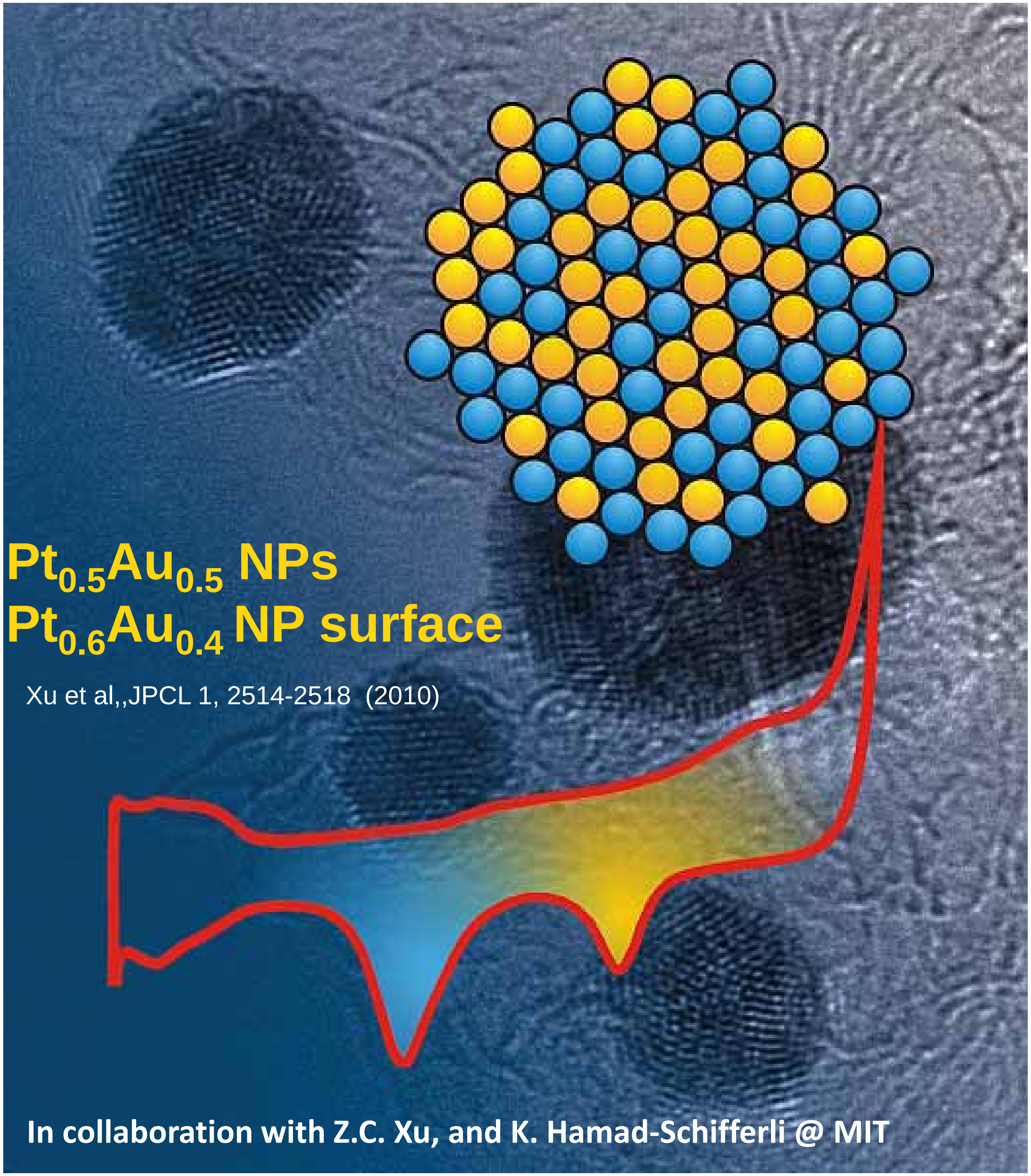
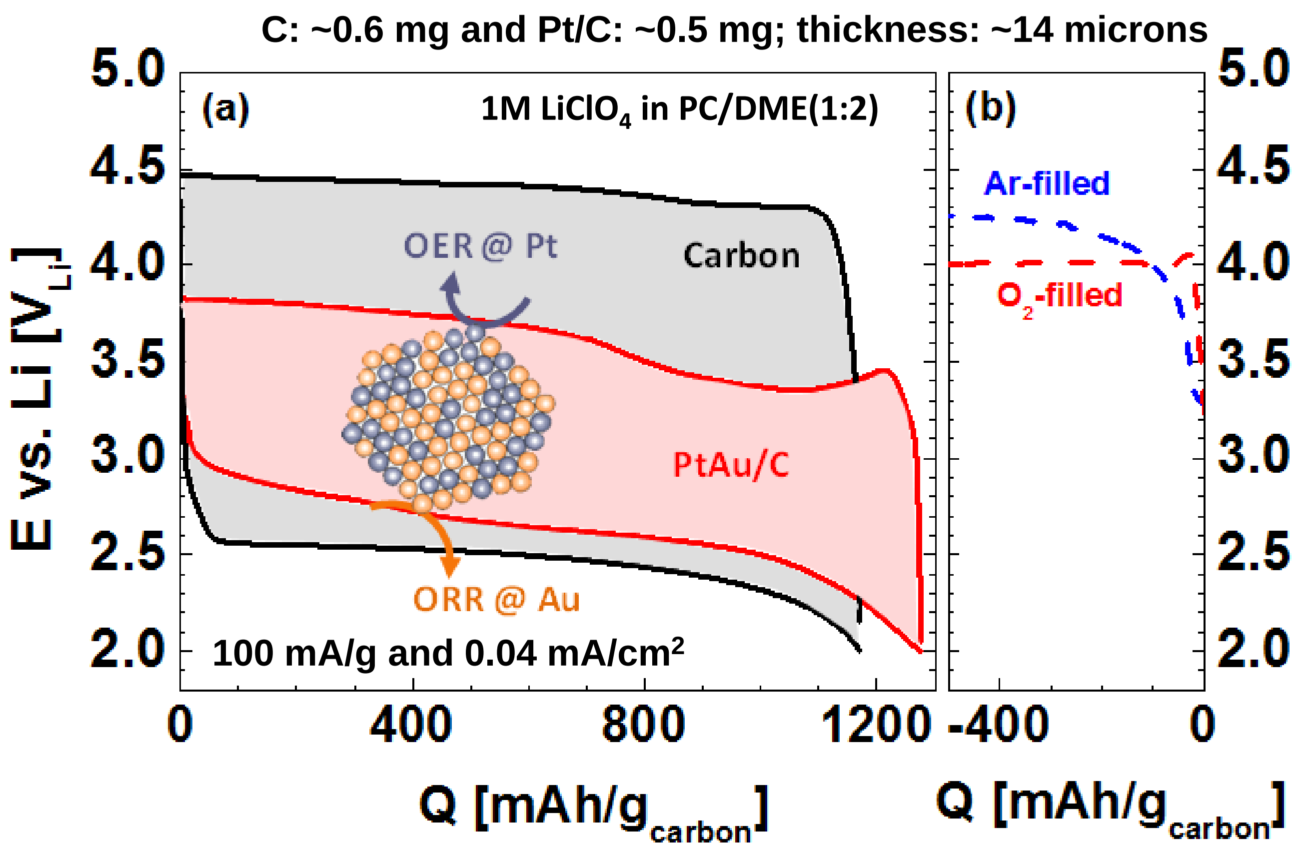
Bifunctional Catalysts



$Pt_{0.5}Au_{0.5}$ NPs
$Pt_{0.6}Au_{0.4}$ NP surface
Xu et al,,JPCL 1, 2514-2518 (2010)
In collaboration with Z.C. Xu, and K. Hamad-Schifferli @ MIT

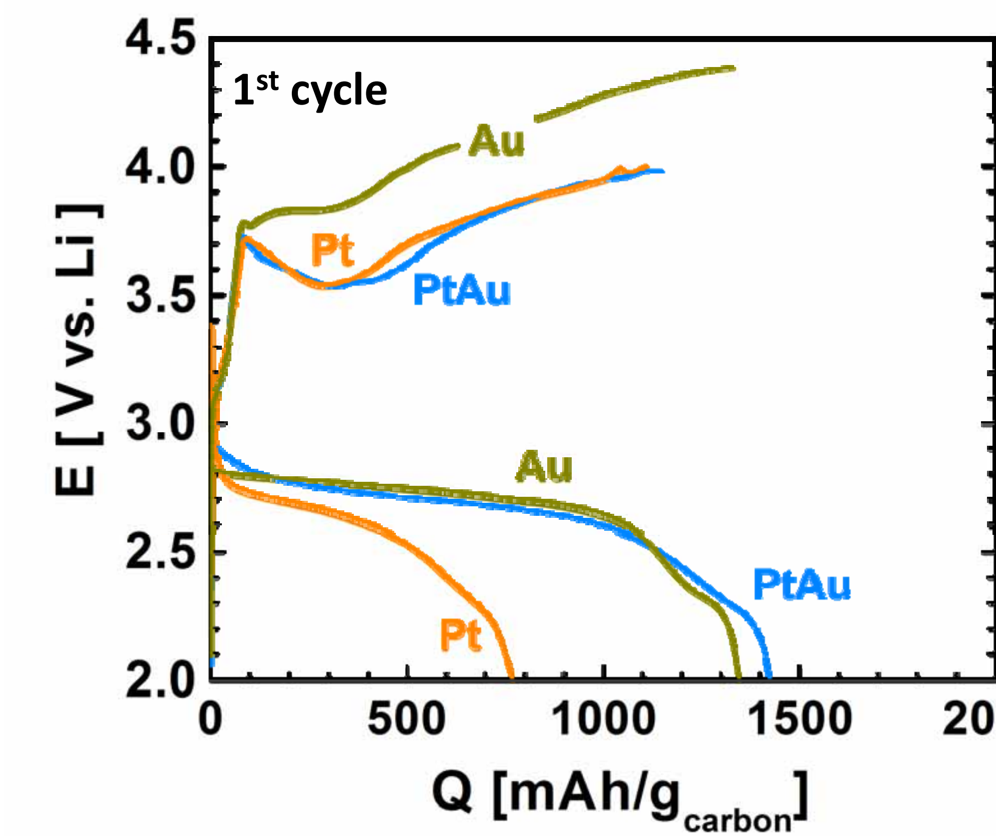
PtAu/C exhibits record round-trip efficiency to date

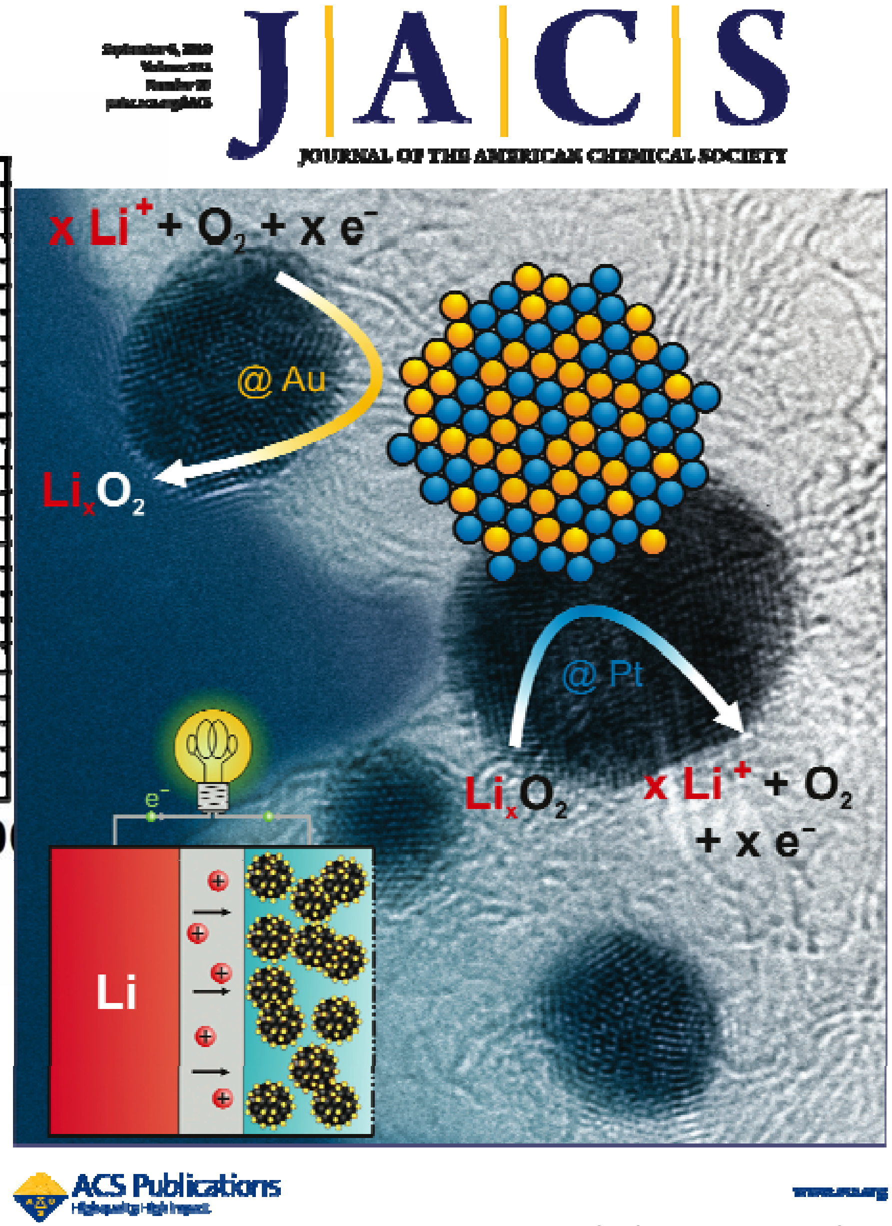


Achieved round-trip efficiency: 75%

Yi-Chun Lu, Zhichuan Xu, Hubert Gasteiger, Shuo Chen, Kimberly Hamad-Schifferli, and Yang Shao-Horn, *JACS,* 132(35) 12170-12171 (2010)

Au is responsible for ORR ; Pt is responsible for OER



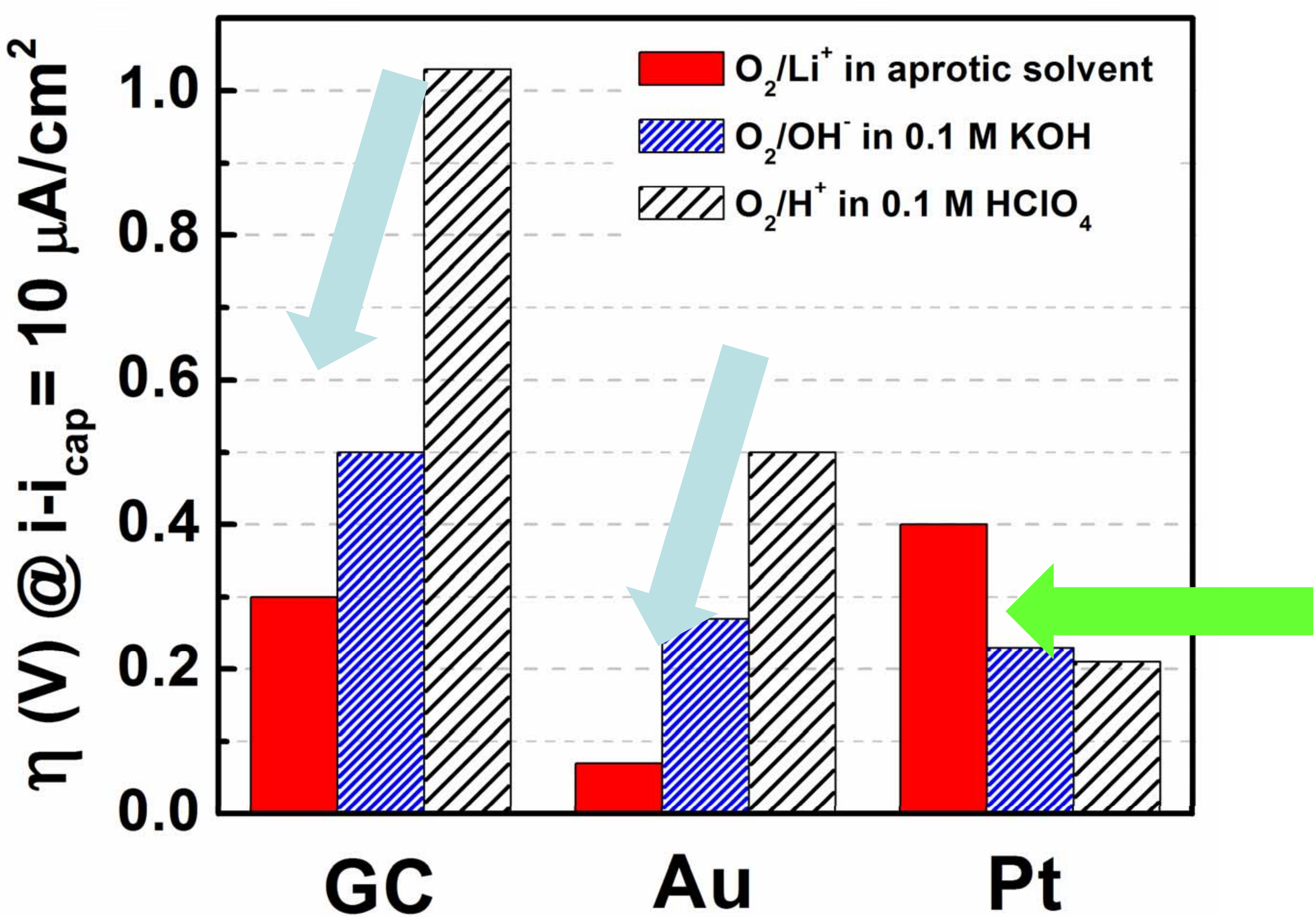


Yi-Chun Lu, Zhichuan Xu, Hubert Gasteiger, Shuo Chen, Kimberly Hamad-Schifferli, and Yang Shao-Horn, *JACS,* 132(35) 12170-12171 (2010)

Challenges in rechargeable Li-air batteries

- **Reaction kinetics**
  - **Poor round-trip efficiencies (<70%)**
  - **Low rate capability (0.01 mA/cm^2 - 0.1 mA/cm^2)**
  - **Solvent reactivity with O_2 reaction intermediate products (e.g. superoxide)**
  - **Cycle life (10-100 cycles)**

Comparing Li^+-ORR activity with H^+-ORR activity



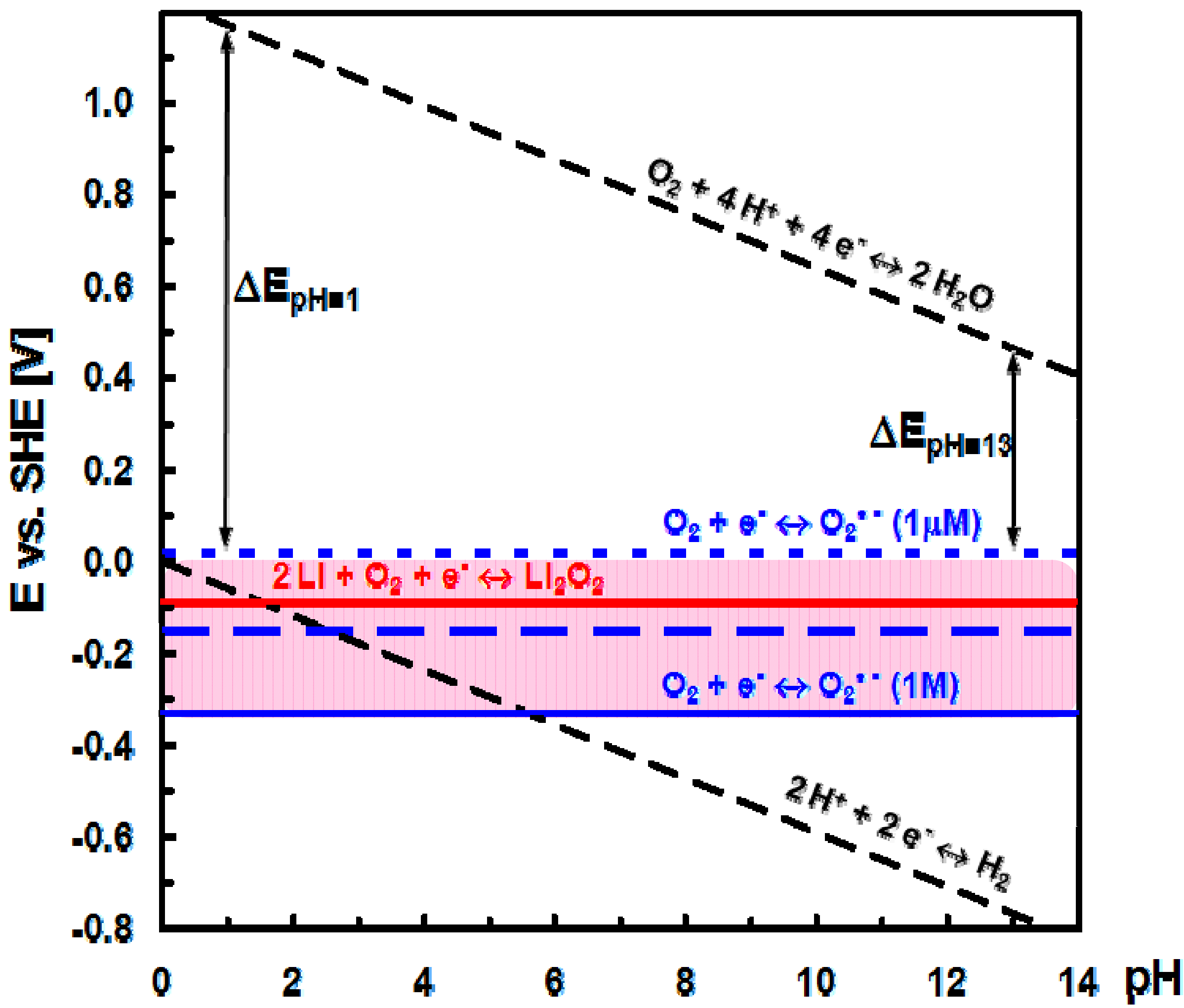
Yi-Chun Lu, Hubert A Gasteiger, Ethan Crumlin, Robert McGuire, and Yang Shao-Horn, , *J. Electrochem. Soc. 157(9) A1016* (2010)

$$O_2 + e^- \dashrightarrow (O_2^-) \xrightarrow{+X\ (H^+,\ Li^+)} (XO_2)_{adsorbed}$$

Step 1	Step 2
Equilibrium voltage is ***independent*** of pH	Equilibrium voltage is ***dependent*** of pH, just like E_{rev}
Overpotential vs. RHE ↓ as pH ↑	Overpotential vs. RHE **≠ f(pH)**
GC & Au	Pt

Yi-Chun Lu, Hubert A Gasteiger, Ethan Crumlin, Robert McGuire, and Yang Shao-Horn, , *J. Electrochem. Soc. 157(9) A1016* (2010)

Why $\eta_{aprotic, Au/GC}$ are smaller than $\eta_{aqueous}$?

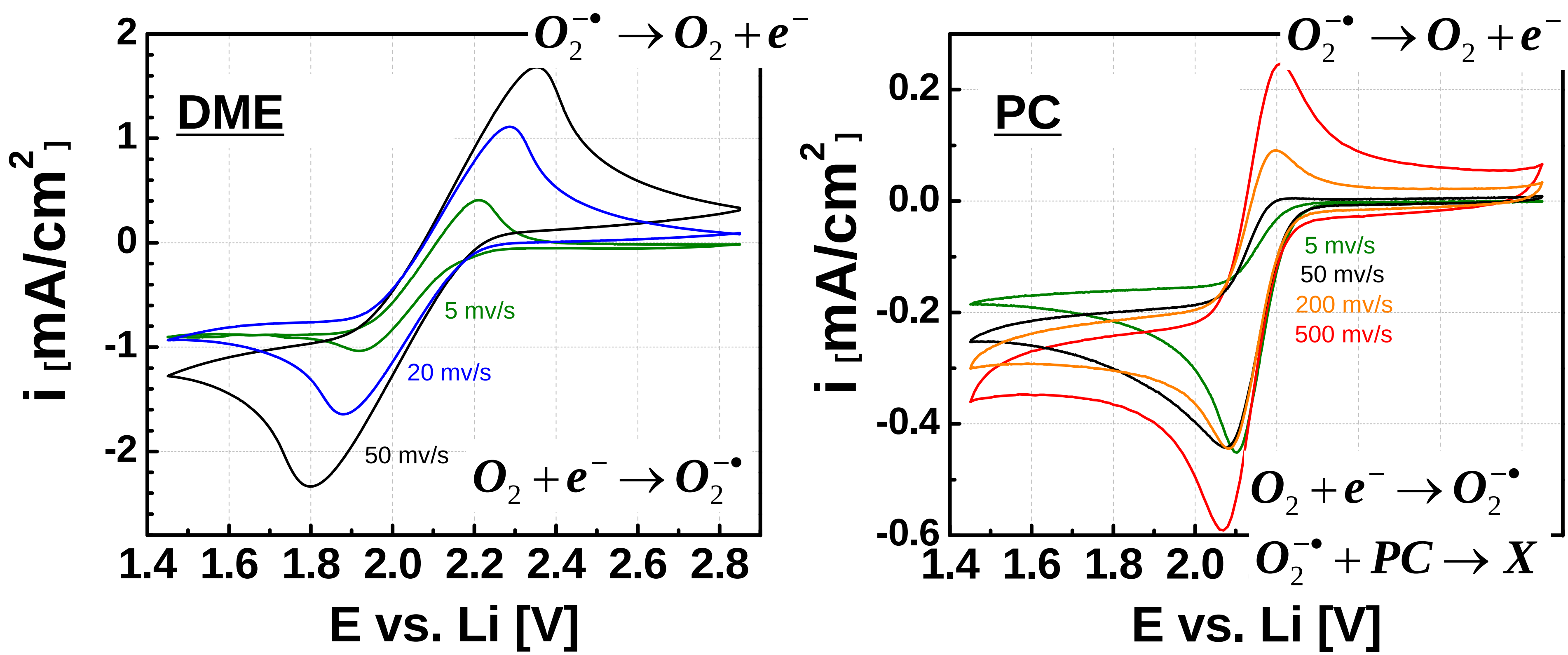


Yi-Chun Lu, Hubert A Gasteiger, Ethan Crumlin, Robert McGuire, and Yang Shao-Horn, , *J. Electrochem. Soc. 157(9) A1016* (2010)

Li-air cathode potential is very close to the stable region of the ORR intermediate species

O_2 Reduction in Li^+ - Free Electrolyte

- ORR on glassy carbon (GC) in 0.5 M $TBAClO_4$ (stagnant electrolyte)



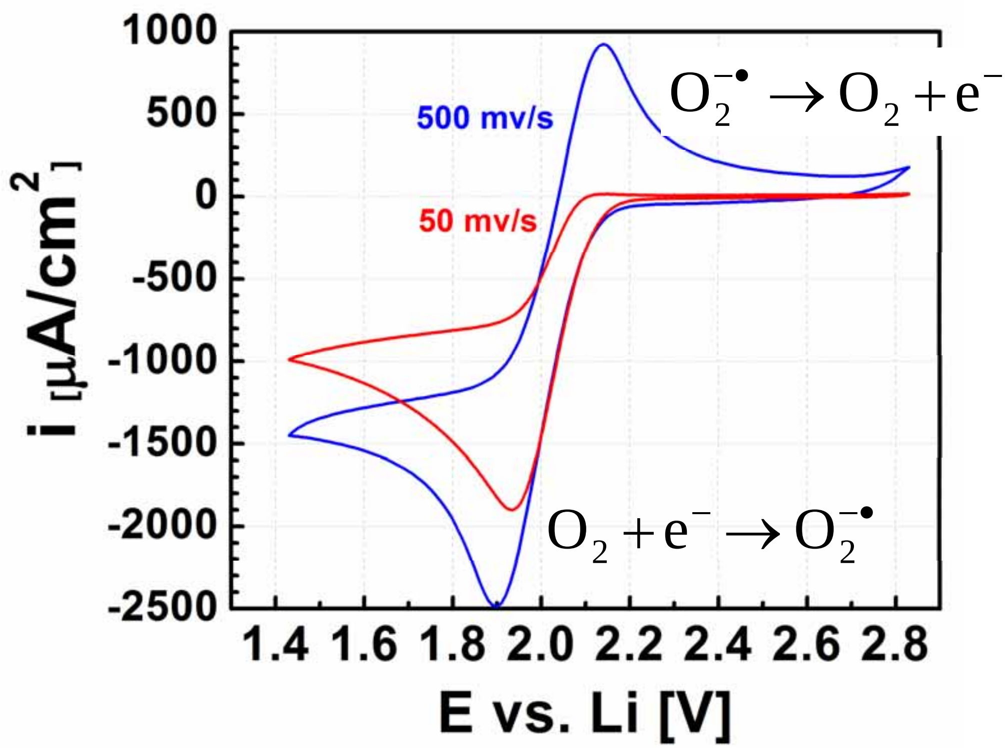
↳ **reaction of reversibly formed superoxide radical, $O_2^{-\bullet}$, with PC*)**

*) **D. Aurbach, M. Daroux, P. Faguy, E. Yeager, *J. Electroanal. Chem. 297* (1991) 225.**

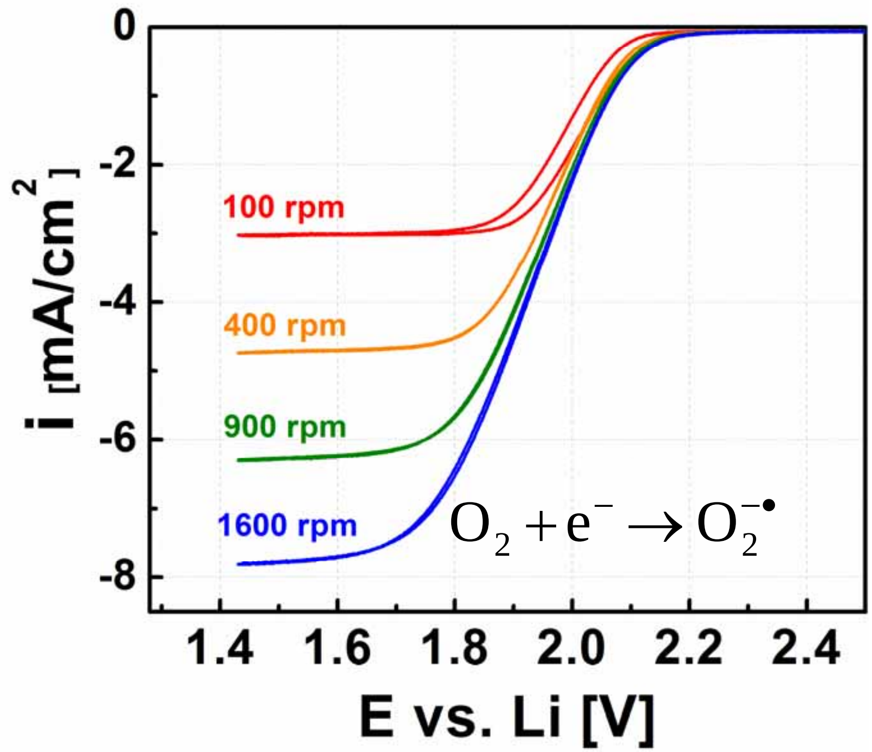
O_2 Reduction in Li^+ - Free Electrolyte

- ORR on glassy carbon (GC) in PC/DME (1/2 v/v) and 1 M $TBAClO_4$

ORR in stagnant electrolyte:

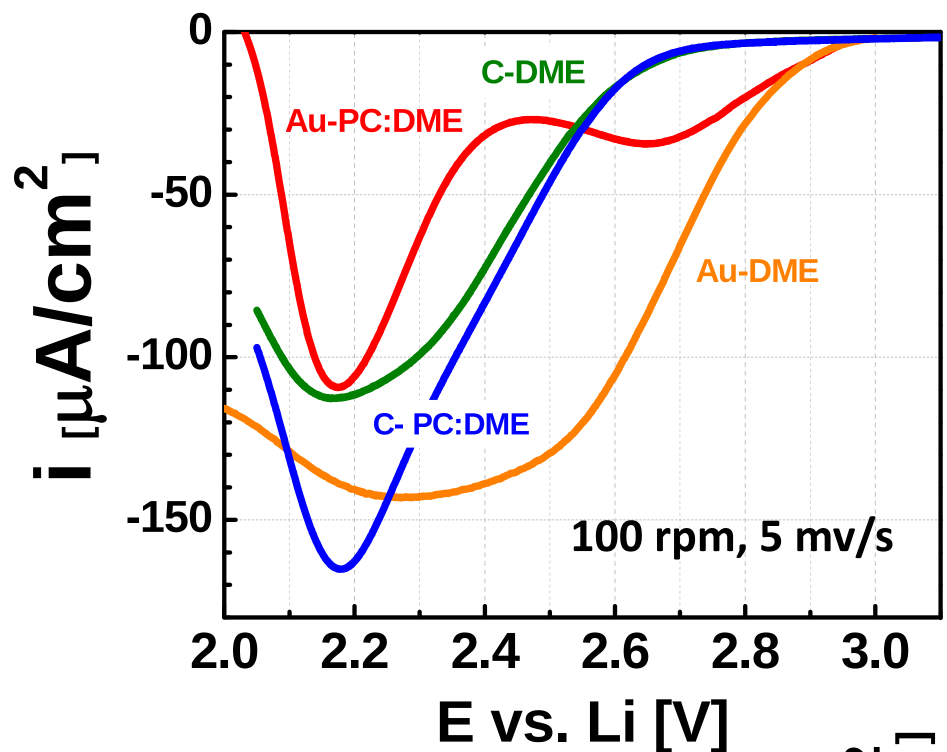


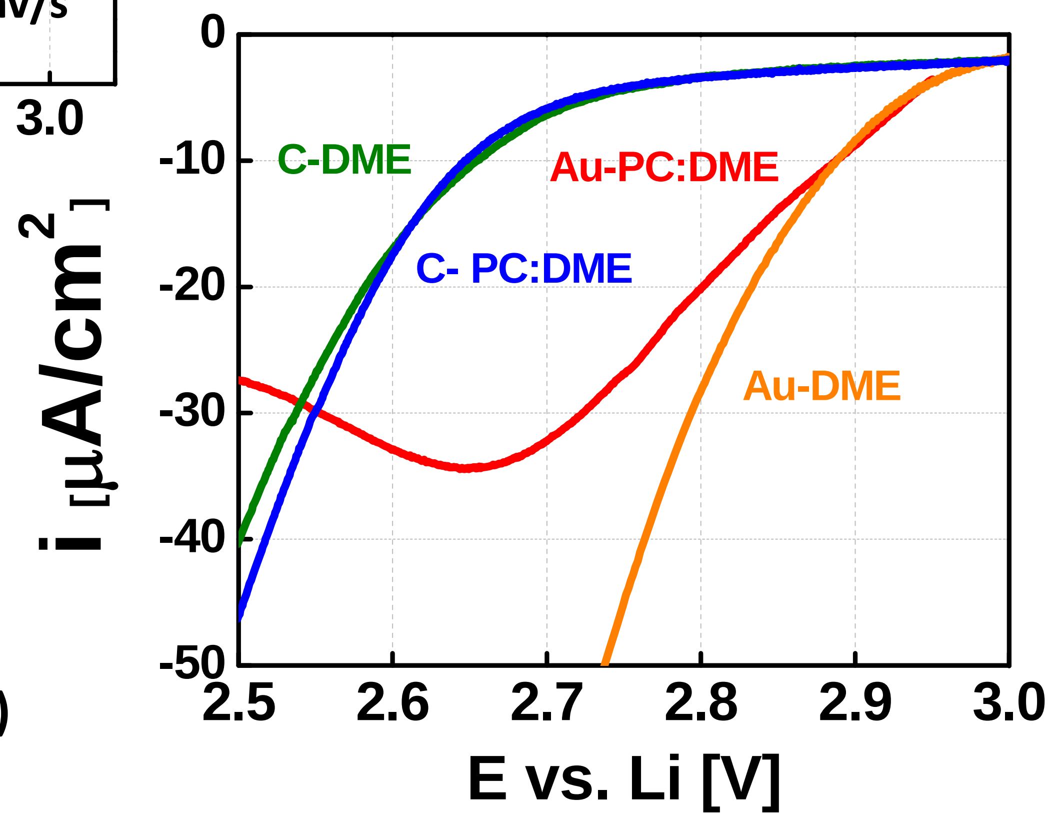
ORR with rotating disk electrode:



reaction of $O_2^{-\bullet}$ with PC/DME

well-defined 1-electron $i_{diffusion}$





PC:DME → 1M $LiClO_4$ PC:DME(1:2)

DME → 0.1M $LiClO_4$ DME

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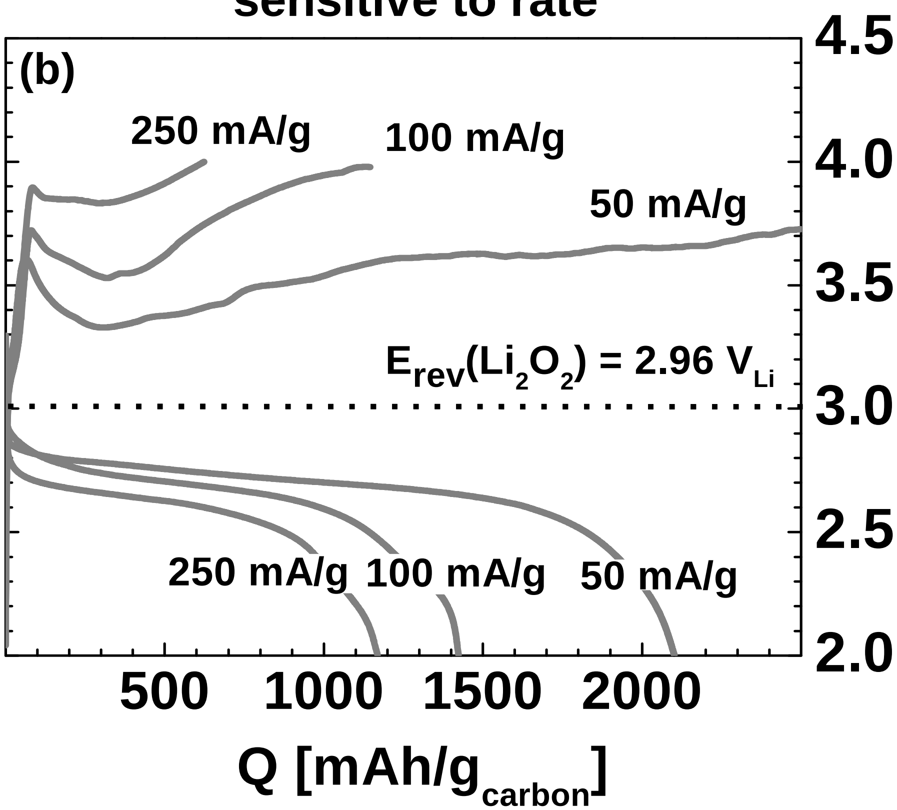
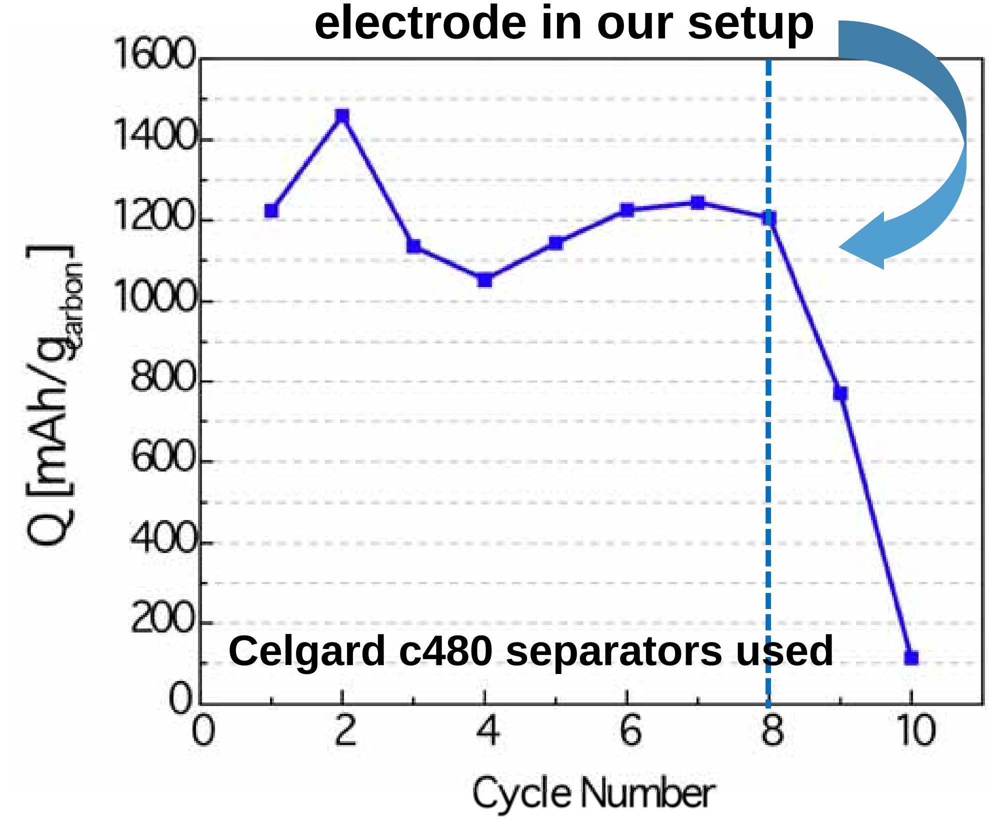
  - **Solvent reactivity with O_2 reaction intermediate products (e.g. superoxide)**
  - **Cycle life (10-100 cycles)**

What about rate capability and cycle life?

Capacity and Efficiency sensitive to rate



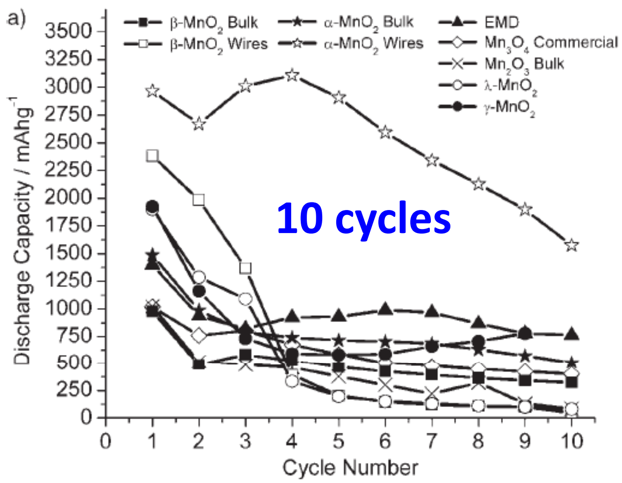
Cycle life limited by lithium electrode in our setup



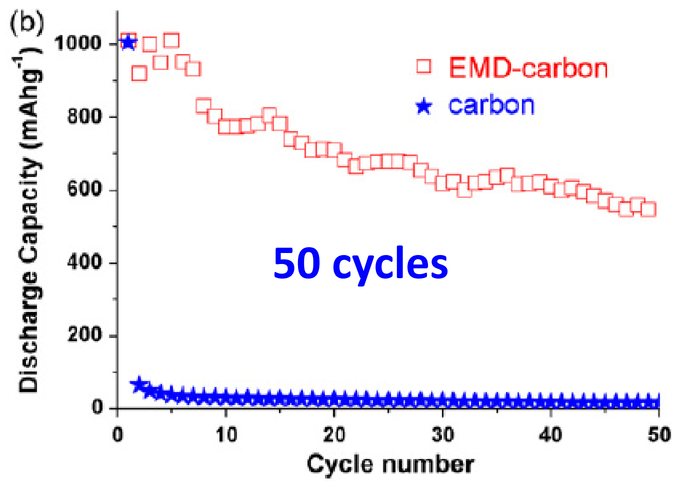
No capacity loss over 8 cycles

Much to be done…

Cycle Life - Achieved Lab Performance



A. Débart et al, *Angew. Chem. Int. Ed. 47* (2008) 4521



A. Débart et al, *J. Power Sources 174* (2007) 1177

100 cycles

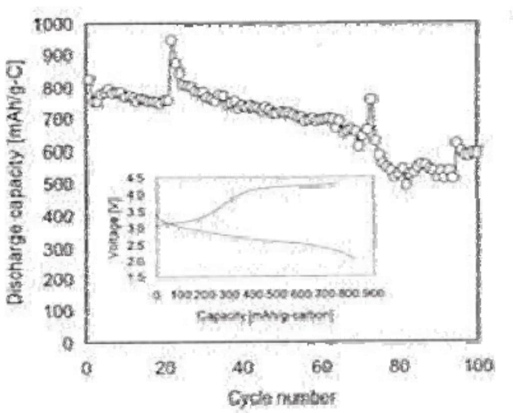


Fig. 1 Discharge capacity of Li-air battery as a function of cycle number. The first discharge-charge curves are also shown in the inset figure.

Mizuno et al, *Electrochem. 78* (2010) 403

Keys to achieve long cycle life:

1. Highly-active bifunctional catalyst to effectively regenerate batteries
2. Li-anode protection
3. Stable electrolyte

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