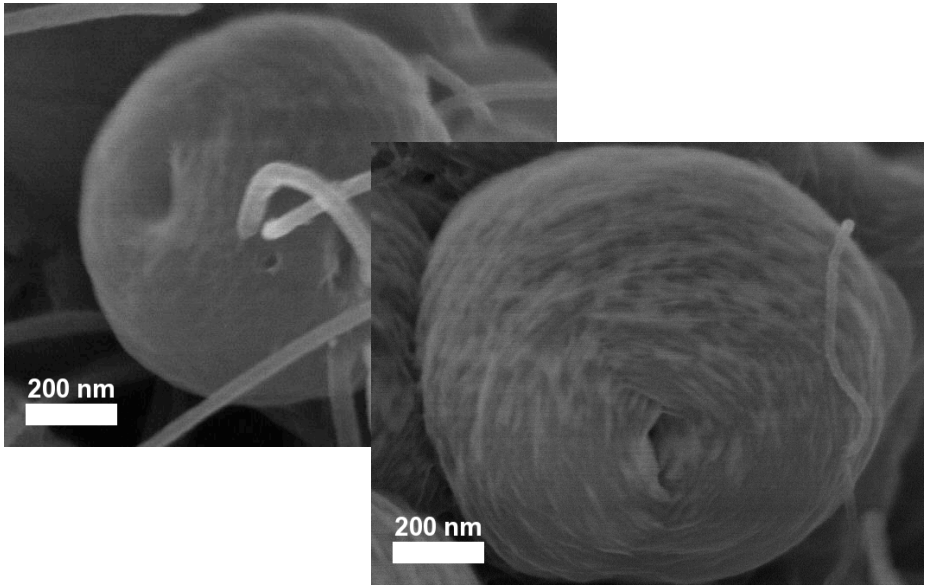
US-China EV battery workshop 2012

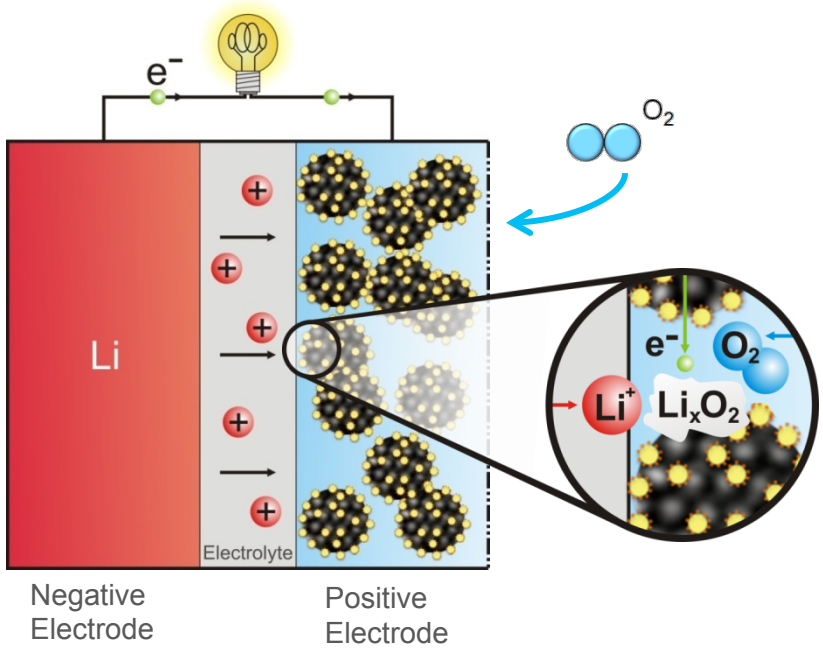


Challenges and Recent Advances In Rechargeable Li-air Batteries

Y. Shao-Horn

Department of Mechanical Engineering and
Department of Materials Science and Engineering
Massachusetts Institute of Technology, USA

Working Principles of An Li-Air Battery

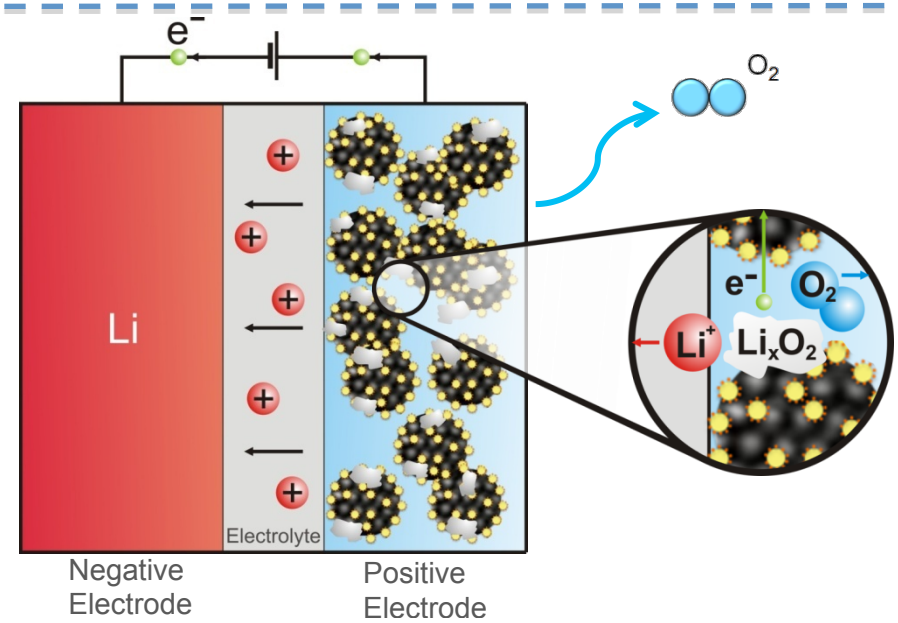


Discharge (ORR)

$$O_2 + xLi^+ + x\,e^- \Rightarrow (Li_xO_2)_{solid}$$

$$x\,Li \Rightarrow x\,Li^+ + x\,e^-$$

$$x\,Li + O_2 \Rightarrow (Li_xO_2)_{solid} \quad \sim 2.91\text{-}\ 2.96V$$



Charge (OER)

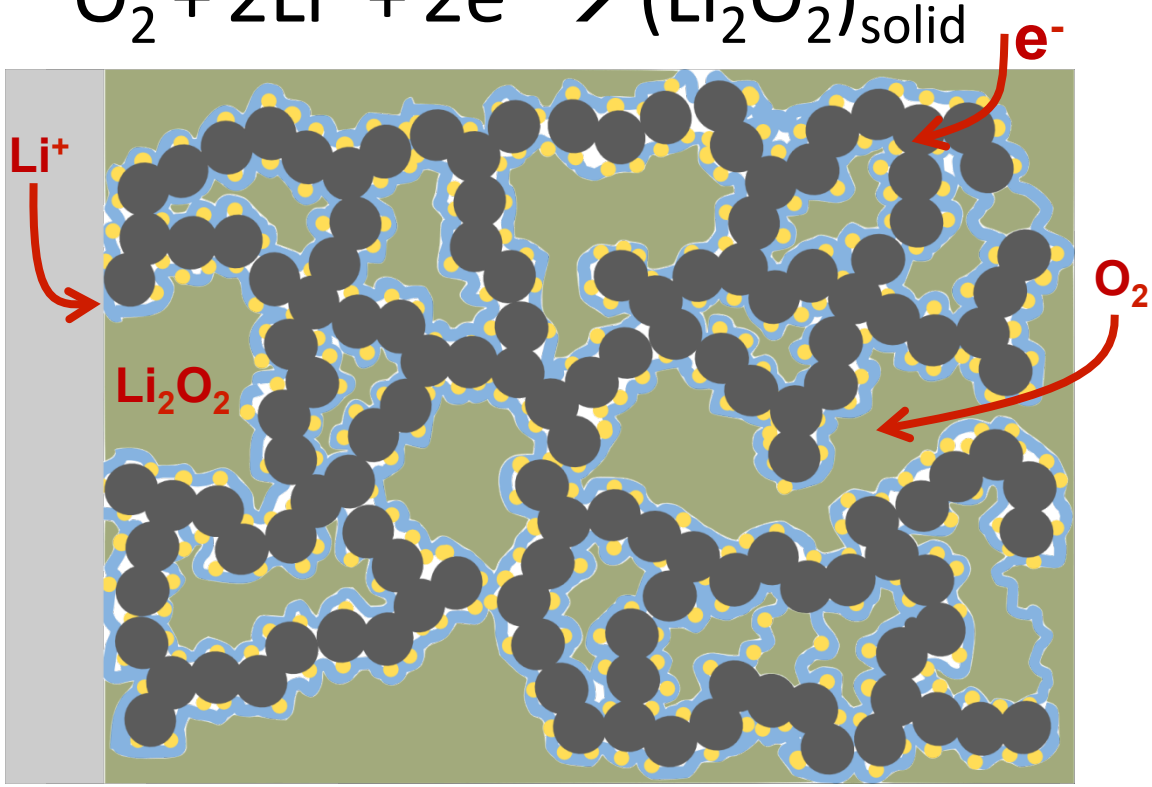
$$O_2 + xLi^+ + x\,e^- \Leftarrow (Li_xO_2)_{solid}$$

$$x\,Li \Leftarrow x\,Li^+ + x\,e^-$$

$$x\,Li + O_2 \Leftarrow (Li_xO_2)_{solid} \quad \sim 2.91\text{-}\ 2.96V$$

Discharge (Oxygen Reduction Reaction ORR)

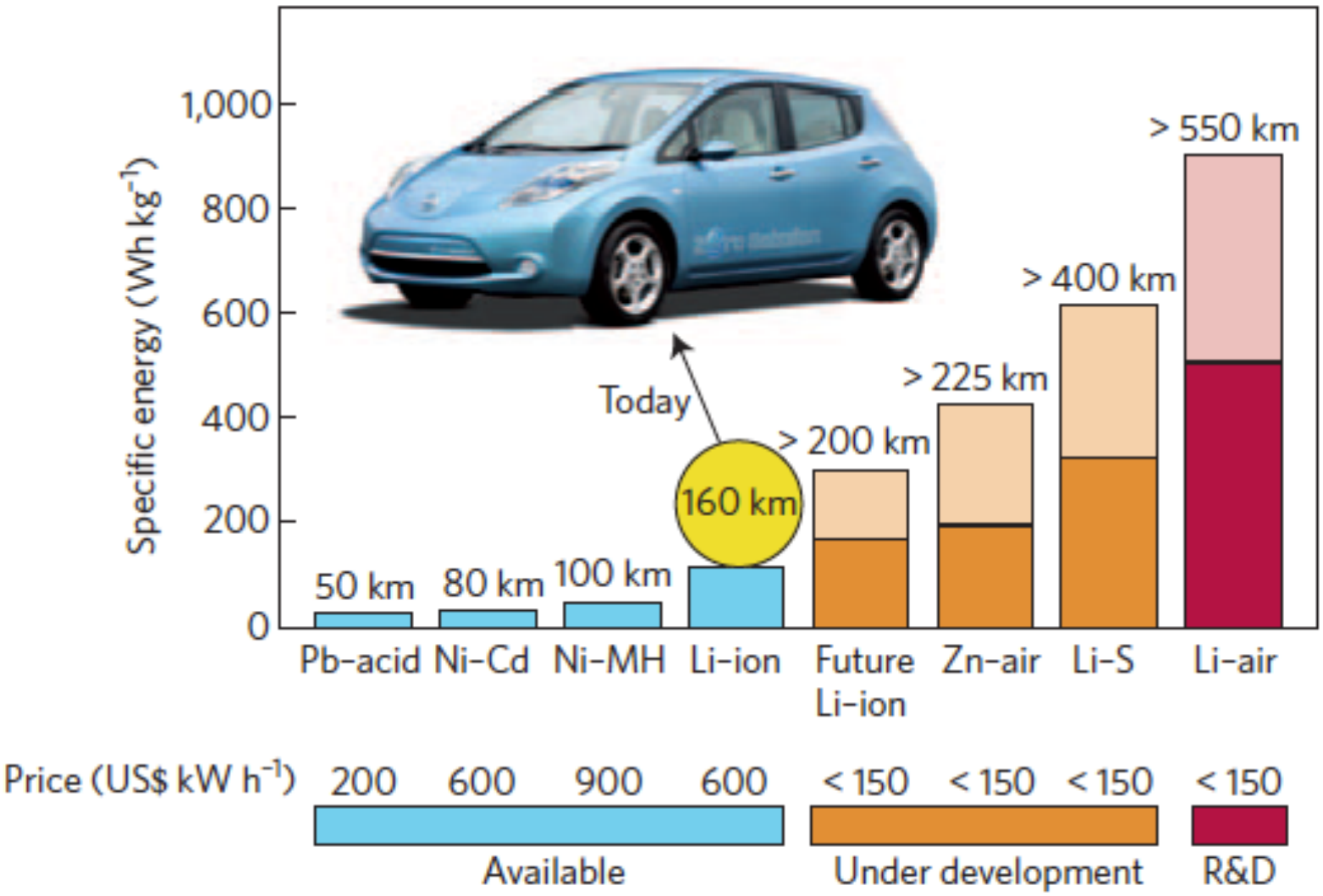
$$O_2 + 2Li^+ + 2e^- \rightarrow (Li_2O_2)_{solid}$$



$$O_2 + 4Li^+ + 4e^- \rightarrow 2(Li_2O)_{solid}$$

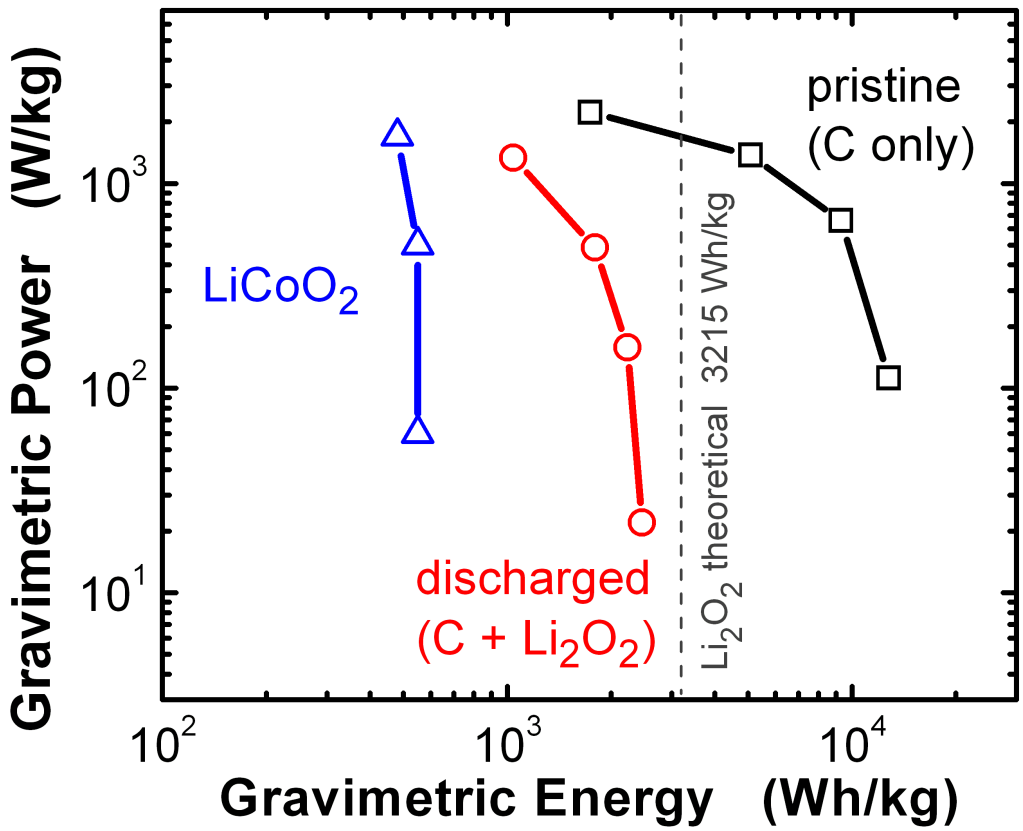
Y.C. Lu, D. Kwabi, K.P.C. Yao, J. Harding, J. Zhou, L. Zuin, Y. Shao-Horn, Energy Environ. Sci., 4, 2999 (2011)

Motivation for High-Energy Lithium Storage



Bruce, P. G. et al. *Nature Materials* **(2011)**

~ 4X Higher Gravimetric Energy than Li-Ion Batteries



~ 75% of theoretical energy density at low-power

R. R. Mitchell, B. M. Gallant, C. V. Thompson and Y. Shao-Horn, Energy & Environmental Science **4 (8), 2952 (2011).**
H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot and J.-M. Tarascon, ChemSusChem **1 (4), 348-355 (2008).**

Major Challenges of Rechargeable Li-Air Batteries

Electrodeposition of Li – Li dendrite

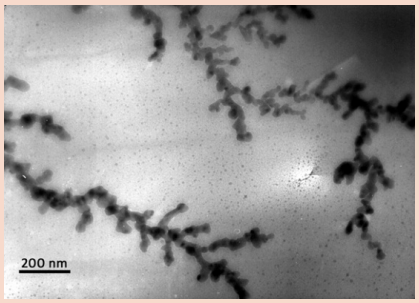
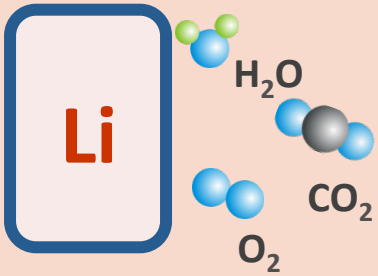
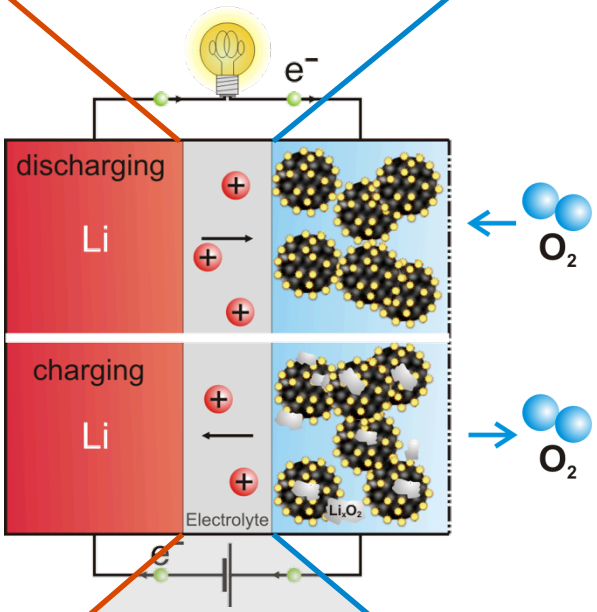


Image courtesy of G.M. Stone /UC Berkeley and LBNL

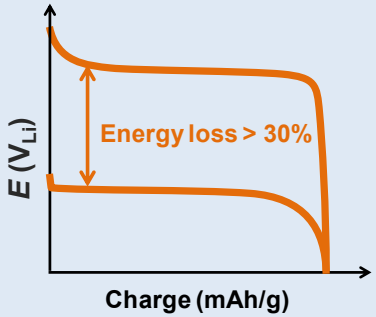
Contamination : H_2O, air – Protected lithium



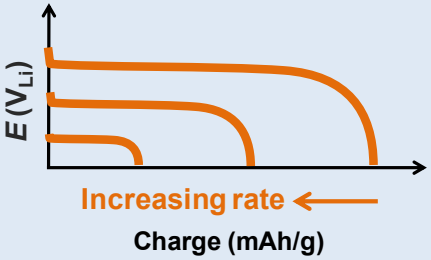


Low solvent stability
Low oxygen solubility
Contamination, e.g., air, H_2O
High volatility

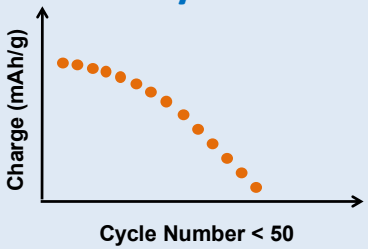
Poor round-trip efficiency



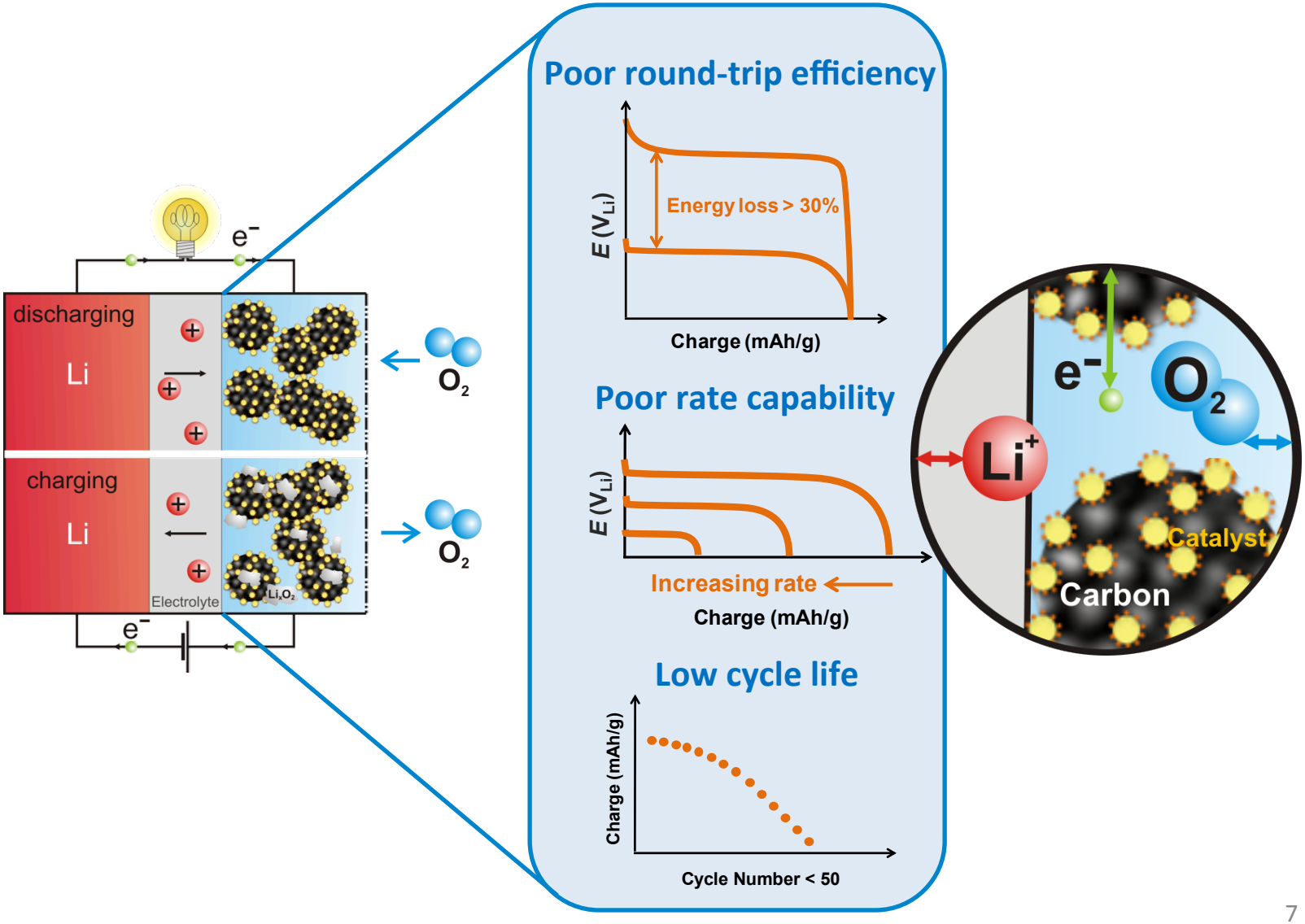
Poor rate capability



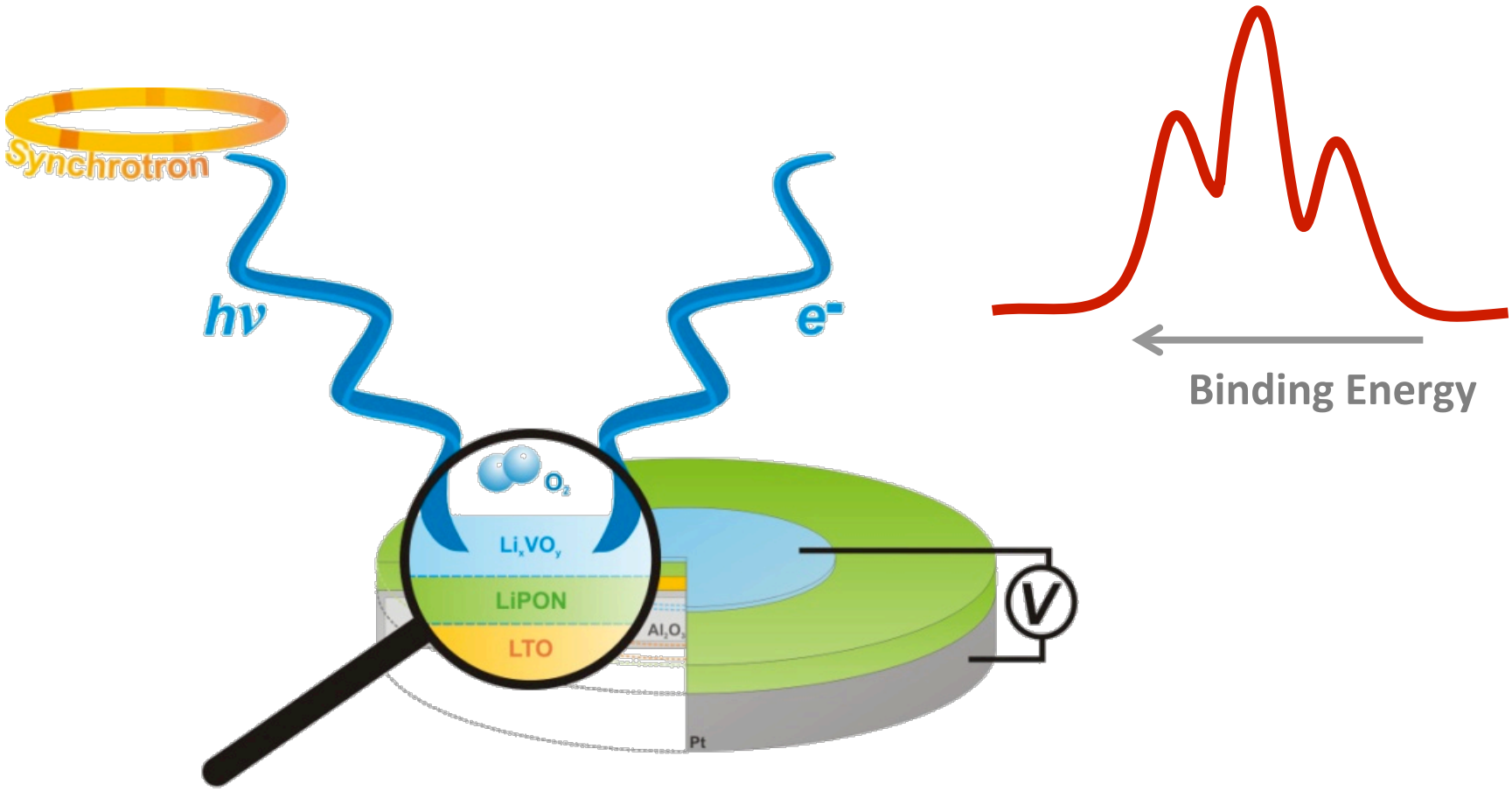
Low cycle life



Oxygen Electrocatalysis => Efficient Li-Air Batteries



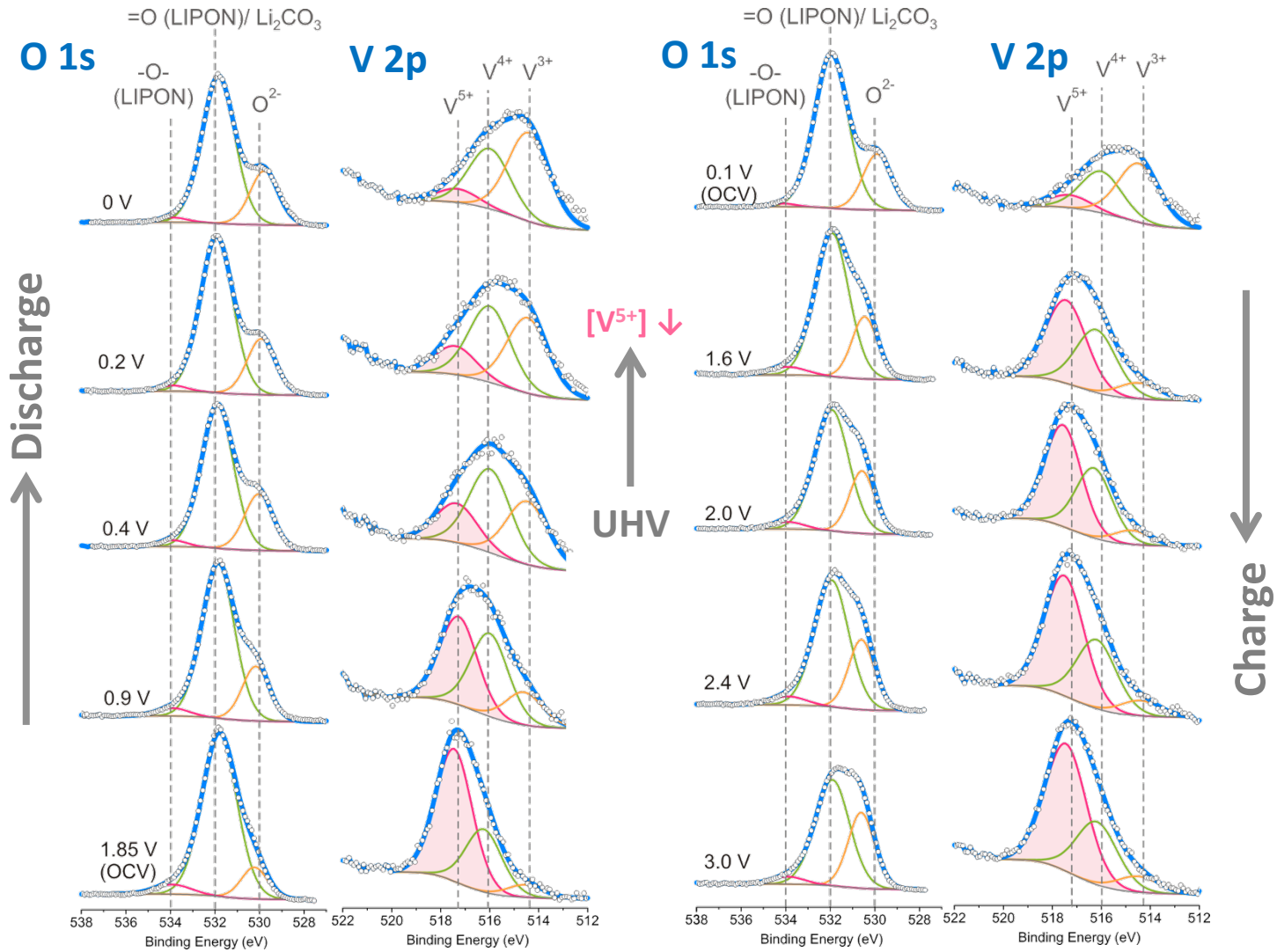
Probing Li-O_2 reaction products via *In situ* XPS



p(O_2) 380 mTorr

In collaboration with Veith G.M. & Dudney N.J. et al. at Oak Ridge National Laboratory and Liu Z. at Advanced Light Source, LBNL

UHV



LiV_2O_5 to $Li_3V_2O_5$

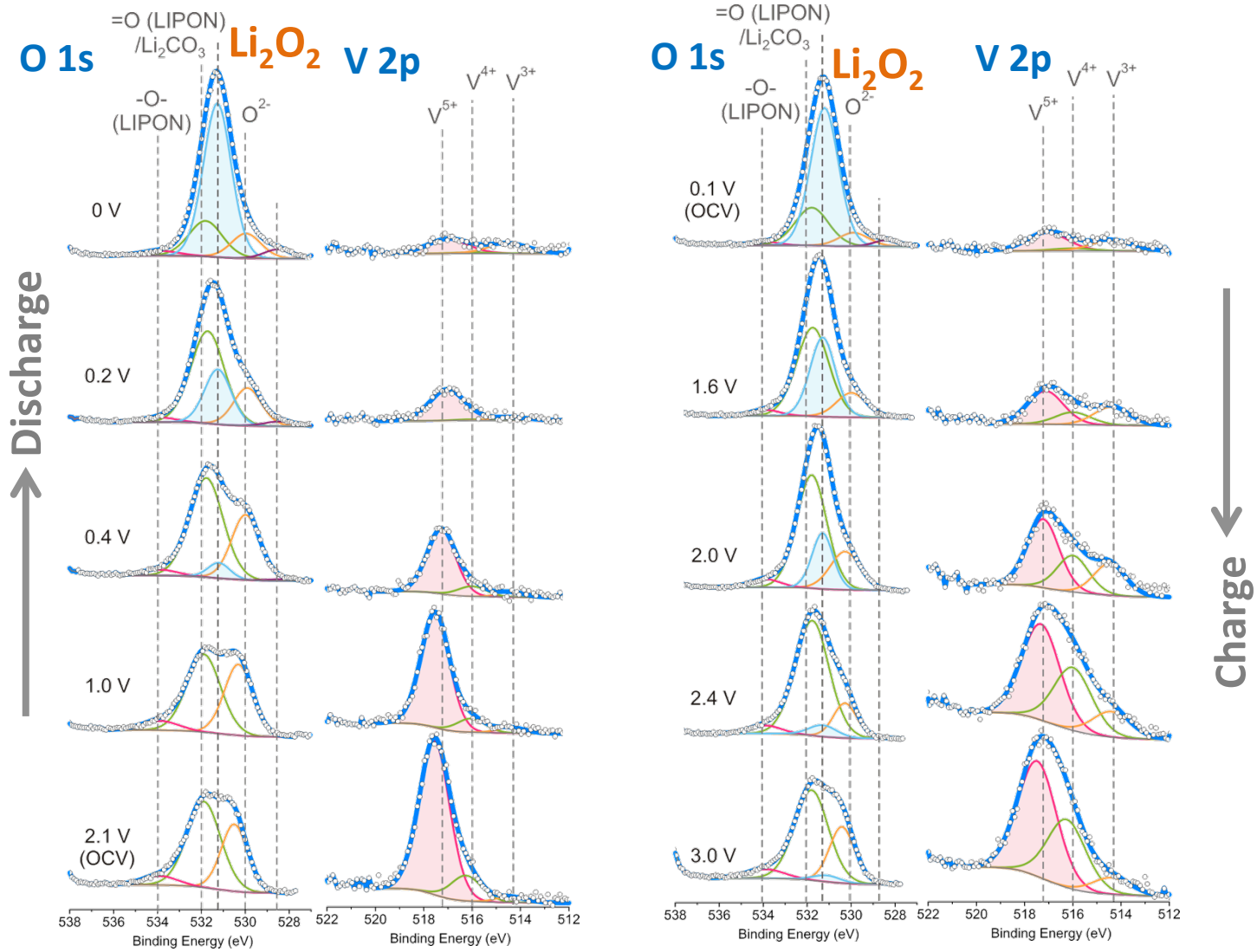
4.5 → 3.5

3.5 → 4.5

$Li_3V_2O_5$ to LiV_2O_5

submitted, 2012

O_2



Lithiation of V_2O_5 & new phases formation

LiV_2O_5 to $Li_{1.5}V_2O_5$

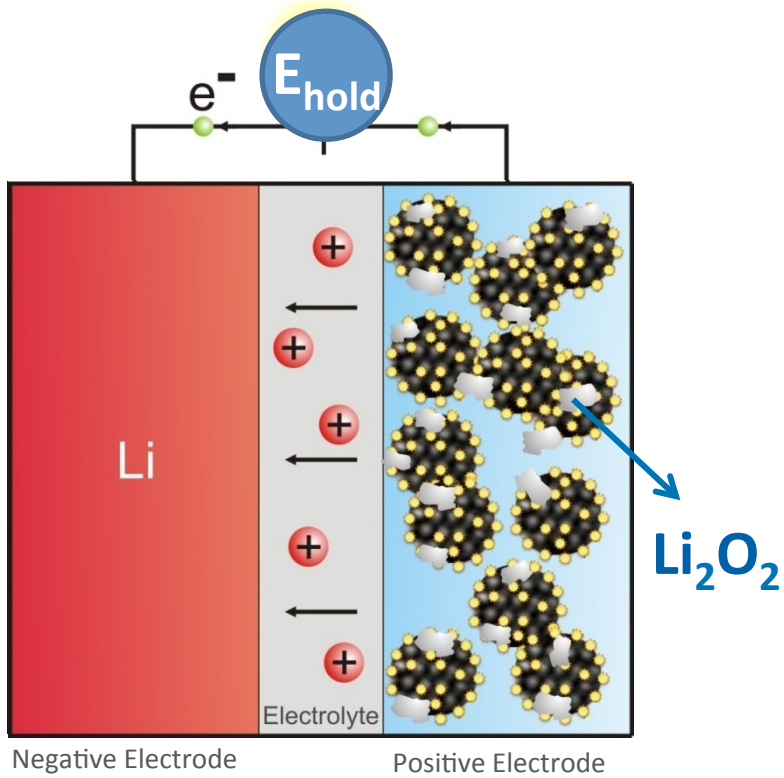
4.5 → 4.3 4.3 ↗ 4.8

Delithiation of V_2O_5 & new phases decomposition

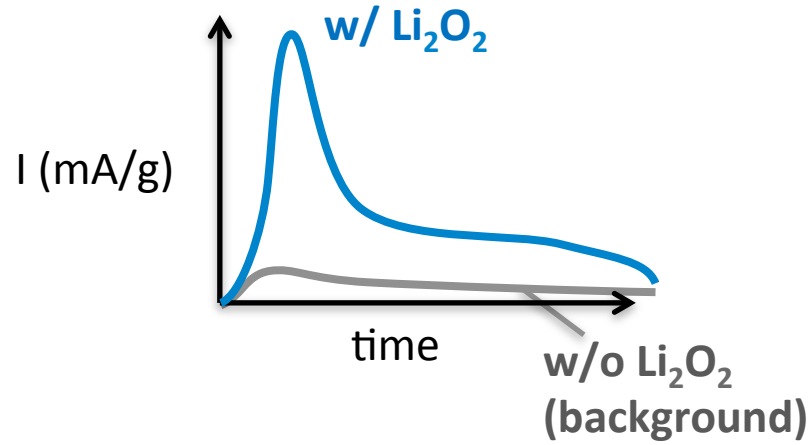
$Li_{1.5}V_2O_5$ to $Li_{0.4}V_2O_5$

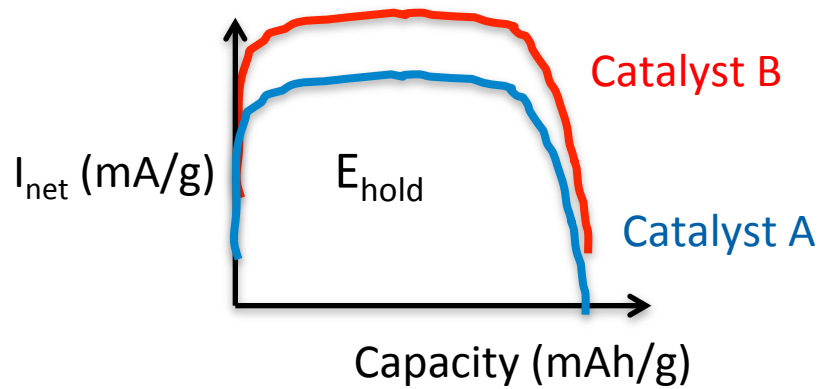
submitted, 2012

Examine Li_2O_2 oxidation with controlled capacity and morphologies



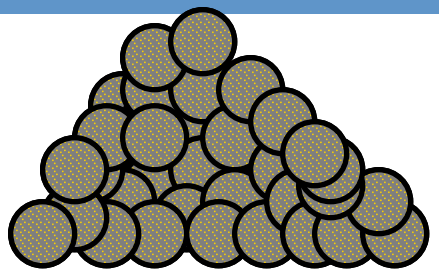
0.1 M $LiClO_4$ DME





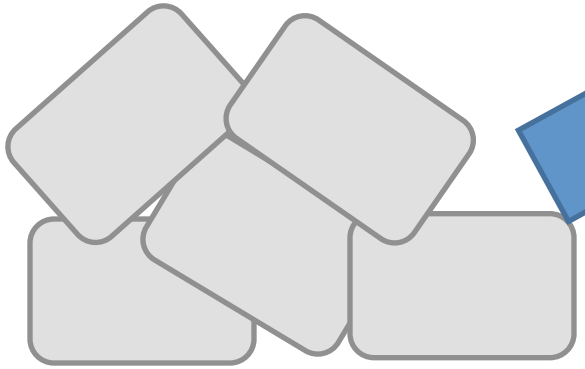
Y.C. Lu, H.A. Gasteiger, M.C. Parent, V. Chiloyan, Y. Shao-Horn, Electrochem. Solid State Lett. 13, A69 (2010)
J. Harding, Y.C. Lu, Y. Tsukada, Y. Shao-Horn, Manuscript in preparation, 2012

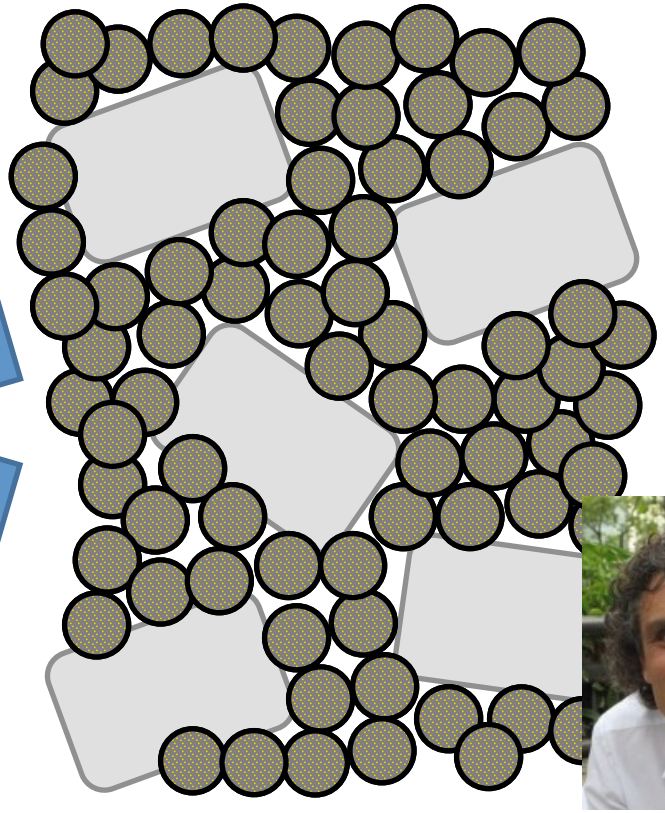
Li_2O_2-Filled Electrodes to probe Li_2O_2 oxidation kinetics



Catalyst+ XC-72 Vulcan C +
Lithiated Nafion®

Li_2O_2 Particles



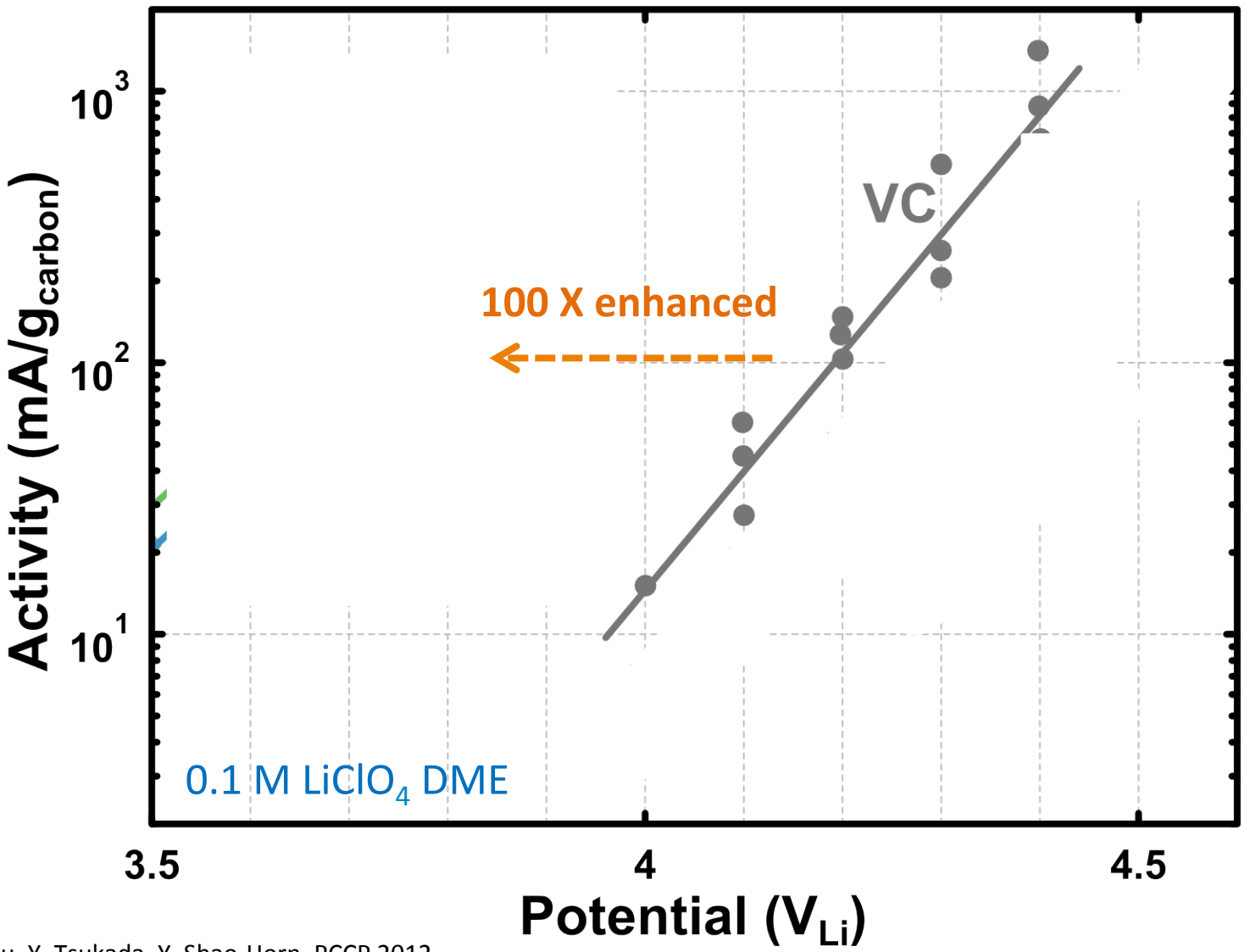


Prof. Hubert A. Gasteiger
(formerly MIT, currently TUM)

Use Au, Pt, and Ru nanoparticles

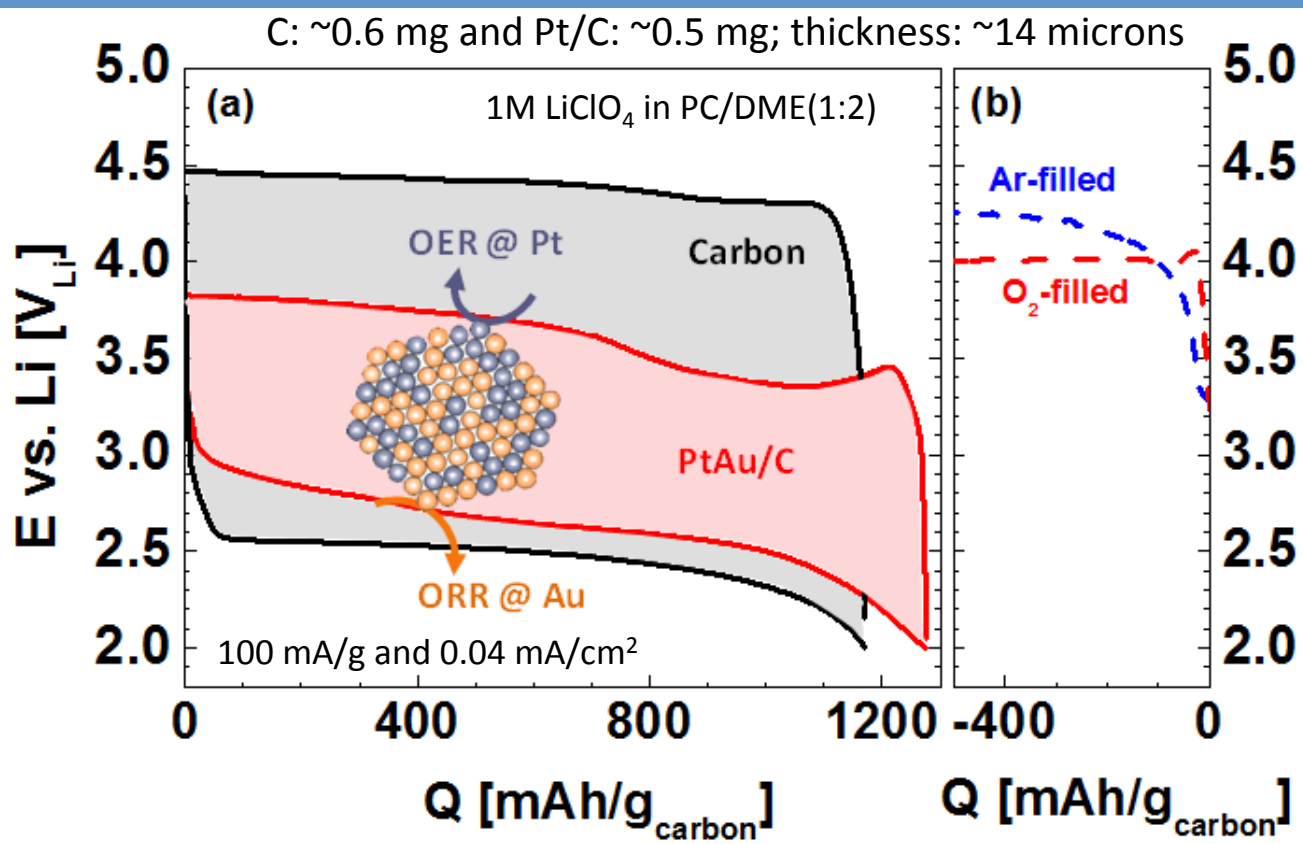
Y.C. Lu, H.A. Gasteiger, M.C. Parent, V. Chiloyan, Y. Shao-Horn, Electrochem. Solid State Lett. 13, A69 (2010)
J. Harding, Y.C. Lu, Y. Tsukada, Y. Shao-Horn, PCCP 2012

Oxidation kinetics of submicron Li_2O_2 particles enhanced by Ru & Pt



J. Harding, Y.C. Lu, Y. Tsukada, Y. Shao-Horn, PCCP 2012

Pt-based NPs promote round-trip efficiency

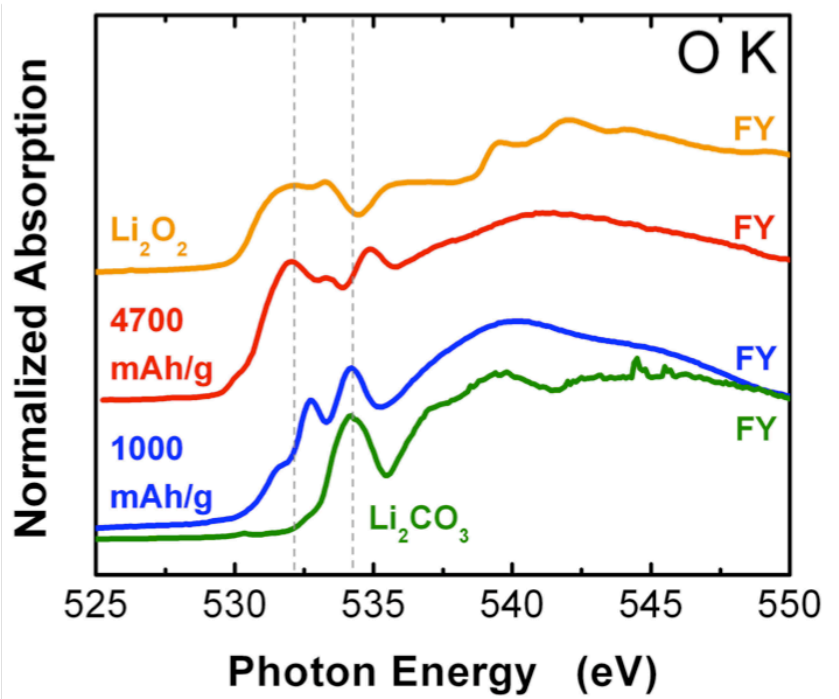


Achieved Record Round-trip efficiency: 75%

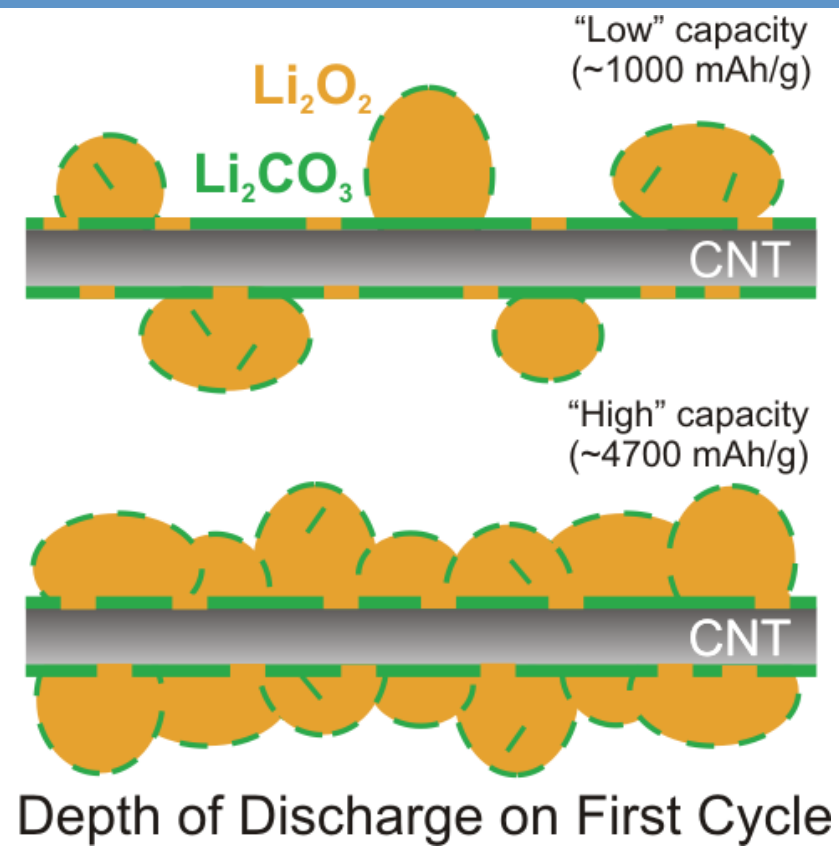
Yi-Chun Lu, Zhichuan Xu, Hubert Gasteiger, Shuo Chen, Kimberly Hamad-Schifferli, and Yang Shao-Horn, *JACS,* (2010)

Li_2O_2 Coats the Surface of Carbon and Li_2CO_3 Forms at Carbon Surface on First Discharge

XANES Flourescence Yield
penetration depth = hundreds of nm



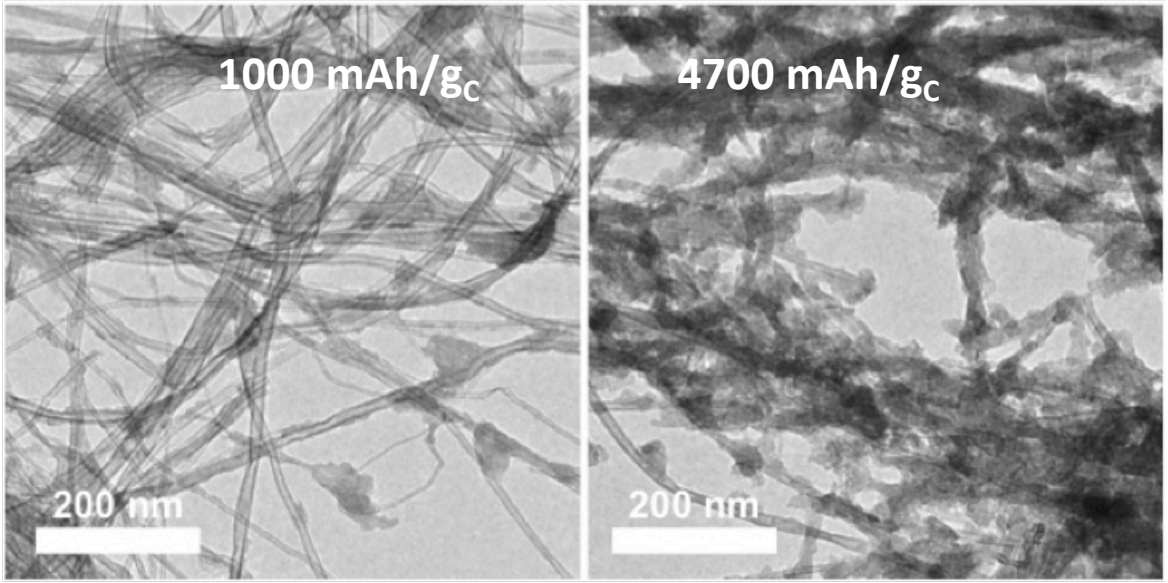
Li_2CO_3 at low capacity
Li_2O_2 at high capacity

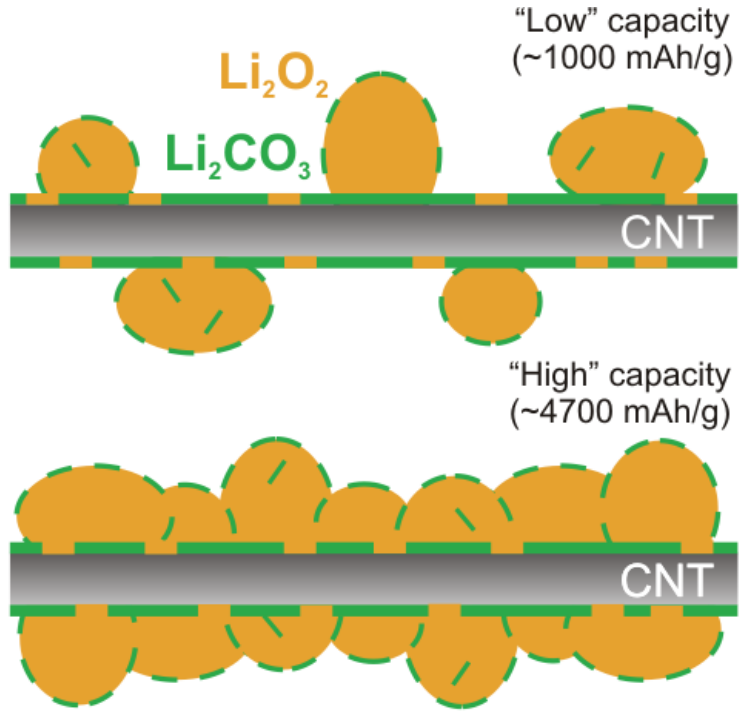


Li_2CO_3 is not detected on the surface of Li_2O_2 at high capacity

B. M. Gallant, R. R. Mitchell, D. G. Kwabi, J. Zhou, L Zuin, C. V. Thompson and Y. Shao-Horn, *submitted.*

Surface of Li_2O_2 is Stable on First Discharge



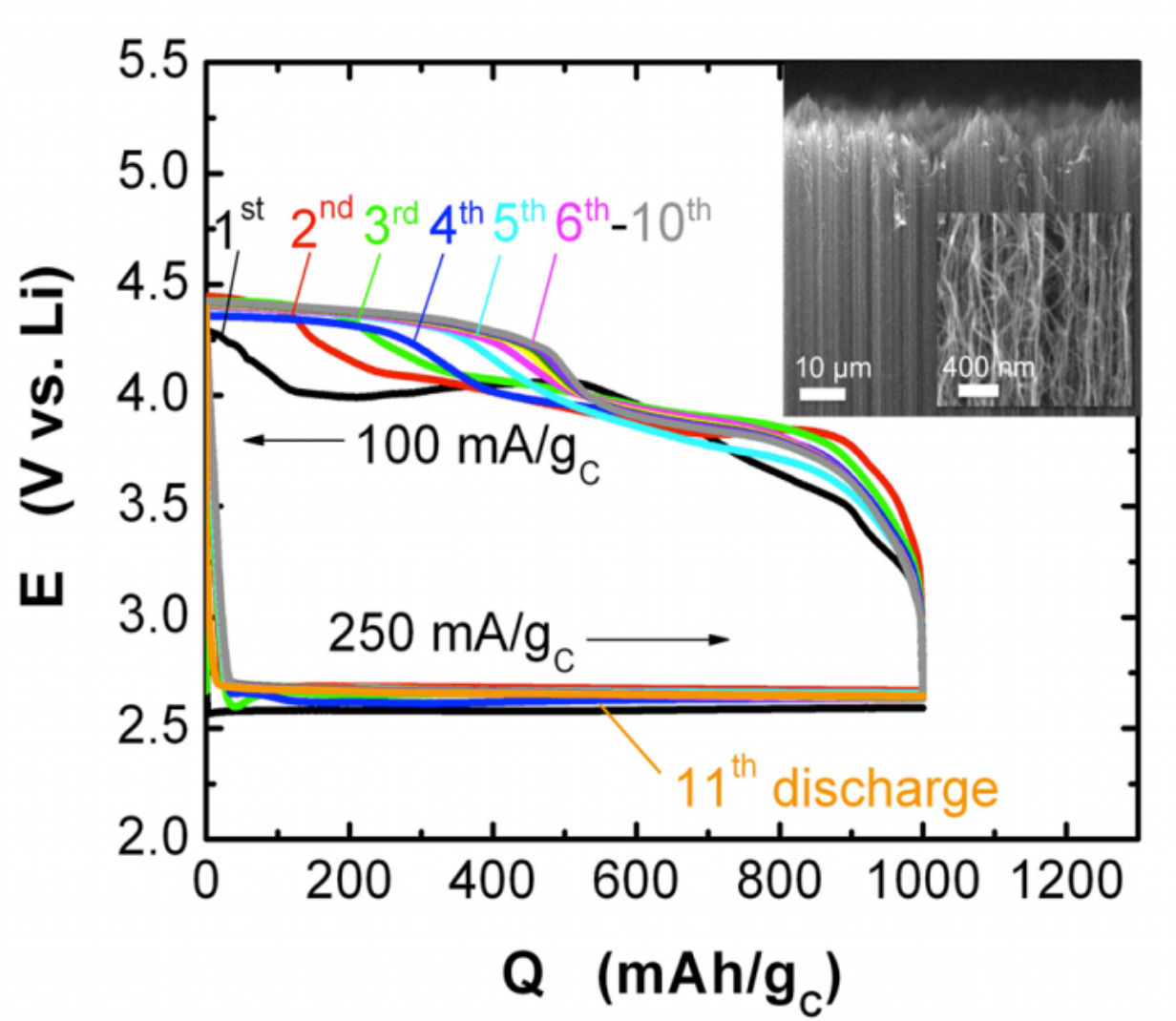


Depth of Discharge on First Cycle

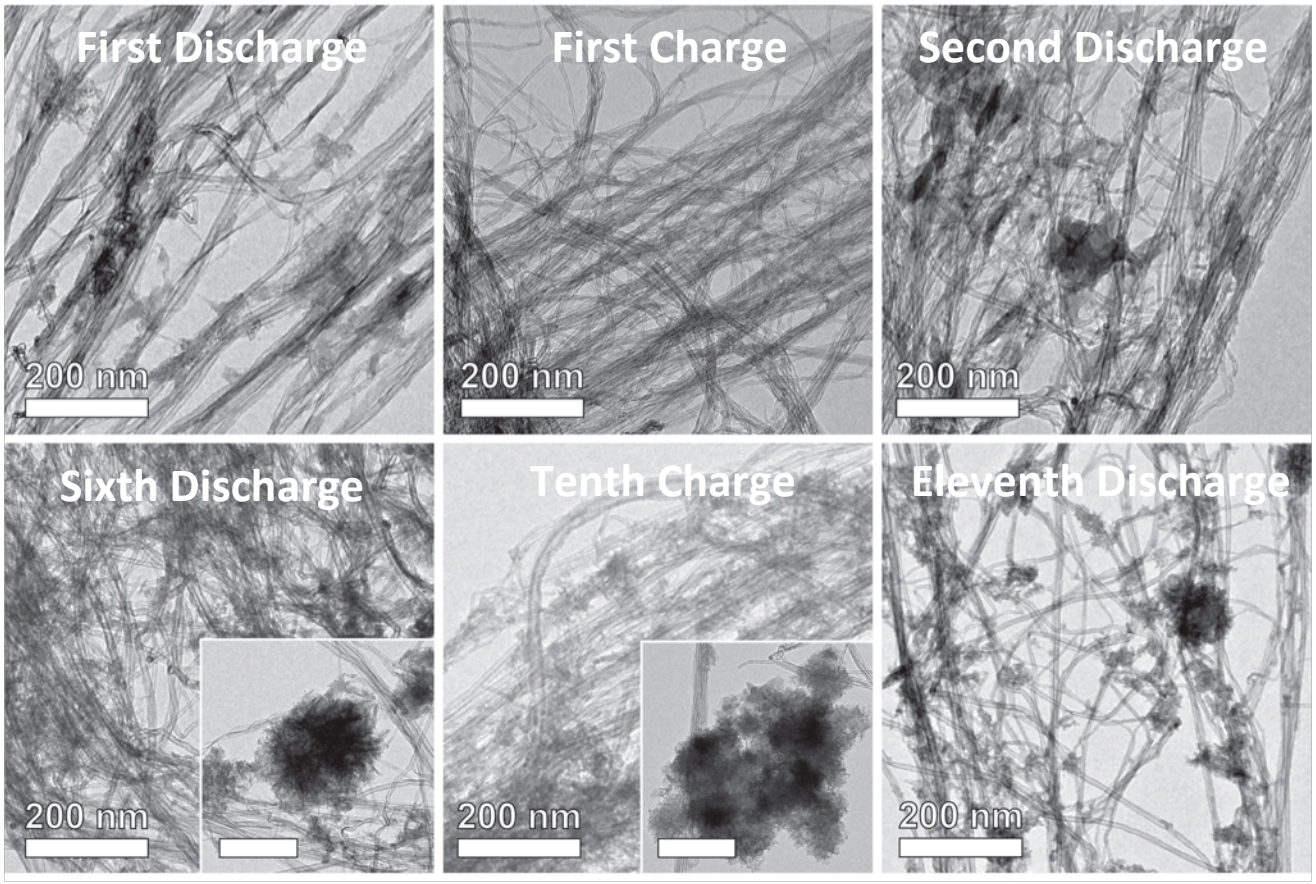
Li_2O_2 covers Li_2CO_3 on the CNT/Li_2O_2 interface upon discharge

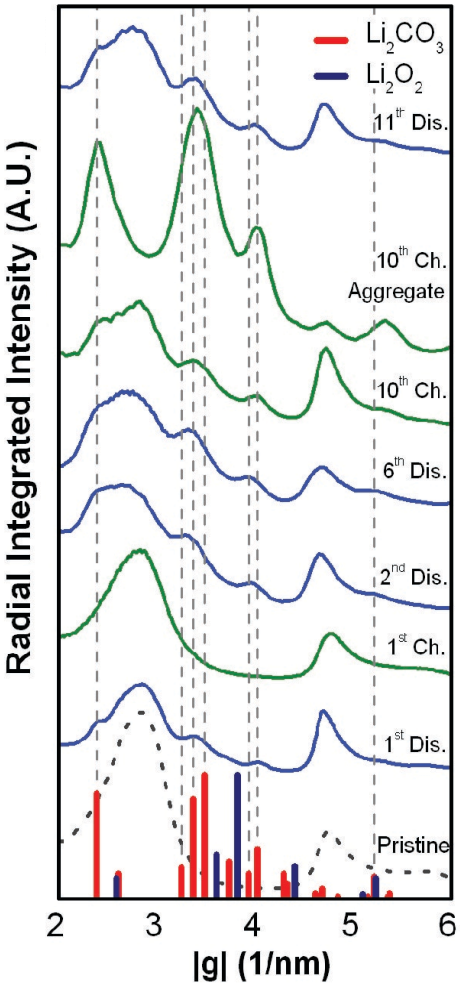
B. M. Gallant, R. R. Mitchell, D. G. Kwabi, J. Zhou, L Zuin, C. V. Thompson and Y. Shao-Horn, *submitted.*

Cycling of Li-O_2 batteries using free-standing CNT carpets (DME)



Li_2CO_3 Agglomerates with Cycling

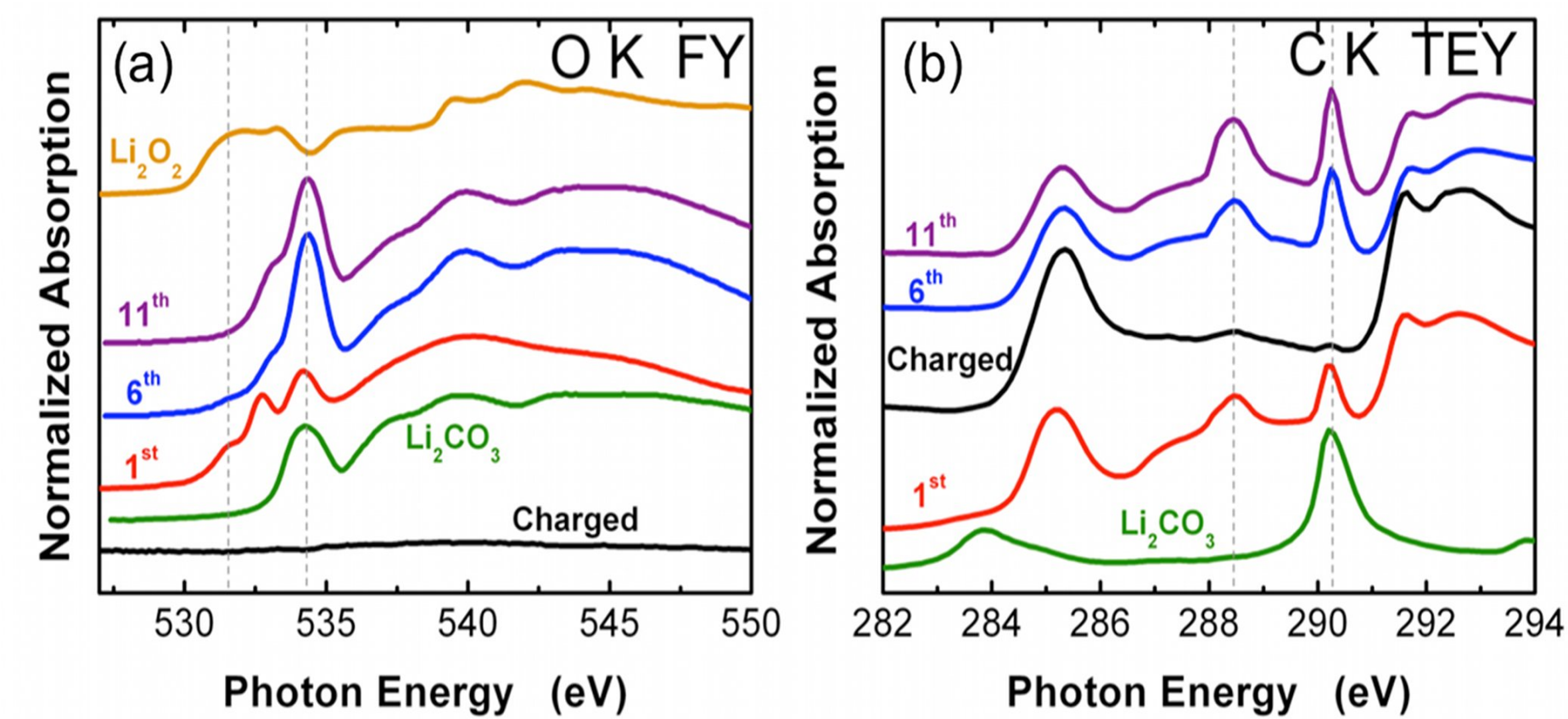




Observe roughening of discharge product morphology with cycling and aggregation of Li_2CO_3.

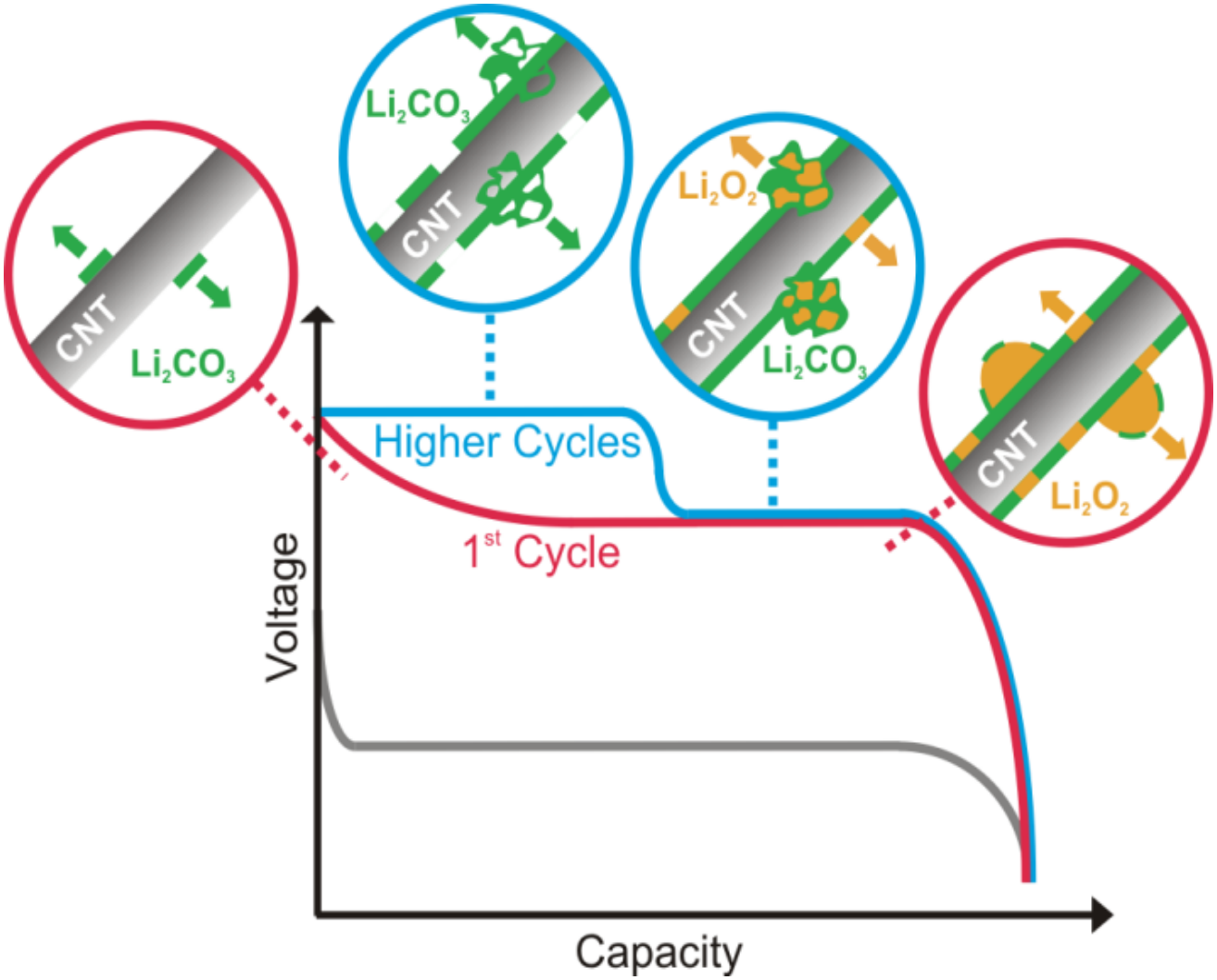
B. M. Gallant, R. R. Mitchell, D. G. Kwabi, J. Zhou, L Zuin, C. V. Thompson and Y. Shao-Horn, *submitted.*

Soft X-ray Absorption Spectroscopy



B. M. Gallant, R. R. Mitchell, D. G. Kwabi, J. Zhou, L Zuin, C. V. Thompson and Y. Shao-Horn, *submitted.*

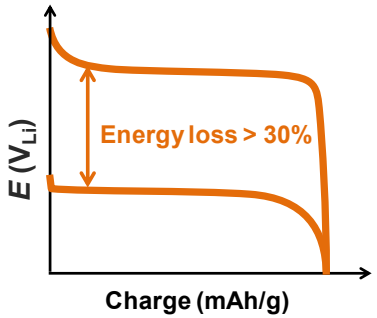
Li_2CO_3 Agglomerates with Cycling => Li-O_2 redox irreversible



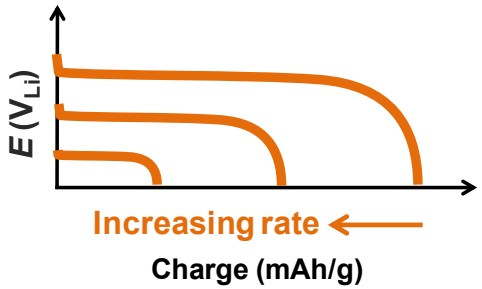
B. M. Gallant, R. R. Mitchell, D. G. Kwabi, J. Zhou, L Zuin, C. V. Thompson and Y. Shao-Horn, *submitted.*

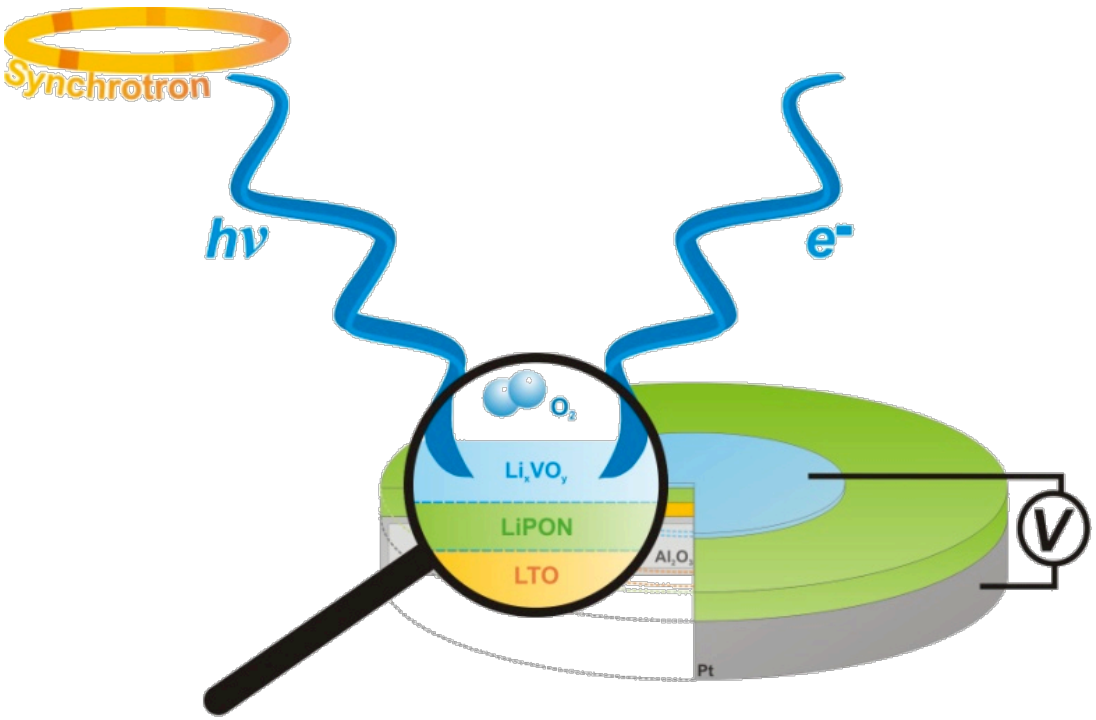
Enabling the reversibility of O_2 electrocatalysis in aprotic electrolytes for Li-air batteries

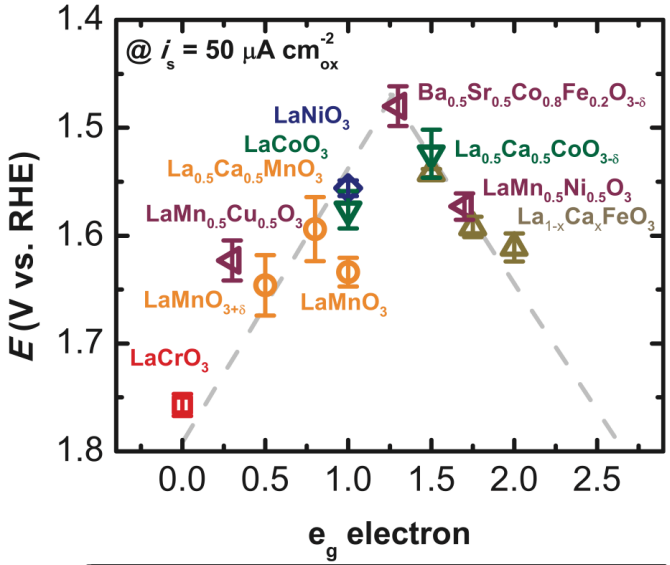
Poor round-trip efficiency

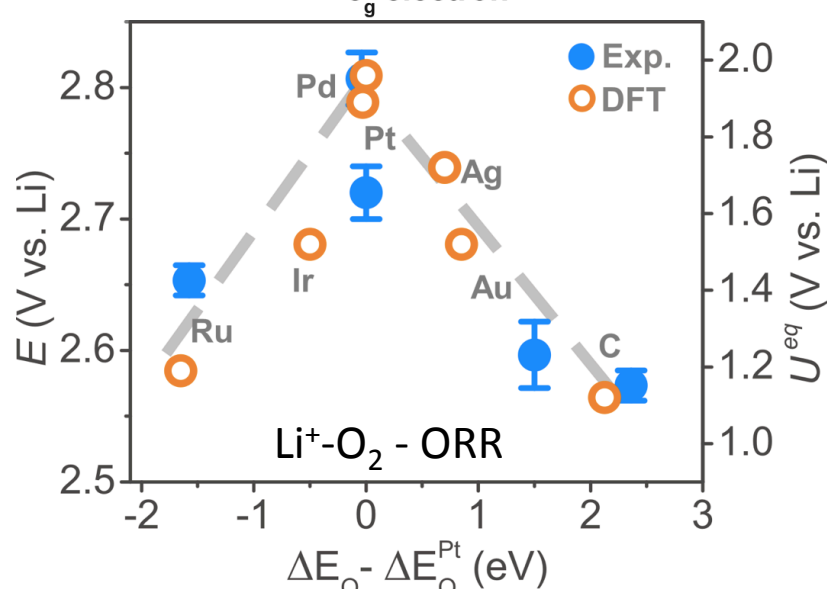


Poor rate capability

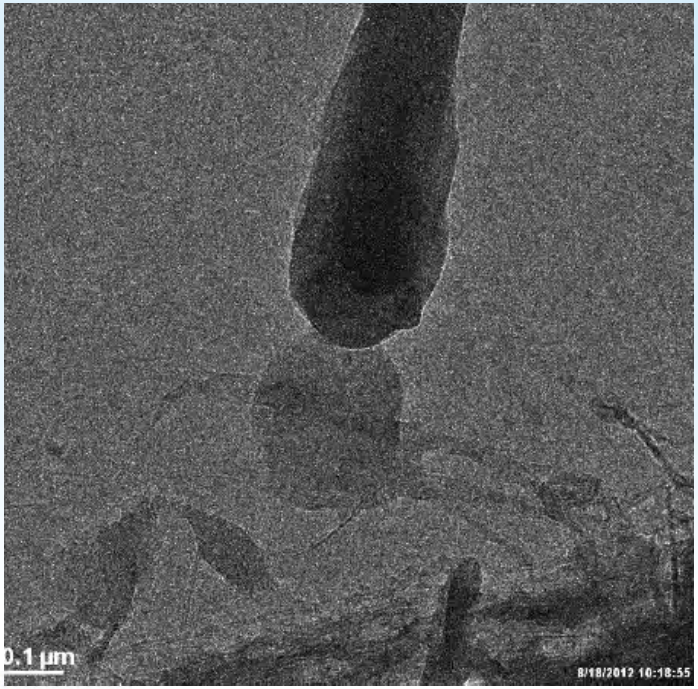








Acknowledgments



O_2 electrocatalysis at high PHs, Jin Sunvtich (MIT), **H. A. Gasteiger** (TUM)
Mechanism discussion: **J.B. Goodenough** (UT-Austin), **J. Freeland** (ANL)
Toyota Motor Company
DOE BES Catalysis (DE-FG02-05ER15728)
Chesonis Family Fellowship

O_2 electrocatalysis for Li-air, Yi-Chun Lu, David Kawabi, Pierre Claver, Hubert A. Gasteiger (TUM) Zhichuan Xu, Jonathon Harding, Ethan Crumlin, Eva Mutoro, Robert McGuire
XANES, Jigang Zhou, Lucia Zuin (Canadian Light Source Inc)
XPS: Azzam Mansour (NSWC)
NP synthesis: Kimberley Hamad-Schifferli (MIT)
In-situ TEM: Y. Liu, Zhong Li, Jianyu Huang (SNL)
In-situ XPS: Zhi Liu, Ethan Crumlin (ALS/LBNL)
DOE EERE (BATT Program)
National Science Foundation MRSEC program
MIT-Ford Alliance
Toyota Motor Company