IBM Almaden Research Center, San Jose, California

Solid-State Li-Ion Conducting Membranes for Lithium Batteries

June 23, 2015

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Advanced Energy Storage, IBM Research

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Why Research in Energy Storage?

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Fossil Fuels

- **500, 000, 000** years in the making
- **87.7%** of world energy consumption
- **200** years of use
- **53.3** years worth oil reserves left

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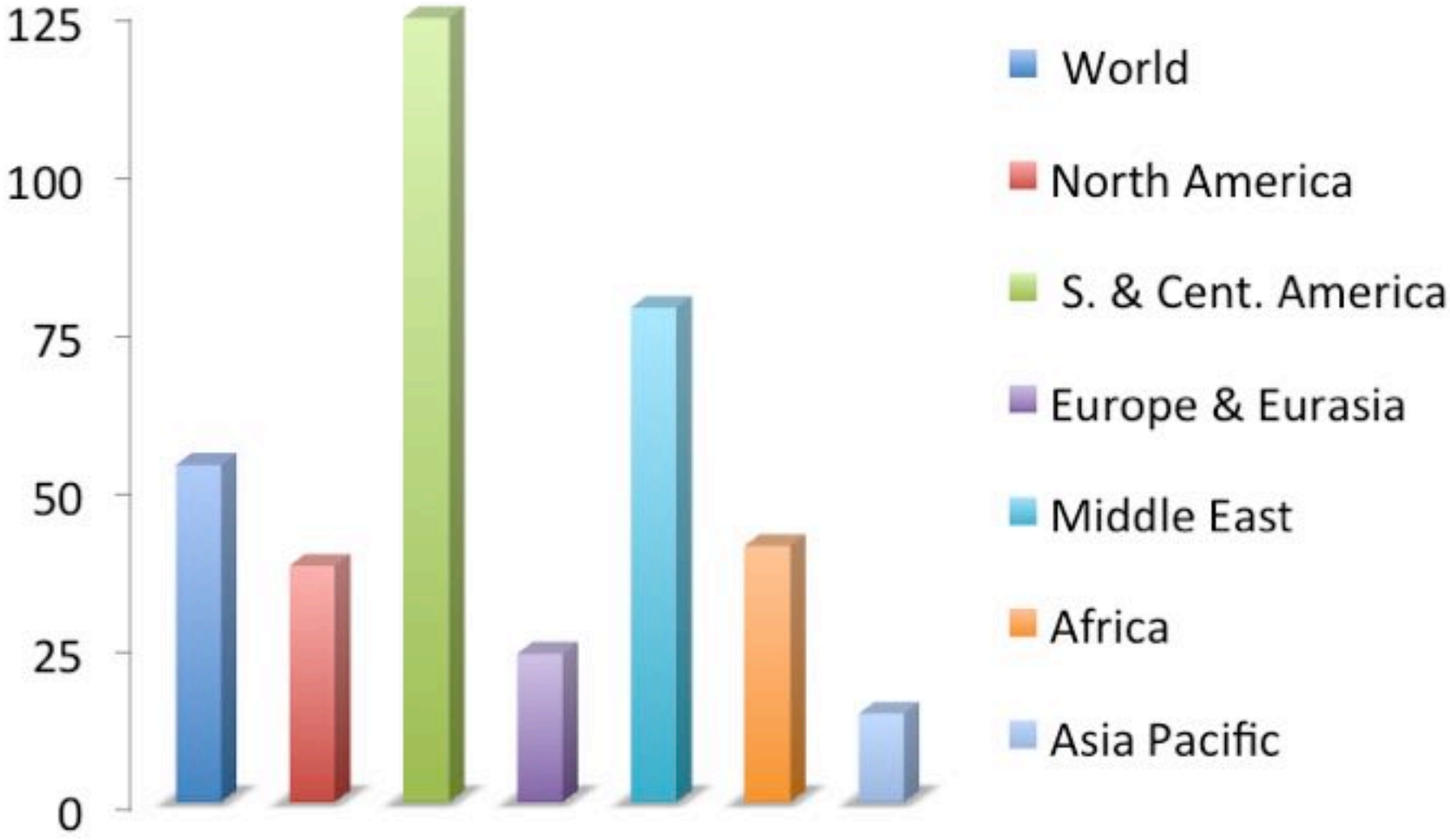
Oil Reserves to Production Ratio in Years



Adapted from BP Statistical Review of World Energy 2014

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Energy Storage Critical to Conserve Natural Resources

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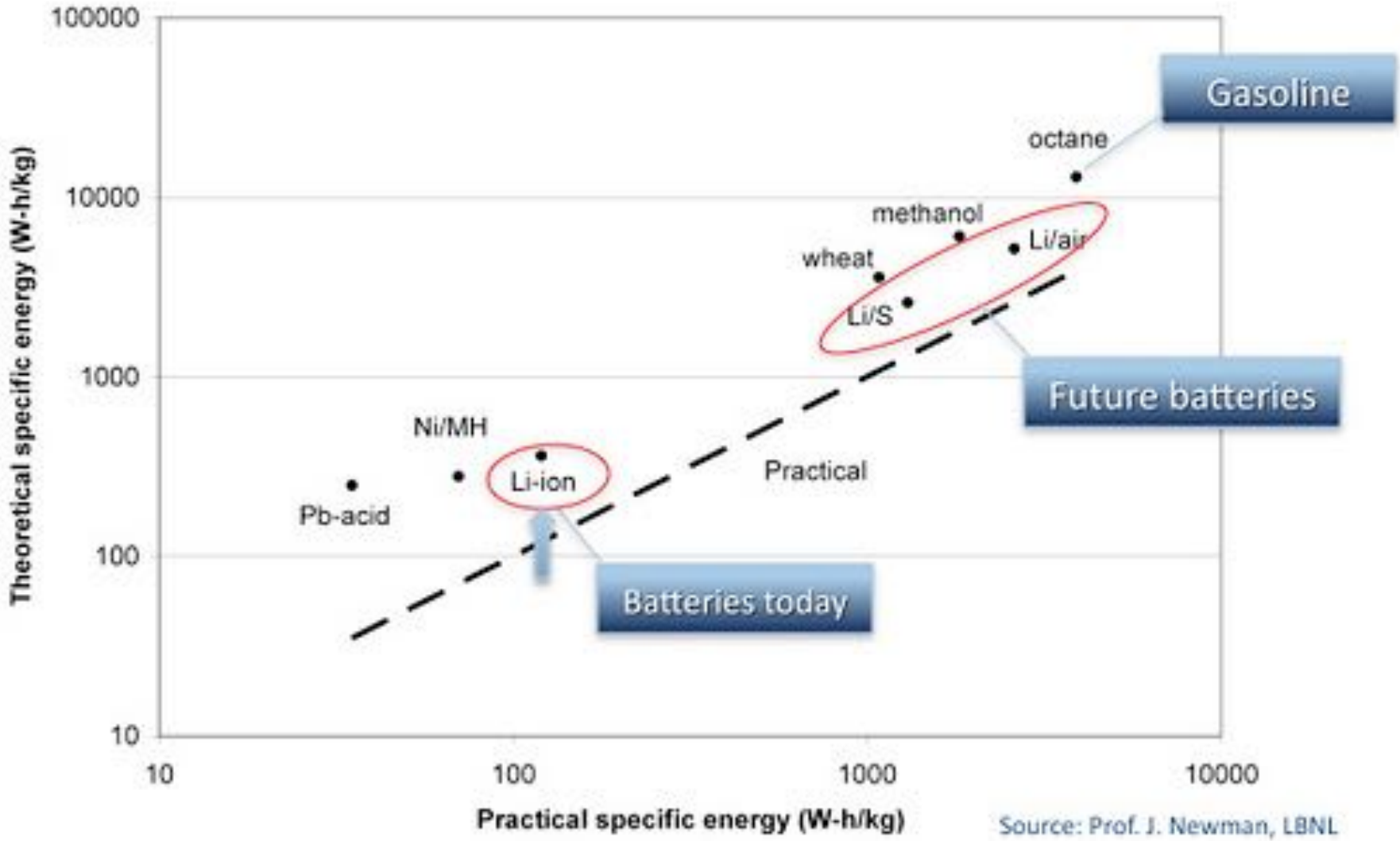
Comparison of Battery Technologies



Li-Air Offers the highest practical specific energy

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Basic Electrochemistry in a Li-O_2 Battery

$$2Li^{+} + O_2 + 2e^{-} \rightleftarrows Li_2O_2$$

$$E_0 = 2.96\ V$$

→ **Forward Reaction: Discharge**

→ **Reverse Reaction: Charge**

Hummelshoj, J. S. et al. J. Chem. Phys. 132, 071101 (2010); Laoire, C. O., Mukerjee, S., Abraham, K. M., Plichta, E. J. & Hendrickson, M. A. J. Phys. Chem. C 114, 9178–9186 (2010).; Laoire, C. O., Mukerjee, S., Abraham, K. M., Plichta, E. J. & Hendrickson, M. A.. J. Phys. Chem. C 113, 20127–20134 (2009); Abraham, K. M. & Jiang, Z. J. Electrochem. Soc. 143, 1–5 (1996); Ogasawara, T., Débart, A., Holzapfel, M., Novák, P. & Bruce, P. G. J. Am. Chem. Soc. 128, 1390–1393 (2006).

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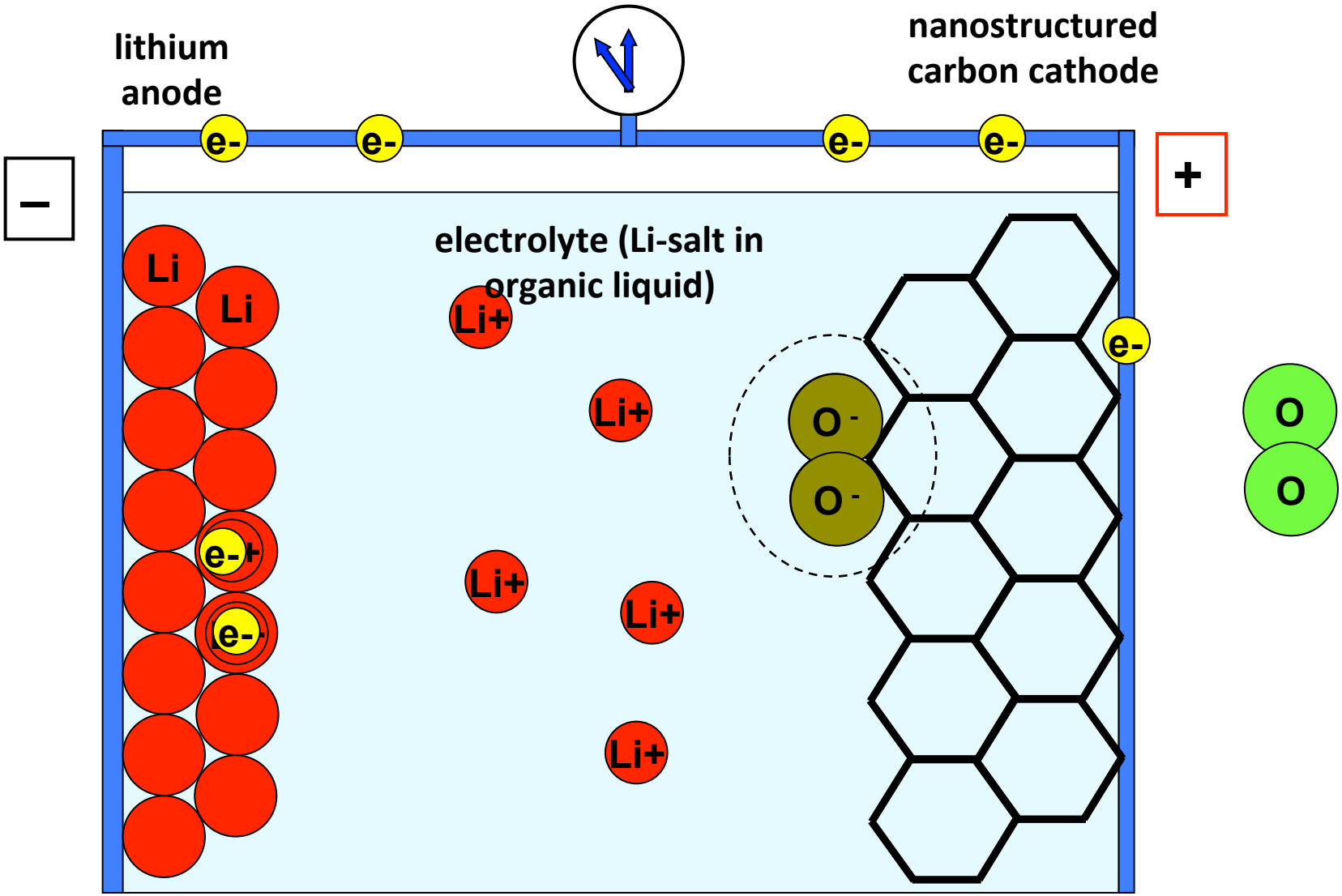
Li-O_2 Battery Concept: Discharge



$$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$$

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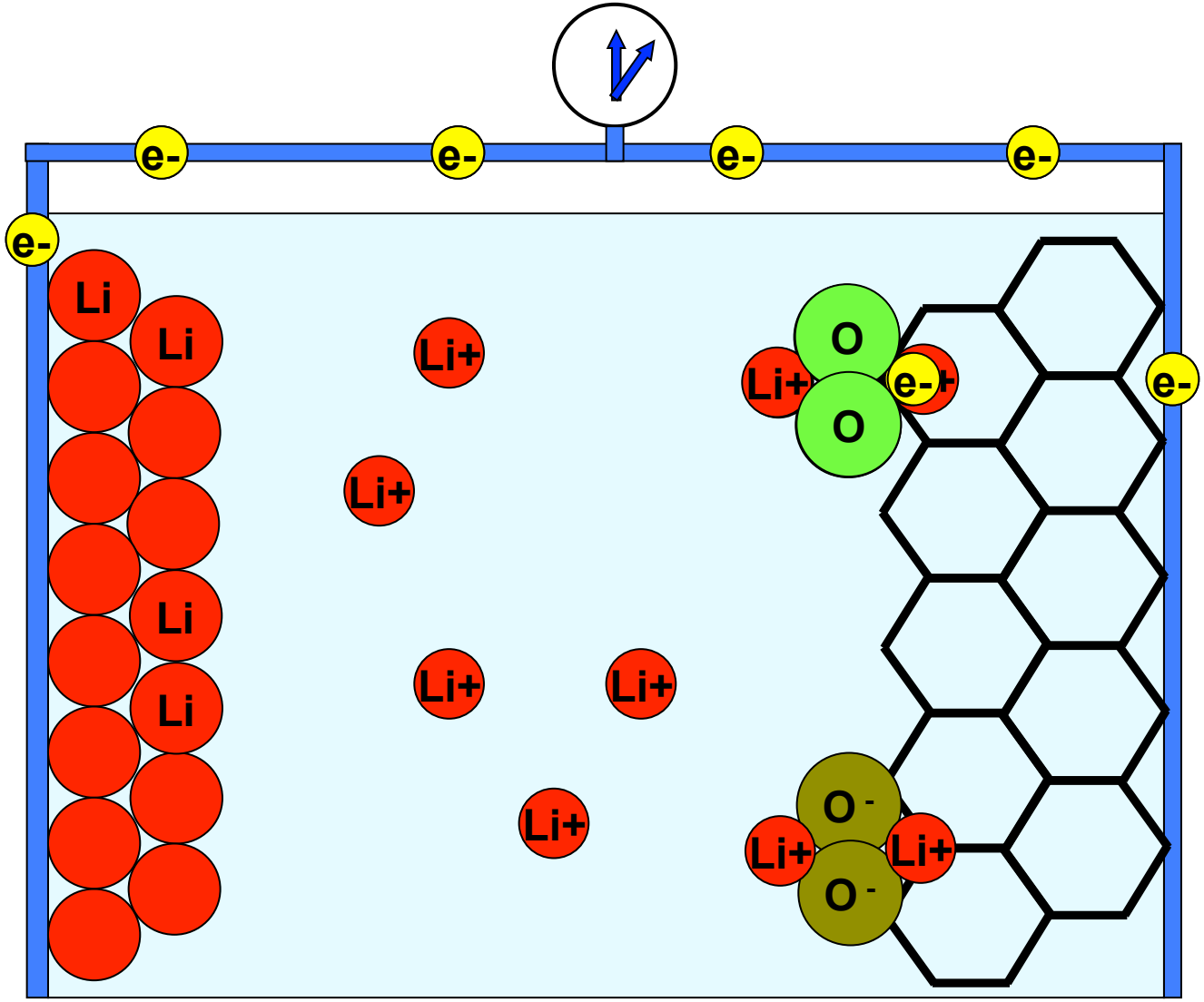
Slide Courtesy: Don Bethune, IBM ARC

Li-O_2 Battery Concept: Charge



$$2Li^{+} + O_2 + 2e^{-} \leftarrow Li_2O_2$$

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Slide Courtesy: Don Bethune, IBM ARC

Basic Electrochemistry in a Li-O_2 Battery

$$2Li^+ + O_2 + 2e^- \rightleftarrows Li_2O_2$$

$$E_0 = 2.96\ V$$

→ **Forward Reaction: Discharge**

→ **Reverse Reaction: Charge**

Ideal: $2e^-$ per O_2 molecule

Simultaneous electron and Gas Analysis necessary

Hummelshoj, J. S. et al. J. Chem. Phys. 132, 071101 (2010); Laoire, C. O., Mukerjee, S., Abraham, K. M., Plichta, E. J. & Hendrickson, M. A. J. Phys. Chem. C 114, 9178–9186 (2010).; Laoire, C. O., Mukerjee, S., Abraham, K. M., Plichta, E. J. & Hendrickson, M. A.. J. Phys. Chem. C 113, 20127–20134 (2009); Abraham, K. M. & Jiang, Z. J. Electrochem. Soc. 143, 1–5 (1996); Ogasawara, T., Débart, A., Holzapfel, M., Novák, P. & Bruce, P. G. J. Am. Chem. Soc. 128, 1390–1393 (2006).

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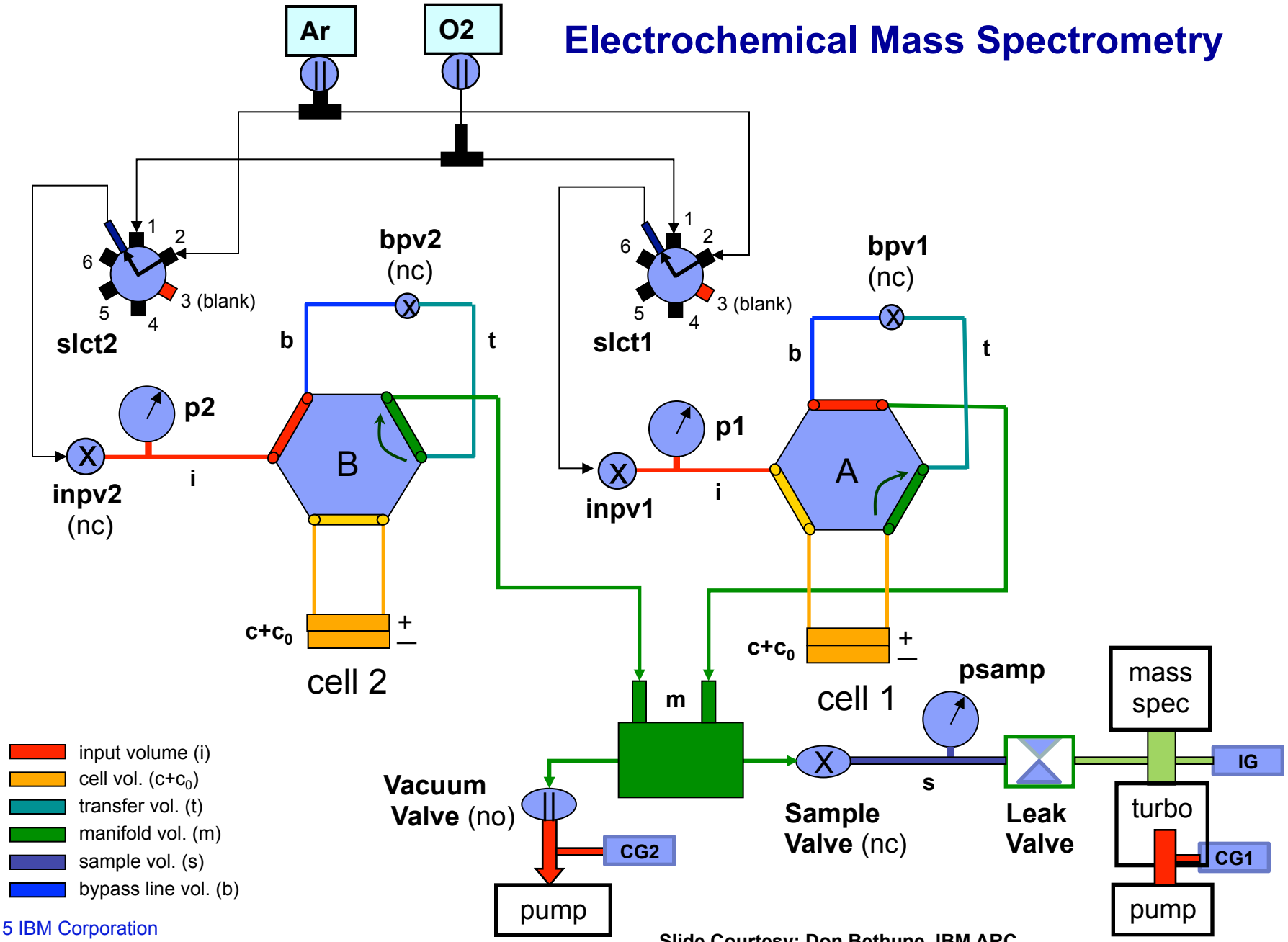
Electrochemical Mass Spectrometry



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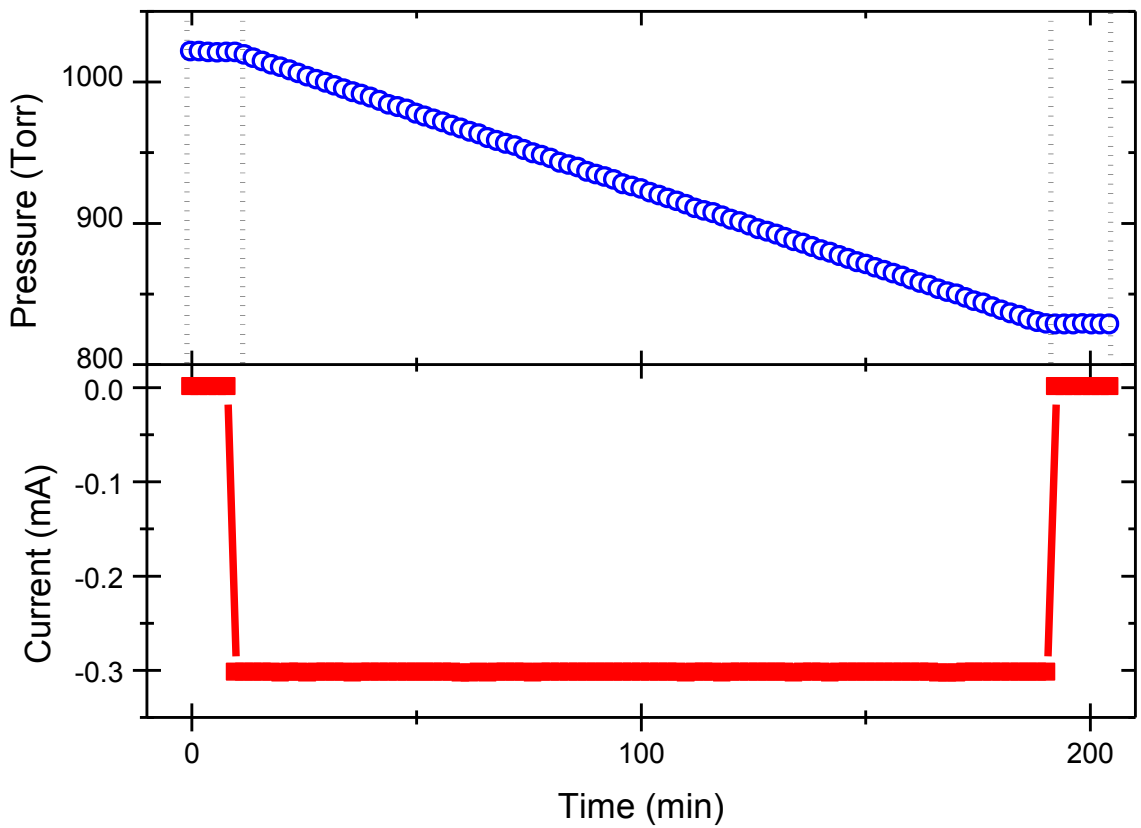
Aprotic Li-O_2 Battery: Near Ideal Discharge

Discharge in Oxygen under Constant Volume Conditions



$$\Delta n_{O_2} = \frac{\Delta P \cdot V}{R \cdot T}$$

$$\Delta n_{e^-} = \left(\frac{1}{e}\right) \cdot \int I \cdot dt$$

This particular sample: 2.003 e-/O_2; Usual variation within ~5% of the ideal value (AvCarb P50 Cathode, Li Anode, 1M LiTFSI in DME Electrolyte)

Discharge Product is predominantly Li_2O_2. But, it is an electronic insulator.

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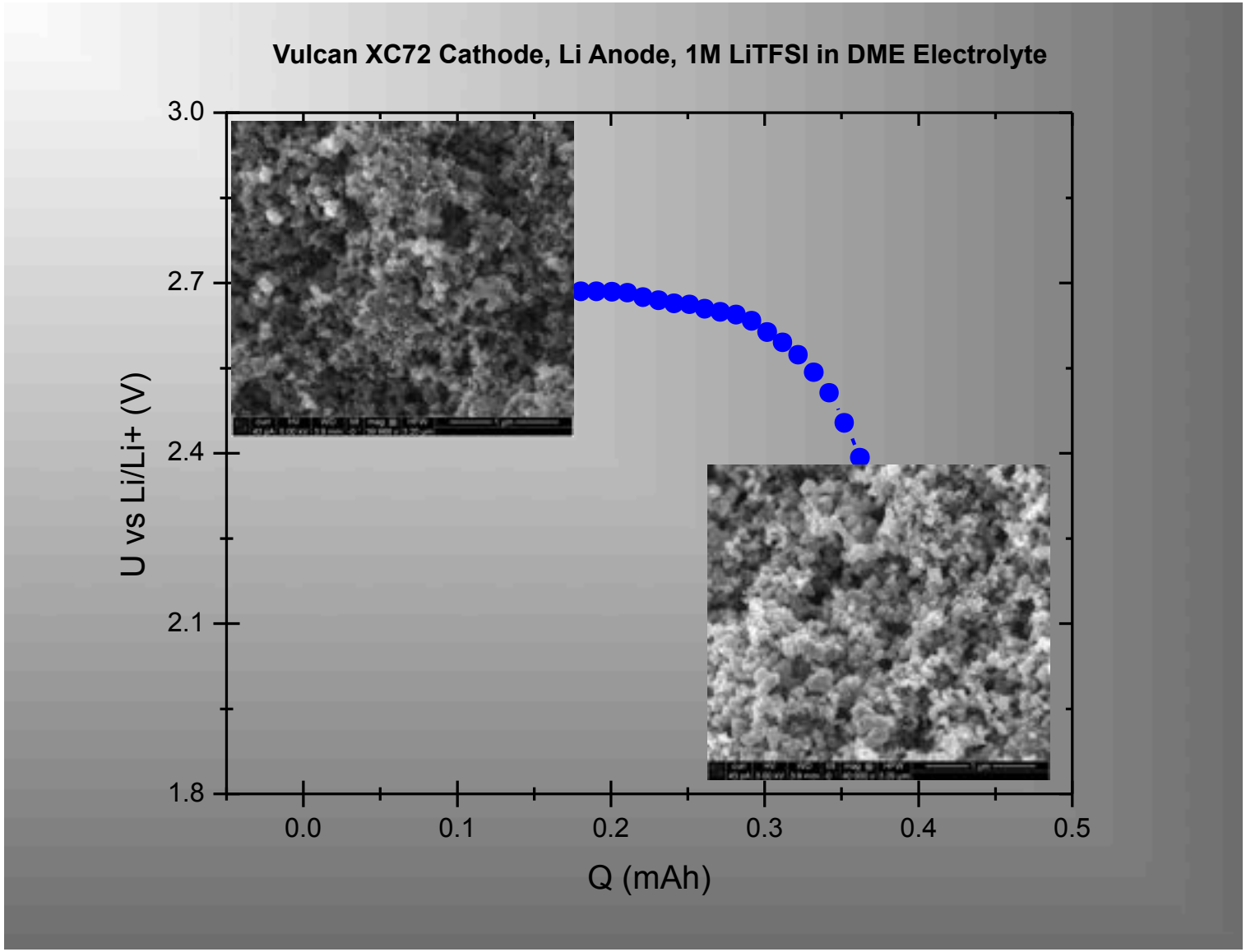
Poor Discharge Capacity



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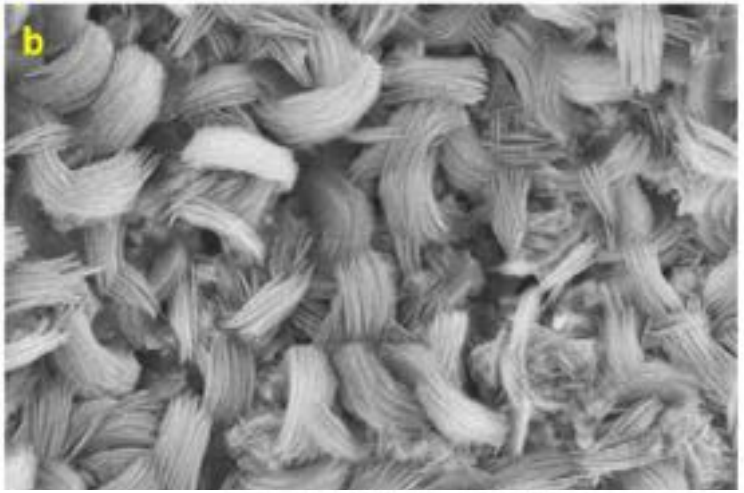
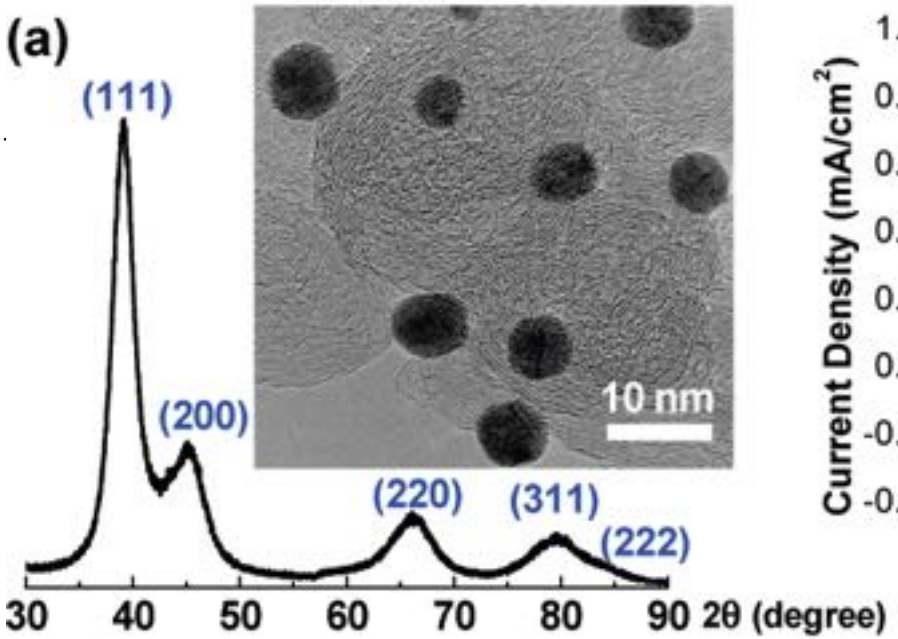
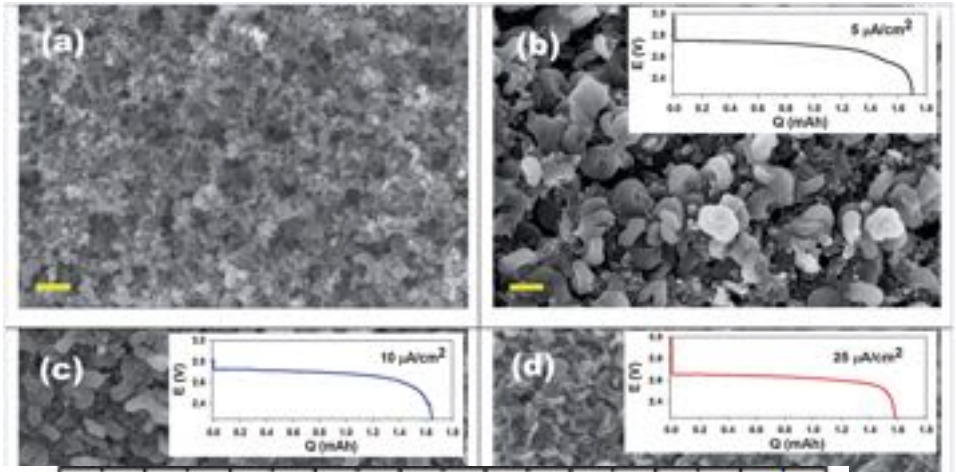
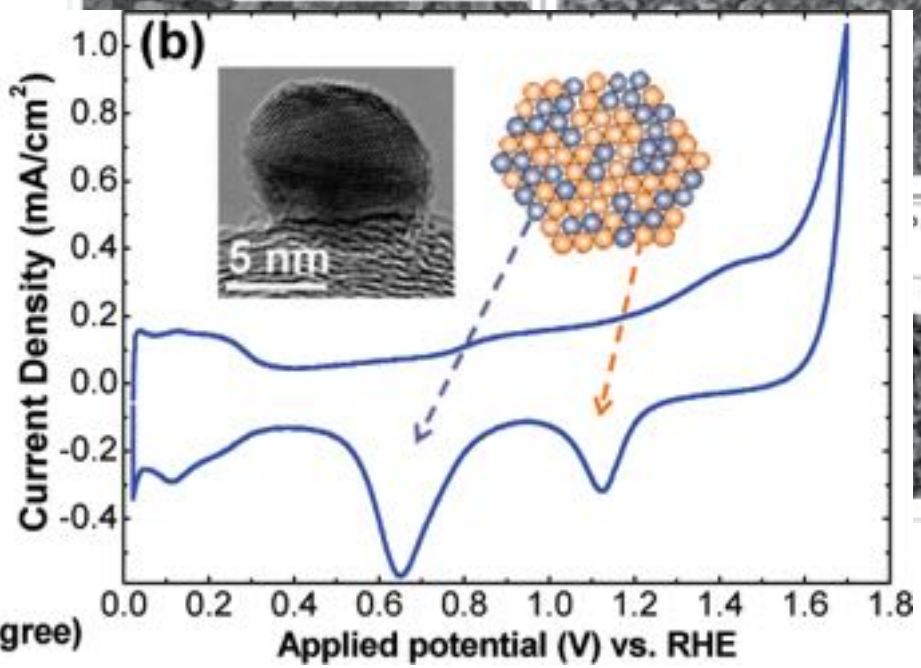
Gravimetric Capacity: ~250 mAh/g_c. ~an order smaller than the theoretical prediction

Toroidal Li_2O_2: Essential for High Specific Capacity









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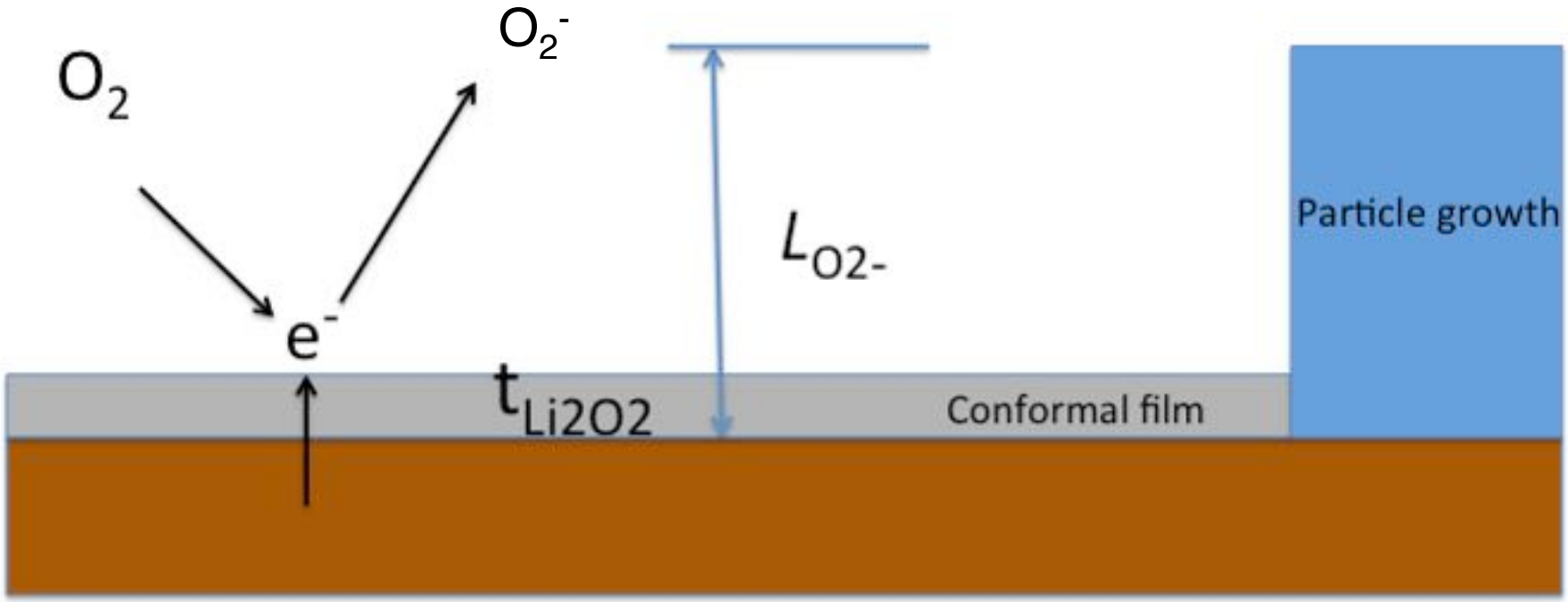
Lu *et al.*, JACS **132**, 12170–12171 (2010).

Practical limitation to high discharge Capacity



→ Li_2O_2 is an electronic insulator.

→ The maximum thickness of Li_2O_2 that can be deposited is limited by quantum mechanical tunneling of electrons.

How do large particles grow?

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How Aprotic are the aprotic solvents?

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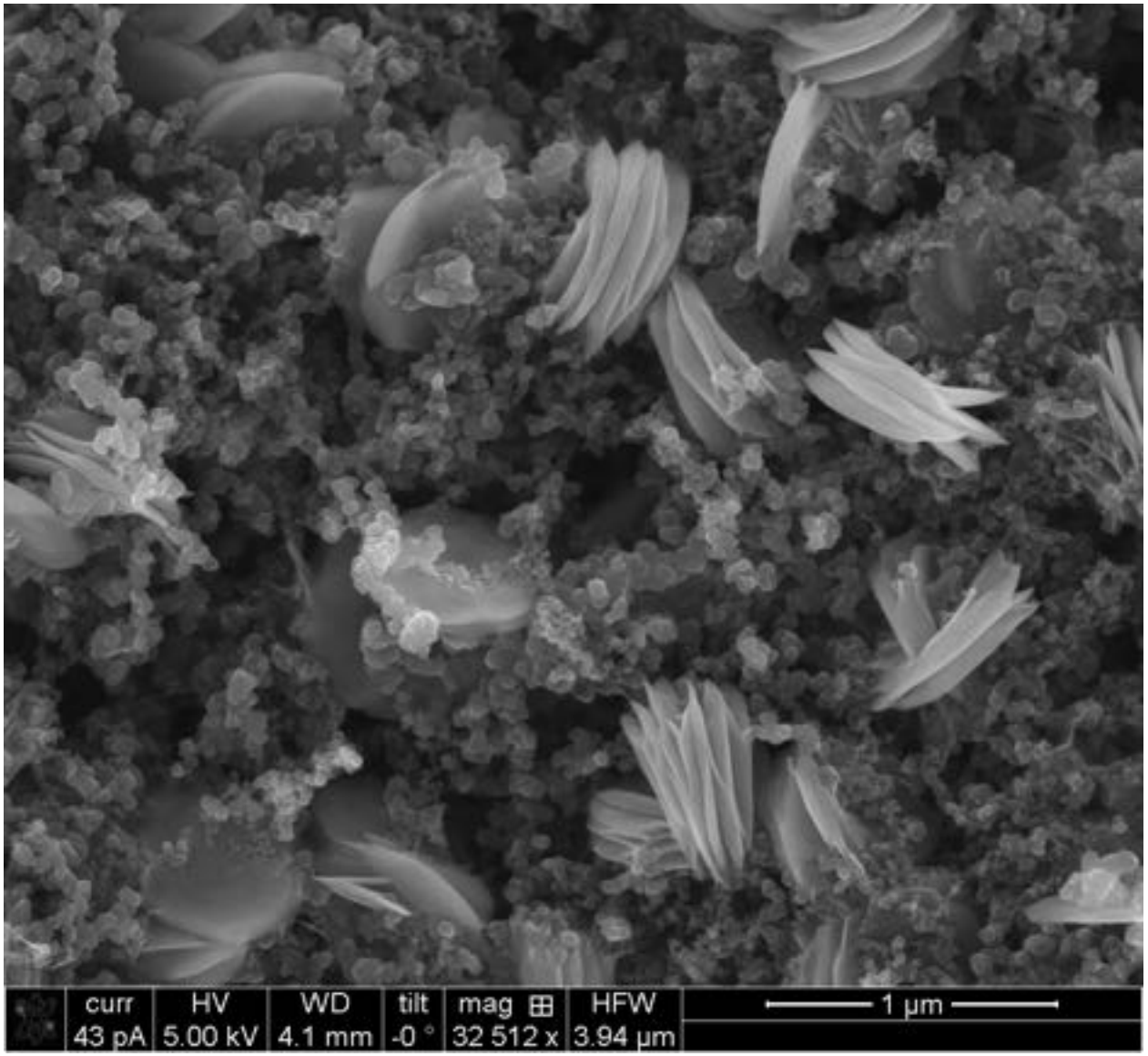
Toroidal Growth with added water

23150 ppm



All cells were discharged at 50uA to 1mAh. XC72 Cathode. Li Anode. 65 µl 1M Li-TFSI in DME

Aetukuri et al., *Nature. Chem.* **7** 50 (2015)

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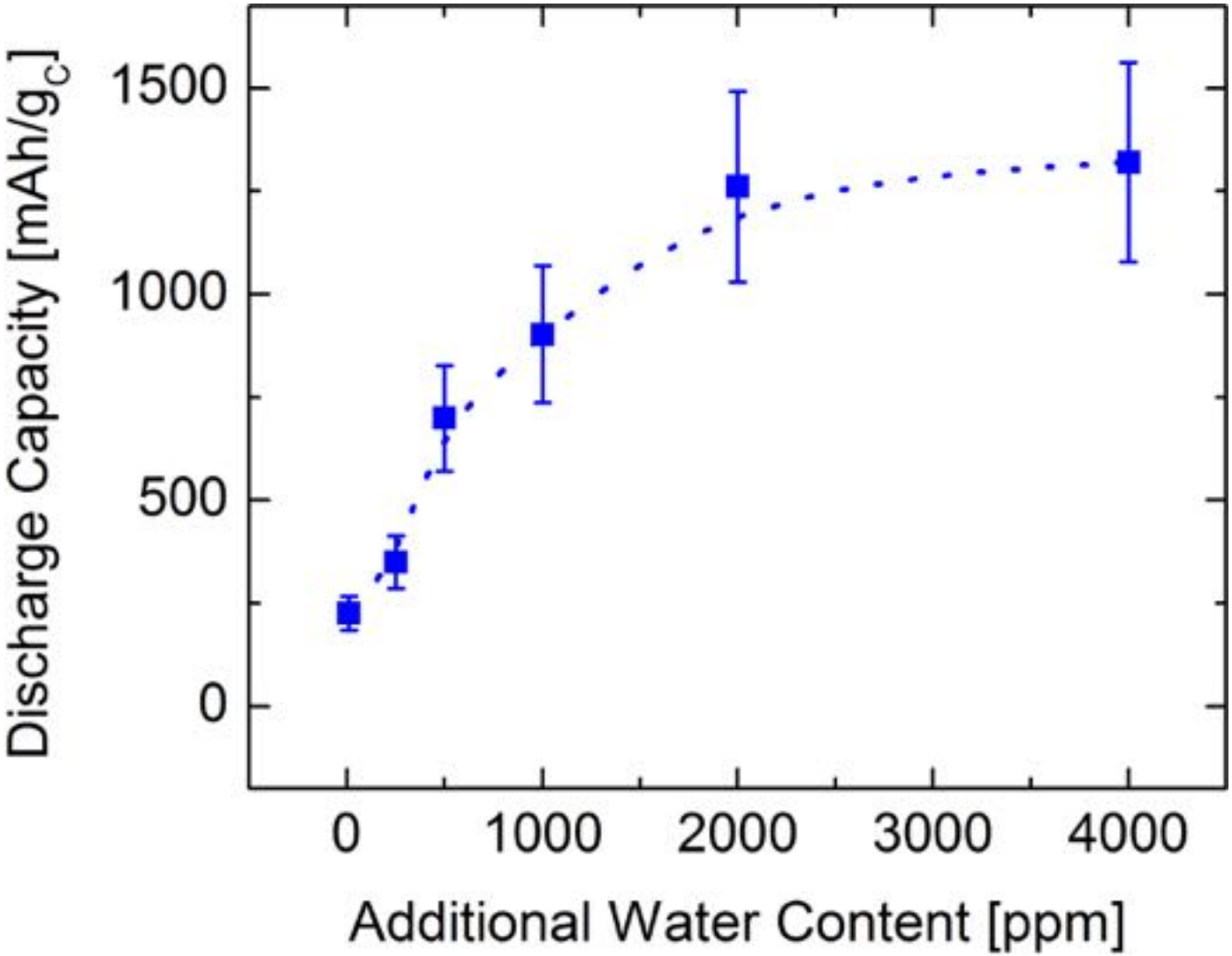
Toroid Formation Correlated with Enhanced Capacity



Aetukuri et al., *Nature. Chem.* **7** 50 (2015)

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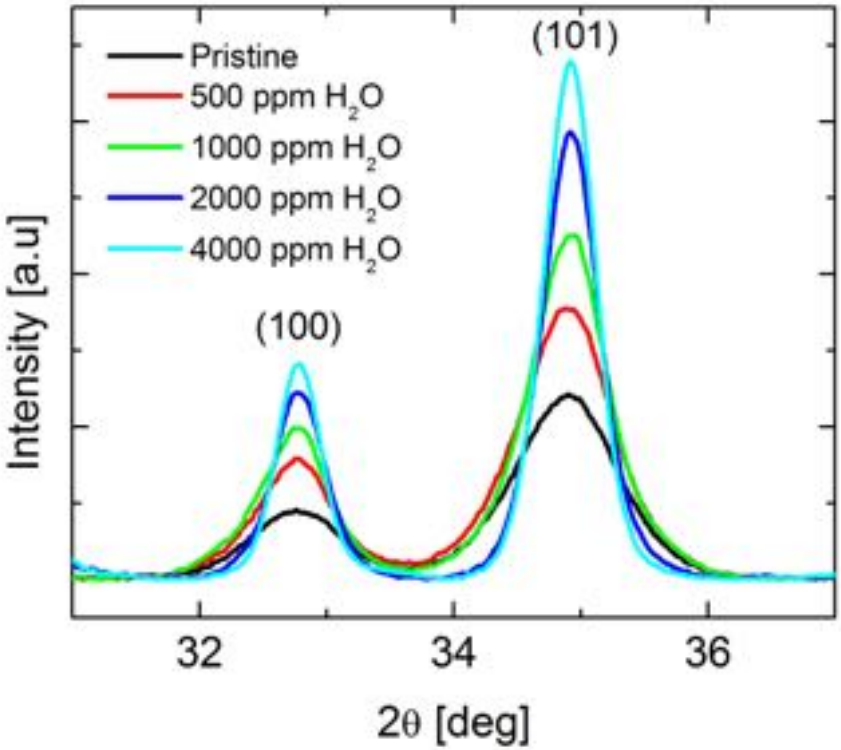
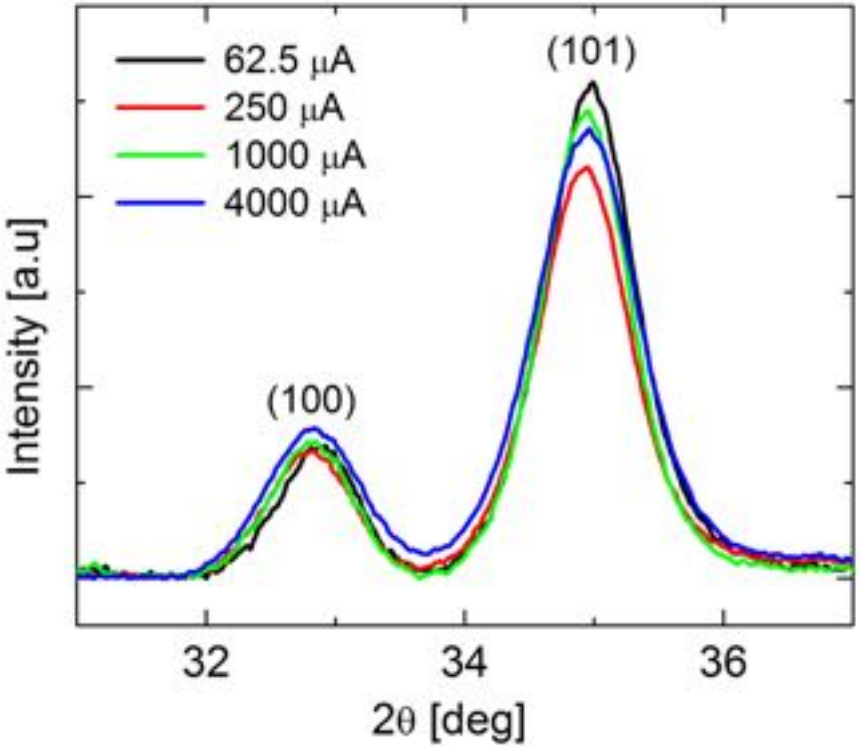
Discharge Phase Purity and Crystallinity from XRD

Water Content Varied



Current Varied – No Water Contamination in Electrolyte



→ **Crystal Size increase in the Samples with increasing water content**

→ **All Samples Discharged to 2mAh on P50. Samples with differing water contents are discharged at 250 uA**

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Two distinct mechanisms for the formation of Li_2O_2

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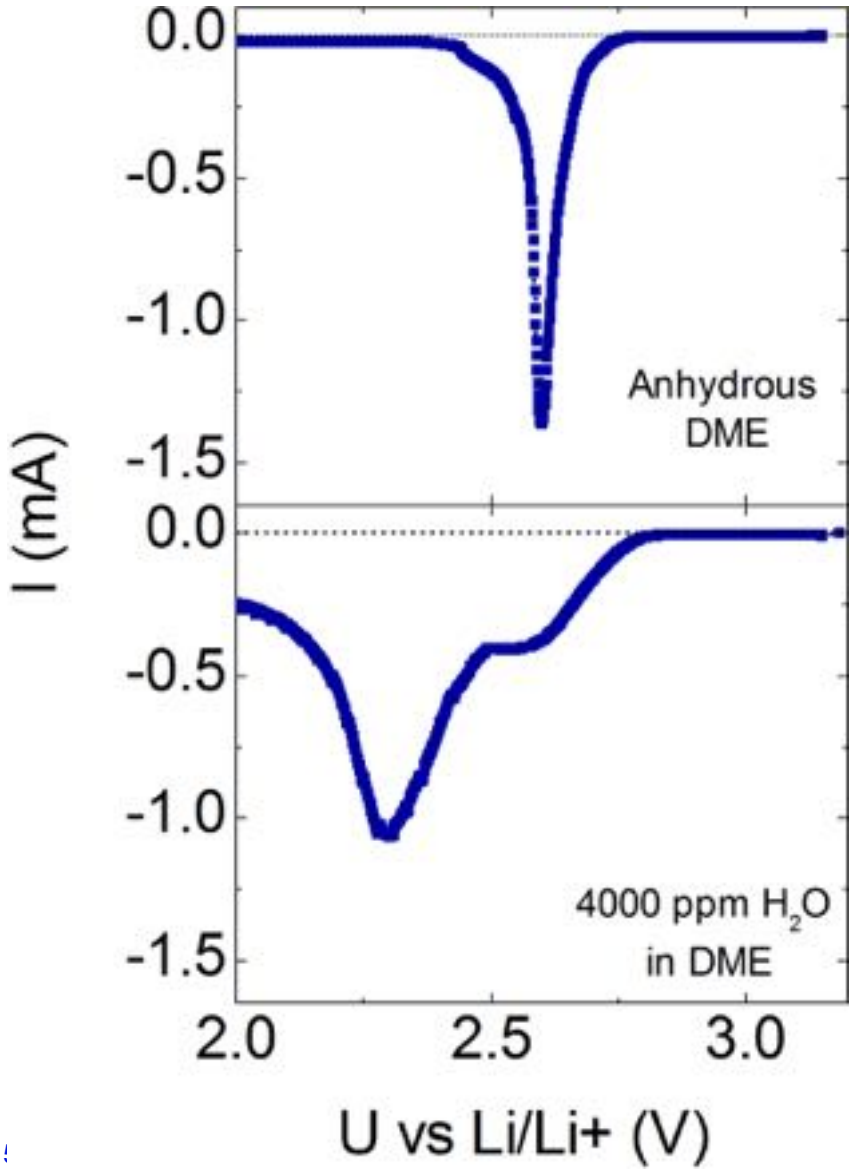
Two Mechanisms for Li_2O_2 growth



Surface Electrochemical Growth

+

LiO_2 Solubility-Mediated Growth

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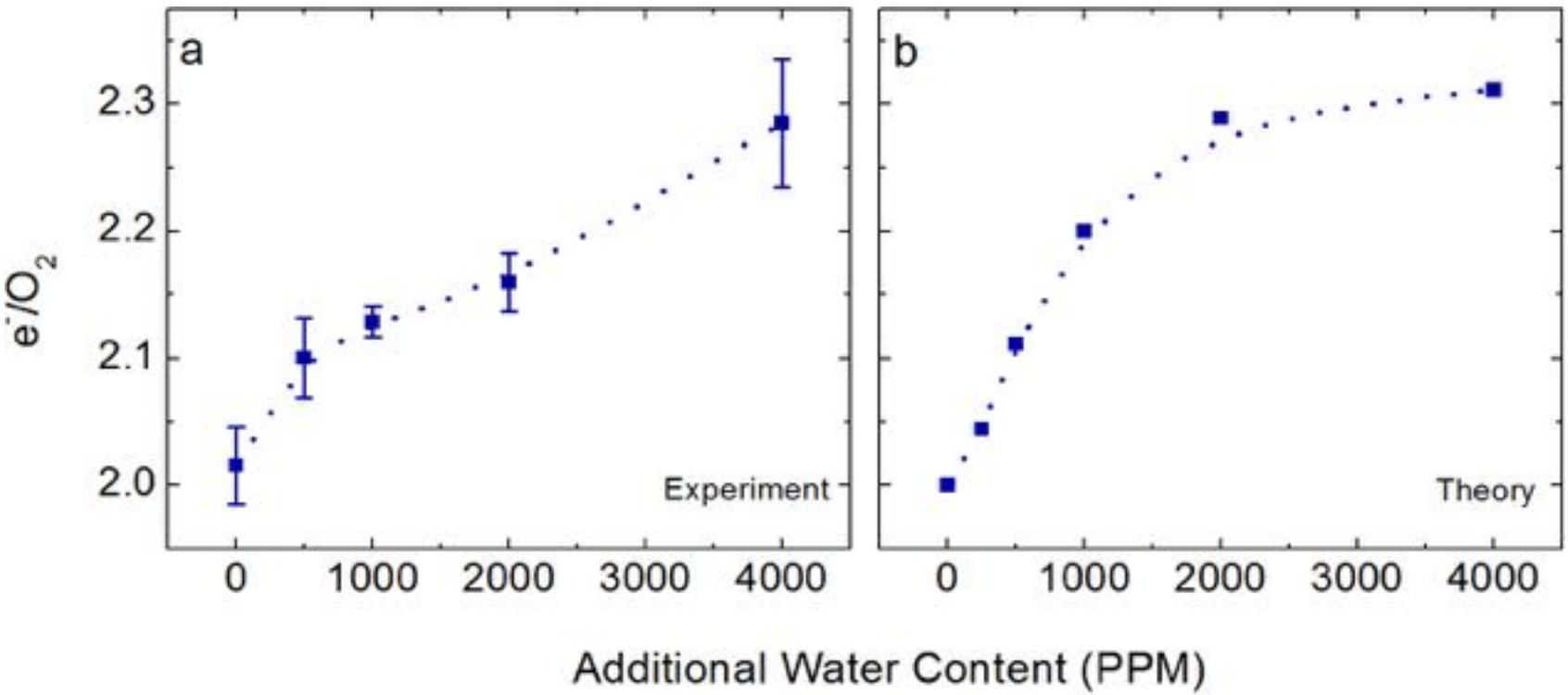
Evidence for Parasitic Electrochemistry



→ Ideal e^-/O_2 is 2.00 for the formation of Li_2O_2.

→ Deviation from 2.00 is an indication for parasitic electrochemistry.

How can we improve capacity while not adversely affecting the electrochemistry?

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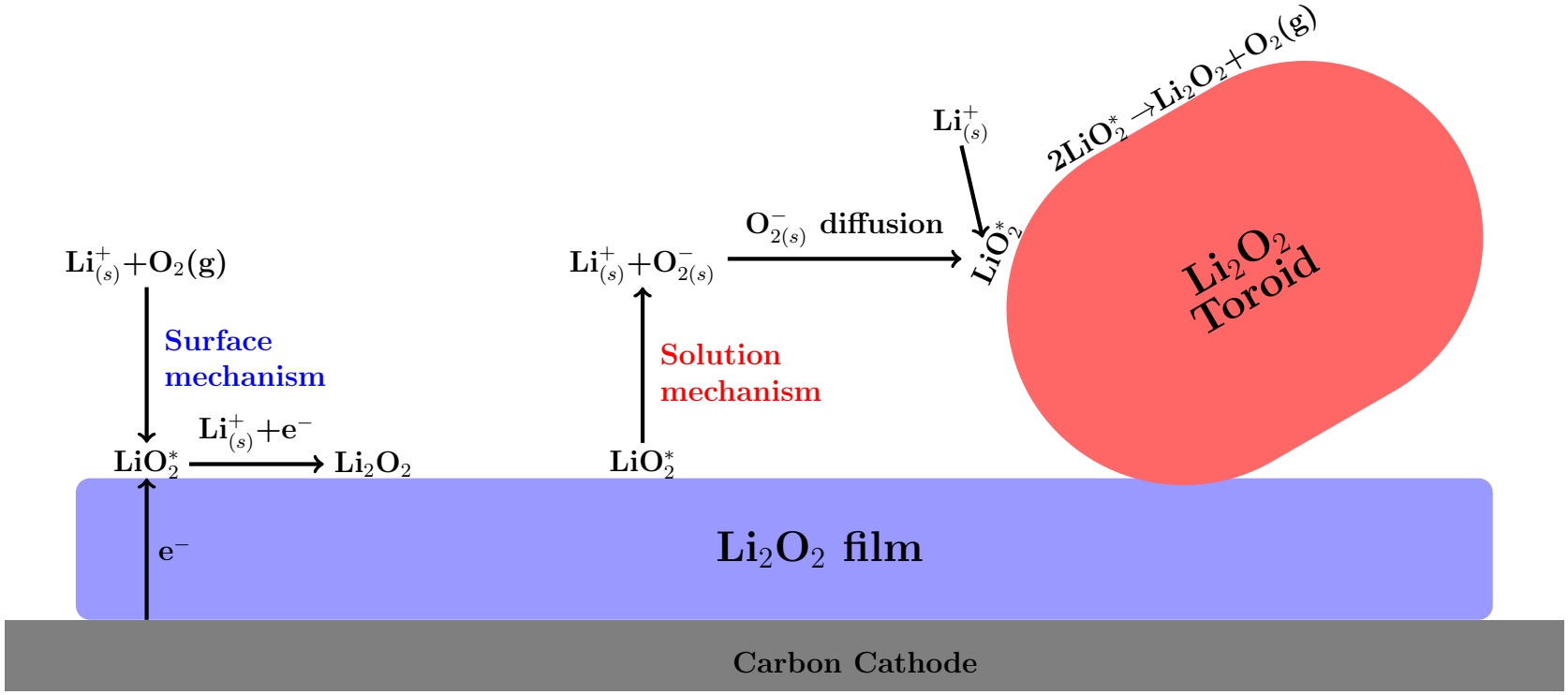
Proposed Microscopic Mechanism



→ **Soluble O_2- as a redox shuttle.**

→ **Solubility determined by the acceptor and donor number of the solvents**

Aetukuri et al., *Nature. Chem.* **7** 50 (2015)

Also see: Johnson et al., *Nature. Chem.* **6** 1091 (2014)

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LiO_2 Solution Thermodynamics

$$LiO_2^* \rightleftarrows Li^+{}_{(sol)} + O_{2\,(sol)}^-$$

$$\Delta G_{(sol)} = G_{LiO_2^*} - G_{Li^+{}_{(sol)}} - G_{O_{2\,(sol)}^-}$$

$$= G_{LiO_2^*} + (G_{Li} - G_{Li^+{}_{(sol)}}) + (G_{O_2} - G_{O_{2\,(sol)}^-}) - (G_{Li} + G_{O_2})$$

$$(G_{Li} - G_{Li^+{}_{(sol)}}) \propto DN$$

$$(G_{O_2} - G_{O_{2\,(sol)}^-}) \propto AN$$

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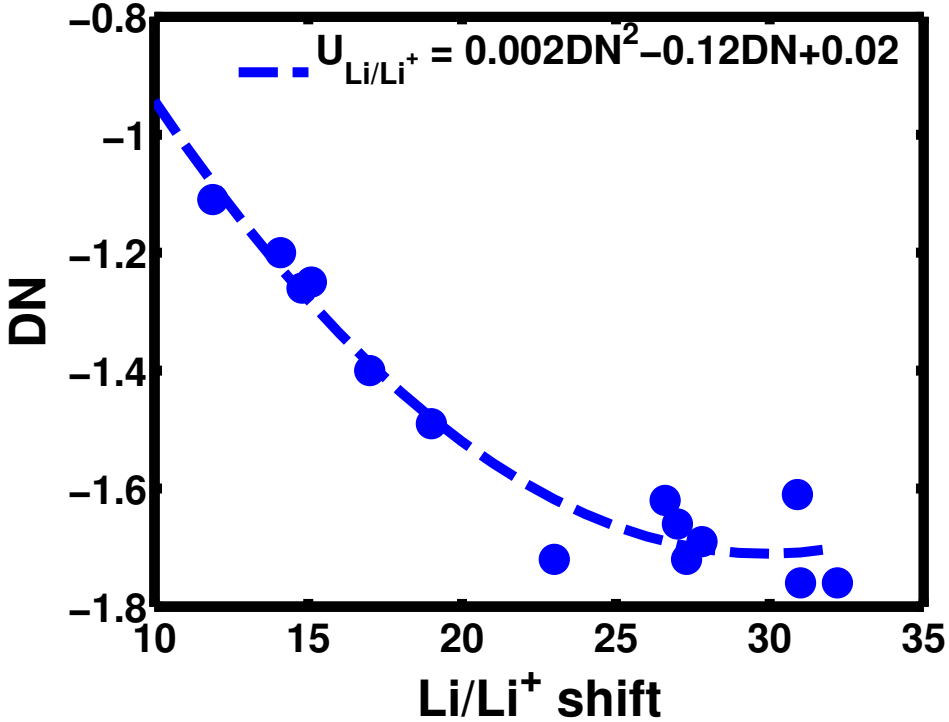
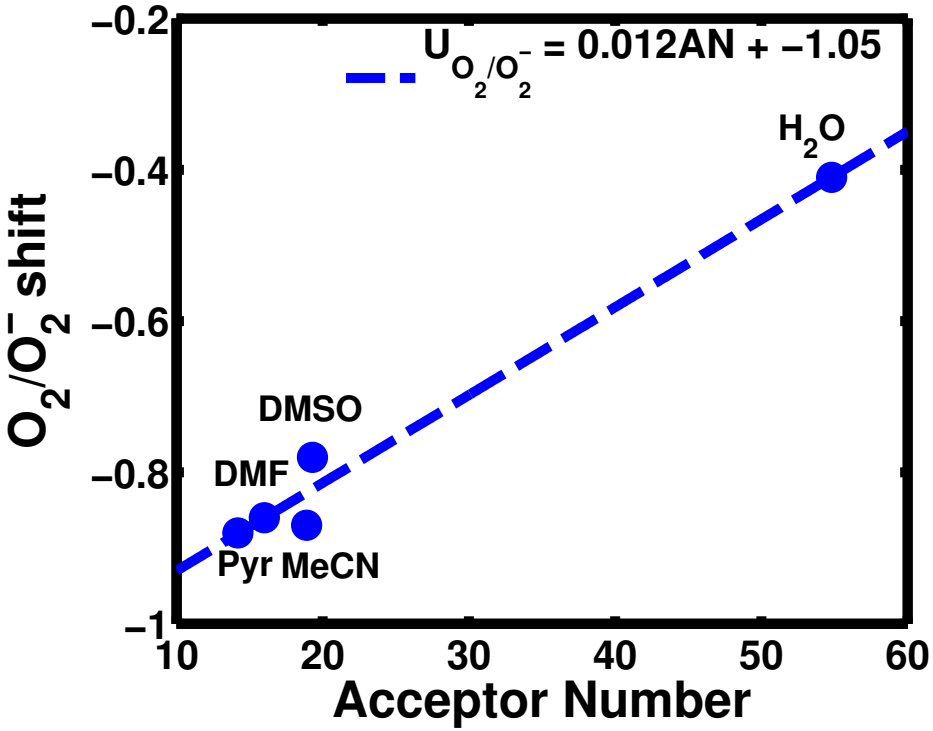
Solvent-Dependent Potential Shifts





Gritzner, G. J. Phys. Chem. 90, 5478-5485 (1986).
Sawyer, D. T., et al. Anal. Chem. 54, 1720-1724 (1982).

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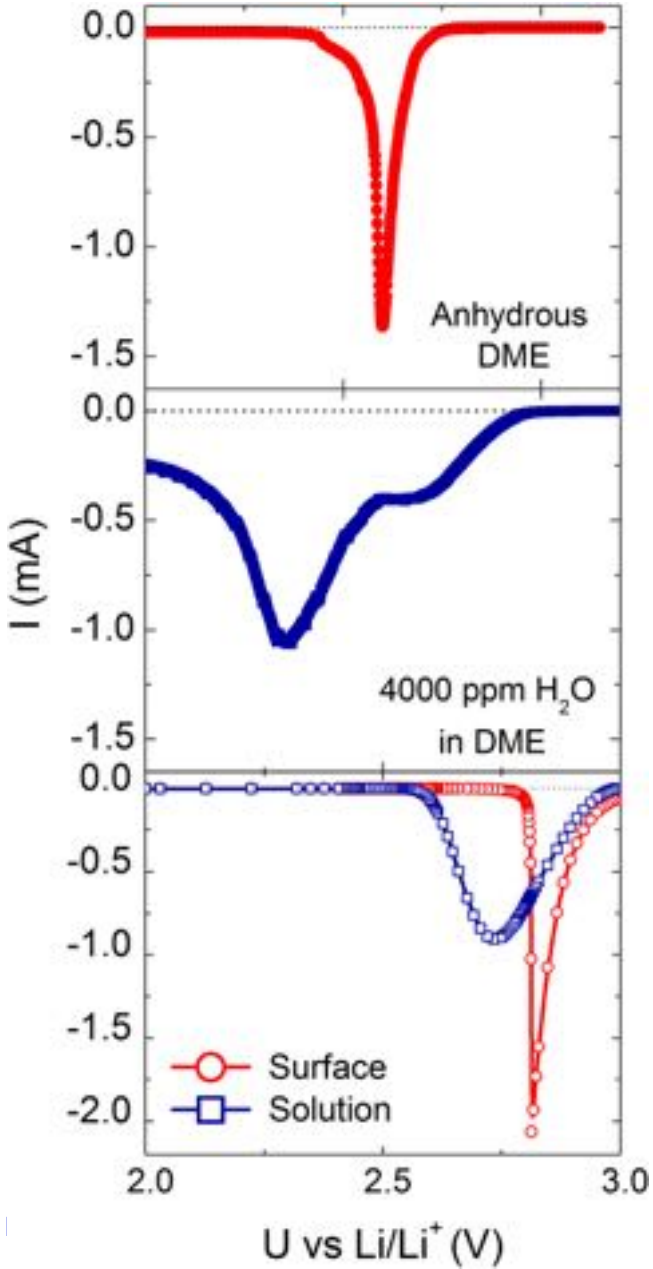
Net Potential Shifts: Experimental Vs Theory



Linear Scanning Voltammograms Experiment and Theory for Li-O_2 cells with water additive

Two distinct electrochemical mechanisms – Theory predicts the potential shifts.

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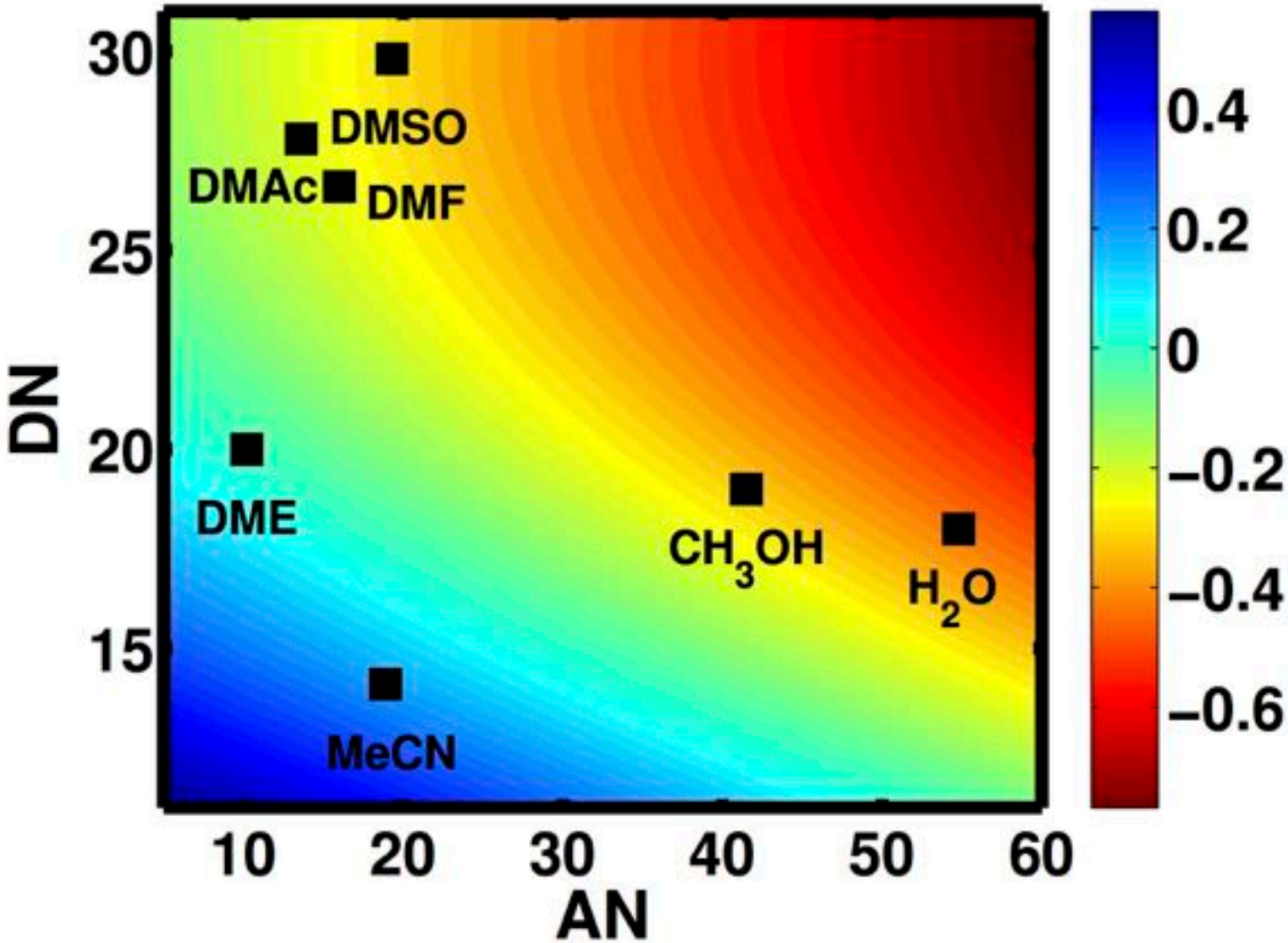
Solvent Phase Diagram



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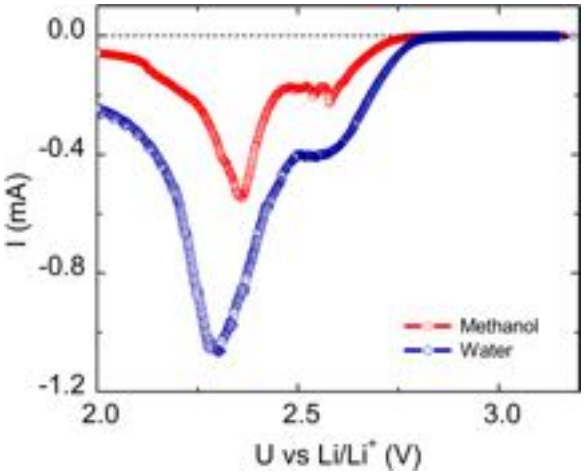
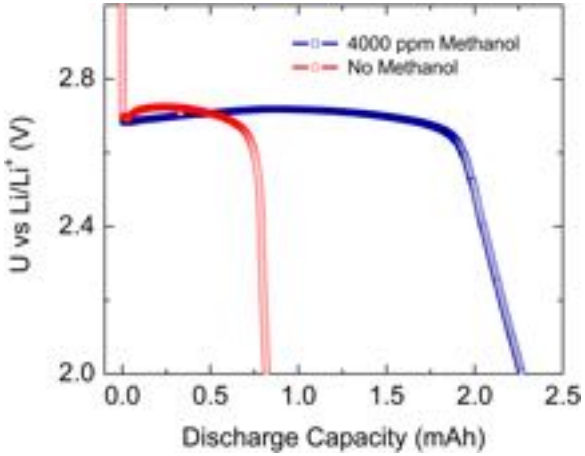
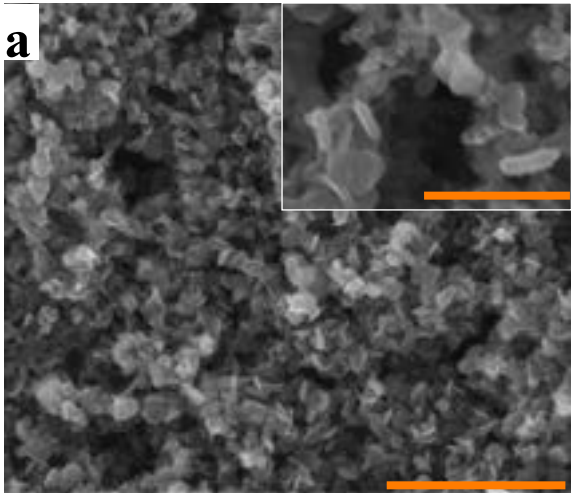
Solution-Mediated Electrochemistry in Methanol and DMSO

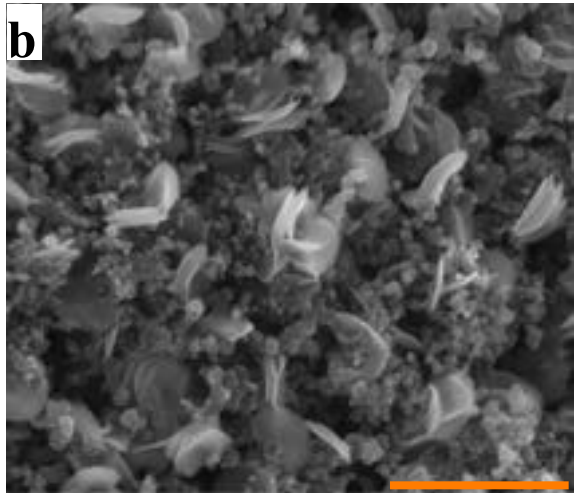
Capacity enhancement with added Methanol

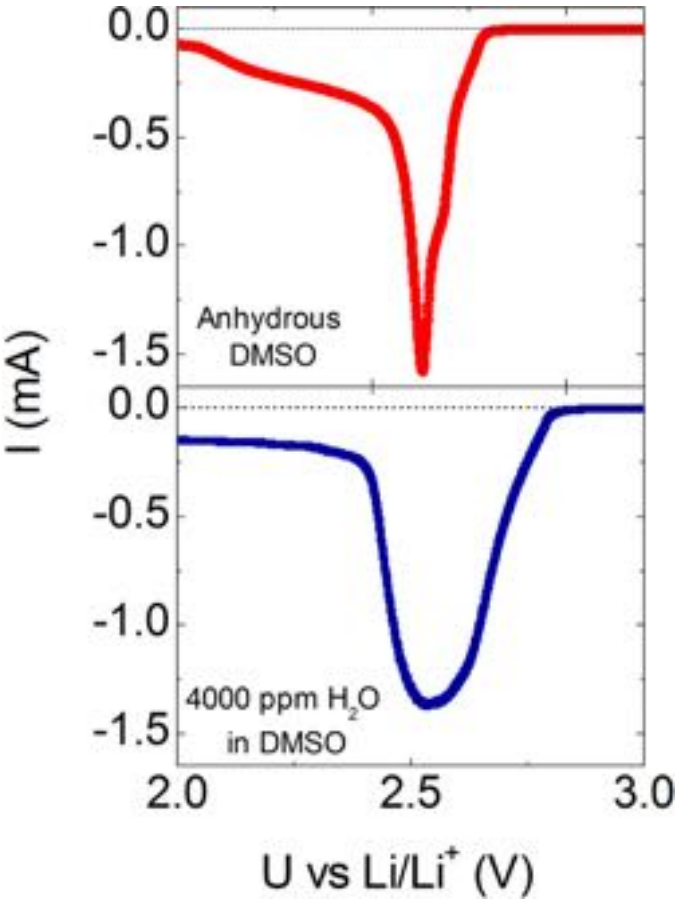




Toroid Growth with DMSO







Poor Rechargeability with DMSO and Methanol.

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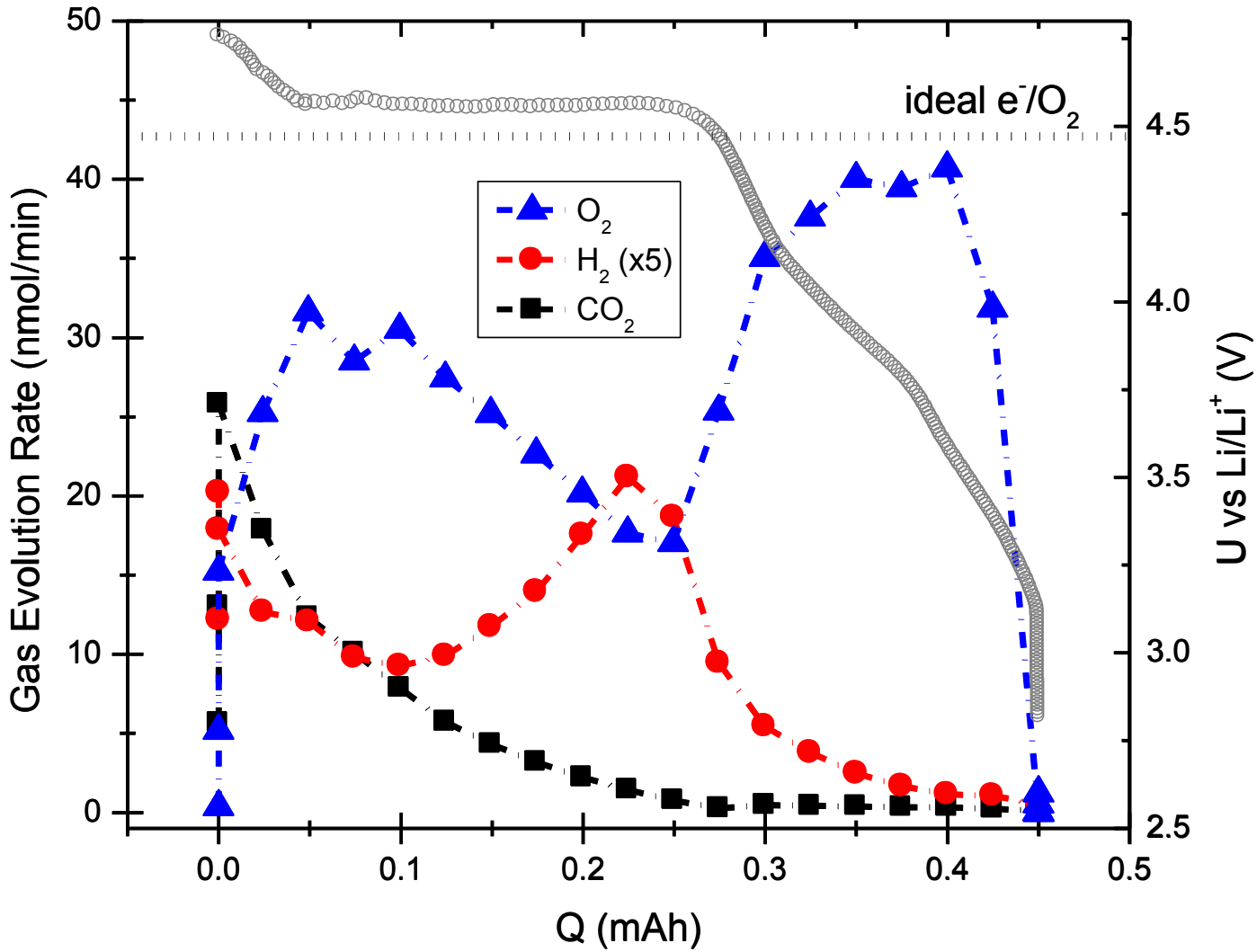
Recharge is still an unsolved problem



(1M LiTFSI in TEGDME, Avcarb P50, 150 uA to 450 uAh)

Increasing Potential Accelerates Electrolyte Decomposition

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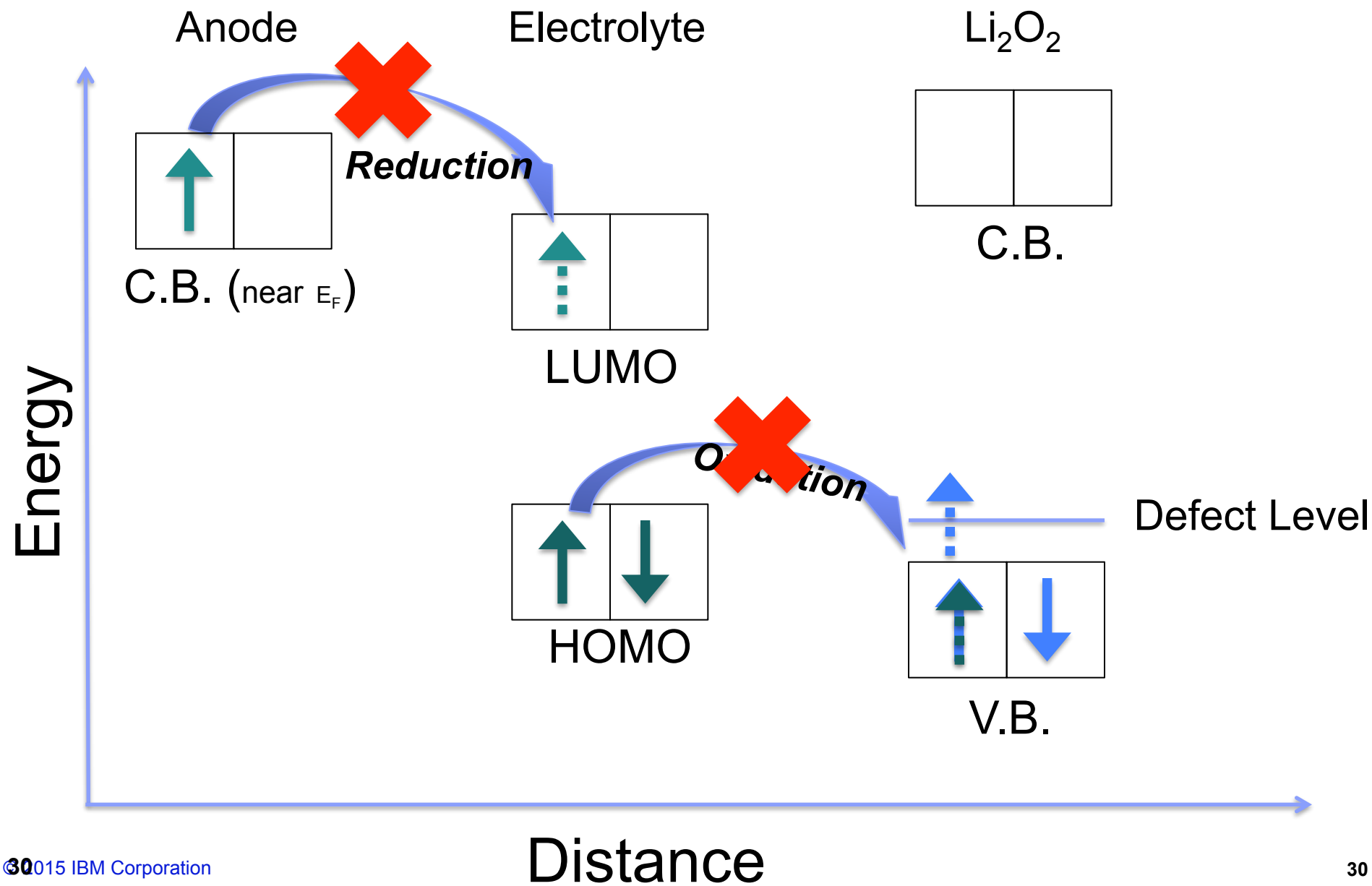
A plausible Mechanism



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Ideal Solvent: Have a large HOMO-LUMO Gap

But, the electrostatics associated makes it a hard problem

How about using two electrolytes?

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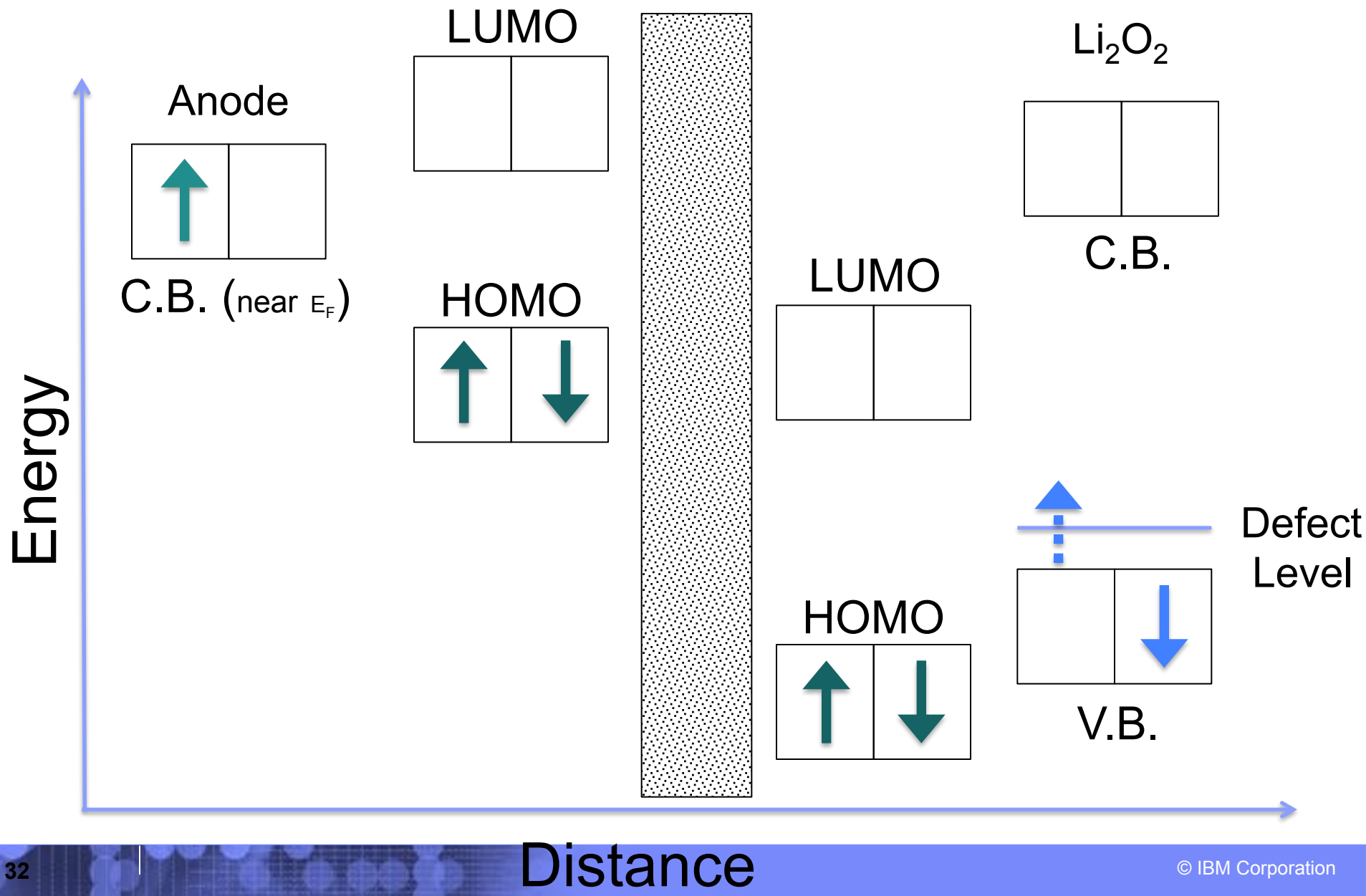
Using a Solid State Ion-Conducting Membrane



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Ideal Ion-Conductor:

- → Li – Ion Conductivity ~1 mS/cm
- → Resist Dendrite Penetration
- → Should be mechanically robust
- → Stable in Li-Air environment

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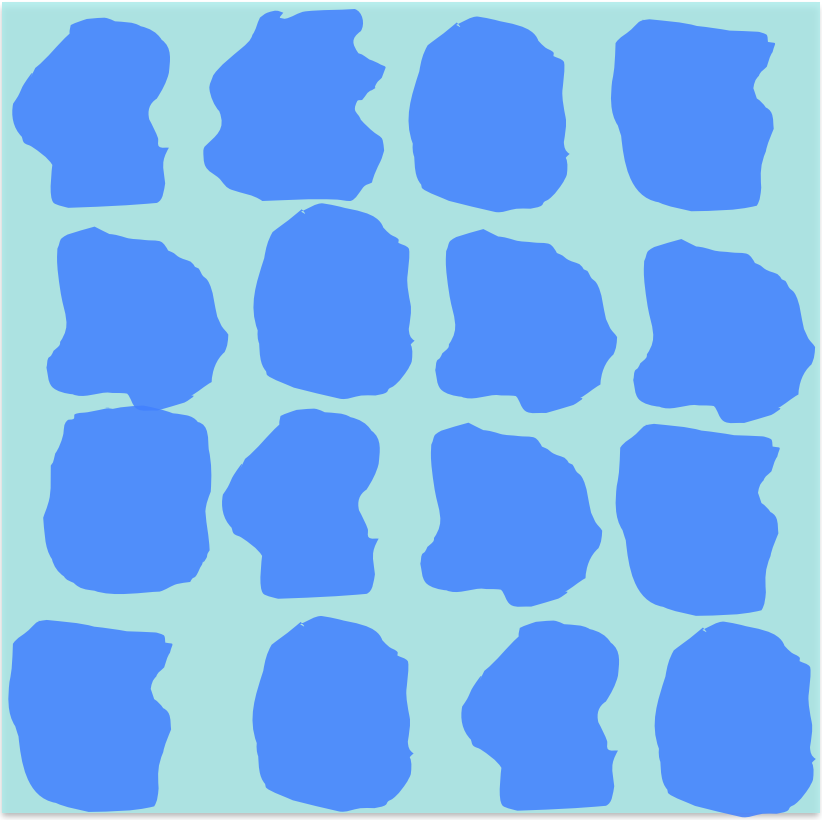
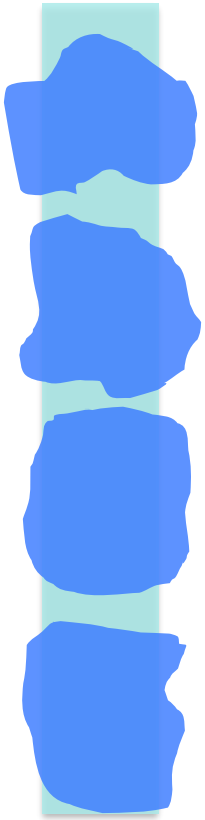
Composite Membranes

Conventional Composite Membrane



Li-Ion Conducting Ceramic in a
Li-Ion <u>conducting</u> Polymer Matrix

One-Particle Thick Membrane



Li-Ion Conducting Ceramic in a
Li-Ion **INSULATING** Polymer Matrix

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Li-Ion Conducting One-particle Thick Membranes

→ $Li_{1.6}Al_{0.5}Ti_{0.95}Ta_{0.5}(PO_4)_3$ (LATTP) Ceramic Particles

→ Cyclo Olefin Polymer

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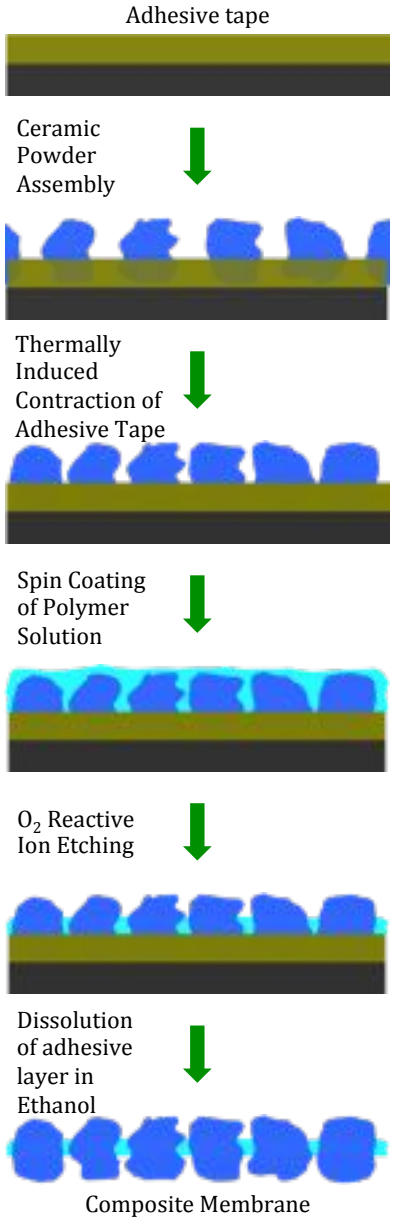
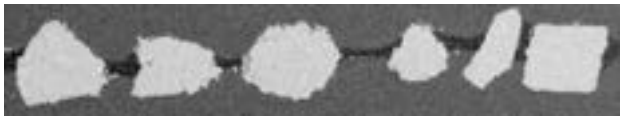
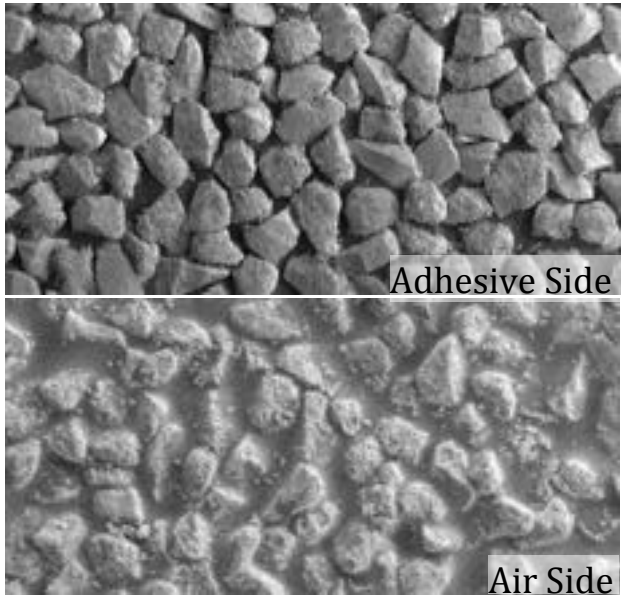
One-Particle Thick Ion-Conducting Composite Membranes







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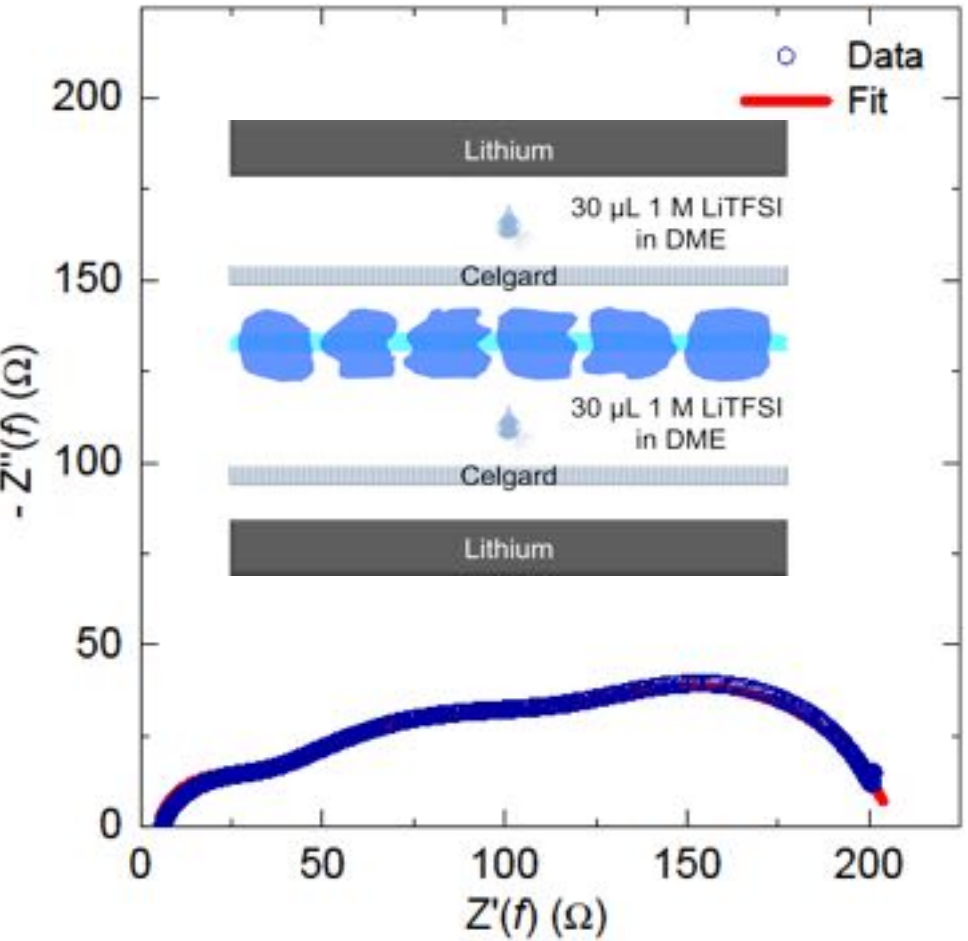
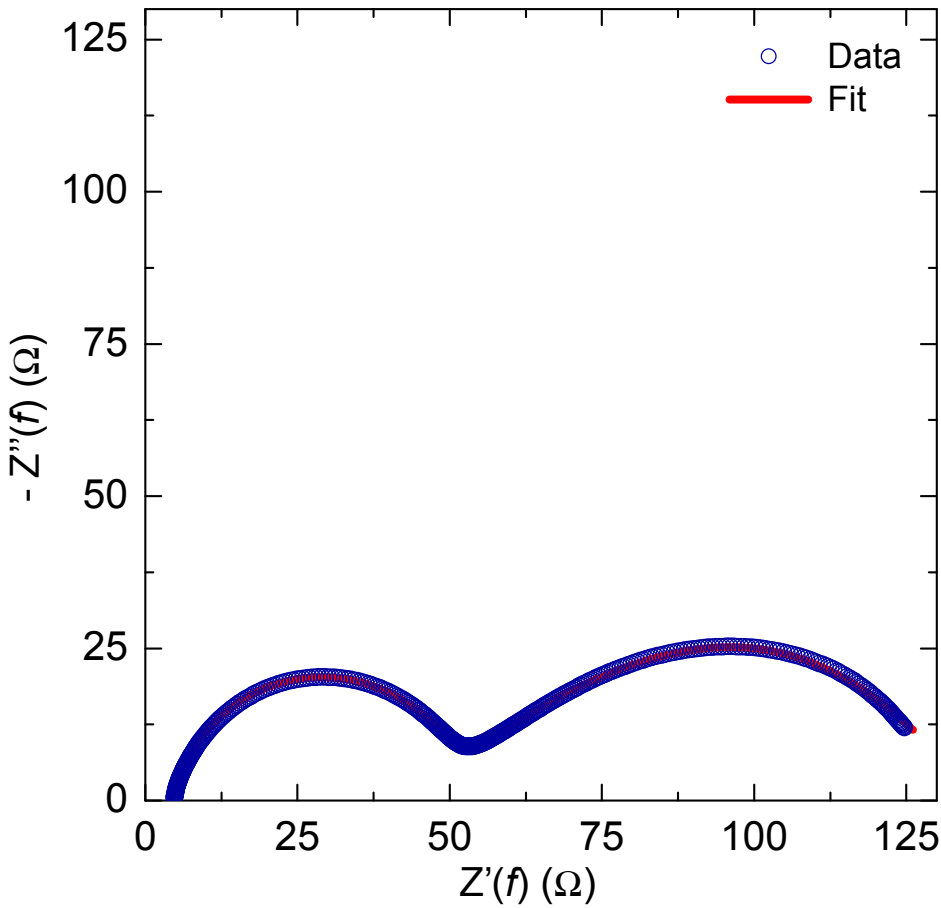
Membranes are Flexible

Membranes have High Ion-Conductance



$Li_{1.6}Al_{0.5}Ti_{0.95}Ta_{0.5}(PO_4)_3$



$Li_7La_3Zr_2O_{12}$

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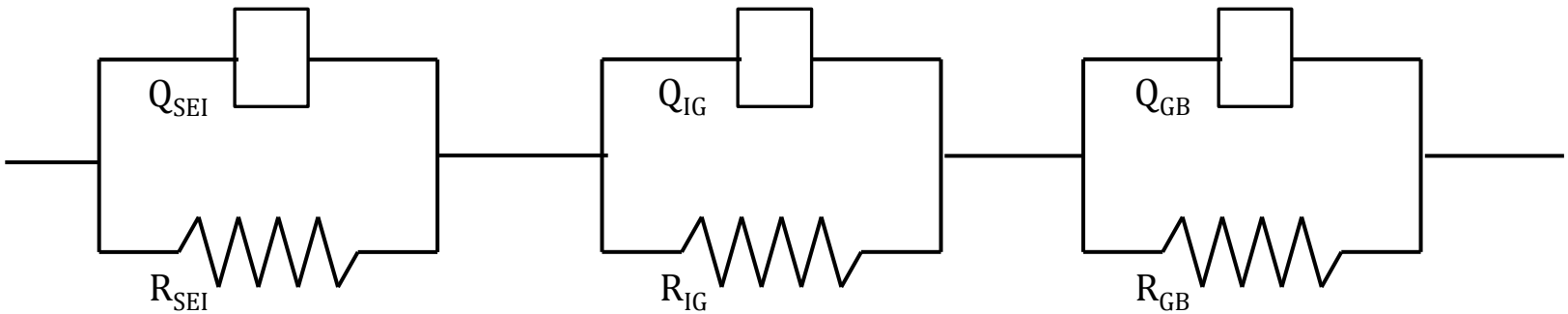
A Quick detail into impedance analysis



$$Z = \frac{R}{1 + i(\omega \mathrm{RC})^n}$$

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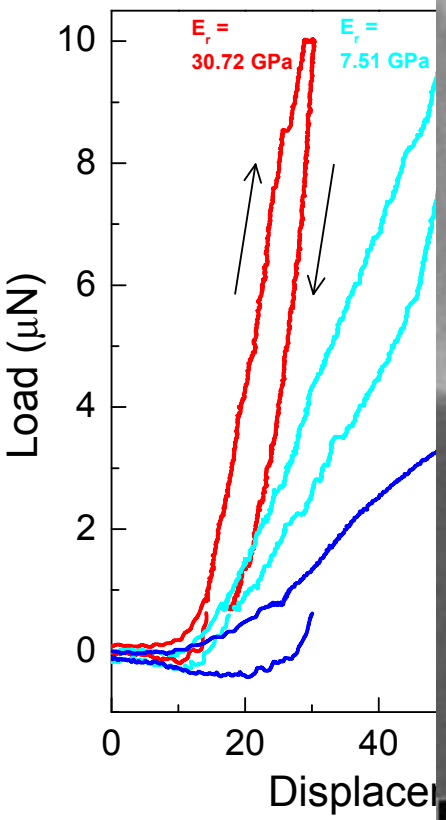
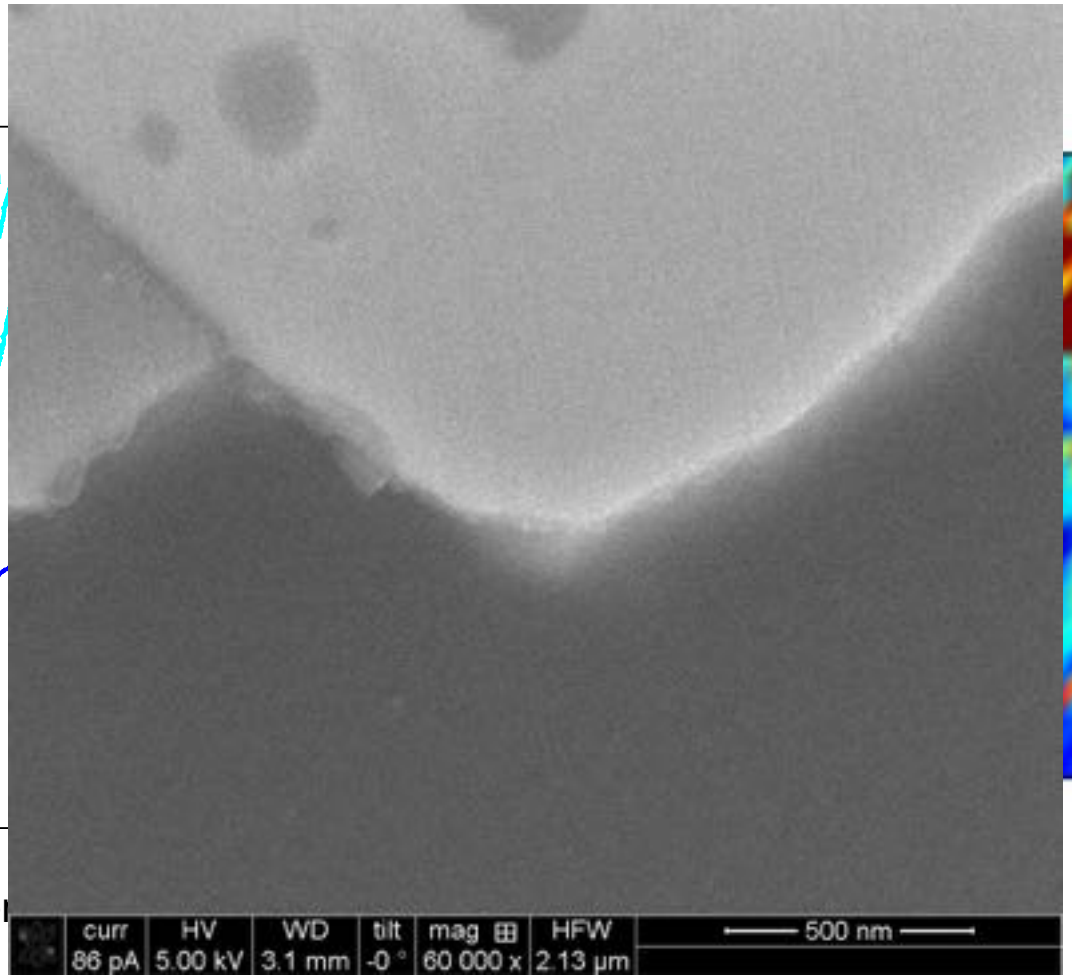
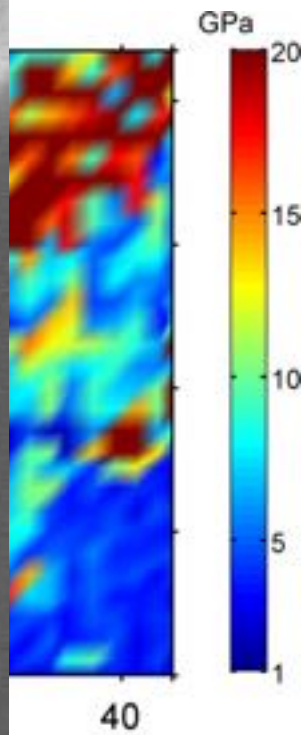
Excellent Particle-Polymer Interface Bonding







Nano-indentation measurements show interface continuity

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Membranes Resist Dendrite Penetration

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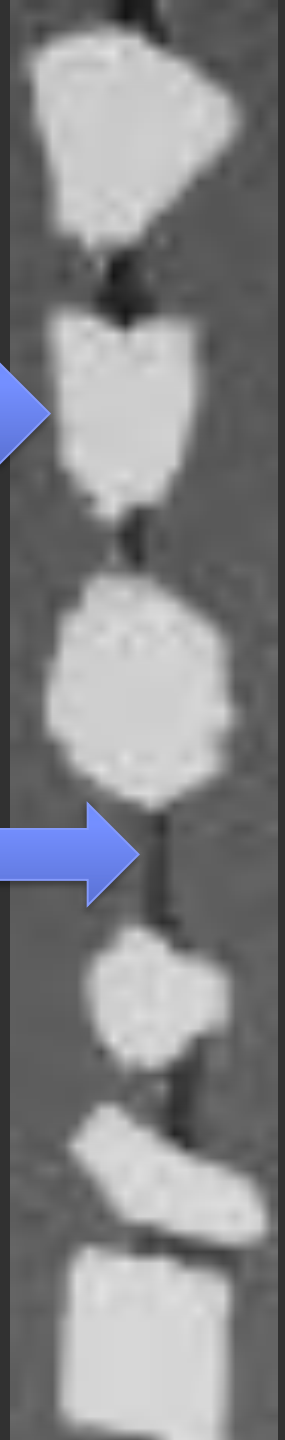
$G_{LATTP} >> G_{Li}$

$G_{polymer} << G_{Li}$

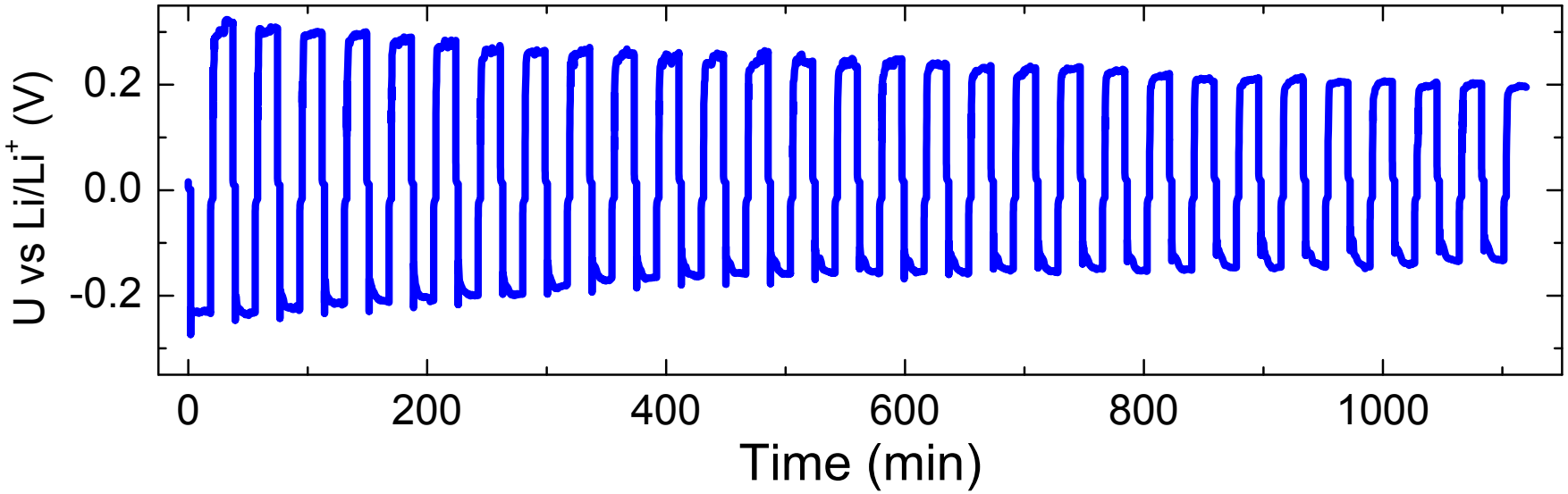
$$\Delta P \propto i_A = 0$$



Modulus of Polymer irrelavent for Supressing Dendrite Growth as long as it is Li-Ion Insulating

Monroe and Newman, JES 152 A396-404, 2005.

Li-Li Cyling With OPTMs



About 200 mV Over Potential at 250 μA/cm^2

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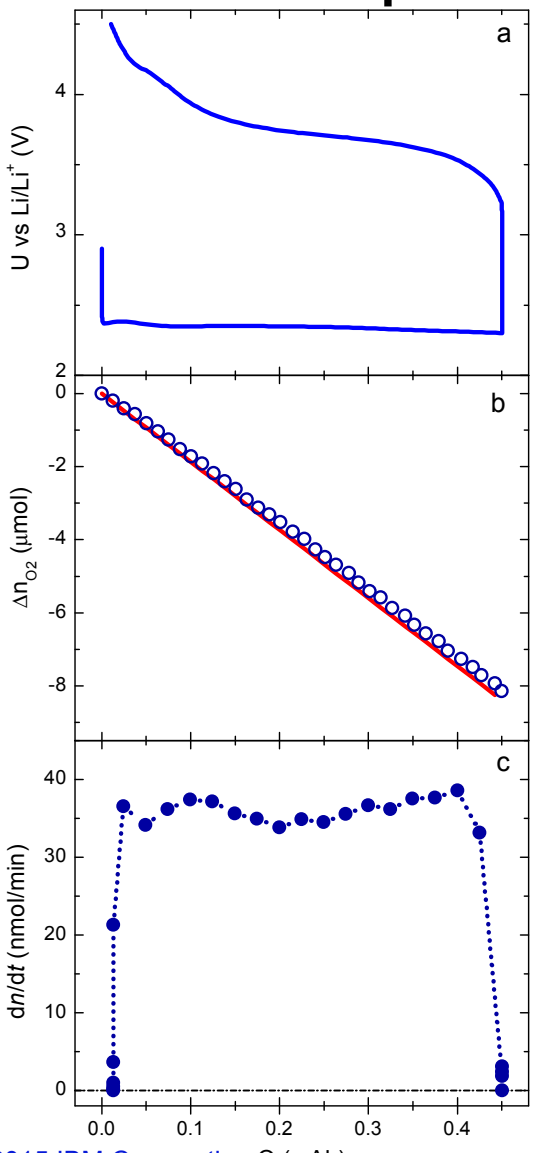
Membranes in Li-O_2 Batteries

Membrane Separator



Battery Measurements performed using LiI as a redox mediator.

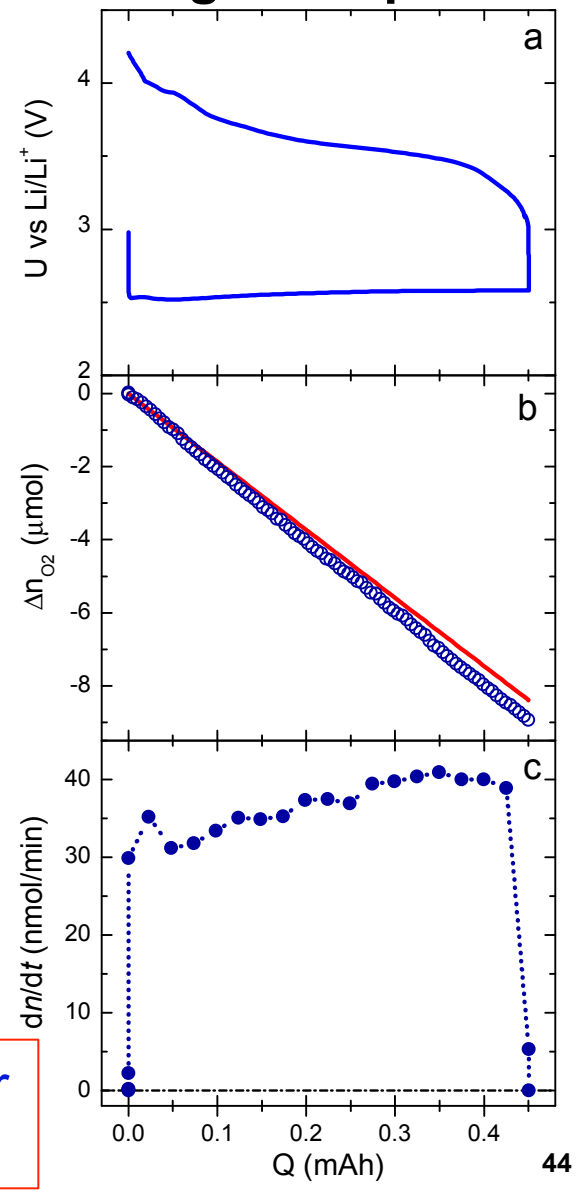
$3I^-/I_3^-$ redox couple enables Li_2O_2 oxidation at low charge overpotentials

Separator	e^-/O_2	η (%)
Membrane	2.06	78
Celgard	1.88	74
Celgard (no LiI)	2.05	61
Ideal	2.00	100

η is the ratio of oxygen evolved to the oxygen consumed and represents the reversibility of the cell

Membranes stable and better than conventional separator

Celgard Separator



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Summary and Outlook

Solution Chemistry in Li-O_2 Batteries

- Enhancing LiO_2 Solubility critical for high discharge capacity Li-O_2 batteries
- Cell Designs with distinct Catholyte and Anolyte compartments → possible path for stable cycling

Composite Membranes

- Developed a General protocol for flexible membrane fabrication
- Recently, developed a manufacture-friendly technique that does not involve Spin coating and Etching
- Possible applications in Li-Air and High Voltage Li-Ion batteries

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Acknowledgements

- Robert Miller, Greg Wallraff, Iwnetim Abate, Leslie Thompson, Don Bethune
- Bryan McCloskey, Alan Luntz, Venkat Viswanathan.
- Winfried Wilcke, Ho-Cheol Kim and other members of the IBM Battery Team

nature chemistry ARTICLES
PUBLISHED ONLINE: 15 DECEMBER 2014 | DOI: 10.1038/NCHEM.2132

Solvating additives drive solution-mediated electrochemistry and enhance toroid growth in non-aqueous Li-O_2 batteries

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Flexible Ion-Conducting Composite Membranes for Lithium Batteries

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FULL PAPER

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Thank you All and especially the BLI Organizing Team for giving me this opportunity to Present

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