Transport Phenomena in Metal-Oxygen Batteries: A Multi-Scale Perspective

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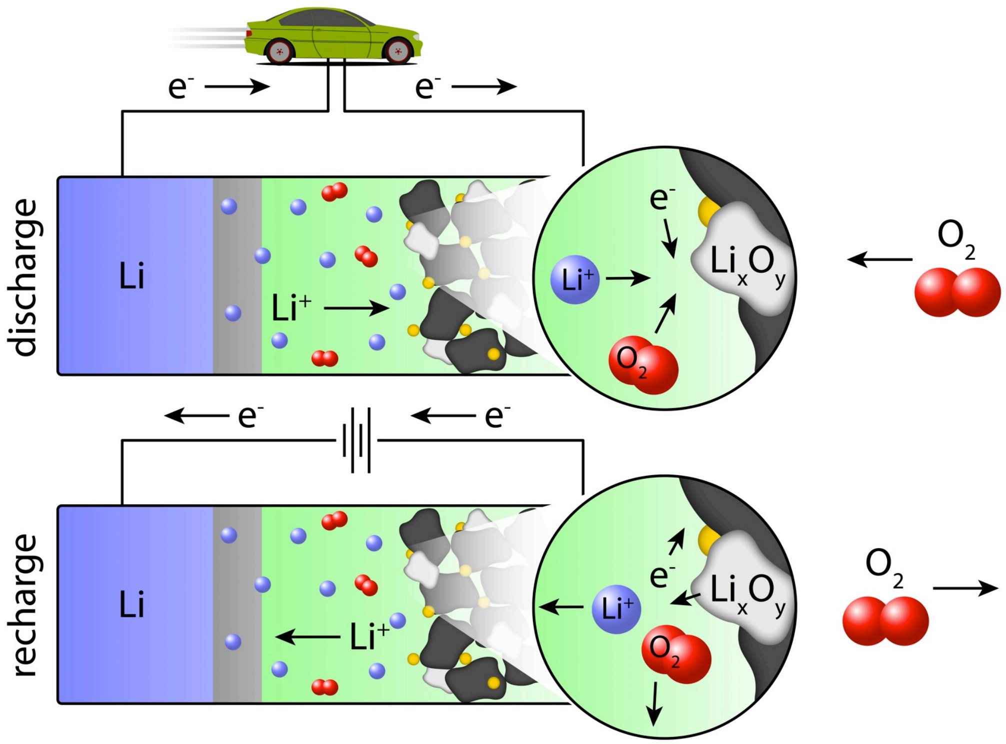
Nordbatt 2

Trondheim, December 3rd, 2015

Introduction

M/O_2 Batteries: Opportunities for high specific energies

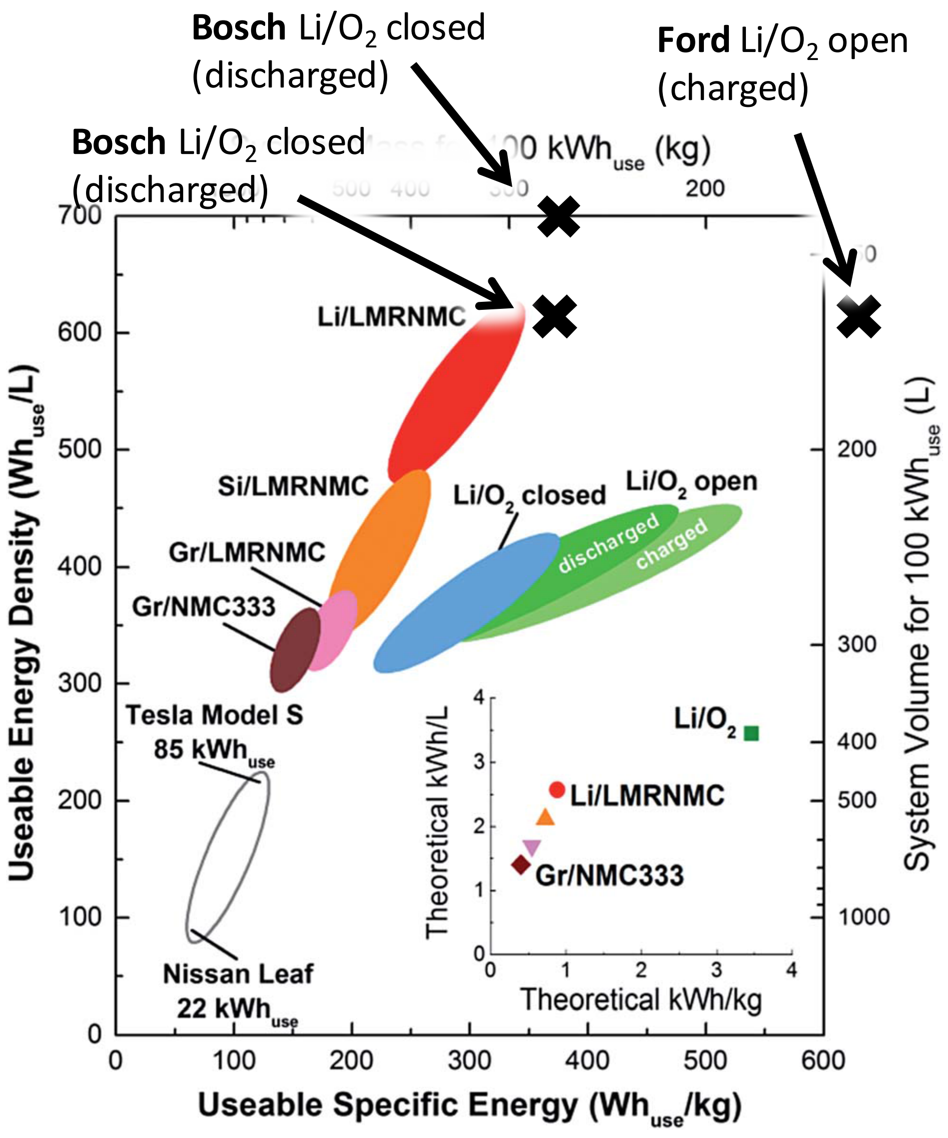


J. Mater. Sci. 47, 7564 (2012)

Li-air projected cost: \$100-240/kWh[1,2]

[1] Johnson Controls, Battery Congress, April, 2011

[2] J. Power Sources 199 (2012) 247–255


Bosch Li/O_2 closed (discharged)

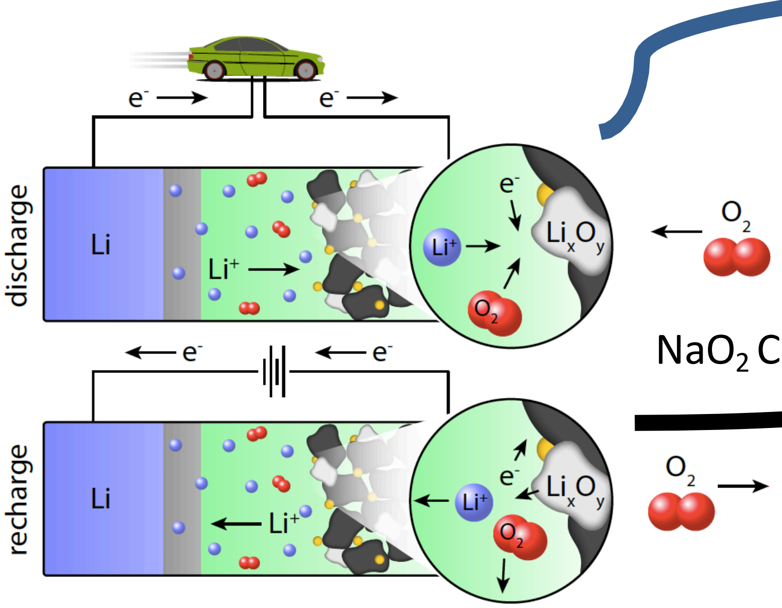
Ford Li/O_2 open (charged)

Bosch Li/O_2 closed (discharged)

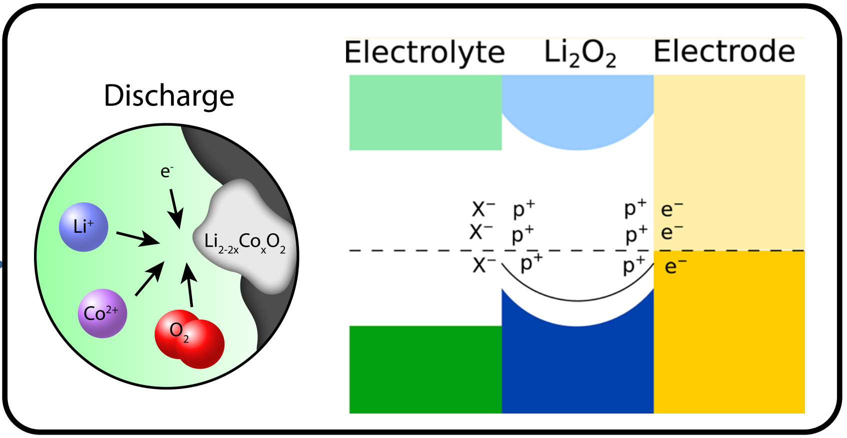
Energy Environ. Sci. DOI:10.1039/c3ee43870h (2014)
J. Electrochem. Soc. 159, R1 (2012)
J. Power Sources 199, 247 (2012)

Other Metal/O_2 Systems

M/O_2 Battery

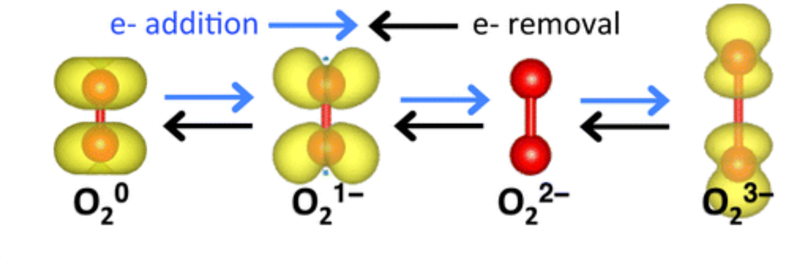


Promoters and transport in Li_2O_2 films



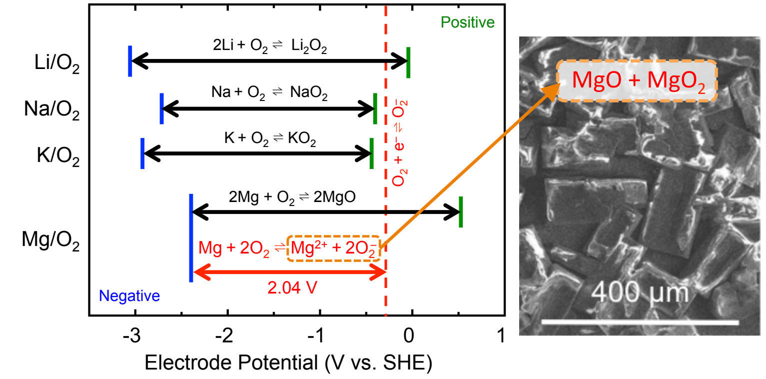
NaO_2 Conductivity

10.1021/acs.chemmater.5b00285



Mg/O_2 Battery

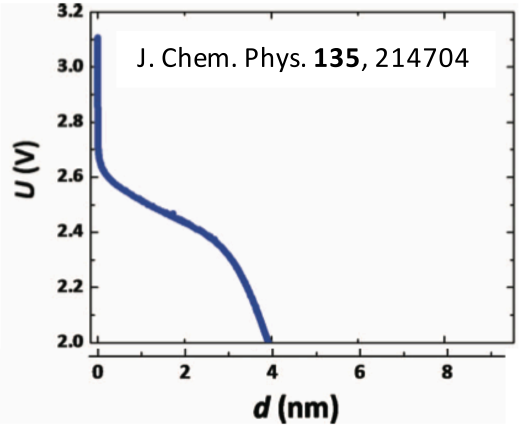
10.1021/acs.chemmater.5b03608



Electrical Passivation: A Limiting Factor

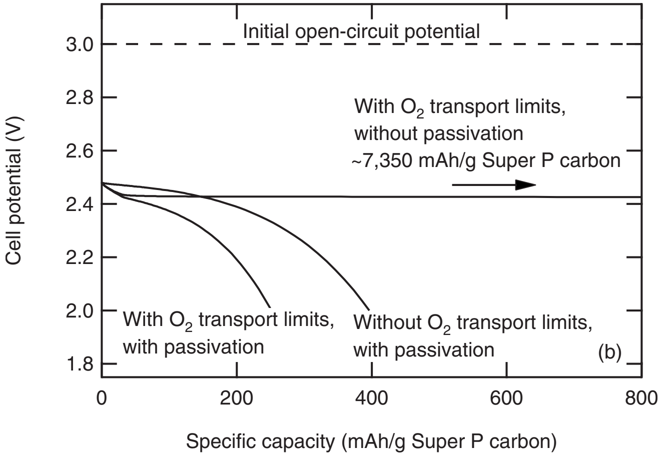
Sluggish electronic transport may limit performance in Li-air batteries

Discharge profile vs Li_2O_2 film thickness



J. Chem. Phys. **135**, 214704

Simulated discharge curves

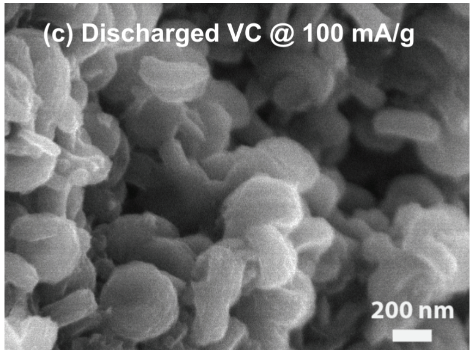


J. Electrochem. Soc. 158, A343 (2011)

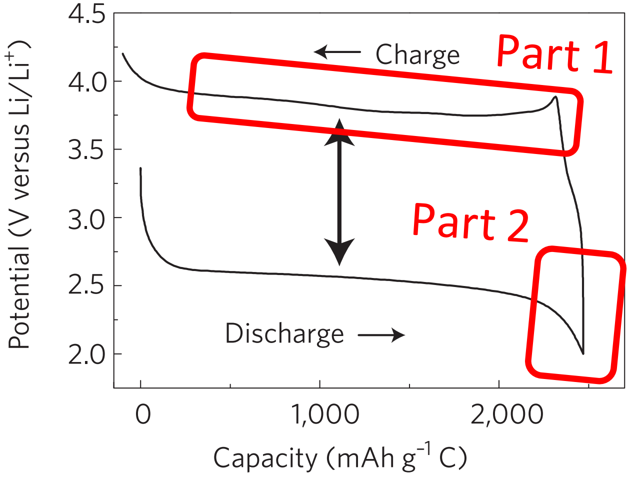
Calculated Li_2O_2 band gap

Method	Li_2O_2 Band Gap (eV)
GGA	2.35
HSE06	4.57
GGA+G_0W_0	5.70
GGA+scGW	7.76

Energy Environ. Sci. 4, 2999 (2011)



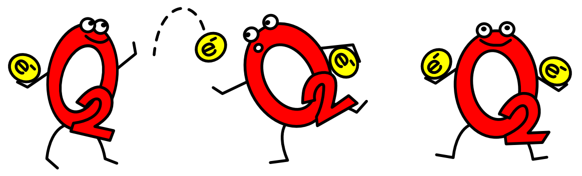
Voltage gap

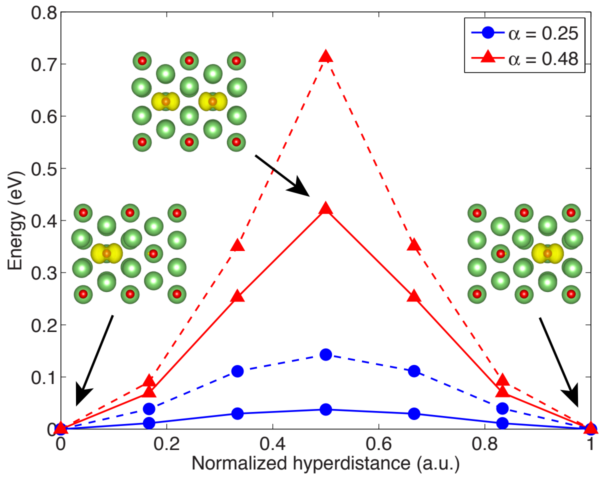


Nature Materials **11**, p12 (2012)

Our Prior Studies of Transport

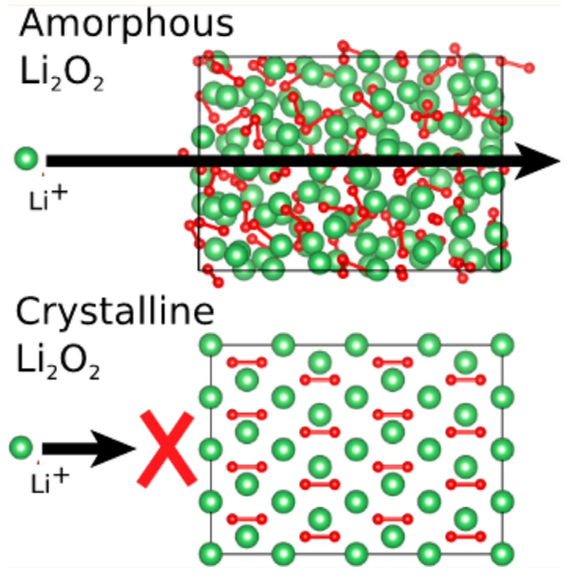
Crystalline Li_2O_2





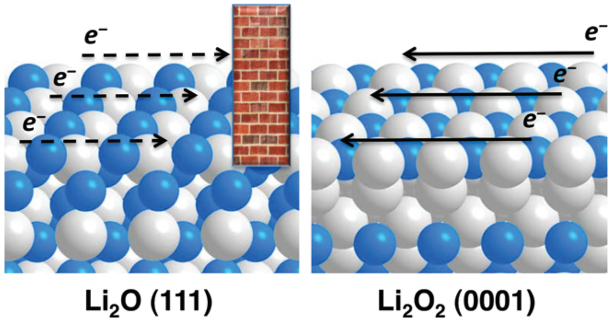
Energy Environ. Sci., 2013, **6**, 2370

Amorphous Li_2O_2



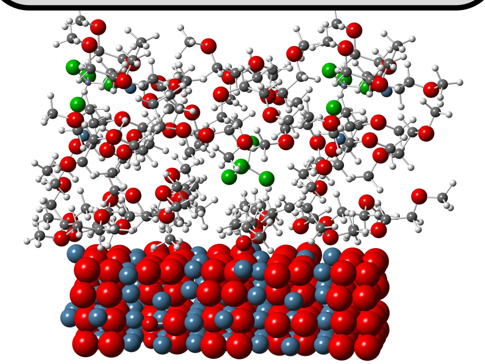
Chem. Mater. 2014, **26**, 2952

Li_2O_2 Surfaces



J. Am. Chem. Soc. 2012, **134**, 1093

Electrolyte Decomp.

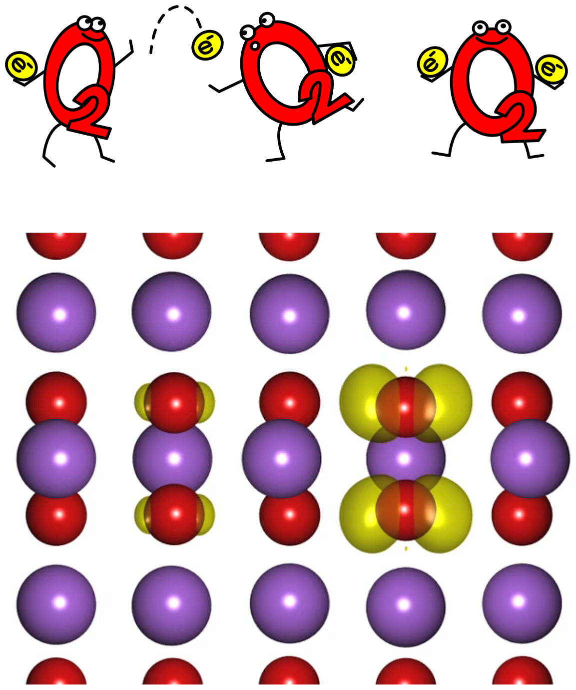


J. Phys. Chem. C 2015, **119**, 9050

- Bulk Li_2O_2 is a very good insulator: $\sigma \sim 10^{-19}$ S/cm
- Hole polarons and V_{Li}^- are the primary (intrinsic) charge carriers, $C \sim 10^7$ cm^3

Our Prior Studies of Transport

Crystalline Li_2O_2



Energy Environ. Sci., 2013, **6**, 2370

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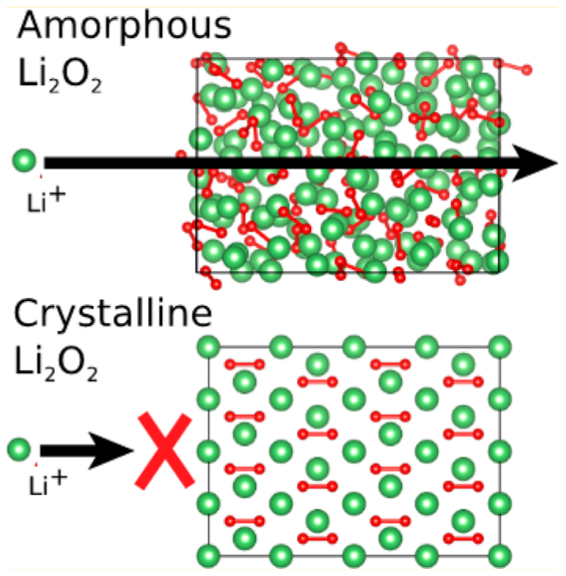
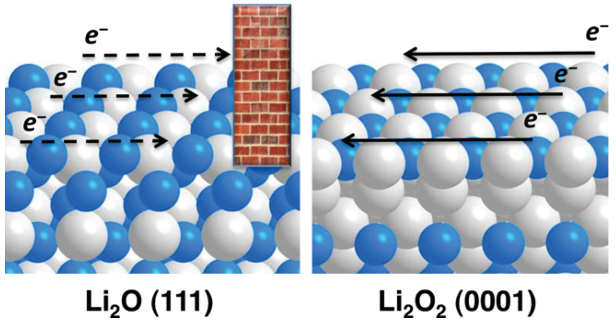


Chem. Mater. 2014, **26**, 2952

Li_2O_2 Surfaces



J. Am. Chem. Soc. 2012, **134**, 1093

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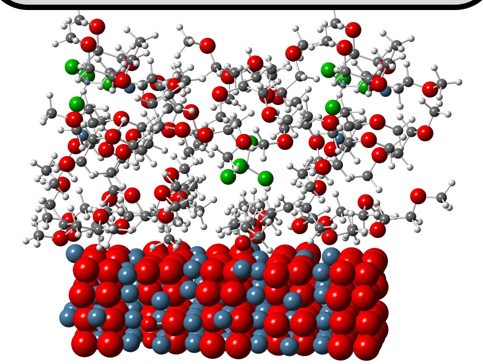

J. Phys. Chem. C 2015, **119**, 9050

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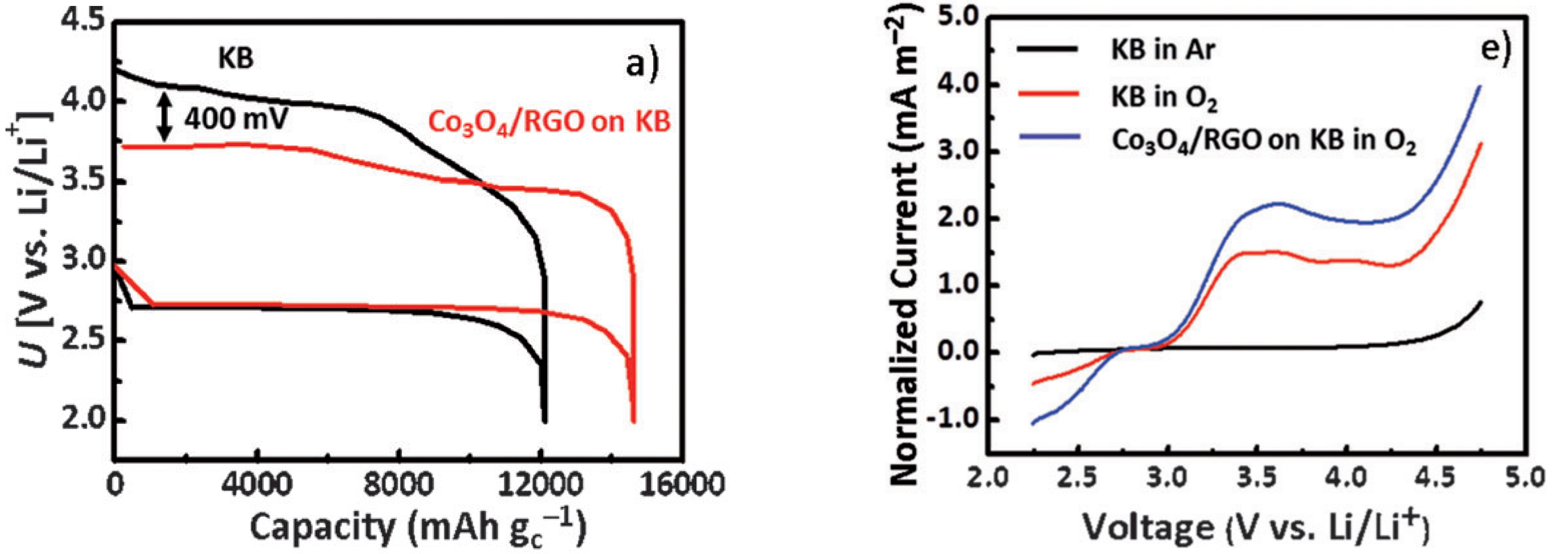
Promoting Charge Transport in Li_2O_2

Li/O_2 OER improves upon addition of metal-oxides to cathode



Black, R.; Lee, J.-H.; Adams, B.; Mims, C. a; Nazar, L. F. *Angew. Chem., Int. Ed*. 2013, 52, 392–396.

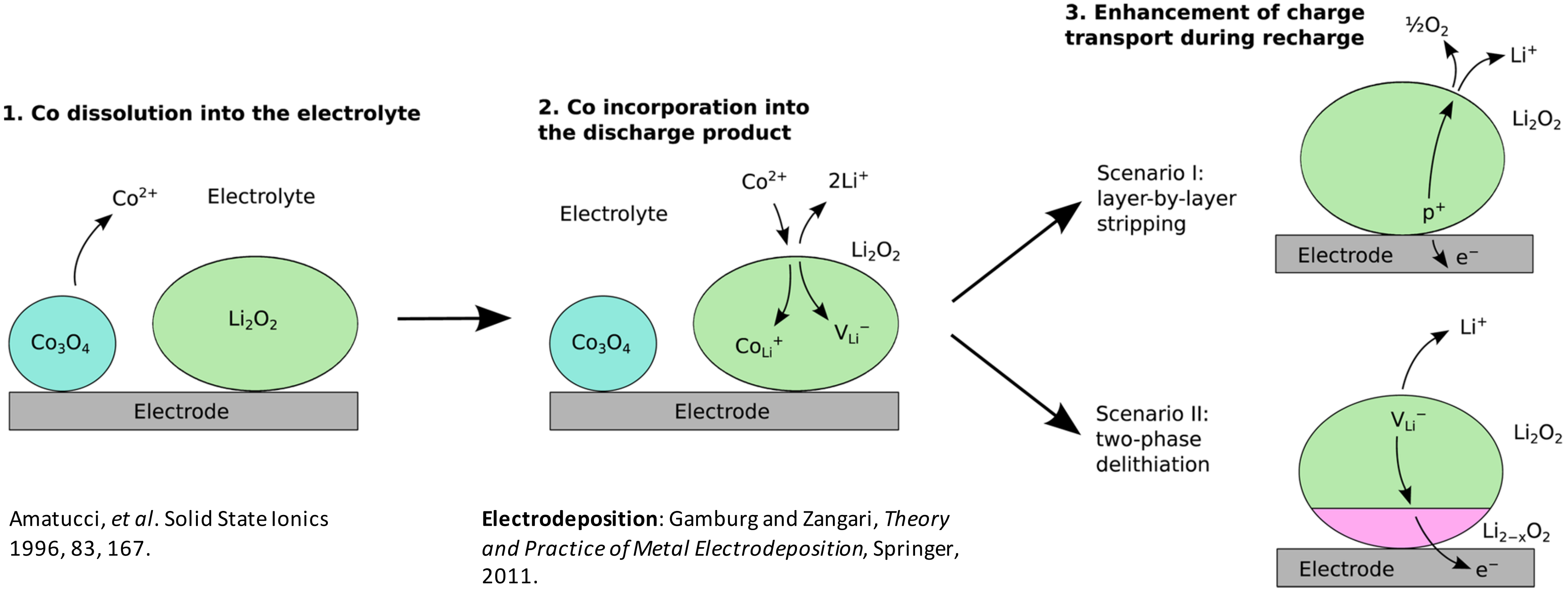
Black *et al.*: Co_3O_4 additions lower the charging plateau in Li/O_2 cells by 400 mV

- Additions do not influence morphology of discharge product, nor contribute to electrolyte oxidation
- Additions do not lower voltage for current onset in LSV → not an electrocatalyst

How do cathode additions “promote” OER in Li/O_2 batteries?

A Mechanism for OER Promotion

Hypothesis: Dissolution of Co^{2+} followed by its incorporation into the Li_2O_2 discharge product results in enhanced charge transport in Li_2O_2



Amatucci, *et al*. Solid State Ionics 1996, 83, 167.

Electrodeposition: Gamburg and Zangari, *Theory and Practice of Metal Electrodeposition*, Springer, 2011.

SEI: Zhang, *et al*. Power Sources 2006, 162, 1379.

Li_2O_2 discharge: Veith, *et al*. J. Phys. Chem. Lett. 2012, 3, 1242.

Multi-scale model predicts transport in doped Li_2O_2 films

Model Description: Atomistic Input

First principles calculations were used to parameterize the continuum model

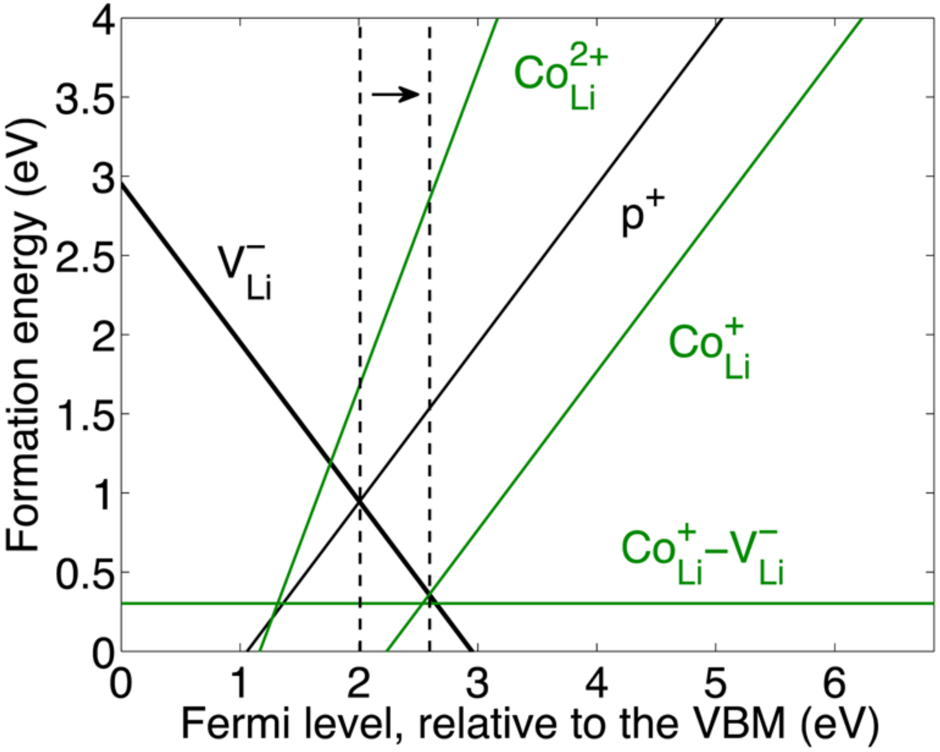
- Formation energy calculations (HSE$_\alpha$ level) reveal that dopants shift the concentration of intrinsic defects
- Equilibrium concentrations establish a boundary condition at the electrolyte/Li_2O_2 interface
- Calculated diffusion coefficients provide input regarding mobility of hole polarons and Li-ion vacancies:

$D_{p+} = 9 \times 10^{-10}$ cm^2/s

$D_{VLi-} = 6 \times 10^{-9}$ cm^2/s

Radin & Siegel, Energy Environ. Sci. 2013, 6, 2370

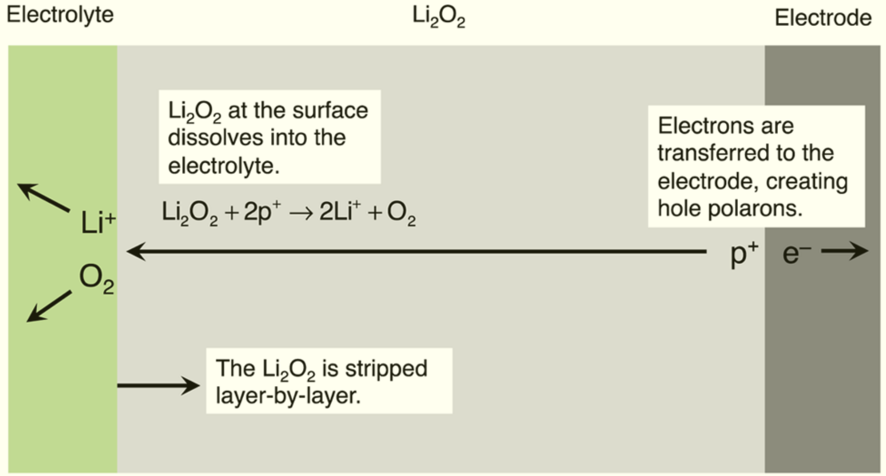
Formation energy for Co substitutions and intrinsic defects in Li_2O_2 *vs.* Fermi level



Calculations predict equilibrium Co doping of 13 ppm

Description of Continuum Model

A 1D transport model based on Nernst-Planck theory predicts the quasi-steady-state voltage drop Δφ associated with charge transport through doped Li_2O_2



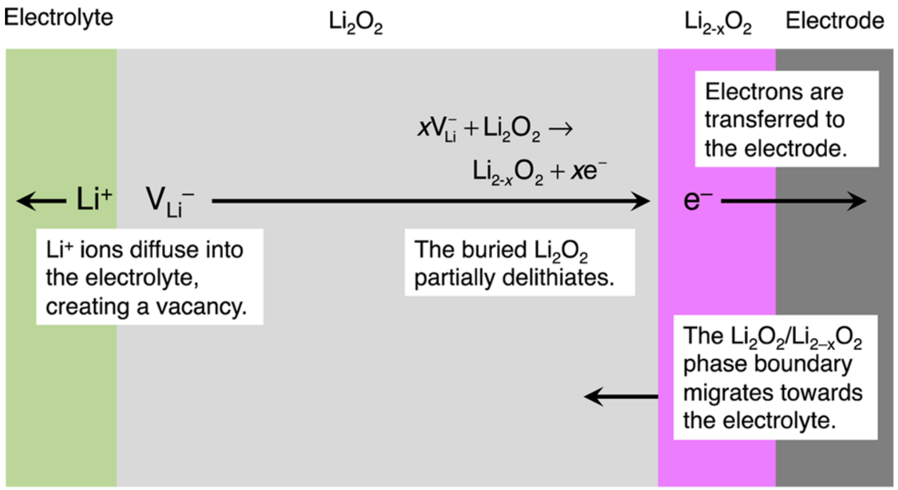
Li_2O_2 at the surface dissolves into the electrolyte.

$Li_2O_2 + 2p^+ \rightarrow 2Li^+ + O_2$

Electrons are transferred to the electrode, creating hole polarons.

The Li_2O_2 is stripped layer-by-layer.

Layer-by-layer stripping (Scenario I)



$xV_{Li}^- + Li_2O_2 \rightarrow Li_{2-x}O_2 + xe^-$

Electrons are transferred to the electrode.

Li^+ ions diffuse into the electrolyte, creating a vacancy.

The buried Li_2O_2 partially delithiates.

The $Li_2O_2/Li_{2-x}O_2$ phase boundary migrates towards the electrolyte.

Two-phase delithiation (Scenario II)

- Model accounts for non-uniform concentrations and potentials
- 4 mobile species: V_{Li}^-, p^+, Co_{Li}^+, and V_{Li}^-–Co_{Li}^+
- Applied to films 10 – 1000 nm (beyond tunneling regime)

Flux law for species *k*:

$$N_k = -D_k \frac{dc_k}{dy} - \frac{D_k z_k e}{k_B T} c_k \frac{d\Phi}{dy}$$

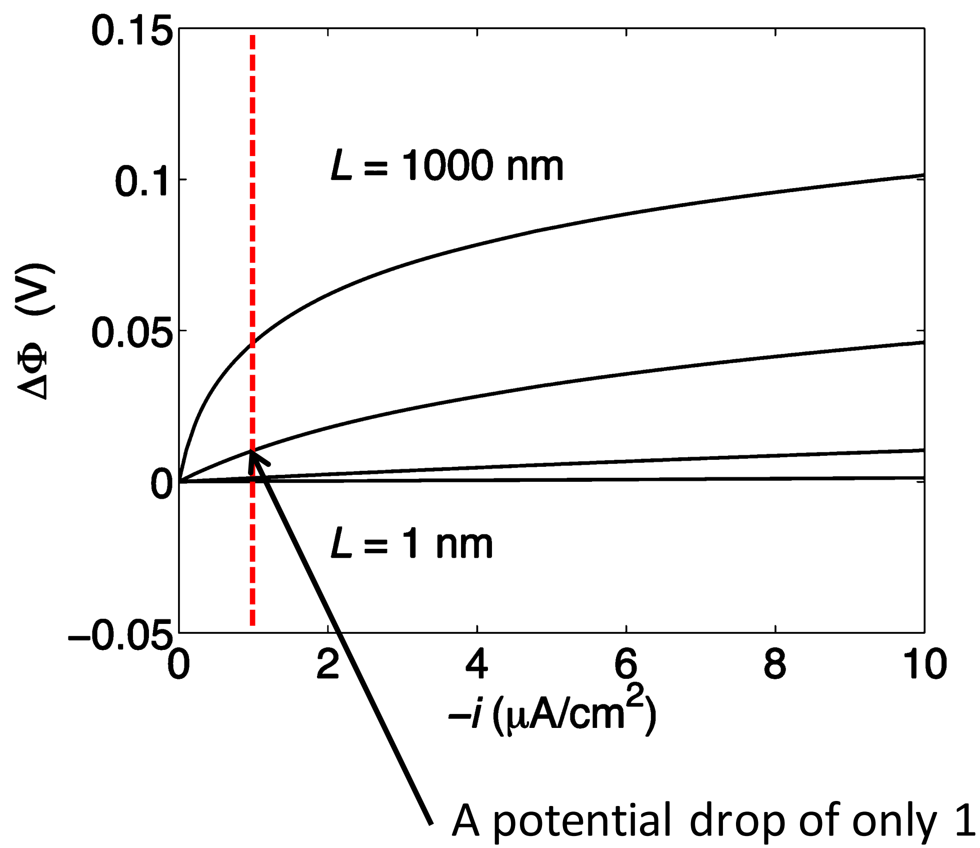
Faraday's law:

$$i = e\left(N_{p^+} - N_{V_{Li}^-} + N_{Co_{Li}^+}\right)$$

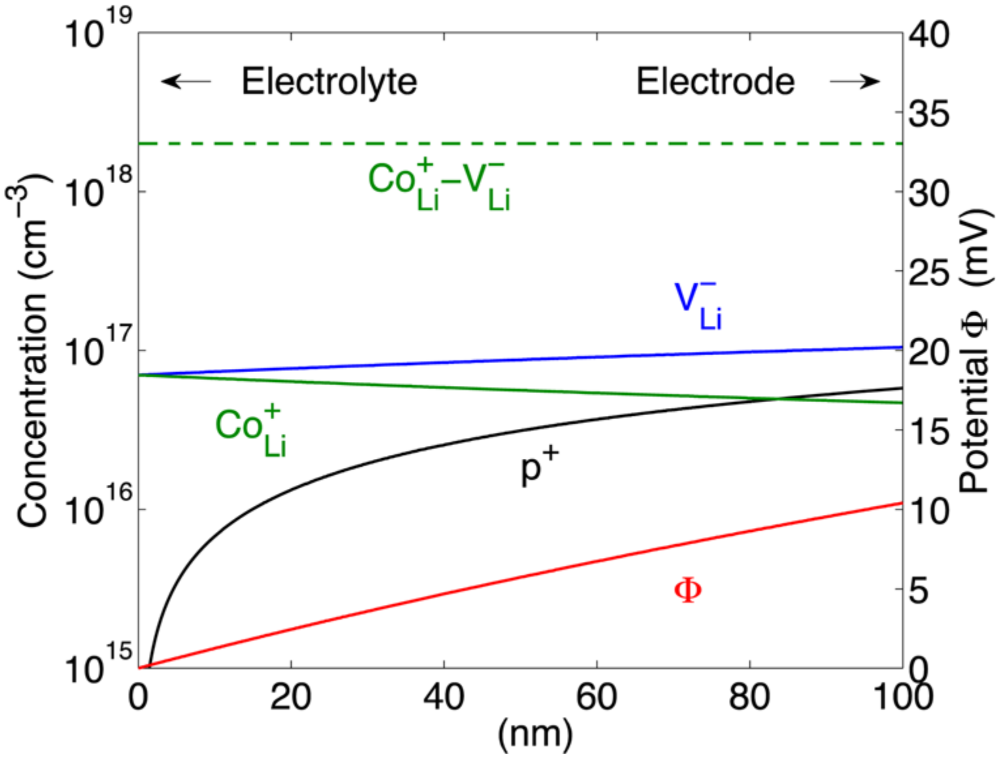
Results: Layer-by-Layer Stripping

A Li_2O_2 film doped with 13 ppm Co has a very low potential drop during charging, and much higher conductivity than bulk Li_2O_2: **$\sigma \sim 10^{-9}$ S/cm**

Potential drop across Co-doped Li_2O_2 film *vs.* current density and film thickness



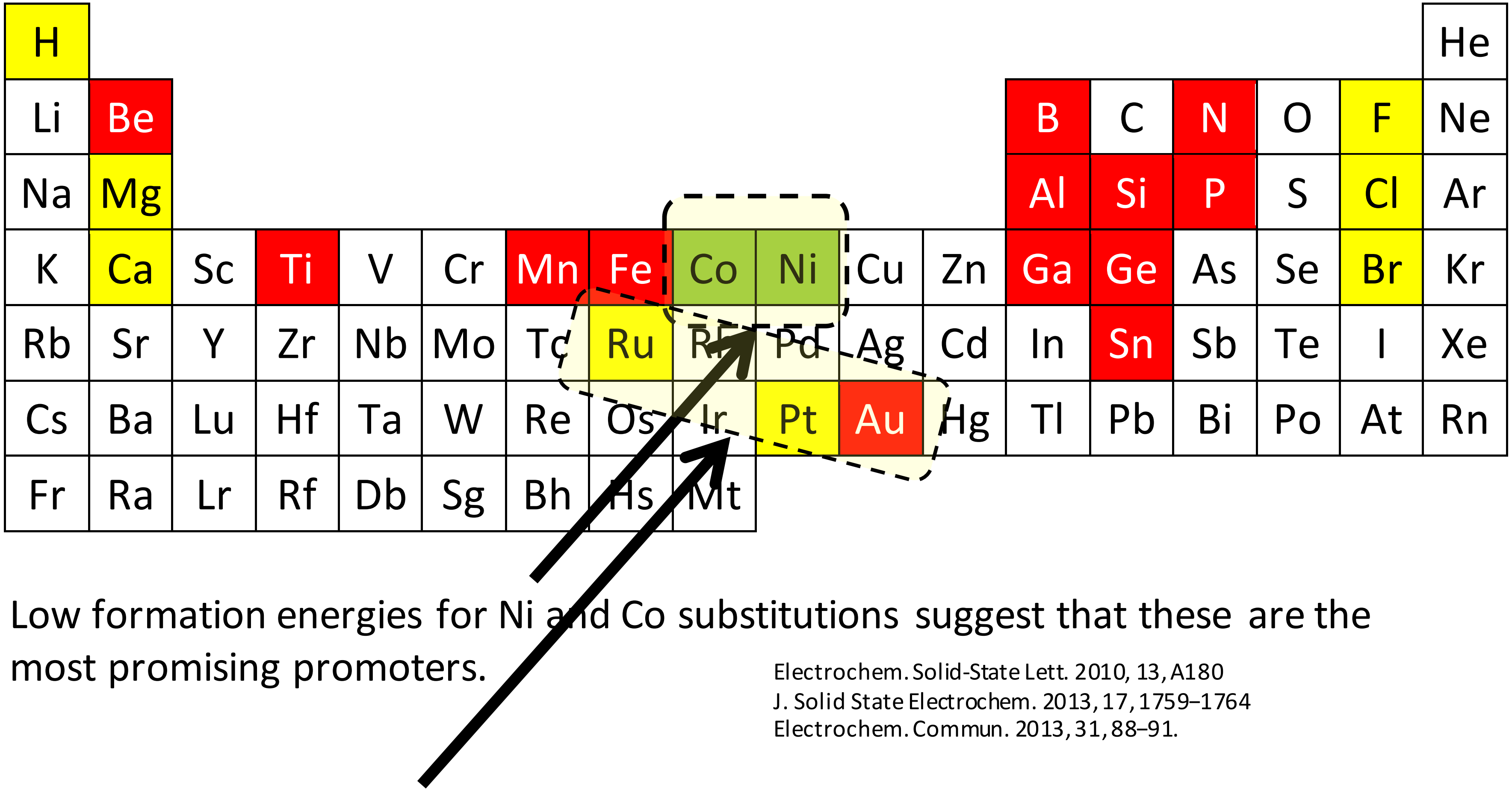
Defect concentration *vs.* position in 100 nm Li_2O_2 film



A potential drop of only 10 mV is needed to drive 1 μA/cm² through a 100 nm Co-doped film

Other Promoters?

22 additional promoters were screened computationally



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt									

Low formation energies for Ni and Co substitutions suggest that these are the most promising promoters.

Electrochem. Solid-State Lett. 2010, 13, A180
J. Solid State Electrochem. 2013, 17, 1759–1764
Electrochem. Commun. 2013, 31, 88–91.

Trend in the calculated formation energies for Pt, Ru, and Au correlates with the trend in OER activity reported by Harding *et al.*
Phys. Chem. Chem. Phys. 2012, 14, 10540–10546.

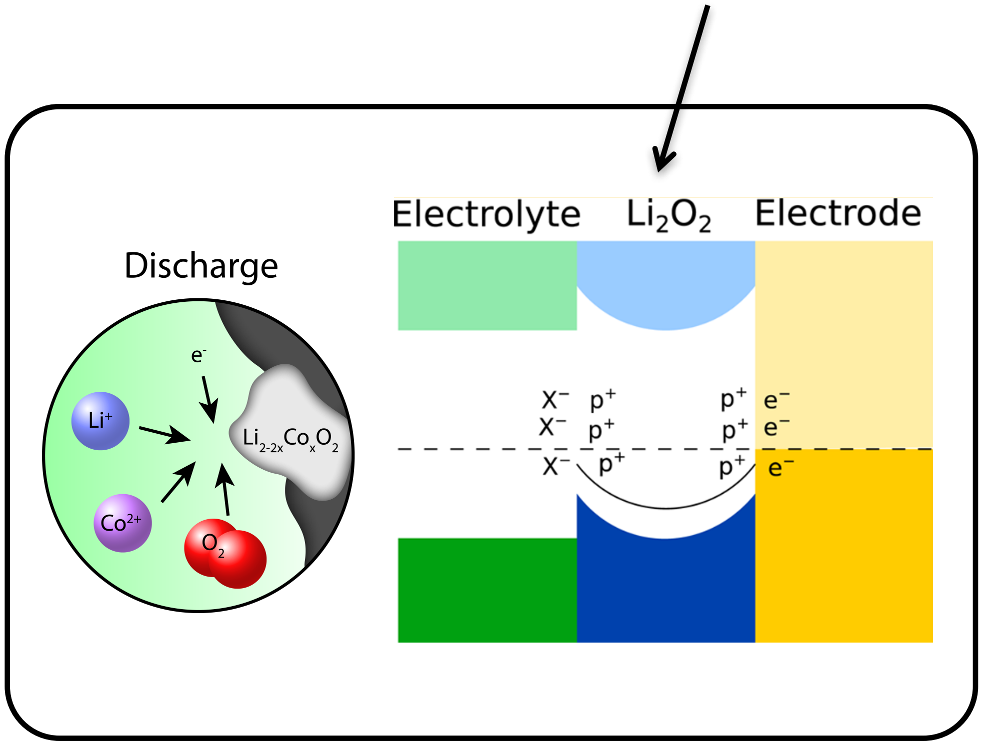
Summary: OER Promoters

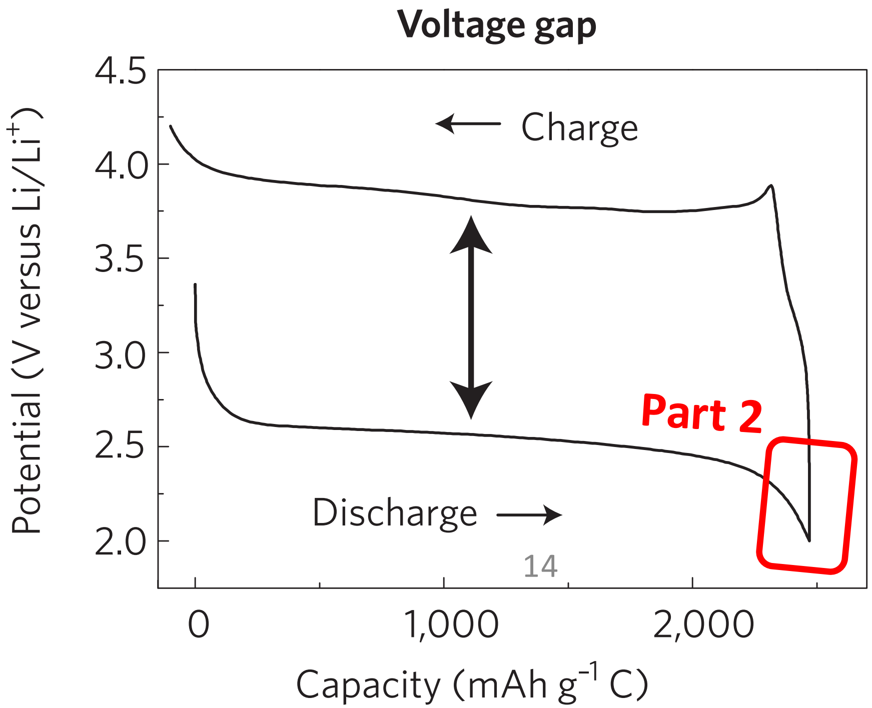
- Understanding ‘OER promotion’ is necessary for rational design of efficient Li/O_2 batteries
- Promotion is hypothesized to arise from enhanced transport in Li_2O_2 resulting from *in situ* doping with metal cations
- Multi-scale transport model reveals that a Li_2O_2 film doped at ppm-levels will have a conductivity > 10^{-9} S/cm during recharge
  - This is 10 orders of magnitude greater than bulk Li_2O_2
  - Contributions to the overpotential from charge transport limitations are reduced to milli-Volts for Co-doped Li_2O_2
- Assessment of 23 promoters suggests that Ni & Co compositions are best
  - Recommended experiment: addition of Co or Ni salts to Li/O_2 electrolyte

M. D. Radin, C. W. Monroe, and D. J. Siegel,
How Dopants can Enhance Charge Transport in Li_2O_2
Chemistry of Materials **27**, 839 (2015).
DOI: 10.1021/cm503874c

Part 2: Sudden Death

Part 2





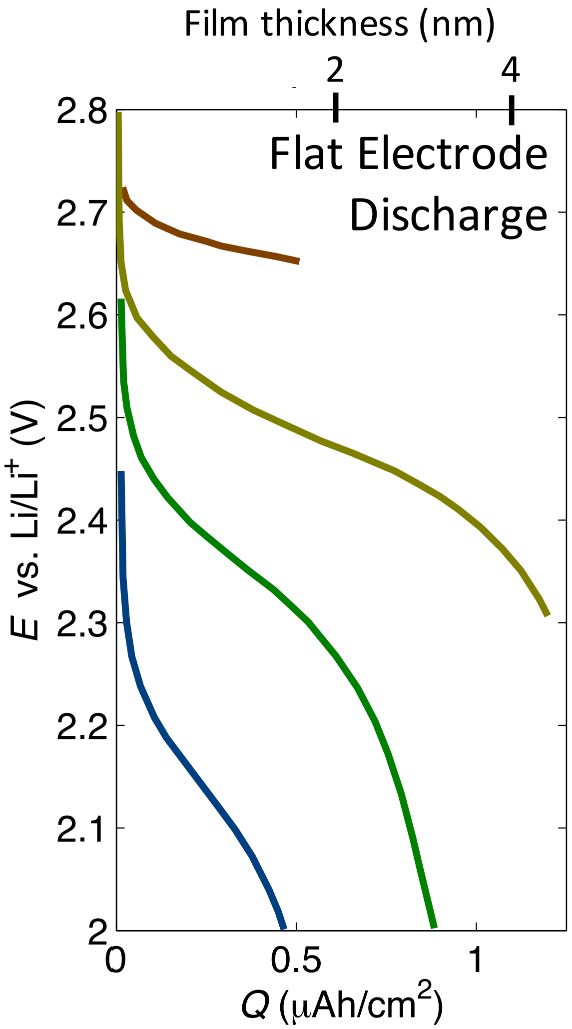
Nature Materials **11**, p12 (2012)

‘Sudden Death’ in Li/O_2 Batteries

Sluggish charge transport has been suggested to limit discharge capacity

- Electron tunneling and the hopping of small hole polarons have been proposed as charge transport mechanisms in Li_2O_2
- Luntz *et al.* argued that hole polaron transport could not explain ‘sudden death’ in Li/O_2 cells which discharge to thin films
  - Model assumed uniform polaron concentration
  - Electron tunneling was suggested as the primary transport mechanism

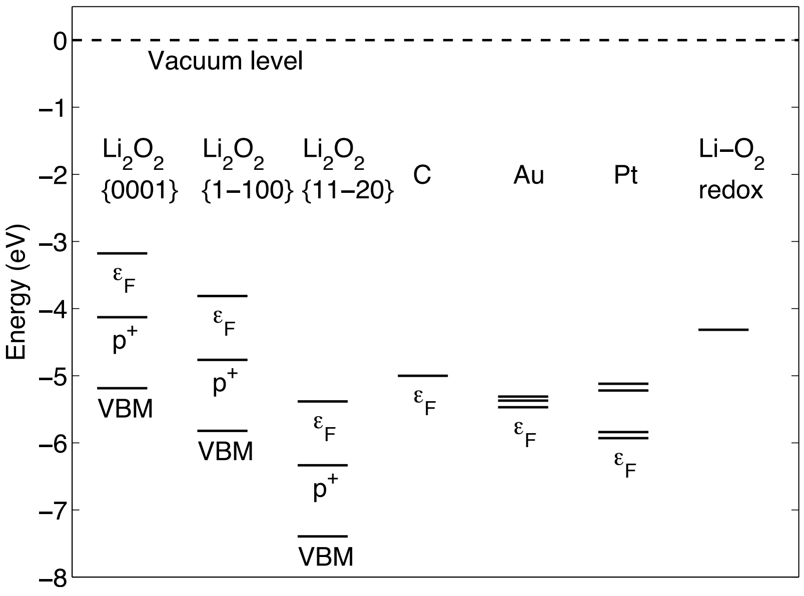
Does this conclusion hold if we allow for a non-uniform concentration of charge carriers?

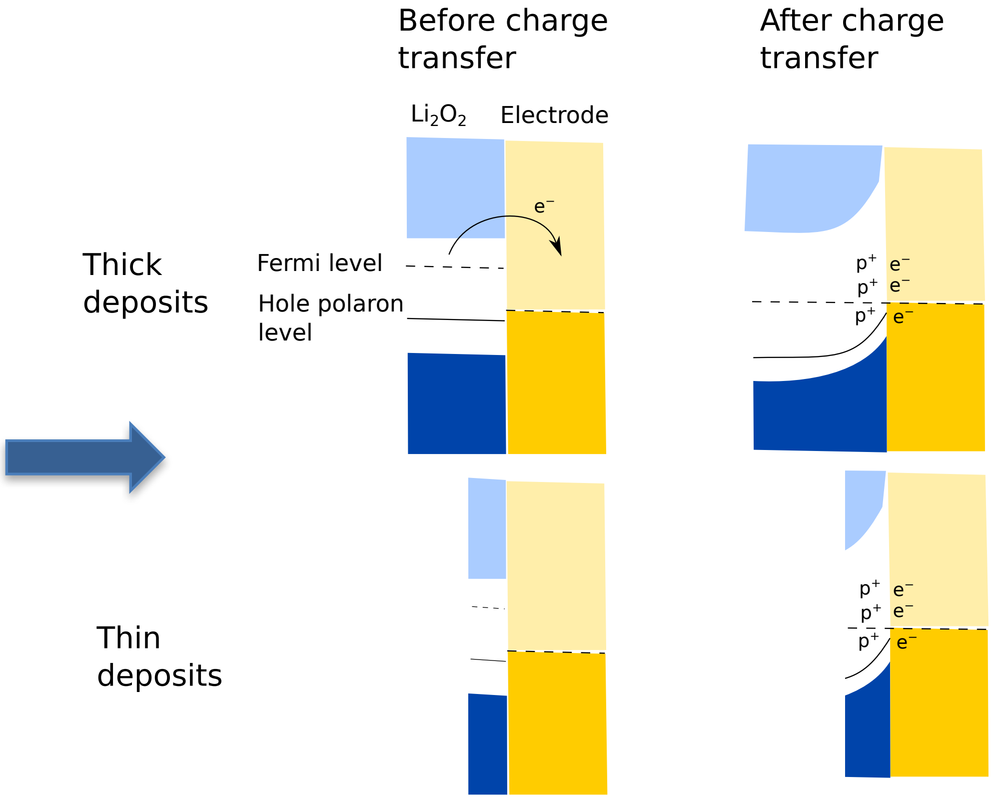


Luntz, et al. *J. Phys. Chem. Lett.* **2013**, *4*, 3494

Space-Charge Layers in Li_2O_2

Polaron-rich space-charge layers are expected to form in Li_2O_2 at interfaces with the electrode and electrolyte





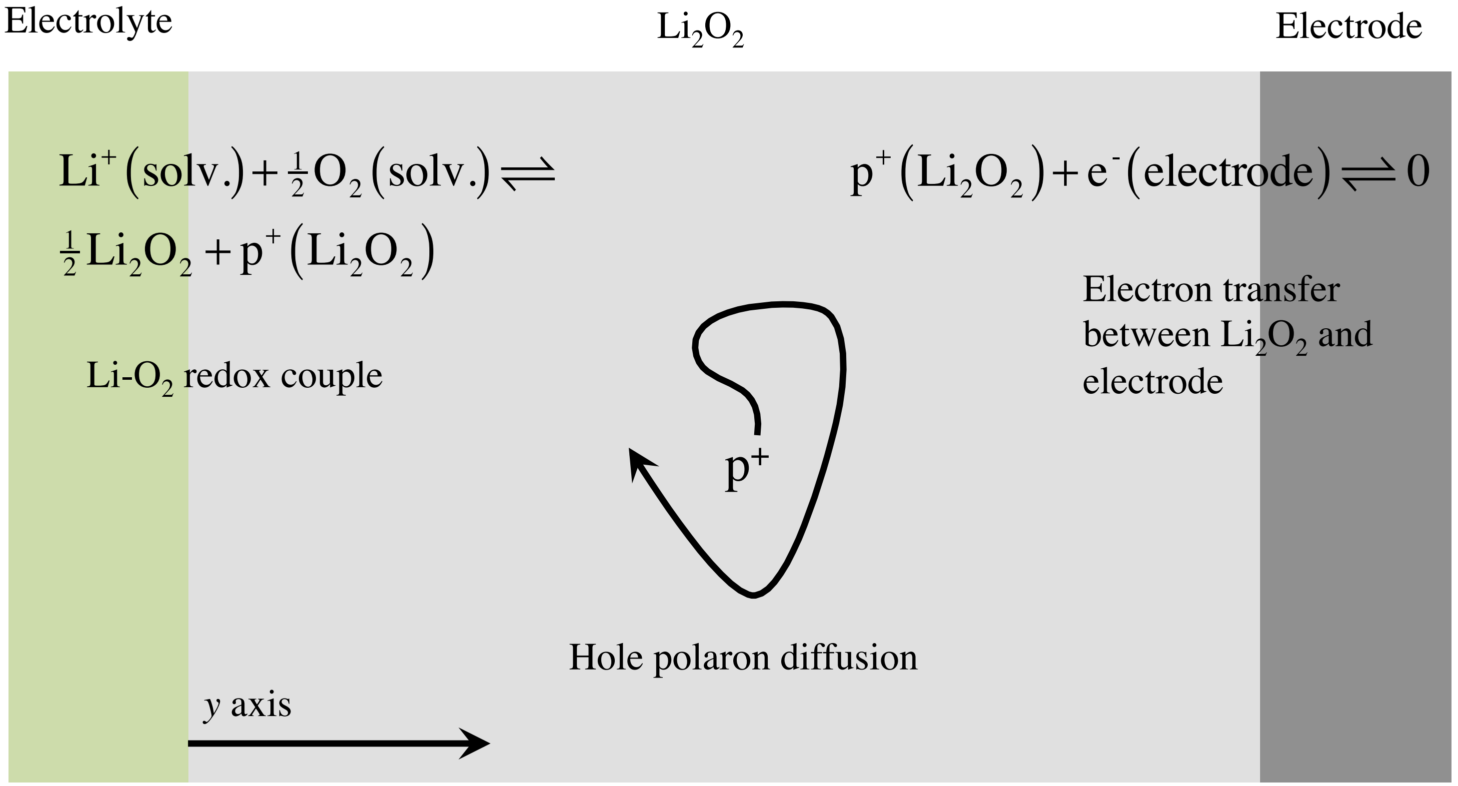
DFT calculations (HSE_α) suggest that the Fermi level of Li_2O_2 is above that for common electrode materials

Electron transfer from Li_2O_2 to electrode creates a space-charge layer that is rich in polarons

Continuum Model for Polaron Transport

We have constructed a 1D transport model based on *non-electroneutral* Nernst-Planck theory

Model schematic



Electrolyte

Li_2O_2

Electrode

$$\mathrm{Li^+(solv.)} + \tfrac{1}{2}\mathrm{O_2(solv.)} \rightleftharpoons \tfrac{1}{2}\mathrm{Li_2O_2} + \mathrm{p^+(Li_2O_2)}$$

$$\mathrm{p^+(Li_2O_2)} + \mathrm{e^-(electrode)} \rightleftharpoons 0$$

Li-O_2 redox couple

Electron transfer between Li_2O_2 and electrode

Hole polaron diffusion

Parameterization of Continuum Model

Model input parameters are taken from a combination of calculated and experimental data

Parameter	Description	Value used in model	Other reported values
D	Polaron diffusion coefficient	3×10^{-13} cm^2/s	9×10^{-10} cm^2/s (in-plane)[3] 2×10^{-14} cm^2/s (out-of-plane)[3]
ε	Li_2O_2 dielectric constant	10	$\varepsilon_{xx} = \varepsilon_{yy} = 7.5$; $\varepsilon_{zz} = 12.5$[3]
i_0	Exchange current density	5×10^{-9} A/cm^2	10^{-5} A/cm^2 [15] 10^{-9} A/cm^2 [16]
$c_1 = c_2$	Polaron concentration at interfaces	3×10^{20} cm^{-3} (1% occupancy)	

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[3] Energy Environ. Sci. 2013, 6, 2370–2379

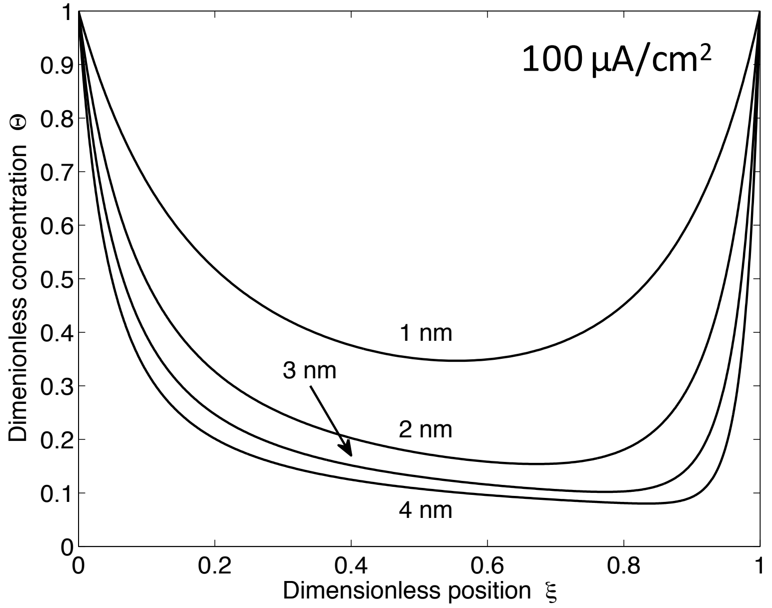
[15] J. Phys. Chem. Lett. 2012, 3, 997–1001

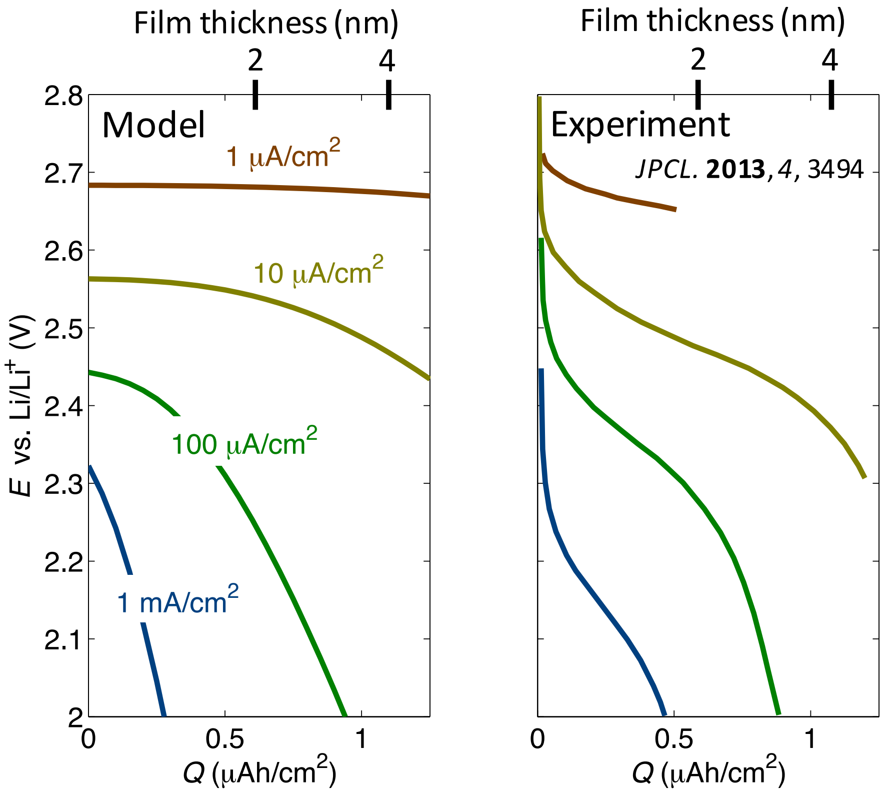
[16] The Lithium Air Battery: Fundamentals; Springer: New York, 2014.

Results

Discharge curves predicted by the model are in good agreement with flat electrode experiments

Concentration of polarons in Li_2O_2 film for thicknesses of 1-4 nm





- Sudden death occurs when the thickness of the growing film exceeds the thickness of the space charge layer, ~ 3 nm
- In this regime charge transport is limited by the low concentration of polarons in the bulk

Design Strategies

A contribution to transport from polaron hopping suggests avenues for performance improvement

- **Temperature dependence** of polaron diffusivity:

$$D \sim T \exp(-E_a/k_B T)$$

- Increasing the temperature of the cell will enhance discharge capacity
  - Confirmed by flat-electrode experiments[1] and by other experiments using porous electrodes[2,3]

- **Crystallite orientation** has implications for cell performance
  - Anisotropy in the dielectric and polaron-diffusion tensors
    - In-plane polaron hopping barrier in Li_2O_2 is 0.3 eV smaller than the out-of-plane barrier
    - Transport overpotentials will be lower in films where the Li_2O_2 {0001} axis lies in the plane of electrode surface

[1] J. Phys. Chem. Lett. 2013, 4, 3494–34997

[2] Energy Environ. Sci. 2012, 5, 8927

[3] J. Solid State Electrochem. 2014, 18, 739–745

Summary: Sudden Death

- Developed a new model for charge transport in thin Li_2O_2 films
  - Model accounts non-uniform distribution of charge carriers (space charge layers)
- Sudden-death during discharge is consistent with limitations in polaron hopping
  - Sudden death occurs when the film thickness exceeds the thickness of the space-charge layers, which contain a sufficient concentration of polarons to satisfy current density requirements
- Model captures the impact of temperature on the experimental discharge curve
- Agreement between the model and experimental data as a function of current, film thickness, and temperature, suggests that polaron migration contributes significantly to charge transport in Li_2O_2 films

Maxwell D. Radin, Charles W. Monroe, and Donald J. Siegel
Impact of space-charge layers on charge transport in Li_2O_2
J. Phys. Chem. Lett. 2015, 6, 3017–3022

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