Transparent Conducting Oxides as Cathodes in Li-O_2 batteries: A First Principles Computational Investigation

Balachandran Radhakrishnan

John W Lawson

Motivation

- Li-O_2 electrochemistry

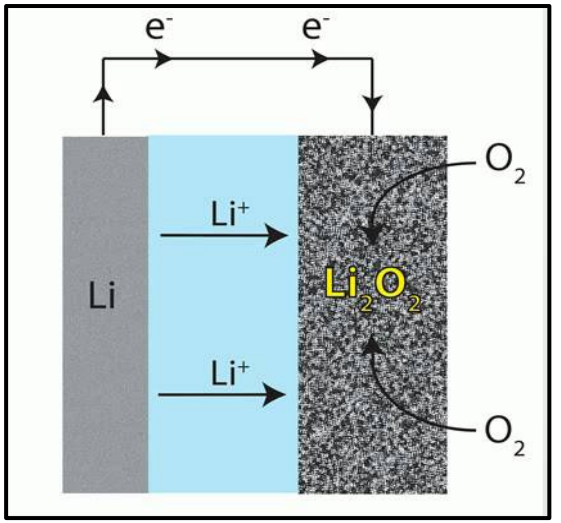
$$Li^+ + O_2(g) + 2e^- \leftrightarrow Li_2O_2^*$$

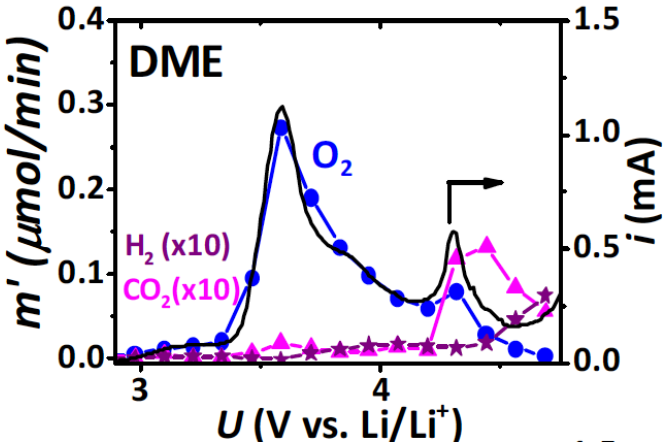
- Parasitic reactions with electrode and electrolyte lead to capacity loss and abysmal cycles

- Carbon cathodes decay over the charge-recharge cycle

$$Li_2O_2 + \frac{1}{2}O_2 + C \leftrightarrow Li_2CO_3^*$$

- Possible solution: Search for non-carbon cathodes with desired properties





J. Phys. Chem. Lett. 2012, 3, 3043−3047

Non-carbon ideal electrode

Preferred properties of cathode in Li-O_2 battery:

1. Stability against Li_2O_2, the deposition product
2. No side reactions with electrolytes and intermediates in the electrochemistry
3. Electrochemical stability in the operating voltage range
4. Promoting formation of Li_2O_2

Transparent Conducting Oxides as cathodes

1. Stable in ether type electrolytes (DME, TEGDME etc)
2. Band gap controlled and commercially available
3. Stable in oxygen rich environment
4. Can they satisfy requirements of cathode in Li-O_2 battery?

Chemical Stability: Phase Diagrams

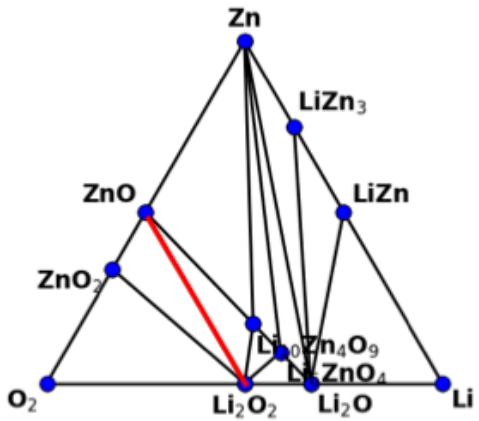
Phase Diagram constructed using DFT energies from [1]Materials Project

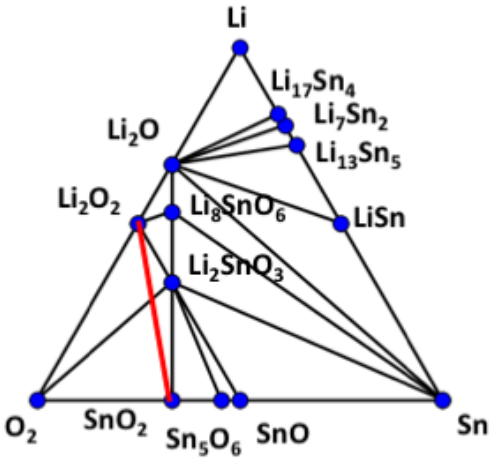
Any chemistry that has a non-intersecting tie-line with Li_2O_2 is stable against it

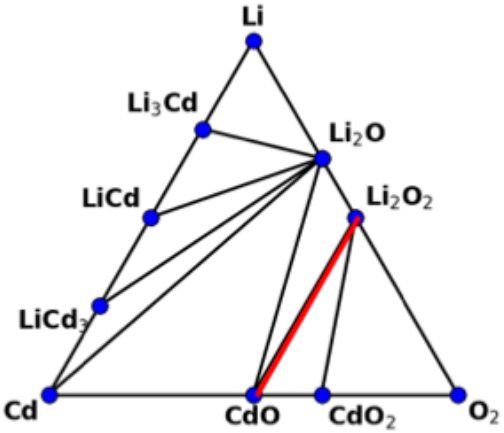
Intersecting tie-line gives the reaction products with Li_2O_2

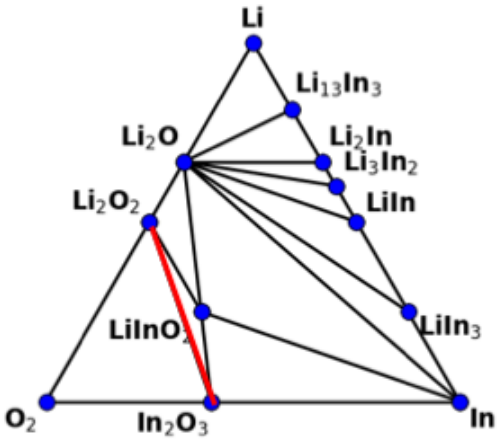
ZnO, In_2O_3 and CdO are stable against Li_2O_2

SnO_2 reacts with Li_2O_2 to form Li_2SnO_3









$$\Delta E(\in, Li_2O_2) = \min_{0 \le x \le 1} E_{x.\in-(1-x).Li_2O_2} - x.E_{\in} - (1-x).E_{Li_2O_2}$$

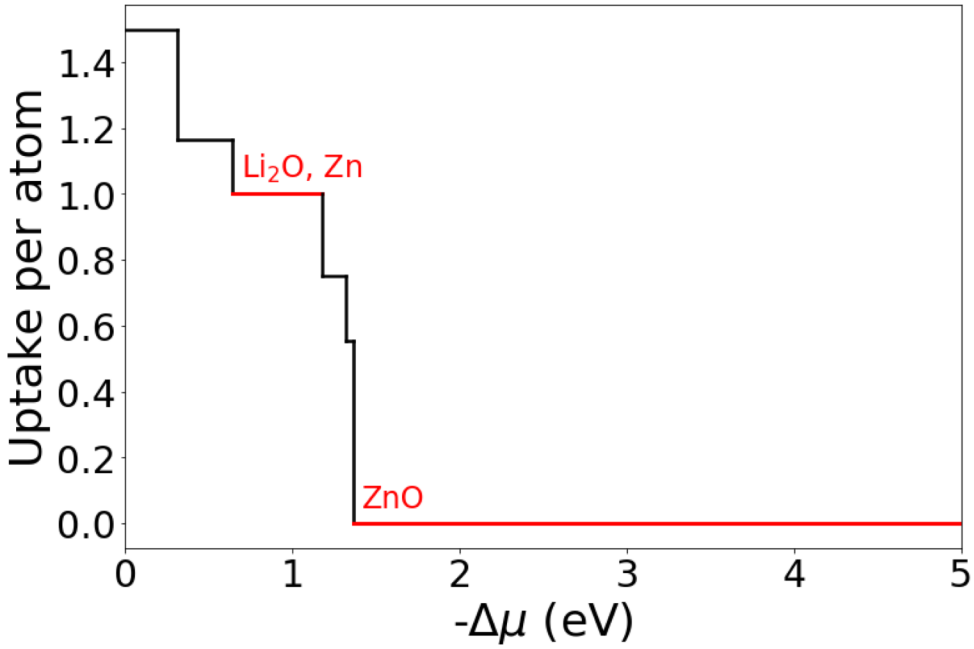
1. Comp. Mater. Sci., 68, 314–319 (2013)

Ref: J. Phys. Chem. C 2019, 123, 8, 4623-4631

Electrochemical stability

Grand potential phase diagram is constructed to predict electrochemical stability range of the electrode

$$\emptyset = E - \mu_{Li} N_{Li}$$



Cathode	Electrochemical stability (V) (vs Li)
SnO_2	>1.98
CdO	>1.72
In_2O_3	>1.58
ZnO	> 1.36

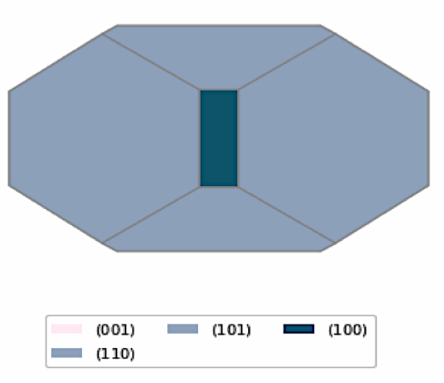
All the TCOs considered in this study are stable in the operating voltage of 2-4.5 V

APL Materials 1 , 011002 (2013); Comp. Mater. Sci., 68, 314–319 (2013)

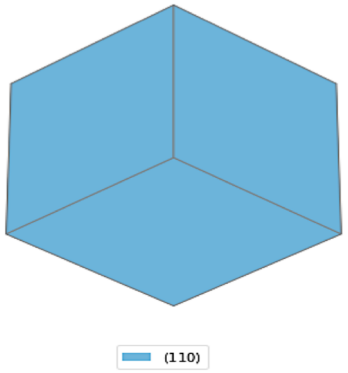
Ref: J. Phys. Chem. C 2019, 123, 8, 4623-4631

Surface of interest

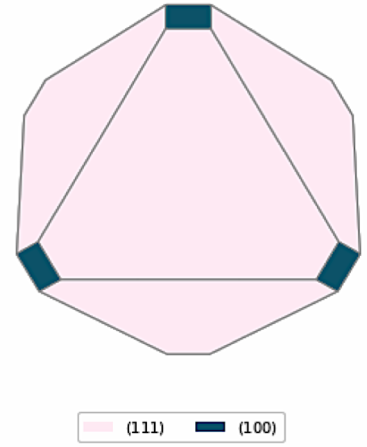
- Identify surfaces of interest using Wulff shape construction
- Surface energy is a function of chemical potential of oxygen
- Oxygen rich and oxygen deficient environments produce different crystal shapes
- ZnO can be synthesized as thin film (0001) as well as needle structures $(10\bar{1}0)$



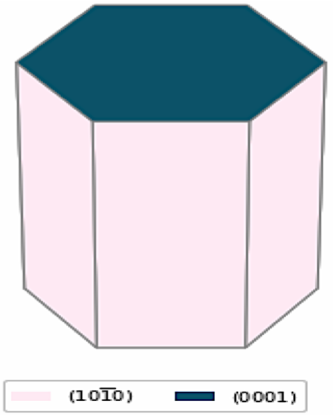
SnO_2



CdO



In_2O_3



ZnO

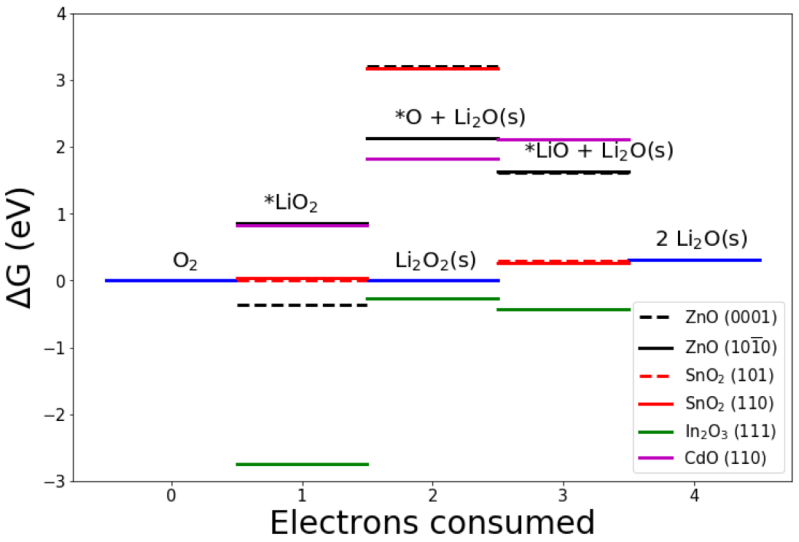
$$\gamma_{surf} = \frac{1}{2A}\left[E_{slab}(N_M N_O) - \frac{N_M}{x}E_{bulk}(M_x O_y) + \left(\frac{N_M}{x}y - N_O\right)\mu_O\right]$$

Adsorption Studies

Li_2O_2: 2 electron process:

a. $Li^+(solv) + O_2(g) + e^- \leftrightarrow LiO_2^*$

b. $Li^+(solv) + LiO_2^* + e^- \leftrightarrow Li_2O_2(s)$



Li_2O: 4 electron process

a. $Li^+(solv) + O_2(g) + e^- \leftrightarrow LiO_2^*$

b. $Li^+(solv) + LiO_2^* + e^- \leftrightarrow Li_2O(s) + O^*$

c. $Li^+(solv) + Li_2O(s) + O^* + e^- \leftrightarrow LiO^* + Li_2O(s)$

d. $Li^+(solv) + LiO^* + Li_2O(s) + e^- \leftrightarrow 2Li_2O(s)$

- ZnO (0001) most suitable for Li_2O_2 formation
- SnO_2 will lead to mix of Li_2O and Li_2O_2 formation
- In_2O_3 and CdO promote Li_2O formation

ACS Energy Lett., 1, 162−168 (2016)

Ref: J. Phys. Chem. C 2019, 123, 8, 4623-4631

Doping TCOs

- TCOs are small band-gap materials in pristine condition
- Vacancy induced electronic conductivity observed
- Considered %~2 at. wt. doping in ZnO
- Used thermodynamic energetics to determine interstitial vs substitutive doping

Substitutional dopant 48 ZnO + X → $Zn_{47}XO_{48}$ +Zn		Interstitial dopant 48 ZnO + X → $Zn_{48}XO_{48}$	
Doped Chemistry	Dopant Formation Energy (eV)	Doped Chemistry	Dopant Formation Energy (eV)
$Zn_{47}AlO_{48}$	-1.75	$Zn_{48}AlO_{48}$	2.153
$Zn_{47}GaO_{48}$	0.83	$Zn_{48}GaO_{48}$	4.417
$Zn_{47}GeO_{48}$	2.56	$Zn_{48}GeO_{48}$	5.502
$Zn_{47}InO_{48}$	1.97	$Zn_{48}InO_{48}$	5.182
$Zn_{47}SiO_{48}$	-1.608	$Zn_{48}SiO_{48}$	2.536
$Zn_{47}SnO_{48}$	4.15	$Zn_{48}SnO_{48}$	7.52

Al, Si and Ga substitutional doping was considered for further studies

Ref: J. Phys. Chem. C 2019, 123, 8, 4623-4631

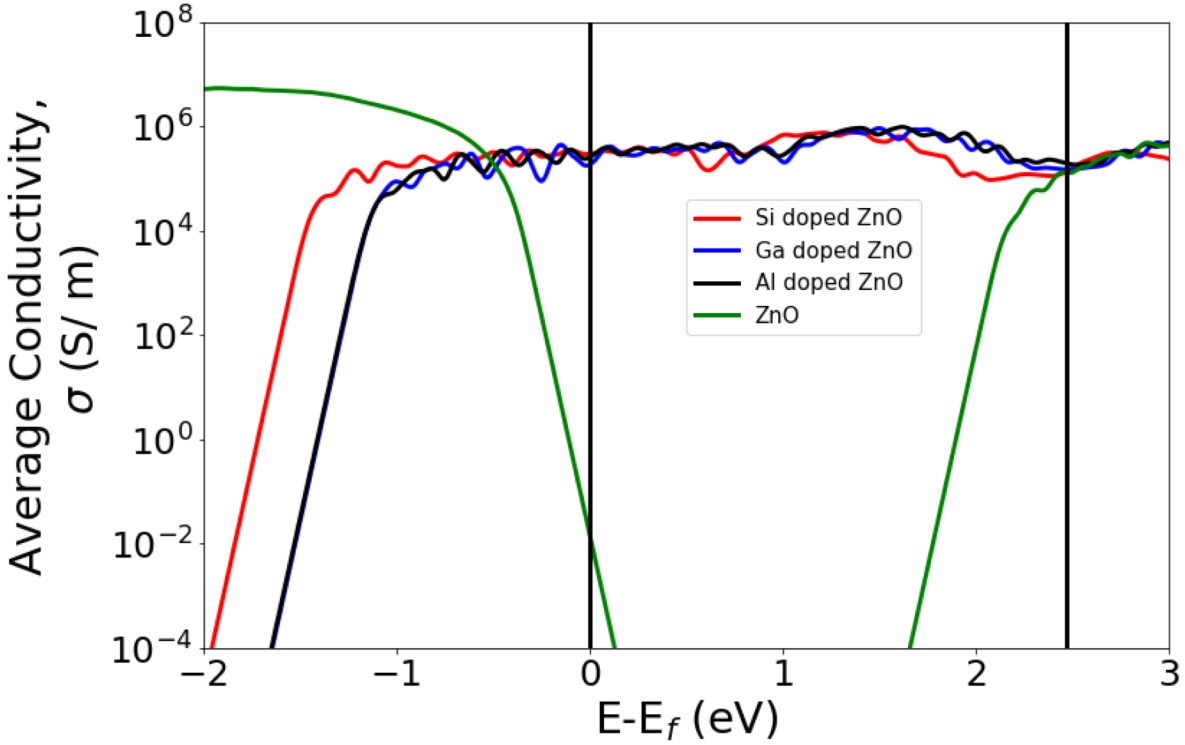
Effect of Doping

Boltzmann semi-classical equations

$$\sigma_{\alpha\beta\gamma}(i,k) = e^3.\tau^3_{(i,k)}.\varepsilon_{\gamma uv}.v_{\alpha(i,k)}v_v(i,k)M^{-1}_{\beta u}$$

$$M^{-1}_{\beta u}(i,k) = \frac{1}{\hbar^2}\frac{\partial^2\varepsilon_(i,k)}{\partial k_\beta \partial k_u}$$

DFT computations using HSE06 hybrid functional

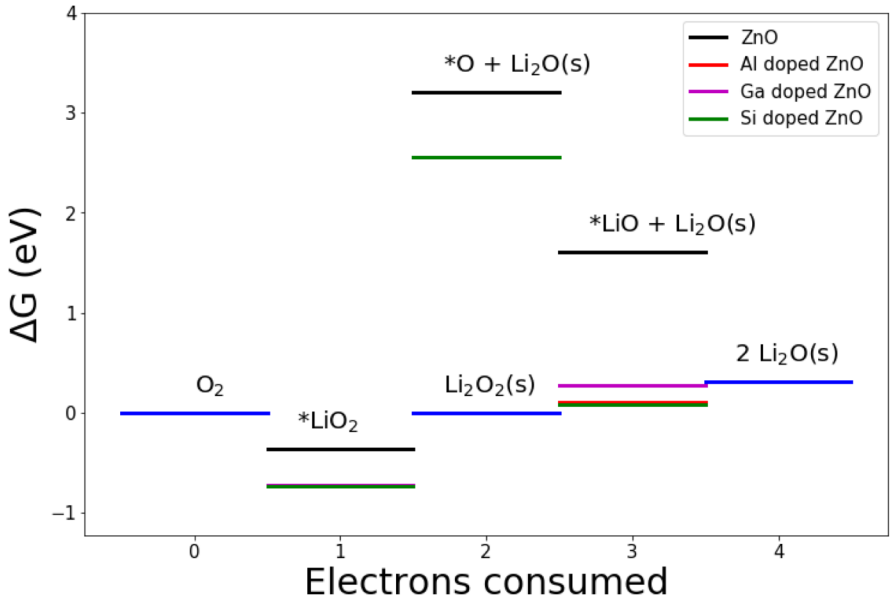


BoltzTraP: Computer Physics Communications 2006, 175, 67-71

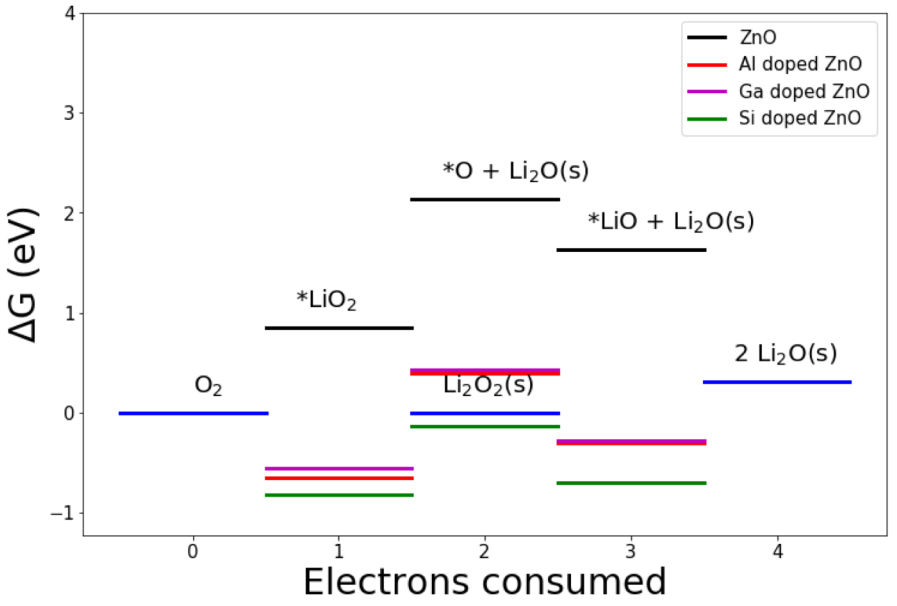
Ref: J. Phys. Chem. C 2019, 123, 8, 4623-4631

Effect of doping

Doped (0001) ZnO



Doped (10$\bar{1}$0) ZnO



- Doping leads to better adsorption of LiO_2^* intermediate
- (10$\bar{1}$0) surface, on doping, promotes formation of Li_2O
- Doped (0001) surface binds LiO_2^* favorably while maintaining a viable path to Li_2O_2 formation

Ref: J. Phys. Chem. C 2019, 123, 8, 4623-4631

Other oxides…

Only those oxides that are chemically stable against Li_2O_2 were considered

Chemistry	Electrochemical stability range (V) (vs Li/Li^+)	Notes
BeO	≥ 0	Toxic
MgO	≥ 0.64	Insulator
K_2O_2	≥ 2.4	Prone to Li^+attack
CaO	≥ 0	Promising candidate with doping
SrO_2	≥ 2.89	Prone to Li^+attack
BaO_2	≥ 2.68	Prone to Li^+attack
CsO_2	≥ 2.88	Conductor
Y_2O_3	≥ 0	Promising candidate with doping
La_2O_3	≥ 0	Promising candidate with doping
CeO_2	≥ 1.22	Used as coating[42]
Sm_2O_3	≥ 0	Rare earth mineral
Gd_2O_3	≥ 0	Rare earth mineral
Tb_2O_3	≥ 0	Rare earth mineral
Dy_2O_3	≥ 0	Rare earth mineral
Er_2O_3	≥ 0	Rare earth mineral
Tm_2O_3	≥ 0	Rare earth mineral
Lu_2O_3	≥ 0	Rare earth mineral
HgO	2.45	Toxic

Ref: J. Phys. Chem. C 2019, 123, 8, 4623-4631

Future studies

- Extend to other classes of chemistries
  - Nitrides
- Effect of electrolyte on adsorption
  - Non-interacting dielectric medium (VASPSol)
  - Explicit role in adsorption energetics
- Effect of doping at various levels
  - Dopants considered in this study stay in the bulk
  - Will surface exposed dopants alter the adsorption profile?