Two-electron reduction of ethylene carbonate: theoretical review of SEI formation mechanisms

SAND2013-3422C

Kevin Leung
Sandia National Laboratories

K. Leung, Chem. Phys. Lett. (2013)

Acknowledgement

John Sullivan, Kevin Zavadil, Steve Harris, Yue Qi, Oleg Borodin

Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S.~Deparment of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE

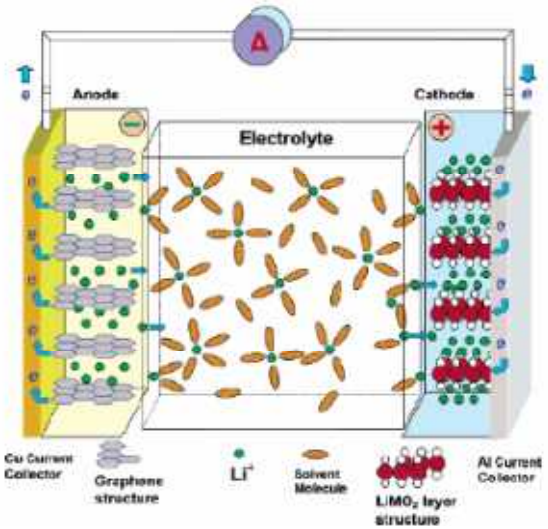
Sandia National Laboratories

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

U.S. DEPARTMENT OF ENERGY

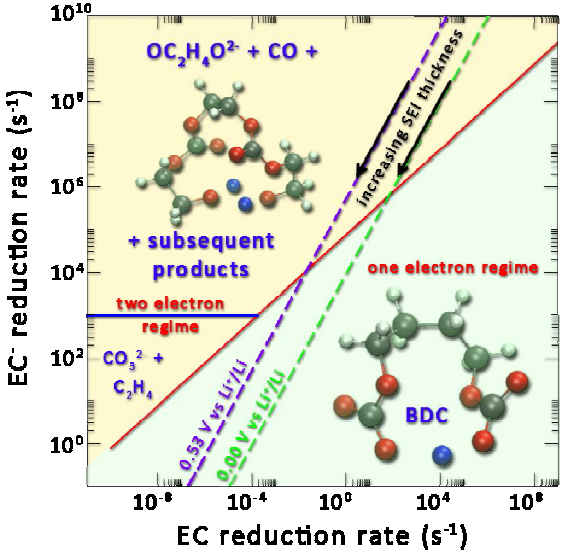
Motivations

- Re-examine electrolyte breakdown and SEI formation mechanisms in light of recent large scale electronic structure calculations
- Integrate new theoretical insights from AIMD simulations into “old” theoretical framework



Objectives

- Construct global picture of SEI growth, incorporating multiple mechanisms, as electron transfer rate varies. Focus on ethylene carbonate (EC), critical for graphite-based anodes.



Technical Approach

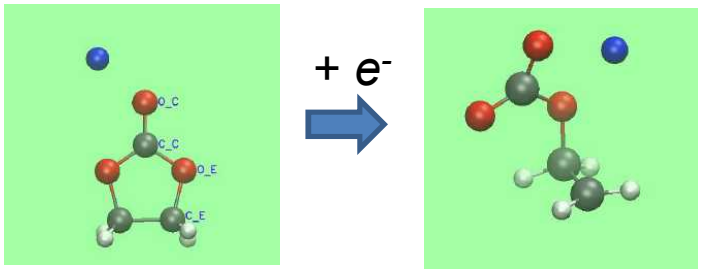
- MP2 calculations, “SMD” dielectric continuum solvent approx. consider only EC (other electrolyte components in the future)

Electrolyte decomposition mechanisms need revision

- widely cited/quoted mechanisms are extrapolation of end product distrbution
- generally not been *proven* (e.g., using labeling, trapping of intermediates)
- recent theoretical work (good at predicting barriers) disagree with some of them

---

widely quoted 1-electron reduction mechanism

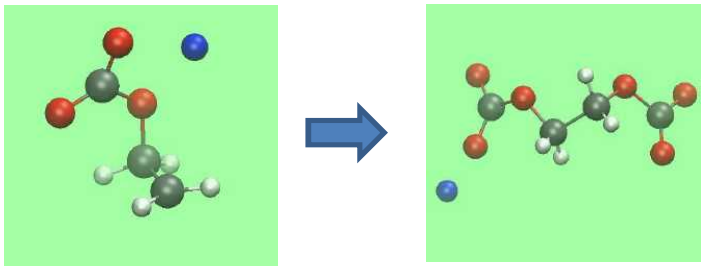


ethylene carbonate (EC)

widely quoted 2-electron reduction mechanism

EC + 2 e^- → $C_2H_4 + CO_3^{2-}$

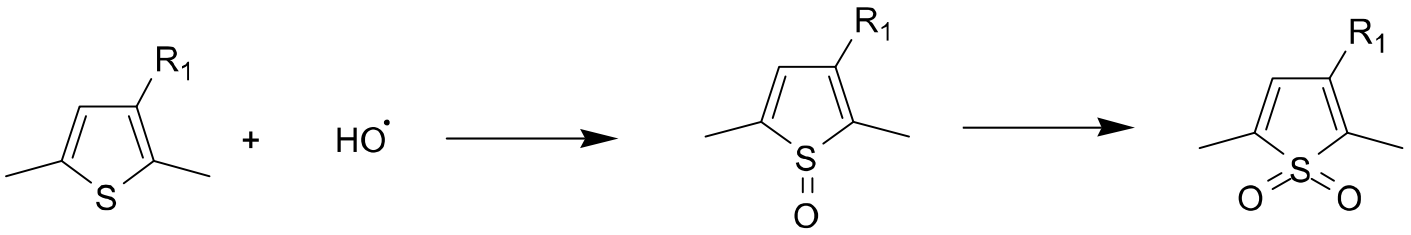
2 x



- will show these are incomplete/incorrect
- first, on the next slide, insight from AIMD

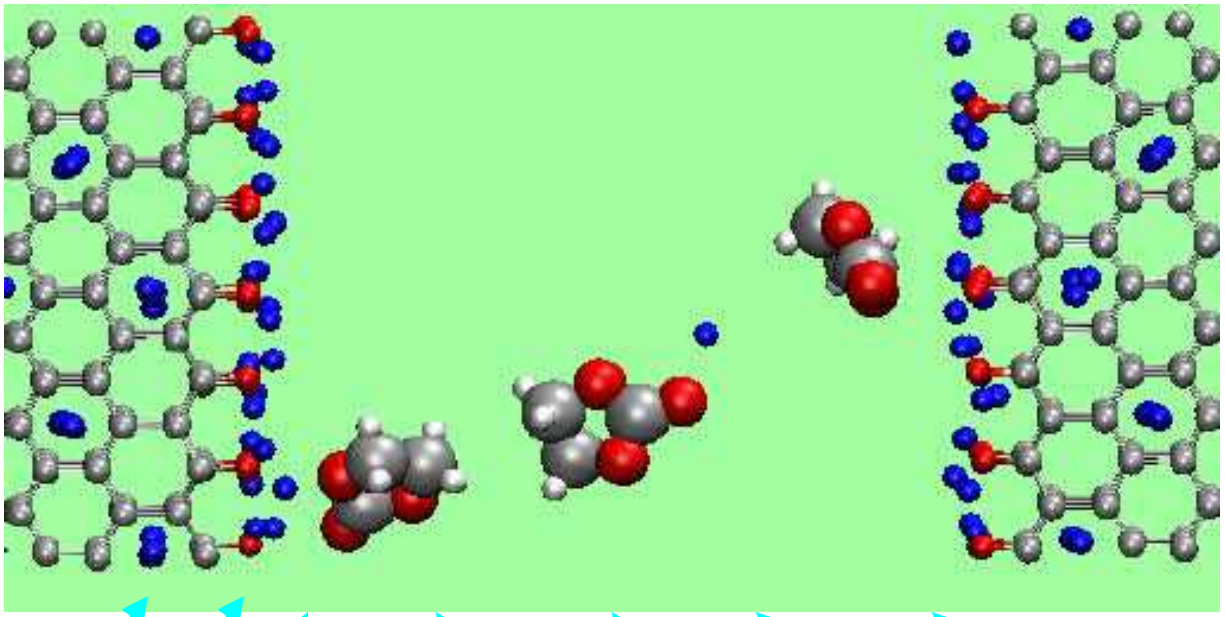
Electrolyte decomposition mechanisms: who cares?

- Additivies like VC, FEC – widely quoted (decomposition) mechanism also wrong; to design of better additives, should know how they work
- Li-air: mechanism via modeling much more integrated into choosing electrolytes
- Organic photovoltaics degradation has similar problems, experimentalist disagree with each other

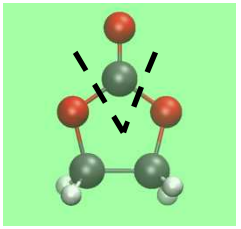


Manceau et al, Polymer Degradation and Stability 94 (2009) 898; Thin Solid Films 518 (2010), 7113

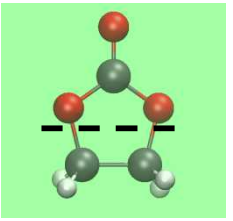
EC breakdown on pristine Li_xC_6 anode: 2-e^- mechanisms



7 ps AIMD trajectory



vs.



Leung, ,Budzien., PCCP 12:6583 (2010)

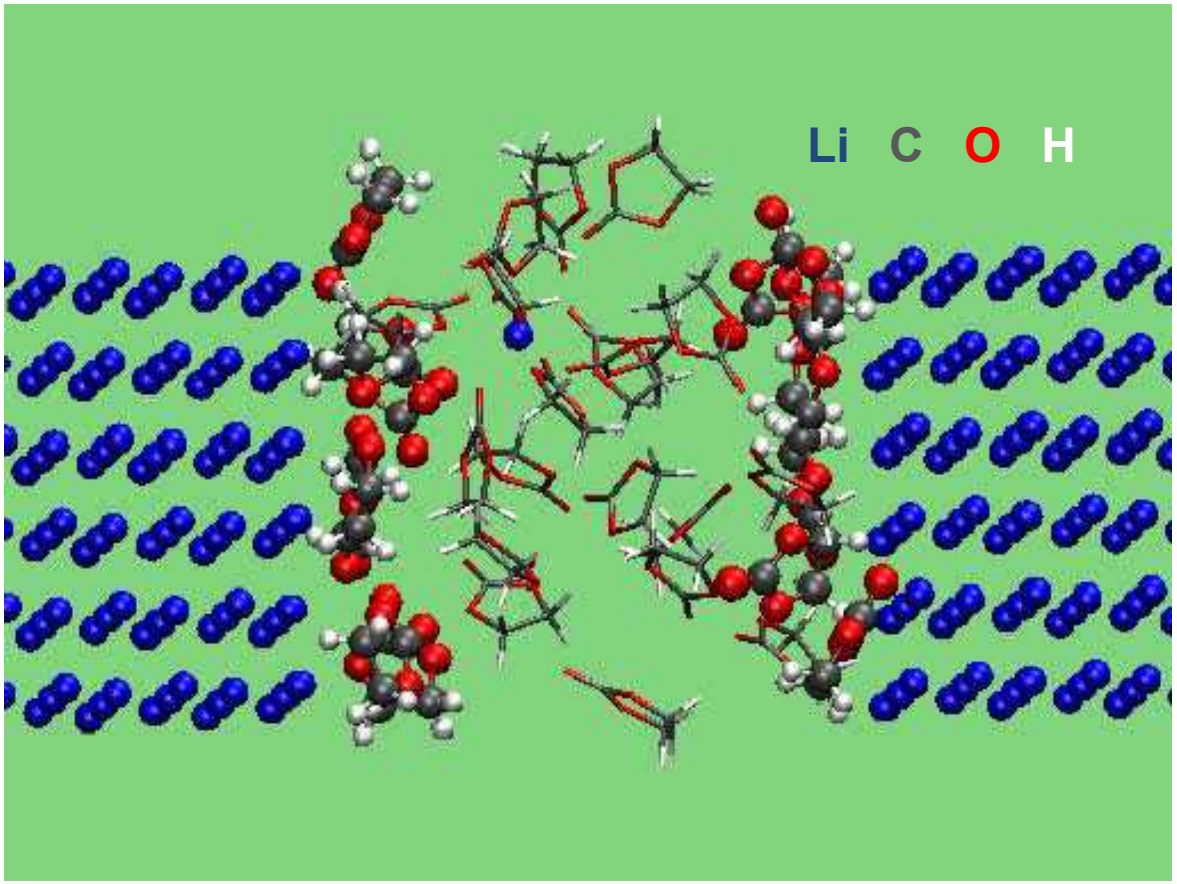
Li^+ O CO_3^{2-} C_2H_4 $C_2H_4O_2^{2-}$ CO $OC_2H_4OCO^{2-}$ → decomposition products

species	CO_3^{2-}	C_2H_4	CO	$OC_2H_4CO^{2-}$
expt.	well known	well known	recent C13 labeling*	N.A.
theory	well known	well known	first predicted, this work	this work

*Onuki et al., JECS 155:A794 (2008)

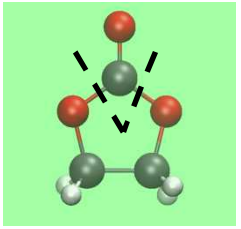
See Mogi et al., JECS (2003) for similar perspectives

EC liquid breakdown on Li metal electrode surface

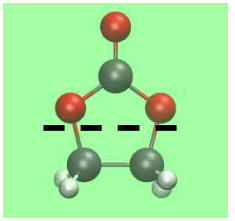


11/12 EC at the interface decomposes into $OC_2H_4O^{2-}$ + CO, not C_2H_4 + CO_3^{2-}

Yu, Balbuena, Budzien, Leung, J. Electrochem. Soc. 158:A400 (2011)



vs.



Li metal SEI "film" Intact EC SEI "film" Li metal

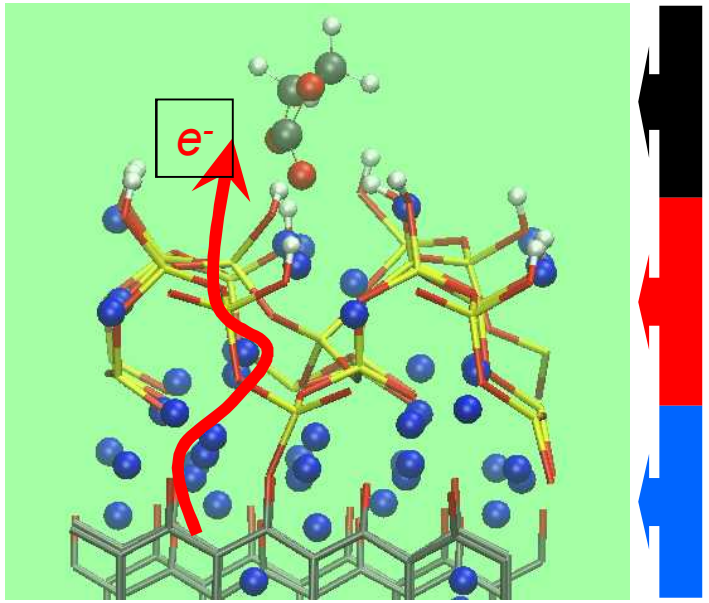
T=350 K, 12 ps

Electrochemical potential of Li well-defined

SEI on LiC_6 and Li metal "similar": Expt: Aurbach, Daroux, Foguy, Yeager, JES 134:1611 (1987)

Estimating e^- tunneling rate through ALD coating

(Emphasizing electron transfer, Marcus theory perspectives)



Leung, Qi, Zavadil,Jung, Dillon, et al., JACS (2011)

using cDFT [*Wu & van Voorhis JPCA 110, 9212 (2006)*]

$$k_{et} = \frac{2\pi}{\hbar}|V_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{(\Delta G^o + \lambda)^2}{4\lambda k_B T}\right]$$

10^{12} /s 10^{-9} overall ~6 x 10^3/s

microgravimetry (Zavadil): thicker ALD layer, less electrolyte decomposition

- state-of-the-art cDFT models e^- transfer through insulator
- 7 A thick ALD layer slows e^- transfer by 10^8 times
- experiments confirm ALD slows electrolyte breakdown

Leung, Qi, Zavadil, Dillon et al., JACS 133:14741 (2011)

E1 E2

Slide 7

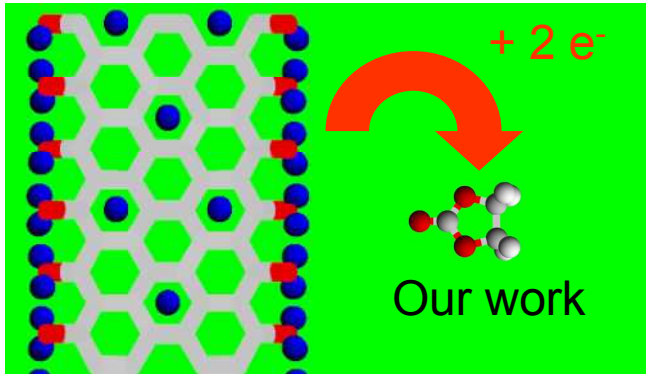
E1 Added footer text.
Ernie, 2/10/2012

E2 Changed slide number style for consistency.
Ernie, 2/10/2012

E3

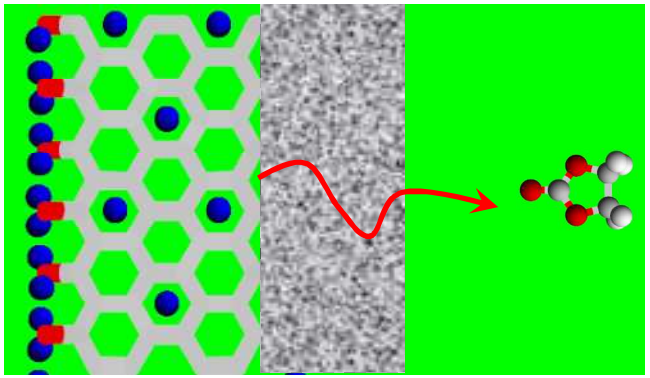
New Predictions of anode SEI formation: 2 regimes

No ALD coating



- first prediction of both fast mechanisms
- adiabatic (fast electron motion)
- DFT, AIMD, PBE suffices
- both CO and CO_3^{2-} product channels are barrierless

thin ALD oxide (intermediate SEI growth?)



- first "DFT" e^- tunneling rate estimate
- non-adiabatic (slow electron tunneling)
- DFT/PBE overestimates rate, use cDFT
- some electrolyte breakdown – agree with microgravimetric measurements

E4

E5

Slide 8

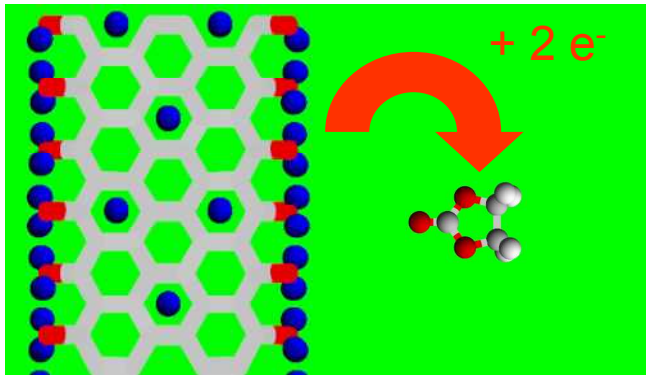
E3 Changed title font for consistency.
Ernie, 2/10/2012

E4 Added footer text.
Ernie, 2/10/2012

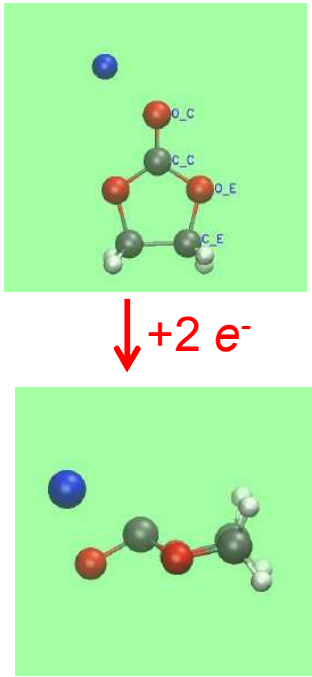
E5 Changed slide number style for consistency.
Ernie, 2/10/2012

New results computed using MP2, cluster + dielectric

I. 2-electron reduction of EC thermodynamically more favorable than 1-*e*$^-$ reduction



oxidized	reduced	Φ (V)
$EC{:}Li^+$	$c\text{-}EC^-{:}Li^+$	+0.53
$c\text{-}EC^-{:}Li^+$	$c\text{-}EC^{2-}{:}Li^+$	+1.16



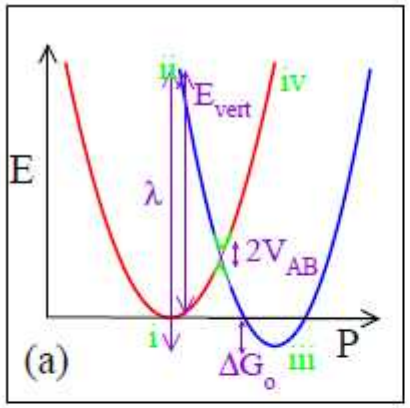
- Reduction potentials favor 2-e$^-$ attack on EC
- 2-e$^-$ attack *also* faster via Marcus theory

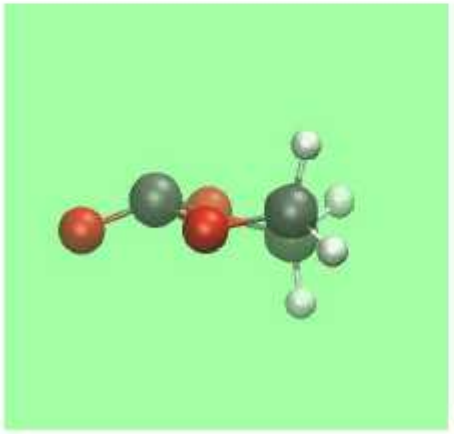
$$k \sim V_o^2 \exp\{-\beta(\lambda + \Delta G^o)^2/4\lambda\}$$

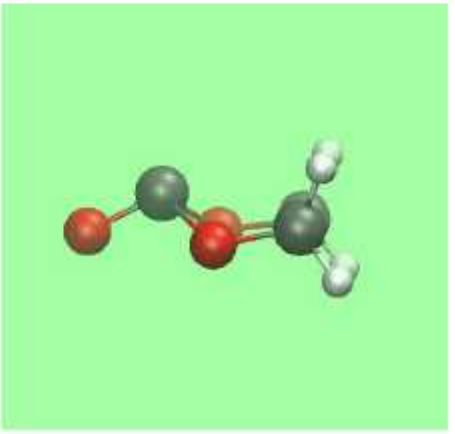
reorganization (free) energy

II. Adding 2nd electron also kinetically viable via Marcus theory

$$k \sim V_o^2 \exp\{-\beta(\lambda + \Delta G^o)^2/4\lambda\}$$





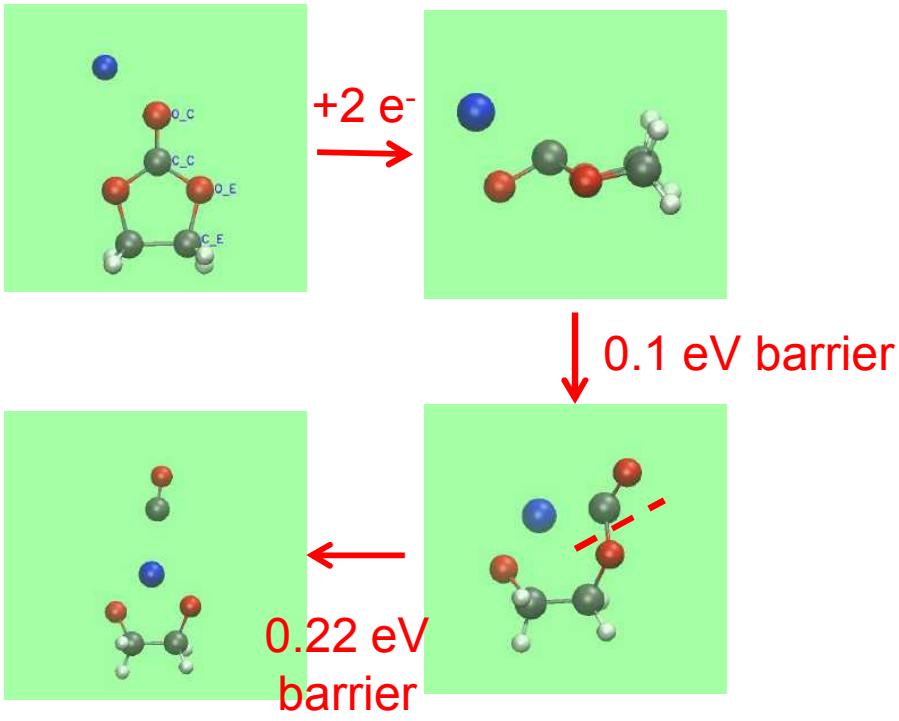


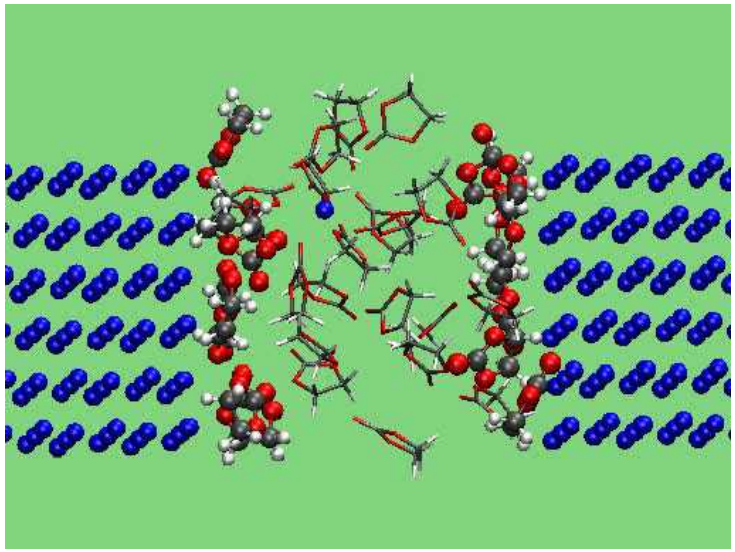
ground	excited	$\lambda_{\epsilon=2.62}$	$\lambda_{\epsilon=40}$
EC	$[c\text{-}EC^-]^+$	1.863	1.916
$c\text{-}EC^-$	$[c\text{-}EC]^-$	1.731	1.639
$c\text{-}EC^-$	$[c\text{-}EC^{2-}]^+$	0.427	0.657
$c\text{-}EC^{2-}$	$[c\text{-}EC^-]^-$	0.802	0.980
$EC{:}Li^+$	$[c\text{-}EC^-]^+{:}Li^+$	2.018	2.000
$c\text{-}EC^-{:}Li^+$	$[c\text{-}EC]^-{:}Li^+$	1.383	1.543
$c\text{-}EC^-{:}Li^+$	$[c\text{-}EC^{2-}]^+{:}Li^+$	0.723	0.987
$c\text{-}EC^{2-}{:}Li^+$	$[c\text{-}EC^-]^-{:}Li^+$	0.955	0.960

λ contributes to electron transfer "barrier" – adding 2nd electron equal or smaller than 1st

At conditions where 1st electron is added, must consider possibility of adding 2nd electron!

III. 2-electron bond-break reaction to yield CO exhibits lower barriers than any other breakdown pathway

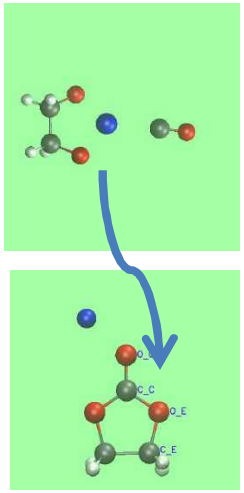


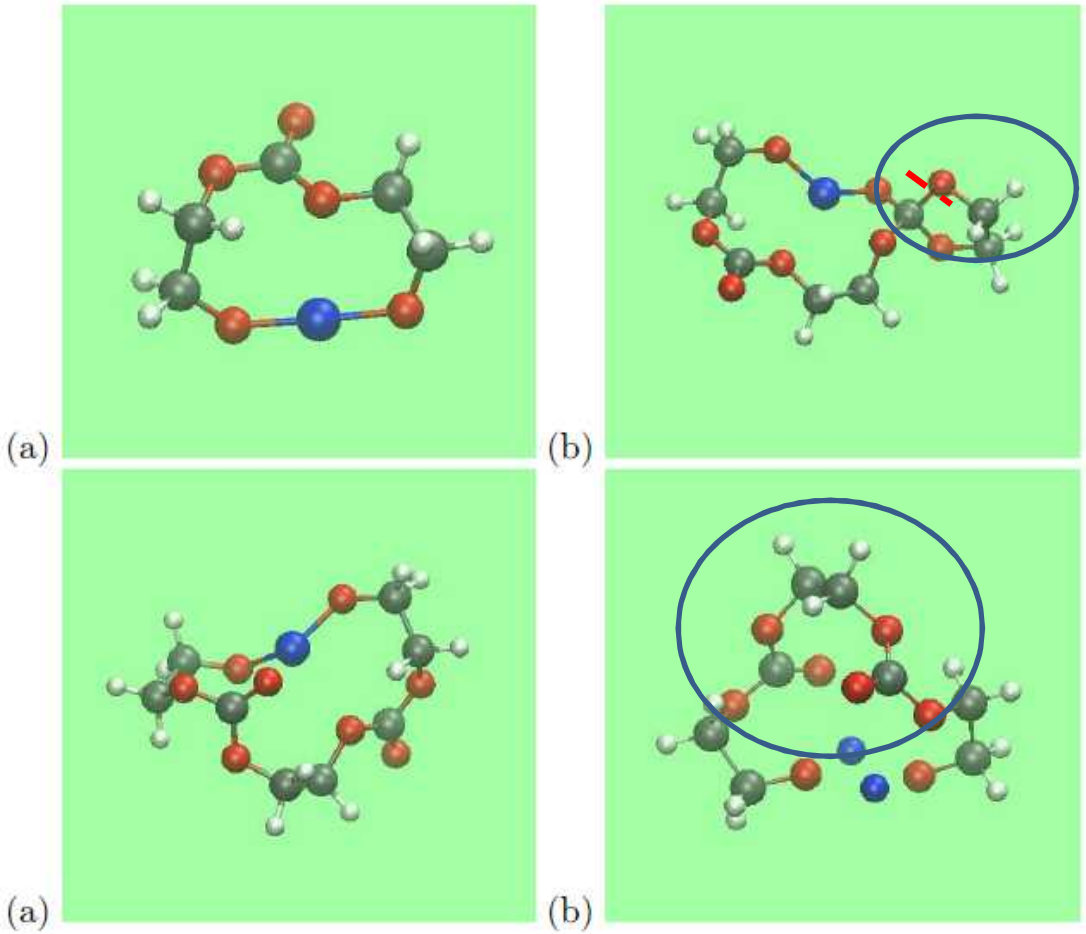


- lowest barrier pathway of all.
- low barriers consistent with fast decomposition dynamics in AIMD simulations of electrolyte-electrolyte interface.

- All 12 EC touch Li metal have accepted 2 e^- and decomposed. 11 of the 12 yield CO + $OC_2H_4O^{2-}$
- CO_3^{2-} pathway larger (0.4 eV) barrier

IV. Ultimate fate of $OC_2H_4O^{2-}$ which is very reactive





- these oligomers will further be reduced

- This fragment looks like EDC, the main SEI component. (from 2-e^-, not 1-e^-, route!)

$$OC_2H_4O^{2-} : Li^+ + EC \rightarrow OC_2H_4OCO_2C_2H_4O^{2-} : Li^+$$

$$OC_2H_4O - EC^{2-} : Li^+ + EC \rightarrow EC - OC_2H_4OCO_2C_2H_4O^{2-} : Li^+$$

$$OC_2H_4O - EC^{2-} : (Li^+)_2 + EC \rightarrow O(C_2H_4OCO_2)_2C_2H_4O^{2-} : (Li^+)_2$$

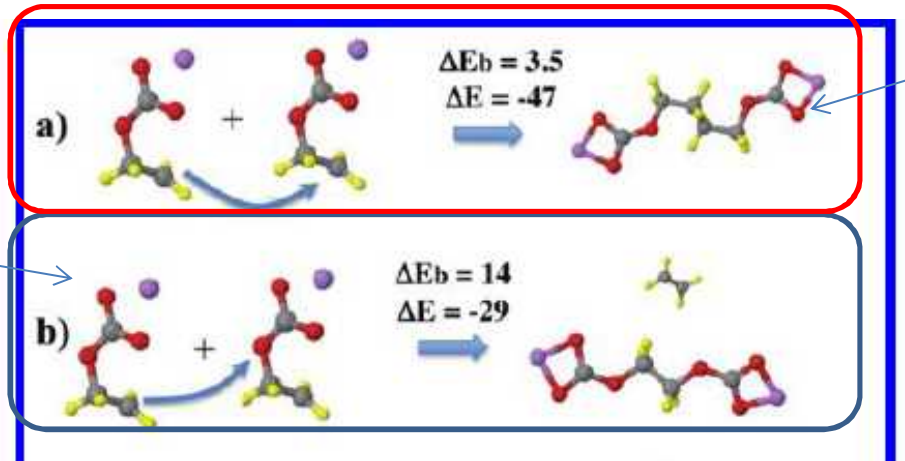
Good that we have a new mechanism for BDC formation

- Other theoretical work cast significant doubt on old, widely accepted BDC formation mechanism!

one-electron reduction

BDC formation predicted to be more kinetically and thermodynamically favored than EDC

D. Bedrov, G.D. Smith, and A.C.T. van Duin, *J. Phys. Chem. A* 116 (2012) 2978.



more favored

widely quoted

Assemble these to give rate equations (assuming no spatial inhomogeneity)

$$d[\mathrm{EC}]^-/dt = k_e[\mathrm{EC}] - k'_e[\mathrm{EC}^-] - k_1[\mathrm{EC}^-]^2;$$

$$d[\mathrm{EC}^{2-}]/dt = k'_e[\mathrm{EC}^-] - k_2[\mathrm{EC}^{2-}].$$

$$k_1 = 4\pi D a_o$$

k_1	bimolecular EC^- recombination rate to form BDC
k_2	unimolecular EC^{2-} decay rate
k_3	unimolecular EC^- ring-opening rate ($\mathrm{C_E}$-$\mathrm{O_E}$ bond)
k_e	rate of electron tunneling to EC
k'_e	rate of electron tunneling to EC^-

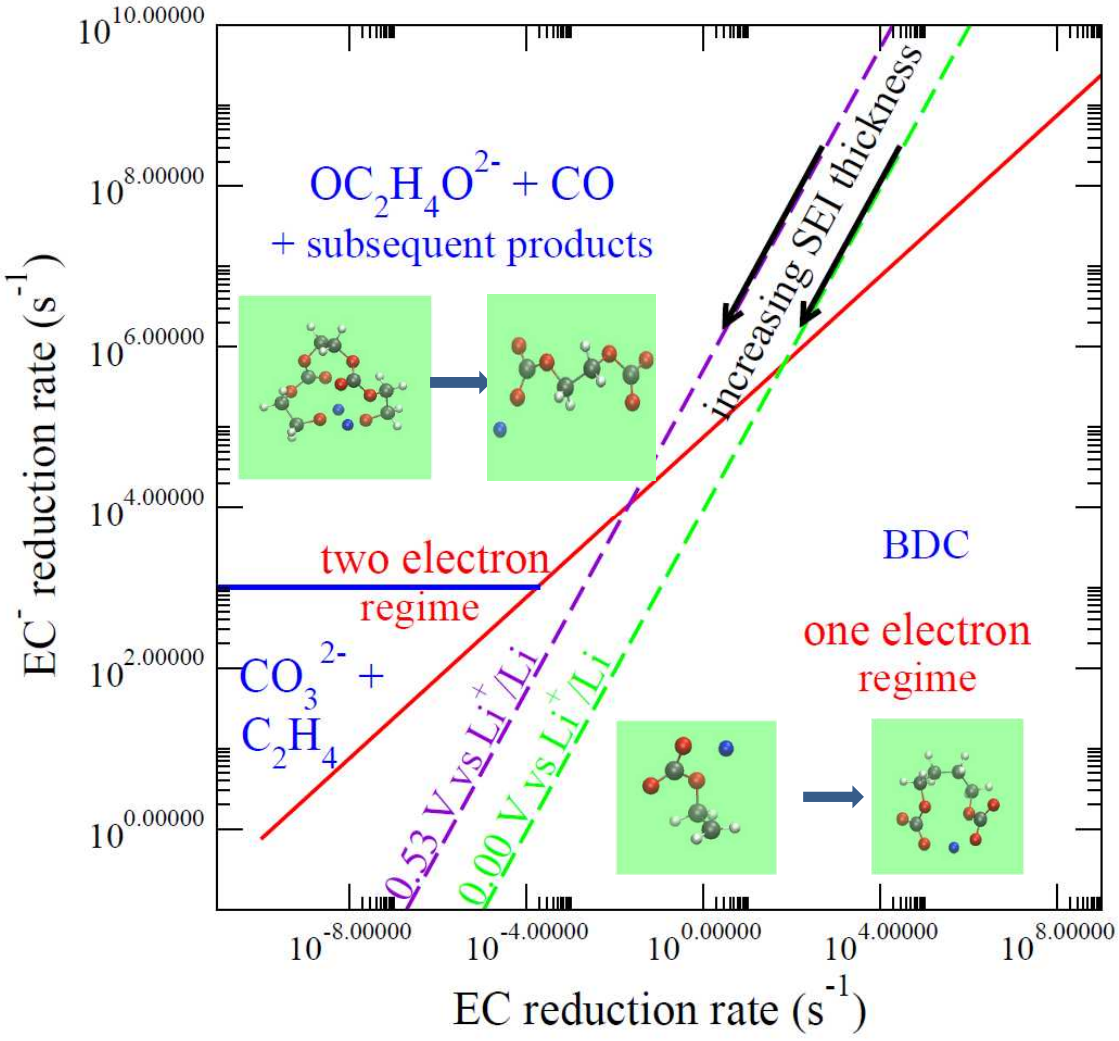
At steady state:

$$[\mathrm{EC}^{2-}] = k'_e[\mathrm{EC}^-]/k_2;$$

$$[\mathrm{EC}^-] = \{-k'_e + (k'^2_e + 4k_1k_e[\mathrm{EC}])^{1/2}\}/2k_1.$$

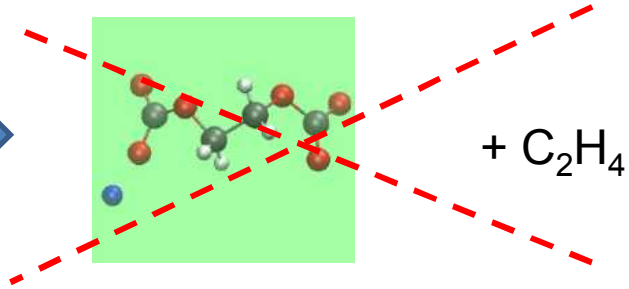
Crossover between 1- and 2-e$^-$ processes: $k'^2_e = 4k_1k_e[\mathrm{EC}]$

V. Global SEI formation picture, assuming spatial homogeneity (no electrodes) and steady state

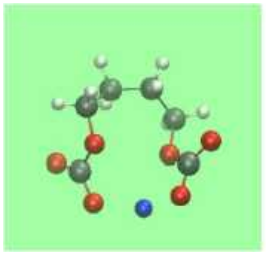


Proposed ethylene dicarbonate formation mechanism

2 

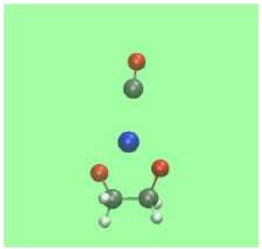


+ C_2H_4

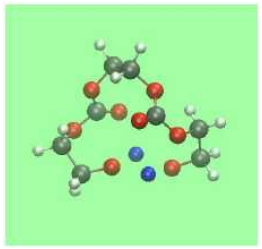


We propose

+2 e^-



+ n EC

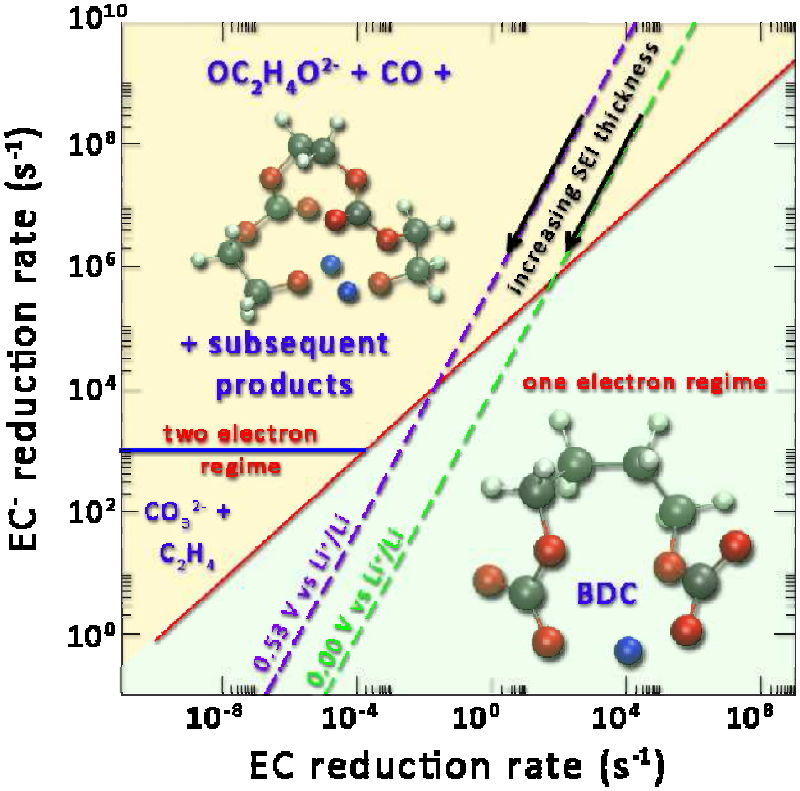


+2 e^-

?

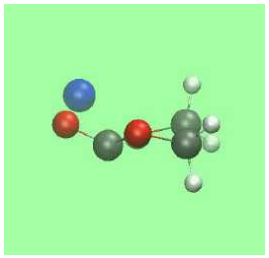
Conclusions

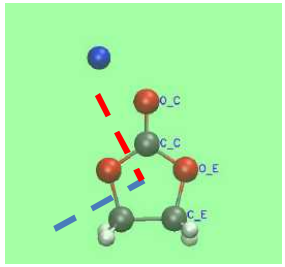
- Quantum chemistry calculations predict accurate reaction barriers
- existing SEI formation mechanisms needs to be revised
- 2 e^- attacks, formation of CO, breaking C_C-O bond in EC crucial
- Results dovetail with AIMD simulations, gas chromatography results



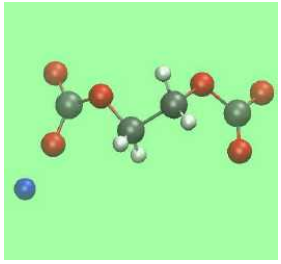
Supplementary slides follow

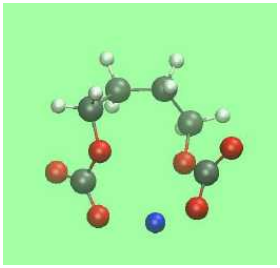
Products/intermediates





EC	charge neutral ethylene carbonate
c-EC$^-$	intact ethylene carbonate radical anion
o-EC$^-$	ring-opened ethylene carbonate radical anion
EDC	ethylene dicarbonate
BDC	butylene dicarbonate





Proposed mechanisms in literature

$$\mathrm{EC} + 2e^- \rightarrow \mathrm{CO_3^{2-}} + \mathrm{C_2H_4}; \quad (1)$$

$$\mathrm{EC} + e^- \rightarrow \mathrm{c-EC^-}; \quad (2)$$

$$\mathrm{c-EC^-} \rightarrow \mathrm{o-EC^-}; \quad (3)$$

$$2\ \mathrm{o-EC} \rightarrow \mathrm{EDC} + \mathrm{C_2H_4}; \quad (4)$$

$$2\ \mathrm{o-EC^-} \rightarrow \mathrm{BDC}; \quad (5)$$

$$\mathrm{c-EC^-} + e^- \rightarrow \mathrm{OC_2H_2O^{2-}} + \mathrm{CO} \quad (6)$$

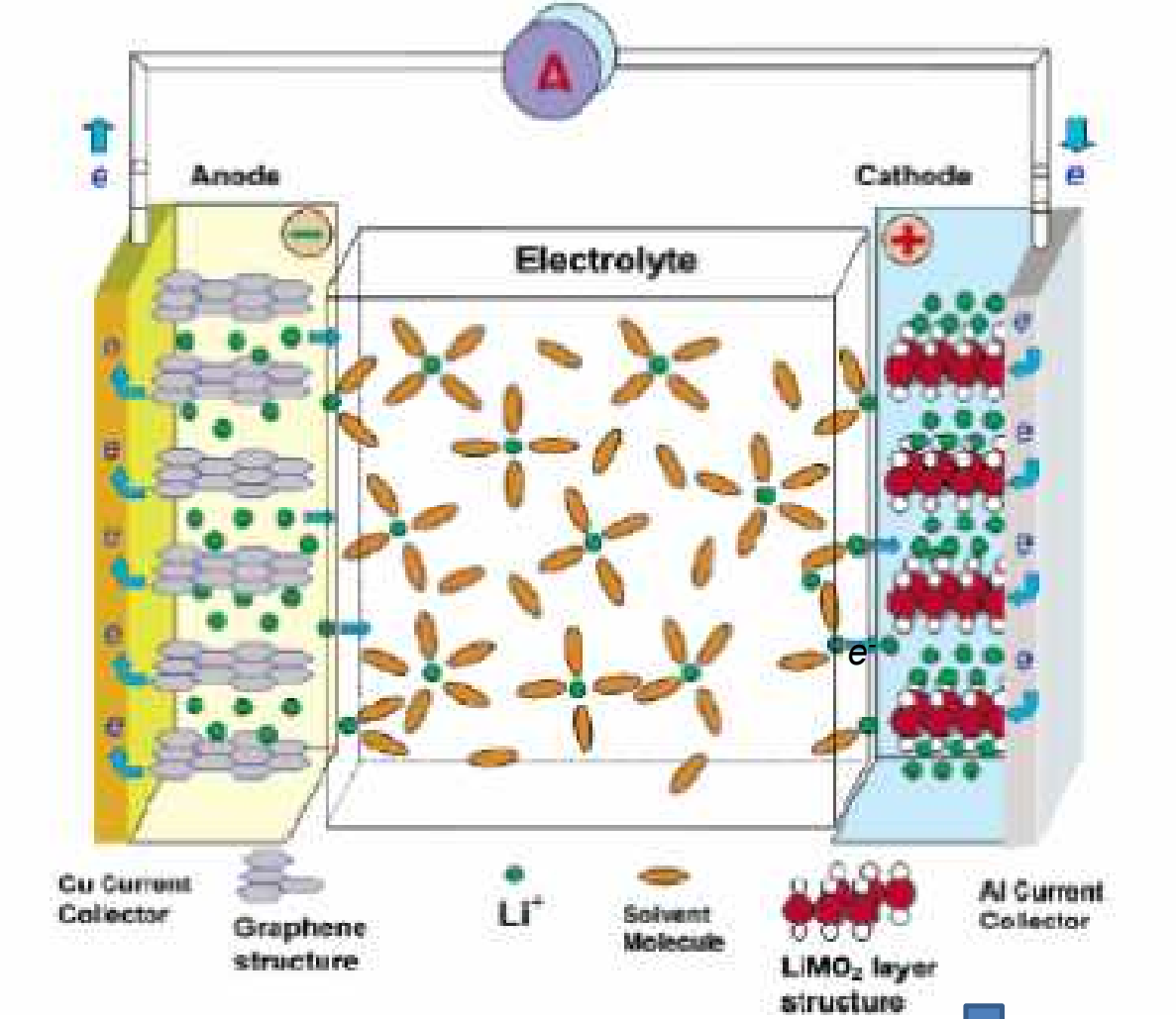
(1) widely quoted 2-e- mechanism

(4) widely quoted 1-e$^-$ pathway, predicted to be slow, not viable!

(5) Fastest 1-e$^-$ mechanism (radical recombination)

(6) Much neglected 2-e$^-$ mechanism

Relevance of Mn(I), Mn(0) in EC



- Mn(II), O^{2-} dissolution
- electrolyte oxidation

Mn(II) diffuses to anode region, gets reduced degrade SEI, battery fails