Supporting Information:

Exploring the Redox Decomposition of Ethylene Carbonate–Propylene Carbonate in Li-Ion Batteries

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**Marcus electron transfer theory** Marcus’ theory of electron transfer describes the rates of electron transfer between weakly coupled donor and acceptor states. It provides a parabolic model to calculate the activation energy of an electron-transfer reaction. The reactant and product energy surfaces were simplified representation of two parabolas. Then, the reorganization energy and change in Gibbs free energy can be obtained for the activation energy. The activation energy can be substituted into the Arrhenius or Eyring equation to calculate a rate constant for an electron-transfer reaction.

**Adiabatic (E_{ad}) and vertical (E_{vert}) oxidation potentials**

To calculate electrochemical stability of the representative complexes versus Li/Li^{+}, the energy cycle shown in Fig. S1 is used. The absolute oxidation potential and vertical oxidation potential of a complex M relative to an electron at rest in vacuum is given by equations (1)-(3).

\[
E_{ad}(M) = \left[ \Delta G_e + \Delta G_{s}(M^+) - \Delta G_{s}(M) \right] / F - 1.4
\]  

\[
E_{vert}(M) = \left[ \Delta G_{e} + \Delta G_{s}(M^+)_{v} - \Delta G_{s}(M)_{v} \right] / F - 1.4
\]

\[
\lambda = E_{vert} - E_{ad}
\]

Where \(E_{ad}\) and \(E_{vert}\) are the adiabatic oxidation and the neutral vertical oxidation respectively; \(\lambda\) is reorganization energy; \(\Delta G_{e}\) is the free energies of the electron attachment; \(\Delta G(M^+)\) and \(\Delta G(M)\) are the free energies of the oxidized solvent-phase, and neutral solvent-phase complexes; and F is the Faraday constant (F=23.061 Kcal mol\(^{-1}\)V\(^{-1}\)); Subscript of “s” and “v” denote the adiabatic oxidation and the vertical
oxidation respectively. In the former, the optimized or relaxed geometry is required during calculation, while the complex geometry does not change during electron transfer in the latter. The Li /Li\textsuperscript{+} oxidation potential is 1.4 V. In this work, we used a value of 1.4 V for to convert from the absolute scale to Li\textsuperscript{+}/Li.

\[ \Delta G_e = \text{IP} - T \Delta S \]

\[ \Delta G^0_s(M) \]

\[ \Delta G^0_s(M^+) \]

\[ M_{(s)} \rightarrow M^+_{(s)} + e^-_{(g)} \]

\[ M_{(g)} \rightarrow M^+_{(g)} + e^-_{(g)} \]

**Fig. S1** Free-energy cycle for the redox reaction \((M \rightarrow M^+ + e^-)\), where \(M_{(g)}\) denotes molecule M in gas-phase, \(M_{(s)}\) denotes the solvated molecule, and IP denotes ionization potential.

**Table S1** The dielectric constants and dipole moments of EC, PC anf FEC.

|            | EC  | PC  | FEC |
|------------|-----|-----|-----|
| Dielectric Constant\(^5, 6\) | 89  | 65  | 78.4 |
| Dipole Moment (Debye)\(^7\)    | 5.64\(^7\), 4.81\(^5\) | 5.36\(^5\) | 4.97\(^7\) |
**Fig. S2** Calculated free energy profile $\Delta G$ of EC (left) and PC (right) decomposition.

**Fig. S3** Calculated free energy profile $\Delta G$ of FEC decomposition.
Fig. S4 3D plots of the HOMO and LUMO orbitals of Product-F1.

Fig. S5 Ring formation of Product-P1.
**Fig. S6** 3D plots of the HOMO and LUMO orbitals of the lithium alkylcarbonate complexes (dimer Product-E1 complex).

**Fig. S7** The reaction between FEC and LiCO$_3^-$ anion to produce inorganic LiF and less-reduced organic intermediate.
Fig. S8 Calculated possible pathways of trans-2,3-butylene carbonate (t-BC) and cis-2,3-butylene carbonate (c-BC) decomposition assisted by Li ions. The hydration energy of the solvated electron in water was -1.63 eV.

Fig. S9 Geometrical structure of dimerized trans-2,3-butylene carbonate (trans-BC).

Fig. S10 Geometrical structure of dimerized cis-2,3-butylene carbonate (cis-BC).
**TS-E1**

imaginary frequency : -734.48 cm⁻¹

| Element | x     | y     | z     |
|---------|-------|-------|-------|
| C       | 1.64927400 | -0.52113700 | 0.00029100 |
| C       | 1.44783700 | 0.96440300  | -0.00026000 |
| C       | -0.65610400 | -0.24789600 | -0.00001800 |
| H       | 2.15581100 | -0.89262800 | -0.89350700 |
| H       | 2.15493500 | -0.89202300 | 0.89483600 |
| H       | 1.69012800 | 1.50379000 | 0.90992000 |
| H       | 1.68964900 | 1.50302300 | -0.91102600 |
| O       | -0.26495000 | 1.01207600 | 0.00016600 |
| O       | 0.31422800  | -1.15860800 | -0.00021100 |
| O       | -1.85174900 | -0.57144200 | -0.00004600 |
| Li      | -2.63893500 | 1.11646900  | 0.00014300 |

**Int-E2**

| Element | x     | y     | z     |
|---------|-------|-------|-------|
| C       | 1.55273000 | -0.27237700 | -0.51160800 |
| C       | 2.18162500 | 0.51004900  | 0.58283000 |
| C       | -0.78770700 | -0.14575900 | -0.02082500 |
| H       | 1.32849400 | 0.35696400  | -1.37572300 |
| H       | 2.17850800 | -1.11339800 | -0.81983200 |
| H       | 2.82067400 | 0.02397400  | 1.31317900 |
| H       | 1.86677200 | 1.53052500  | 0.76910000 |
O  -0.73768200  1.08575900  -0.35438600
O  0.31126700  -0.92256800  -0.08401300
O  -1.85617900  -0.70312900  0.37615300
Li -2.53786300  0.98998800  0.10295400

**TS-E2**

imaginary frequency :-163.09 cm\(^{-1}\)

C  -1.99262200  -0.11045500  0.62681300
C  -2.37993500  0.36610200  -0.58179200
C  0.90840700  -0.15030600  -0.01137600
H  -1.44297800  0.51535800  1.31917700
H  -2.34364900  -1.06919500  0.99424900
H  -2.98267500  -0.22806500  -1.26294700
H  -2.04152900  1.33648100  -0.93111600
O  0.74149500  1.10064800  0.19202900
O  -0.08473500  -1.01226400  -0.02982500
O  2.07216800  -0.65376200  -0.20462200
Li  2.58810500  1.11213500  0.00603600
TS-P1

imaginary frequency : -705.67 cm⁻¹

C 1.29854800 -0.10690700 0.46323600
O -0.24085800 -0.88529200 0.09389100
C -1.08556800 0.10706000 -0.04708900
C 0.91356700 1.26521600 -0.00995400
H 1.31899100 -0.22944000 1.54458500
H 1.28913700 1.47343300 -1.01726500
H 1.21995700 2.06785100 0.66682600
O -0.54612600 1.33317100 -0.06223000
O -2.31368500 -0.04004000 -0.12711600
C 2.33879700 -0.88597500 -0.28426000
H 2.17818800 -0.82566800 -1.36570400
H 3.34679400 -0.50043200 -0.06882500
H 2.32202600 -1.93985100 0.00928000
Li -2.55393600 -1.86165600 0.08771500

Int-P2

C 1.22547300 -0.53142700 0.22315400
O -0.22315800 -0.76823000 0.17950000
C -1.14751000 0.37552900 -0.10111800
| Element | X    | Y    | Z    |
|---------|------|------|------|
| C       | 1.58365500 | 0.48753700 | 1.24733100 |
| H       | 1.59954700  | -1.51230700  | 0.54791900  |
| H       | 1.83150500  | 1.50254800   | 0.96145700  |
| H       | 1.41495500  | 0.27366000   | 2.29879600  |
| O       | -0.67017700 | 1.46686000   | -0.31163800 |
| O       | -2.32591900 | -0.09201200  | -0.05243100 |
| C       | 1.76146200  | -0.22850000  | -1.17365000 |
| H       | 1.37907900  | 0.73123400   | -1.52734700 |
| H       | 2.85653000  | -0.18988400  | -1.15134800 |
| H       | 1.45981900  | -1.01184000  | -1.87764600 |
| Li      | -1.77529400 | -1.75506500  | 0.35013800  |

**TS-P2**

Imaginary frequency: \(-236.40\) cm\(^{-1}\)

| Element | X    | Y    | Z    |
|---------|------|------|------|
| C       | -1.70887400 | 0.52389600 | -0.19995600 |
| O       | 0.44517200  | 0.69049400  | -0.41494000 |
| C       | 1.22177100  | -0.34085100 | 0.11665800  |
| C       | -1.65997000 | 0.70369800  | 1.15524500  |
| H       | -1.84133600 | 1.40642600  | -0.82325300 |
| H       | -1.54066500 | -0.14156600 | 1.82499500  |
| H       | -1.64839100 | 1.69857900  | 1.59084700  |
| O       | 0.75391600  | -1.30761600 | 0.68719500  |
O  2.45463500  -0.02063500  -0.13570400
C  -1.91399900  -0.80111300  -0.86955800
H  -1.48176700  -1.60646200  -0.27307200
H  -2.98986500  -0.98207200  -1.00505100
H  -1.44940800  -0.80953600  -1.85981700
Li  2.02936100  1.67430100  -0.58713200

TS-P1-1

imaginary frequency = -749.69 cm⁻¹

C  -1.31371200  -0.04355400  -0.45130900
O  -0.11698900  -0.92612100  -0.46867000
C  0.97309300  -0.28341900  -0.05493400
C  -0.80786800  1.35548400  -0.23959900
H  -1.74761000  -0.17353500  -1.44711100
H  -1.17576600  1.89385600  0.62840500
H  -0.66216700  1.97482900  -1.11942400
O  0.81491400  0.99428700  0.22863500
O  2.07053200  -0.85291100  0.03132100
C  -2.25815500  -0.55532200  0.62613600
H  -1.81859500  -0.42108400  1.62040400
|    | X      | Y      | Z      |
|----|--------|--------|--------|
| H  | -3.20537900 | -0.00602000 | 0.58730100 |
| H  | -2.46750500 | -1.61869700 | 0.47943800 |
| Li | 3.12307400  | 0.59649100  | 0.54631100 |

**Int-P3**

|    | X      | Y      | Z      |
|----|--------|--------|--------|
| C  | 1.76527800  | -0.54020200 | -0.19917100 |
| O  | -1.41411000 | -1.40782200 | -0.26839800 |
| C  | -1.47002200 | -0.20721700 | -0.13919500 |
| C  | 0.80713200  | -0.36270300 | 0.92402600 |
| H  | 1.52854500  | -1.30386200 | -0.93562100 |
| H  | 1.27039900  | 0.15077800  | 1.77411700 |
| H  | 0.39553300  | -1.32012000 | 1.25052500 |
| O  | -0.32708100 | 0.47581100  | 0.55222000 |
| O  | -2.29976000 | 0.69836600  | -0.45451700 |
| C  | 2.83128300  | 0.45657500  | -0.50982100 |
| H  | 3.20299000  | 0.95109400  | 0.39739100 |
| H  | 3.68471000  | -0.00719400 | -1.01946900 |
| H  | 2.46995800  | 1.25528600  | -1.18287200 |
| Li | -1.27551800 | 2.02148400  | 0.20881600 |

**TS-P3**
imaginary frequency :-156.59 cm⁻¹

C  1.87884800  -0.41315900  -0.25018400
O  -1.33107200  -1.38326900  -0.44090900
C  -1.51541500  -0.23022500  -0.10414300
C  1.29989700  -0.66971800  0.94950400
H  1.55318000  -1.00477300  -1.10432100
H  1.59296500  -0.12727000  1.84493700
H  0.61781500  -1.50169000  1.06553800
O  -0.59400500  0.53079300  0.58725400
O  -2.54017000  0.55533200  -0.28424000
C  2.89199300  0.65580500  -0.50723500
H  3.14812500  1.20535200  0.40463100
H  3.81581700  0.22934400  -0.92266700
H  2.52523100  1.37406500  -1.25448200
Li -1.62103200  2.04863800  0.18062600

TS-F1

imaginary frequency :-743.30 cm⁻¹

C  1.11690500  1.12106500  0.23108100
C  1.34276300  -0.33755400  0.41813900
C  -0.98720700  0.19530800  -0.02203200
|     |      |      |      |
|-----|------|------|------|
| H   | 1.23691900 | 1.67596700 | 1.16502000 |
| H   | 1.74905800  | 1.54358900  | -0.55360500 |
| H   | 1.72733300  | -0.72745800  | 1.35445800 |
| O   | -0.31900000 | -0.83541800  | 0.45353400 |
| O   | -0.27027000 | 1.30816500  | -0.21433600 |
| O   | -2.19388600 | 0.16082900  | -0.29039500 |
| F   | 1.86546900  | -0.97009400  | -0.64810600 |
| Li  | -2.69068400 | -1.56759100 | 0.17117800 |

|     |      |      |      |
|-----|------|------|------|
| Int-F2 | C   | -0.98938400 | -0.23425700 | 0.92914500 |
| C    | -1.79235600  | 0.58763300  | 0.00348200 |
| C    | 1.21196900  | -0.15114400  | 0.00330900 |
| H    | -0.60993900 | 0.38788700  | 1.74240000 |
| H    | -1.59171400 | -1.05366700 | 1.32831200 |
| H    | -1.47401800 | 1.54583500  | -0.39187300 |
| O    | 1.21492500  | 1.09498100  | 0.28428200 |
| O    | 0.13816800  | -0.91506000 | 0.29208400 |
| O    | 2.19354900  | -0.73124100 | -0.54843700 |
| F    | -2.66776400 | -0.06619900 | -0.78594500 |
| Li   | 2.91034600  | 0.97096600  | -0.48146200 |
TS-F3

imaginary frequency : -151.19 cm⁻¹

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | -1.39837700 | 0.00460900 | 1.07005500 |
| C    | -1.89800600 | 0.49250900 | -0.08363300 |
| C    | 1.34495400  | -0.16835100 | -0.01272000 |
| H    | -0.71248800 | 0.61574200  | 1.63826200  |
| H    | -1.79200400 | -0.90565600 | 1.50605000  |
| H    | -1.55965800 | 1.39833700  | -0.57400100 |
| O    | 1.20941100  | 1.09984600  | 0.11930300  |
| O    | 0.36087500  | -1.01304500 | 0.20018100  |
| O    | 2.46260100  | -0.69094800 | -0.35906200 |
| F    | -2.83220700 | -0.16464600 | -0.77592500 |
| Li   | 2.99983100  | 1.07799100  | -0.37085600 |

TS-F2

imaginary frequency : -740.97 cm⁻¹

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | 0.93534700  | 1.27581700 | 0.27066800 |
| C    | 1.34290200  | -0.15904300 | 0.37661400 |
| C    | -0.93261300 | -0.23130000 | 0.05901200 |
| H    | 0.84983600  | 1.82927200  | 1.20029900 |
| H    | 1.35323500  | 1.82920700  | -0.56249500 |
H     1.94077000  -0.41962100  1.25349000
O     0.14234300  -0.93930300  0.46956400
O     -0.69920200  1.03267900 -0.19696500
O     -2.04475700 -0.76153600 -0.00913700
F     2.01950000  -0.55927300 -0.74610000
Li    -3.19341000  0.60901100 -0.50728400

Int-F3
C    -1.67751600  0.89326800 -0.84741900
C    -1.36754600 -0.39786100 -0.18928800
C     1.01876900 -0.11946700 -0.08480600
H    -1.74263100  0.93105200 -1.92896100
H    -1.70555500  1.80488700 -0.26707000
H    -1.99245500 -1.21289400 -0.57291800
O    -0.04816700 -0.89844200 -0.42119000
O     0.85397700  1.05315900  0.37338700
O     2.15698600 -0.64350500 -0.25596000
F    -1.58317800 -0.30883300  1.16855000
Li    2.71487700  0.97037200  0.47039400

TS-F4
imaginary frequency : -287.77 cm\(^{-1}\)

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| C       | 1.90704300 | -0.13972900 | 1.11166300 |
| C       | 1.76117900 | -0.28884000 | -0.23336000 |
| C       | -1.13301500 | -0.18599200 | 0.03756600 |
| H       | 2.11925100 | -1.01100400 | 1.71877900 |
| H       | 1.68753700 | 0.80689900 | 1.58833700 |
| H       | 2.03075900 | -1.18334200 | -0.78193100 |
| O       | -0.17934200 | -1.07984700 | -0.15081700 |
| O       | -0.90752400 | 0.98663900 | 0.49039200 |
| O       | -2.31482800 | -0.57424900 | -0.27346100 |
| F       | 1.59444400 | 0.77020000 | -1.02246800 |
| Li      | -2.72841200 | 1.16089200 | 0.21763200 |

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