

Supplementary Material:

Isothermal Microcalorimetry as a Tool to Study Solid-Electrolyte Interphase Formation in Lithium-Ion Cells

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Reaction Scheme and Energies

Table S1 lists the enthalpy changes for the 18 reactions summarized in Figure S1 and originally presented in Table 5 of Self *et al.*¹ These values were evaluated from the enthalpies of each individual species, as calculated by DFT using B3LYP/6-311++G(d,p)/IEFPCM-UFF ($\epsilon=20$). Figure S2 graphically compares the changes in enthalpy and free energies. It is noted that the original report by Self *et al.* included the electronic energy and the free energy for each structure but not the enthalpy. Therefore, these values were obtained from the authors and are included here in Table S2. The new open-ring structure of $\text{LiO}_3\text{SCHCHCH}_2$ (LiPES) was calculated using the same method as described above. The calculated energies and molecular geometry are reported.

Table S1 The enthalpy changes for the reactions of Li₂PES with PES, EC, EMC. The reaction groups correspond to the four categories discussed in the main article text and as indicated on Figure 5. The reaction numbers correspond to Figure S1.

| Reaction | | ΔH (eV) |
|----------|-------|-----------------|
| No. | Group | |
| (1) | (iii) | -2.357 |
| (2) | (iii) | -2.333 |
| (3) | (iii) | -2.214 |
| (4) | (iii) | -2.575 |
| (5) | (iii) | -2.298 |
| (6) | (iii) | -2.221 |
| (7) | (i) | -3.665 |
| (8) | (i) | -3.629 |
| (9) | (iv) | -0.550 |
| (10) | (iv) | -0.636 |
| (11) | (ii) | -1.976 |
| (12) | (ii) | -1.857 |
| (13) | (ii) | -1.858 |
| (14) | (ii) | -1.684 |
| (15) | (iv) | -0.046 |
| (16) | (iv) | -0.185 |
| (17) | (iv) | -0.051 |
| (18) | (iv) | -0.195 |

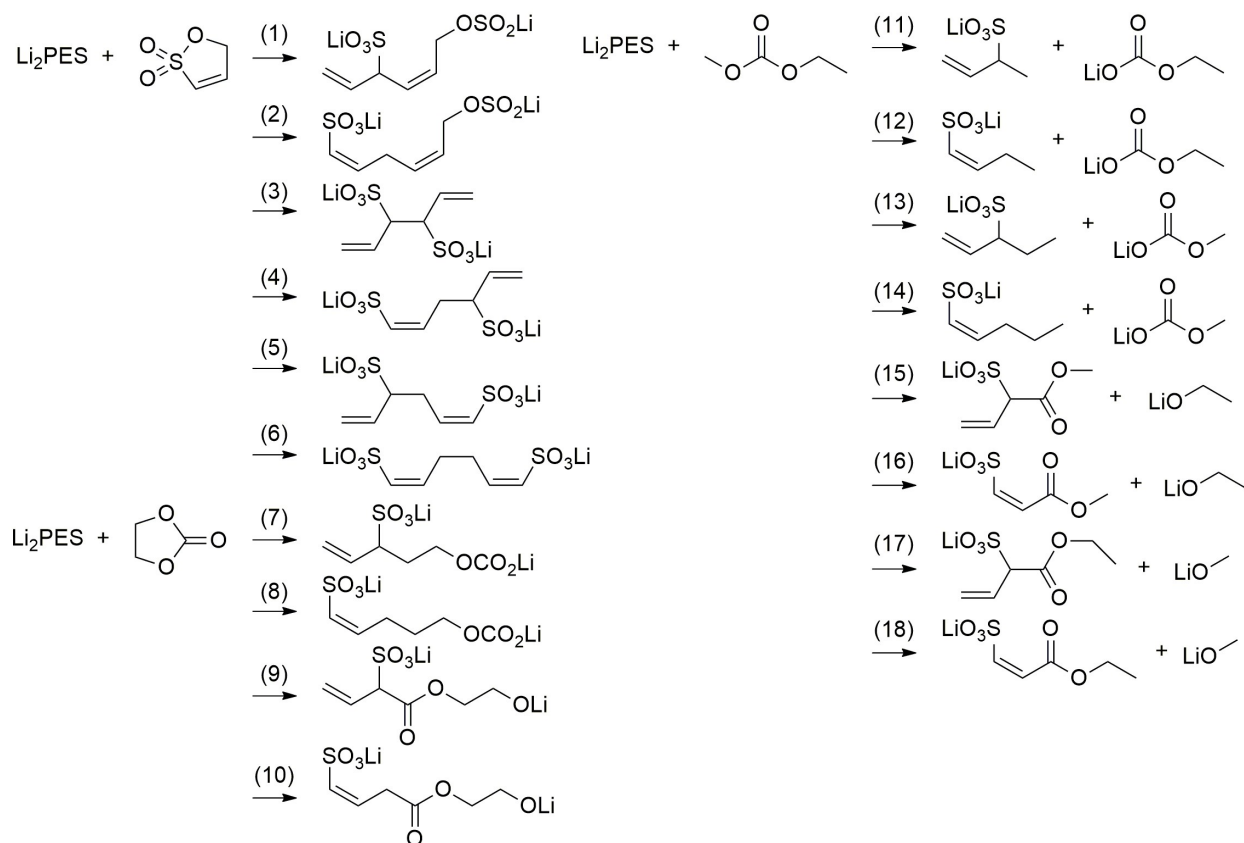


Figure S1 The reactions of Li_2PES with PES, EC, and EMC, as originally proposed by Self *et al.*¹

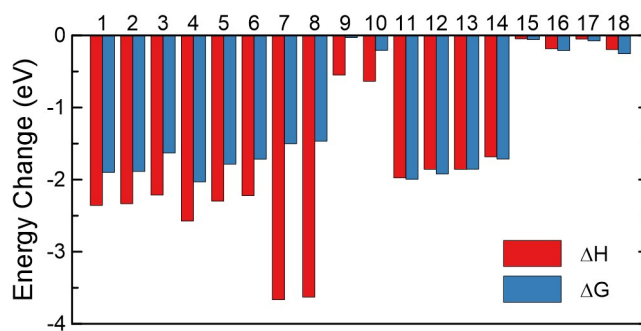


Figure S2 The changes in enthalpy and free energy for the 18 reactions in Figure S1.

Table S2 The enthalpy of the species involved in the reactions in Figure S1, as obtained from Self *et al.* The species are identified by the naming convention in the original article.¹

| Species | H (Ha) |
|----------------------------|--------------|
| PES-MS4c1a | -1496.433145 |
| PES-MS4c1b | -1496.432265 |
| PES-MS4c2a | -1496.42789 |
| PES-MS4c2b | -1496.441134 |
| PES-MS4c3a | -1496.430973 |
| PES-MS4c3b | -1496.428143 |
| EC-MS4c1a | -1098.373398 |
| EC-MS4c1b | -1098.372064 |
| EC-MS4c2a | -1098.258929 |
| EC-MS4c2b | -1098.26206 |
| EMC-MS4c 1a | -788.108665 |
| EMC-MS4c 1b | -788.104304 |
| EMC-MS4c 2a | -827.403958 |
| EMC-MS4c 2b | -827.397563 |
| EMC-MS4c 3a | -976.702414 |
| EMC-MS4c 3b | -976.707541 |
| EMC-MS4c 4a | -1016.002649 |
| EMC-MS4c 4b | -1016.007953 |
| MS4c (Li ₂ PES) | -755.802791 |
| PES | -740.543723 |
| EC | -342.435913 |
| EMC | -382.922145 |
| LiOMe | -122.724146 |
| LiOEt | -162.024197 |
| LiO ₂ COMe | -311.389251 |
| LiO ₂ COEt | -350.688889 |

DFT Calculations – LiPES open ring structure

E = -748.25783616 Ha

H = -748.176763 Ha

G = -748.220635 Ha

| Row | Sym | X | Y | Z |
|-----|-----|------------|------------|------------|
| 1 | C | 0.7270800 | -1.0277150 | -0.2574850 |
| 2 | C | 2.0673960 | -0.7456580 | -0.0202540 |
| 3 | C | 2.6334910 | 0.4678260 | 0.3115000 |
| 4 | S | -0.6125330 | 0.1348600 | -0.1326210 |
| 5 | O | -1.8088270 | -0.5768620 | -0.7048830 |
| 6 | O | -0.8913240 | 0.3461710 | 1.3342970 |
| 7 | O | -0.2302710 | 1.3687120 | -0.8469710 |
| 8 | H | 0.3895720 | -2.0287980 | -0.4920000 |
| 9 | H | 2.7331940 | -1.6011110 | -0.1080830 |
| 10 | H | 3.6996950 | 0.5413050 | 0.4826410 |
| 11 | H | 2.0432060 | 1.3702360 | 0.4021670 |
| 12 | Li | -2.7298550 | -0.5700950 | 1.1250330 |

References

J. Self, D. S. Hall, L. Madec, and J. R. Dahn, *J. Power Sources*, **298**, 369–378 (2015).