Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supporting Information: Solvent Oligomerization Pathways Facilitated by Electrolyte Additives During Solid-Electrolyte Interphase Formation

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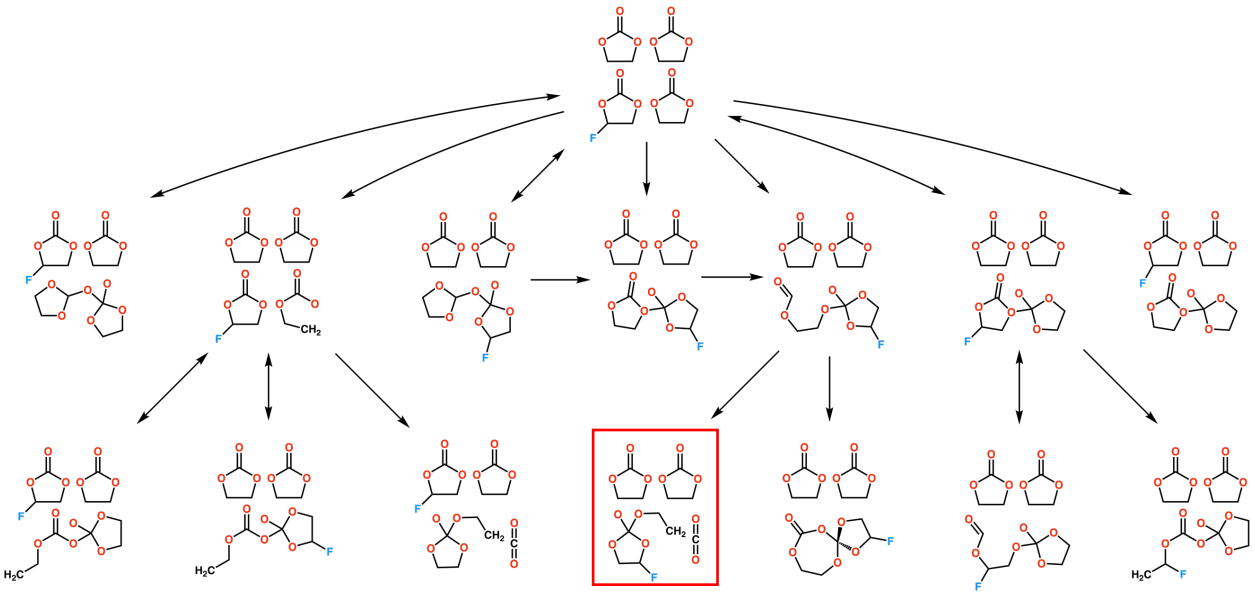

Figure S1: Reaction network of 1 FEC molecule, 3 EC molecules, and 1 $Li^+$ with an extra electron. The boxed molecules indicate the node in the reaction network that contains the open-shell $S_N1$ adduct with FEC, as well as two intact EC molecules and $CO_2$. Constructed from ~50 separate reactive MD trajectories using *mdstates*. Although $Li^+$ was included in the simulations, it is not pictured in the reaction network.

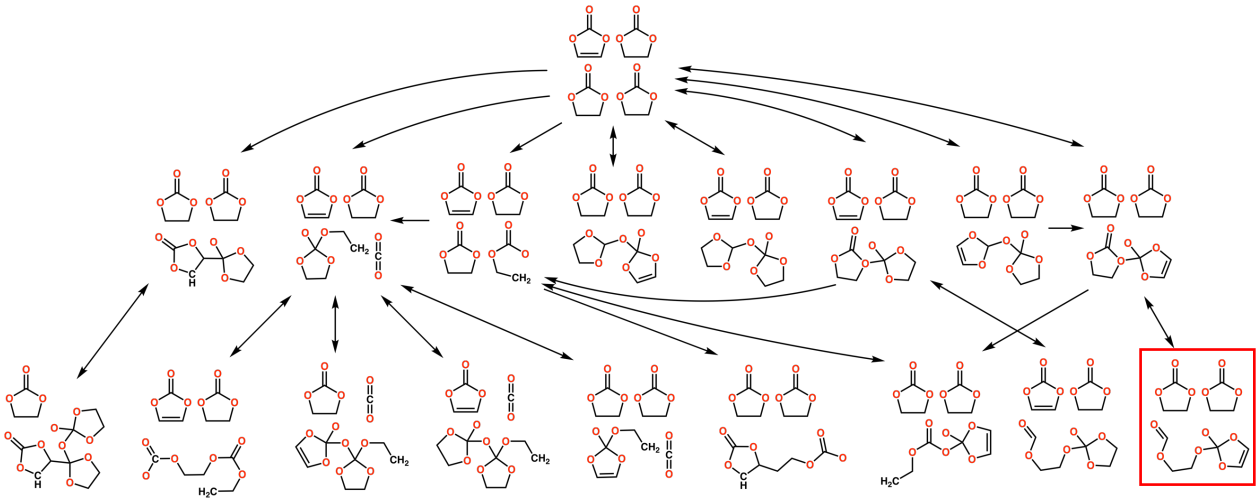

Figure S2: Reaction network of 1 VC molecule, 3 EC molecules, and 1 $Li^+$ with an extra electron. The boxed molecules indicate the node in the reaction network that contains the open-shell $S_N1$ adduct with VC, as well as two intact EC molecules and $CO_2$. Constructed from ~50 separate reactive MD trajectories using *mdstates*. Although $Li^+$ was included in the simulations, it is not pictured in the reaction network.

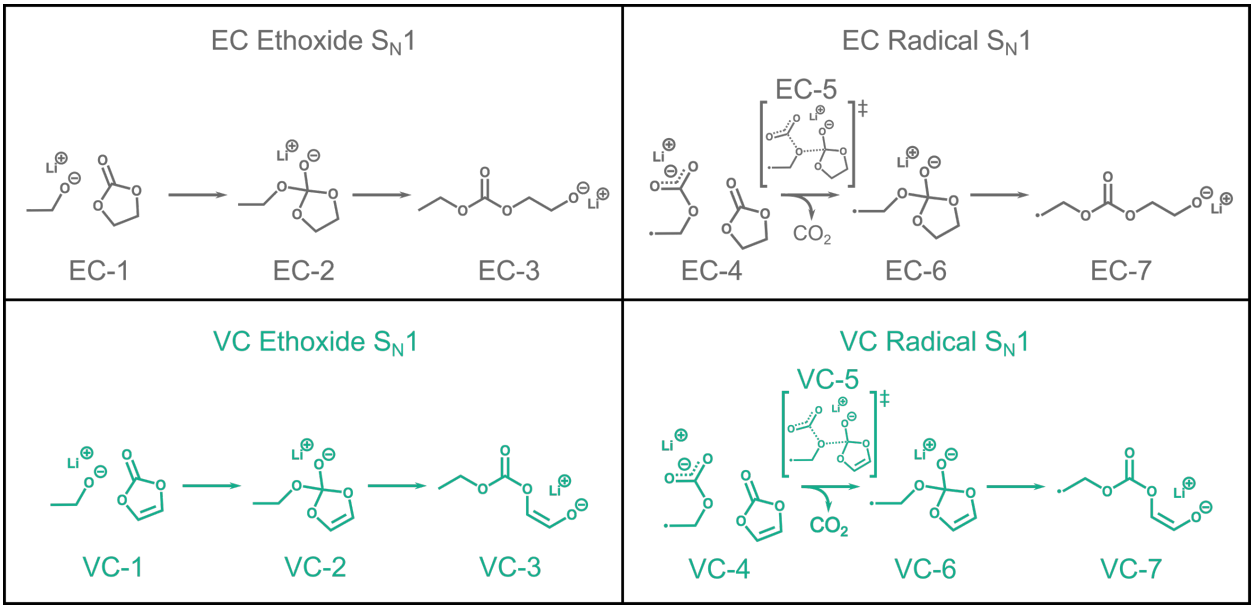


Figure S3: $S_N1$ mechanisms for combinations of EC and VC electrophiles and ethoxide and o-EC nucleophiles.

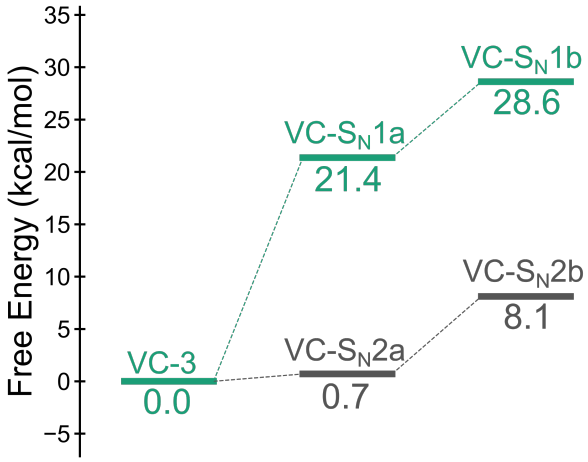


Figure S4: Reaction diagram of VC-3 structure oligomerizing with an EC via $S_N1$(green) and $S_N2$ (gray) mechanisms. The $S_N1$ and $S_N2$ states along the reaction path correspond to the stable structures in Figure 1a and 1b in the main text, respectively.

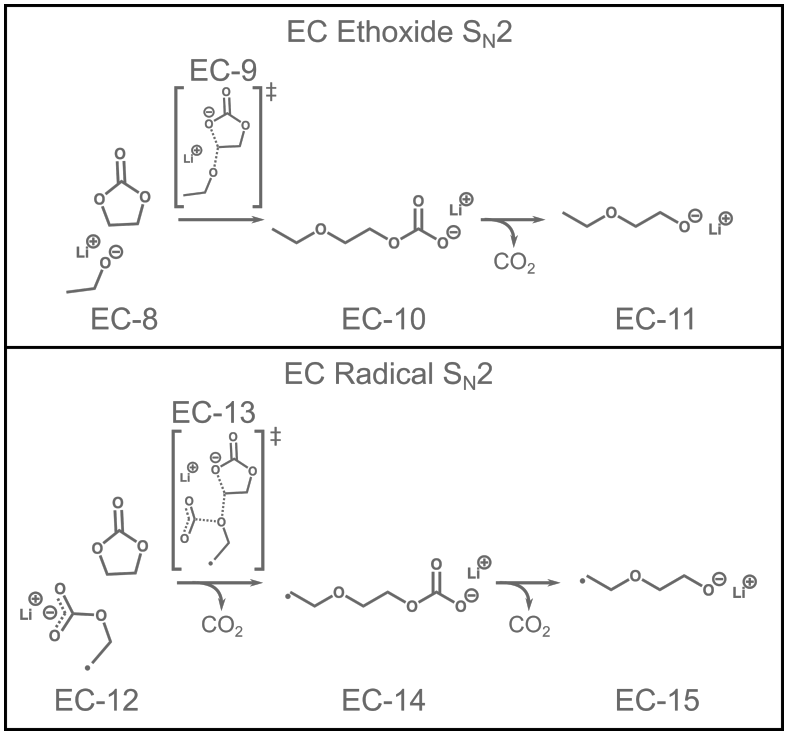


Figure S5: $S_N2$ mechanisms for EC with both ethoxide and o-EC nucleophiles.

Table S1: Transition state (TS) structures with XYZ coordinates in Å.

| TS Description | XYZ coordinates | | |
|---|---|---|---|
| Decarboxylation step during ethenolate formation in Figure 3 in main text | C | -2.36093 | -2.41900 | -3.36309 |
| | O | -3.62781 | -3.29322 | -4.80691 |
| | O | -2.00266 | -1.44127 | -3.90460 |
| | C | -3.77018 | -2.66120 | -5.94483 |
| | C | -4.51189 | -3.04148 | -7.01135 |
| | O | -2.47108 | -3.23595 | -2.52607 |
| | H | -4.54152 | -2.41746 | -7.89772 |
| | H | -3.21283 | -1.71598 | -6.01868 |
| | H | -5.08889 | -3.96265 | -7.01159 |
| | Li | -4.31786 | -4.91547 | -4.16552 |
| EC-5 in Figure 4 in main text | C | 0.85021 | -0.10891 | -0.71284 |
| | O | 1.23043 | -1.17791 | 0.09969 |
| | O | 1.80300 | 0.88689 | -0.56160 |
| | C | 2.13067 | -0.70221 | 1.10582 |
| | C | 2.32425 | 0.77991 | 0.76329 |
| | O | 0.47491 | -0.37396 | -1.88540 |
| | H | 3.05827 | -1.27506 | 1.02863 |
| | H | 1.69844 | -0.84515 | 2.09857 |
| | H | 3.37127 | 1.08391 | 0.74343 |
| | H | 1.76548 | 1.43223 | 1.43958 |
| | C | -1.61675 | -0.96110 | 0.57829 |
| | O | -0.42145 | 0.46408 | 0.17708 |
| | O | -1.65218 | -1.01618 | 1.75135 |
| | C | -1.08747 | 1.55620 | -0.45795 |
| | C | -2.12697 | 2.12636 | 0.42360 |
| | O | -1.98224 | -1.37444 | -0.48735 |
| | H | -1.52036 | 1.24335 | -1.41827 |
| | H | -0.31762 | 2.30953 | -0.69525 |
| | H | -1.96398 | 2.18962 | 1.49421 |
| | H | -2.96970 | 2.65254 | -0.01158 |
| | Li | -1.03653 | -1.33089 | -2.16835 |

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|---|---|---|---|---|
| FEC-5 in Figure 4 in main text | C | 0.85644 | -0.05395 | -0.65468 |
| | O | 1.28926 | -1.10050 | 0.13843 |
| | O | 1.72812 | 1.04181 | -0.40737 |
| | C | 2.00006 | -0.53707 | 1.23980 |
| | C | 2.56939 | 0.73457 | 0.64313 |
| | O | 0.54648 | -0.28179 | -1.84100 |
| | H | 2.77198 | -1.23331 | 1.56431 |
| | H | 1.32207 | -0.30700 | 2.06554 |
| | H | 2.68117 | 1.57582 | 1.32567 |
| | C | -1.59387 | -0.99149 | 0.45605 |
| | O | -0.48796 | 0.42485 | 0.21561 |
| | O | -1.68907 | -1.16036 | 1.62064 |
| | C | -1.17436 | 1.53194 | -0.39050 |
| | C | -2.27638 | 2.00145 | 0.47283 |
| | O | -1.92632 | -1.36908 | -0.64158 |
| | H | -1.54354 | 1.25546 | -1.38596 |
| | H | -0.42132 | 2.32174 | -0.53546 |
| | H | -2.14690 | 2.04871 | 1.54872 |
| | H | -3.14753 | 2.46682 | 0.02554 |
| | Li | -0.94586 | -1.24403 | -2.28209 |
| | F | 3.85318 | 0.48973 | 0.11702 |
| VC-5 in Figure 4 in main text | C | 0.85225 | -0.07900 | -0.65368 |
| | O | 1.24470 | -1.13477 | 0.19802 |
| | O | 1.77436 | 0.95871 | -0.43834 |
| | C | 2.14630 | -0.59621 | 1.09052 |
| | C | 2.45951 | 0.63849 | 0.71459 |
| | O | 0.52451 | -0.34550 | -1.82860 |
| | C | -1.62242 | -0.94264 | 0.54252 |
| | O | -0.46953 | 0.45882 | 0.21113 |
| | O | -1.71351 | -1.03195 | 1.71375 |
| | C | -1.13742 | 1.54939 | -0.43833 |
| | C | -2.19383 | 2.10740 | 0.42951 |
| | O | -1.95377 | -1.36669 | -0.53567 |
| | H | -1.55138 | 1.23047 | -1.40388 |
| | H | -0.36684 | 2.30576 | -0.65685 |
| | H | -2.02902 | 2.20574 | 1.49710 |
| | H | -3.06163 | 2.58081 | -0.01610 |
| | Li | -0.99608 | -1.29235 | -2.19787 |
| | H | 3.13329 | 1.37384 | 1.12390 |
| | H | 2.47889 | -1.21244 | 1.91035 |

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| EC-9 in Figure 5 in main text | O | -0.62501 | -0.76477 | -2.12132 |
| | C | 0.20318 | -0.05759 | -2.96403 |
| | C | 0.49212 | -0.79654 | -4.27217 |
| | H | 1.18901 | 0.16936 | -2.49017 |
| | H | -0.21469 | 0.94074 | -3.23187 |
| | H | 1.14989 | -0.21145 | -4.92677 |
| | C | -0.01033 | 0.51457 | 2.05209 |
| | O | -0.88041 | 1.02422 | 1.25884 |
| | O | 0.70427 | -0.49188 | 1.52998 |
| | C | -0.73758 | 0.21840 | -0.27458 |
| | C | 0.28881 | -0.79670 | 0.16937 |
| | O | 0.21093 | 0.86788 | 3.21208 |
| | H | -0.42317 | 1.08992 | -0.82868 |
| | H | -1.77306 | -0.06640 | -0.35560 |
| | H | 1.18288 | -0.76047 | -0.44845 |
| | H | -0.12175 | -1.80409 | 0.17428 |
| | Li | -0.48703 | 2.32622 | 4.27160 |
| | H | 0.97673 | -1.75849 | -4.07223 |
| | H | -0.43897 | -0.99479 | -4.81446 |
| FEC-9 in Figure 5 in main text | O | -1.00321 | 1.21907 | -0.10000 |
| | C | -0.05740 | 1.84837 | -0.90129 |
| | C | -0.06886 | 1.32644 | -2.33435 |
| | H | 0.96673 | 1.71564 | -0.49533 |
| | H | -0.22462 | 2.94327 | -0.92919 |
| | H | 0.68453 | 1.83705 | -2.94410 |
| | C | -0.12391 | 2.26754 | 4.09570 |
| | O | -1.08900 | 2.74616 | 3.40598 |
| | O | 0.57267 | 1.27475 | 3.41071 |
| | C | -0.99422 | 2.00583 | 1.76925 |
| | C | -0.07129 | 0.90825 | 2.23388 |
| | O | 0.24831 | 2.56898 | 5.21047 |
| | H | -0.57587 | 2.89148 | 1.31745 |
| | H | -2.05515 | 1.83622 | 1.71395 |
| | H | 0.68043 | 0.63173 | 1.50074 |
| | F | -0.82686 | -0.23589 | 2.50301 |
| | Li | -2.05668 | -0.27635 | -0.37622 |
| | H | 0.14597 | 0.25280 | -2.35739 |
| | H | -1.04831 | 1.48826 | -2.79636 |

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|---|---|---|---|
| EC-13 in Figure 5 in main text | C | -0.90500 | 0.12480 | -0.98772 |
| | O | -1.23626 | 1.37502 | -0.26684 |
| | O | 0.27955 | -0.04662 | -1.20371 |
| | C | -0.15117 | 2.18822 | 0.26325 |
| | C | 0.28025 | 1.75726 | 1.60890 |
| | O | -1.93795 | -0.50460 | -1.24497 |
| | H | -0.52026 | 3.21538 | 0.25687 |
| | H | 0.65591 | 2.11305 | -0.47296 |
| | H | 0.45809 | 0.70833 | 1.81474 |
| | C | -5.52389 | 1.75651 | 0.62353 |
| | O | -4.96841 | 1.89083 | -0.64404 |
| | O | -4.67331 | 1.80149 | 1.56069 |
| | C | -3.60112 | 2.27773 | -0.59591 |
| | C | -2.88148 | 1.56943 | 0.52626 |
| | O | -6.74038 | 1.59896 | 0.67655 |
| | H | -3.52633 | 3.36191 | -0.46660 |
| | H | -3.16988 | 1.99849 | -1.55526 |
| | H | -2.45704 | 2.11651 | 1.35308 |
| | H | -3.02745 | 0.50736 | 0.64534 |
| | Li | -2.21959 | -2.08214 | -2.31598 |
| | H | 0.54018 | 2.49325 | 2.35950 |
| FEC-13 in Figure 5 in main text | C | -0.64842 | 0.07917 | -0.97464 |
| | O | -1.25358 | 1.30184 | -0.35760 |
| | O | 0.56007 | 0.11534 | -1.08127 |
| | C | -0.35941 | 2.27362 | 0.25392 |
| | C | 0.00489 | 1.92265 | 1.64216 |
| | O | -1.53241 | -0.72901 | -1.26876 |
| | H | -0.87386 | 3.23547 | 0.19715 |
| | H | 0.51468 | 2.32264 | -0.40373 |
| | H | 0.31433 | 0.91331 | 1.88667 |
| | C | -5.37106 | 2.12315 | 0.92991 |
| | O | -4.63287 | 2.91859 | 0.00959 |
| | O | -4.80400 | 1.02974 | 1.19256 |
| | C | -3.59171 | 2.24246 | -0.57954 |
| | C | -2.95709 | 1.21868 | 0.33778 |
| | O | -6.41251 | 2.60922 | 1.33346 |
| | H | -2.87669 | 2.98244 | -0.93541 |
| | F | -4.06438 | 1.57347 | -1.71419 |
| | H | -2.63041 | 1.52304 | 1.32084 |
| | H | -3.03099 | 0.17088 | 0.10086 |
| | Li | -1.77632 | -2.30353 | -2.34766 |
| | H | 0.09621 | 2.69796 | 2.39262 |