Rational electrolyte design to form inorganic–polymeric

interphase on silicon-based anodes

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Experimental Methods

Electrolyte preparation: The cyclic phosphate TFEP used in this study was synthesized according to a procedure described in our previous work.¹ Battery-grade LiFSI salt, LiPF₆ salt, FEMC solvent, FEC solvent, and 1.0 M LiPF₆ in EC/DMC electrolyte were kindly provided by Guangzhou Tinci Materials Technology Co. Ltd. (Guangdong, China). TMP solvent and HFE solvent were purchased from Canrd New Energy Technology (Guangdong, China). The electrolyte was prepared by dissolving the salt in a mixture solvent of TFEP/FEMC/HFE (1:3:1 by volume) or TFEP/FEMC (1:3 by volume) at a salt-to-solvent molar ratio of 1:8 in an Arfilled glovebox. The concentrations were calculated to be 0.93 and 0.95 M, which were referred to as 0.93 M LiFSI in TFEP/FEMC/HFE and 0.95 M LiFSI in TFEP/FEMC, respectively. Commercial 1.0 M LiPF₆ in EC/DMC electrolyte (1:1 by volume) with/without the 5% FEC additive, respectively, were used as references.

Electrode preparation: The NMC622 cathode was purchased from Canrd New Energy Technology (Guangdong, China). The SiO and Si anodes with particle sizes of 1–5 um were provided by BTR New Energy Materials (Shenzhen, China) and Zhongning Silicon (Zhejiang, China). Polyamide imide (PAI, Torlon 4000T-HV) was purchased from Solvay. The NMC622 cathode was prepared by mixing NMC622 with acetylene black (AB, Li400, Denka Black) and polyvinylidene difluoride (PVDF, HSV900, Kynar) in N-methylpyrrolidone (NMP) at a weight ratio of NMC622: AB: PVdF of 80:10:10, which was then coated on an Al foil current collector using a doctor blade. The SiO or Si anode was fabricated by mixing SiO or Si with AB and PAI in NMP at a weight ratio of SiO/Si: AB: PAI of 70:15:15, of which the slurry was coated on a Cu current collector and subsequently dried in a vacuum oven at 60 °C for 2 h. The dried SiO or Si electrode was further treated at 400 °C in a tube furnace for 2 h under an Ar atmosphere to complete the imidization process for the PAI binder. The mass loadings were ~1 mg cm⁻² for both Si-based anodes except for a high mass loading test for SiO (i.e., ~3.5 mg cm⁻²), and 7–8 mg cm⁻² for the NMC622 cathode. For the full-cells, the capacity ratio of SiO: NMC622 was controlled at ~1.1.

Material characterization: The cyclic phosphate TFEP was identified using a 400 MHz NMR spectrometer (Bruker AVANCE NEO). The viscosity and density of the various electrolytes were measured using a viscometer (KF40, BROOKFIELD) and a density meter (DMA 35, Anton Paar), respectively. A Solartron 147055BEC symmetrical Pt/electrolyte/Pt cell (Solartron Analytical) was used to measure the ionic conductivities. The AC impedance spectrum was measured at a temperature range of 298 to 328 K and a frequency range of 100 mHz to 100 kHz. The Raman spectra of the solutions were collected using a QE65 Pro spectrometer (Ocean Optics) with a laser excitation wavelength of 532 nm, and the surface chemical compositions of the electrodes were analyzed using XPS (PerkinElmer PHI 1600 ESCA). The concentrations of the transition metal ions in the electrolyte were analysed by inductively coupled plasma optical emission spectrometer (ICP-OES, SPECTRO ARCOS MV). The morphologies and microstructures of the electrodes before and after electrochemical analyses were studied by SEM (TESCAN Brno, s.r.o. MAIA3) and TEM (FEI Talos F200X). The cells were disassembled in an Ar-filled glovebox, rinsed three times with DMC, and then dried under vacuum, and thus it was assumed that no residual salt or solvent remained on the surface of the electrodes. For XPS measurement, the washed electrodes were transferred from the glovebox to the XPS chamber without exposure to air. The chemical analysis of the SiO electrode was performed using electrospray ionization-quadrupole time-of-flight mass spectrometry (ESI-Q-TOF-MS, UltiMate3000-timsTOF, Bruker).

Theoretical calculations: The HOMOs and LUMOs of the solvents were calculated using DFT at the B3LYP/6-311++G(3df,2p) level of theory, and the radial distribution functions were obtained by MD simulations with the generalized AMBER force field for all chemical species. The atomic point charges were given by the RESP method with the DFT calculations at the B3LYP/cc-pvdz level of theory. The time step was set to 1 fs using the

SHAKE method, which constrains the bond distances between hydrogen atoms and heavy atoms. The sizes of the simulation cells were adjusted by NPT-MD simulations with 1 bar and 298 K (Table S3). Then, using NVT-MD simulations (298 K), the systems were equilibrated for 1 ns, followed by 10 ns production runs. The Gaussian16 and Amber16 packages were used for the DFT calculations and MD simulations, respectively.

Force filed parameters: The intermolecular interaction *V* is calculated by sum of Coulomb and 6-12 Lennard-Jones (LJ) potentials,

$$V(R_{ij}) = \frac{q_i q_j}{R_{ij}} + \varepsilon_{ij} \left[\left(\frac{r_{ij}}{R_{ij}} \right)^{12} - 2 \left(\frac{r_{ij}}{R_{ij}} \right)^6 \right].$$

Here R_{ij} represents the distance between atoms *i* and *j*, *q* is partial atomic charge, and ε_{ij} and r_{ij} are given by Lorentz–Berthelot combining rule,

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, r_{ij} = r_i + r_j$$

The partial atomic charges and LJ parameters corresponding to each atom name of electrolyte molecules and ions (Figure S28) are summarized in Tables S4-7, respectively.

Electrochemical measurements: The oxidative stability of the electrolytes was studied in a three-electrode configuration using a Pt plate as the working electrode and lithium metal as both the reference and counter electrodes via LSV analysis. Cyclic voltammetry (CV) was conducted in a two-electrode coin cell assembly with an SiO electrode as the working electrode and Li metal as the reference/counter electrode at a scan rate of 0.05 mV s⁻¹. The LSV and CV tests were conducted using a VMP3 potentiostat (BioLogic). The SiO|Li, Si|Li NMC622|Li, and SiO|NMC622 cells were assembled in 2032-type coin cells using a glass fiber separator (GC-50, Advantec) and 60 μ L of the electrolytes, the glass fiber was chosen as the separator because it has a better wettability for the electrolytes. Galvanostatic charge–discharge tests were carried out using a M340A charge–discharge tester (Wuhan Land, China). All charge–discharge tests were performed at the same C rate without using a constant voltage mode. Electrochemical impedance spectroscopy was measured for the cells after selected charge–discharge cycles with an amplitude of 5 mV within a frequency range of 10 mHz to 100 KHz.



Figure S1. Raman spectra of 0.93 M LiFSI in TFEP/FEMC/HFE and 0.95 M LiFSI in TFEP/FEMC electrolytes.



Figure S2. Oxidative stabilities of the different electrolytes in a three-electrode cell with Pt as the working electrode and Li as the counter and reference electrodes at a scan rate of 1 mV s⁻¹. It should be noted that the oxidation potentials vary depending on the conditions (e.g., electrodes, impurities, and defined current). The oxidation potential (4.4 V at 0.02 mA cm⁻²) of 1 M LiPF₆ in EC/DMC agrees with some publications²⁻³ but is lower than those reported in others⁴.

Molecule	Structure	HOMO (a.u. ^a)	LUMO (a.u.)	HOMO (eV)	LUMO (eV)
EC		-0.3102	-0.0106	-8.4405	-0.2884
DMC		-0.3008	0.0020	-8.1848	0.0554
EMC		-0.2978	0.0017	-8.1031	0.0463
FEMC		-0.3196	-0.0058	-8.6963	-0.1578
TFEP	CF ₃	-0.3120	-0.0109	-8.4895	-0.2966
HFE		-0.3534	-0.0042	-9.6160	-0.1143

 Table S1. Chemical structures and HOMO/LUMO energies of various organic solvents

^aatomic units.



Figure S3. Temperature-dependent (a) ionic conductivities and (b) viscosities of the different electrolytes.

As shown in Figure S3, 0.93 M LiFSI in TFEP/FEMC/HFE has a lower viscosity than 0.95 M LiFSI in TFEP/FEMC (5.5 versus 6.2 mPa·s at 25 °C, respectively), and a slight lower ionic conductivity (2.0 versus 2.2 mS cm⁻¹, respectively) due to the intensified Li^+ -FSI⁻ association, which is in good accord with the MD simulations (Figure 2) and Raman results (Figure S1).



Figure S4. Flammability tests for the conventional 1 M LiPF₆ in EC/DMC, 0.95 M LiFSI in TFEP/FEMC, and 0.93 M LiFSI in TFEP/FEMC/HFE. The conventional 1 M LiPF₆ in EC/DMC immediately caught fire upon ignition, and continued to burn fiercely even upon removal of the fire torch, while the 0.95 M LiFSI in TFEP/FEMC and 0.93 M LiFSI in TFEP/FEMC/HFE electrolytes did not catch fire, indicating an excellent non-flammability.



Figure S5. The first two cyclic voltammetry curves of the SiO anodes in the 1 M LiPF₆ in EC/DMC (black curve), 0.95M LiFSI in TFEP/FEMC (blue curve) and 0.93 M LiFSI in TFEP/FEMC/HFE (read curve) electrolytes at a scan rate of 0.1 mV s⁻¹. The corresponding dashed and solid lines represent the 1st and 2nd cycles, respectively.



Figure S6. The first charge-discharge curves of the SiO|Li half-cells using 1 M LiPF₆ in EC/DMC (black curve), 0.95 M LiFSI in TFEP/FEMC (blue curve) and 0.93 M LiFSI in TFEP/FEMC/HFE (red curve) at a 0.05 C.



Figure S7. Selected charge-discharge curves for the SiO|Li half-cells at a rate of 0.2C in 0.95 M LiFSI in TFEP/FEMC after three formation cycles at a rate of 0.05C. All tests were conducted at 25 °C. A rate of 1 C corresponds to 1600 mA g^{-1} on the weight basis of the SiO electrode.



Figure S8. Cycling performance of the SiO|Li half-cells using 0.93 M LiFSI in TFEP/FEMC/HFE, conventional 1 M LiPF₆ in EC/DMC and with the 5 vol.% FEC additive at a rate of 0.2 C. All tests were conducted at 25 °C after three formation cycles at 0.05 C. 1 C rate corresponds to 1600 mA g^{-1} on the weight basis of the SiO active material.



Figure S9. Rate performance of the SiO|Li half-cells using 0.93 M LiFSI in TFEP/FEMC/HFE and conventional 1 M LiPF₆ in EC/DMC.



Figure S10. SEM images of (a) the pristine SiO electrode and the electrodes after cycling in (b) 1 M LiPF₆ in EC/DMC, (c) 0.95 M LiFSI in TFEP/FEMC, and (d) 0.93 M LiFSI in TFEP/FEMC/HFE for 100 cycles. The white scale bar represents 3 μ m.



Figure S11. TEM images and corresponding EDS mapping images of the SiO electrodes after cycling in (a) 1 M LiPF₆ in EC/DMC and (b) 0.93 M LiFSI in TFEP/FEMC/HFE for 100 cycles. The white scale bar represents 500 nm.



Figure S12. ESI-Q-TOF-MS spectra collected from the pristine SiO electrode and the SiO electrode after cycling in 0.93 M LiFSI in TFEP/FEMC/HFE for 100 cycles.

To verify the SEI compounds, chemical analysis using electrospray ionization-quadrupole time-of-flight mass spectrometry (ESI-Q-TOF-MS) was performed on the SiO anode recovered from cell after 100 cycles. The cells were disassembled in an Ar-filled glovebox, rinsed three times in 3.0 ml of DMC very carefully (1 min each time), and then dried under vacuum, and thus it was assumed that no residual salt or solvent remained on the surface of the electrodes. The SiO was scraped from the Cu current collector and soaked in acetonitrile (AN), thereafter the formed SEI was dissolved from the SiO surface under sonication for at least 6 h.

As shown in Figure S11, in addition to the 3 peaks detected in AN solution collected from the pristine SiO electrode (could be assigned to the species of PAI binder), there are multi peaks can be detected for the SEI of the SiO electrode after cycling in 0.93 M LiFSI in TFEP/FEMC/HFE for 100 cycles. We are able to identify the chemical formula and speculate the chemical structure for the 7 peaks with a m/z < 500, and the results are summarized in Table S1. As can be seen, phosphate oligomer species ($C_2H_4O_4P^-$, $C_6H_8F_6O_8P_2^{2-}$, $C_4H_7F_3O_5P^-$, $C_9H_{15}F_6O_{12}P_3^{2-}$, $C_6H_8F_6O_5P^-$, $C_6H_{10}F_3O_8P^{2-}$, $C_8H_{10}F_9O_8P^{2-}$) are identified. For the peaks with a m/z > 500, they are most likely related to P-containing oligomers or polymers.

Based on these ESI-Q-TOF-MS data, we can draw the conclusion that P-containing oligomers or polymers (i.e., polyphosphoesters) do exist on the surface of SiO anode. which indicates TFEP solvent was reduced to form polymeric SEI on the surface of SiO anode.

Peak	m/z	Formula	Structure
1	122.985	$C_2H_4O_4P^-$	
2	191.981	$C_6H_8F_6O_8P_2{}^{2-}$	CF_{3} O P CF_{3} CF_{3}
3	222.998	$C_4H_7F_3O_5P^-$	
4	260.984	$C_9H_{15}F_6O_{12}P_3^{2-}$	$CF_3 \qquad 0 \qquad $
5	305.001	$C_6H_8F_6O_5P^-$	-0 0 P -0 CF_3 CF_3 CF_3
6	328.980	$C_6H_{10}F_3O_8P^{2-}$	$ \begin{array}{c} 0 \\ 1 \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ -$
7	466.971	$C_8H_{10}F_9O_8P^{2-}$	CF_{3} CF_{3} CF_{3} CF_{3} CF_{3}

 Table S2. ESI-Q-TOF-MS results collected from SiO electrode after 100 cycles.



Figure S13. Electrochemical impedance spectra of SiO|Li half-cells using different electrolytes after different charge-discharge cycles. The impedance spectra were collected at the fully dilithiated state.



Figure S14. Cycling performance of the SiO|Li half-cells using LiFSI in TMP/FEMC/HFE (i.e., 1.01 M) and LiFSI in TFEP/FEMC/HFE (i.e., 0.93 M) electrolytes, both electrolytes have an identical salt-to-solvent molar ratio of 1:8.



Figure S15. Cycling performance of the SiO|Li half-cells using LiPF₆ in TFEP/FEMC/HFE (i.e., 0.96 M) and LiFSI in TFEP/FEMC/HFE (i.e., 0.93 M) electrolytes, both electrolytes have an identical salt-to-solvent molar ratio of 1:8.



Figure S16. Cycling performance of the SiO|Li half-cells using 0.93 M LiFSI in TFEP/FEMC/HFE and conventional 1 M LiPF₆ in EC/DMC at a rate of 0.2 C with a high SiO mass loading of ~3.5 mg cm⁻².



Figure S17. Cycling performance of the Si|Li half-cells using 0.93 M LiFSI in TFEP/FEMC/HFE, conventional 1 M LiPF₆ in EC/DMC and with the 5 vol.% FEC additive at a rate of 0.2 C. All tests were conducted at 25 °C after three formation cycles at 0.05 C. 1 C rate corresponds to 3579 mA g^{-1} on the weight basis of the Si active material.



Figure S18. High resolution C 1s, F 1s, O 1s, P 2p and S 2p XPS spectra for the SiO electrode cycled in 0.93 M LiFSI in TFEP/FEMC/HFE (top red row), 0.95 M LiFSI in TFEP/FEMC (middle blue row), and the conventional 1 M LiPF₆ in EC/DMC (bottom black row) for 100 cycles.



Figure S19. Cycling performances of the NMC622|Li half-cells using 0.93 M LiFSI in TFEP/FEMC/HFE, 0.95 M LiFSI in TFEP/FEMC and 1 M LiPF₆ in EC/DMC. The tests were conducted at a rate of 0.4 C after three formation cycles at a rate of 0.1 C with a cut-off voltage of 3.0-4.6 V at 25 °C. The 1 C rate corresponds to 200 mA g⁻¹ on the weight basis of the NMC622 electrode.



Figure S20. Selected charge-discharge curves at different cycles for the NMC622|Li half-cells using (a) the conventional 1 M LiPF₆ in EC/DMC, (b) 0.95 M LiFSI in TFEP/FEMC and (c) 0.93 M LiFSI in TFEP/FEMC/HFE.



Figure S21. The first charge-discharge curves of the SiO|NMC622 full-cells using 1 M LiPF₆ in EC/DMC (black curve), 0.95 M LiFSI in TFEP/FEMC (blue curve) and 0.93 M LiFSI in TFEP/FEMC/HFE (red curve) at 0.1 C.



Figure S22. Cycling performance of the SiO|NMC622 full-cells using 0.95 M LiFSI in TFEP/FEMC at 0.4 C after three formation cycles at 0.1 C. A rate of 1 C corresponds to 200 mA g^{-1} on the weight basis of the NMC622 cathode.



Figure S23. Selected charge-discharge curves for the SiO|NMC622 full-cells at a rate of 0.4 C in 0.95 M LiFSI in TFEP/FEMC after three formation cycles at 0.1 C. A rate of 1 C corresponds to 200 mA g^{-1} on the weight basis of the NMC622 cathode.



Figure S24. High resolution C 1s, F 1s, O 1s, P 2p, N 1s, S 2p, Ni 2p and Co 2p XPS spectra for the SiO anode from SiO|NMC622 full-cell cycled in 0.93 M LiFSI in TFEP/FEMC/HFE (top red row) and the conventional 1 M LiPF₆ in EC/DMC (bottom black row) for 100 cycles.



Figure S25. Transition metal ion (TM) concentrations in the electrolytes of the SiO|NMC622 cells after 100 cycles measured by ICP-OES.

The concentrations of the transition metal ions in the electrolyte were further analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). As shown in Figure S25, after 100 cycles, the concentrations of Ni, Co, and Mn in 0.93 M LiFSI in TFEP/FEMC/HFE were only 1/27, 1/10 and 1/9, respectively, to those in the reference electrolyte, clearly validating its superiority in suppressing transition metal dissolution.



Figure S26. High resolution C 1s, F 1s, O 1s and P 2p XPS spectra for the NMC622 from SiO|NMC622 full-cell cycled in 0.93 M LiFSI in TFEP/FEMC/HFE (top red row) and the conventional 1 M LiPF₆ in EC/DMC (bottom black row) for 100 cycles.

XPS was then employed to study the chemical composition of the NMC622 surface after cycled in SiO|NMC622 full cells for 100 cycles. Specifically, the characterized peaks corresponding to CF₃ were observed in both C 1s and F 1s spectra for the NMC622 cycled using 0.93 M LiFSI in TFEP/FEMC/HFE (Figure S14). Furthermore, as shown in the O 1s spectra, the intensity of the peak corresponding to the lattice-oxygen (MO) bonds in the NMC622 cathode is significantly lower comparing to that of cycling in 1 M LiPF₆ in EC/DMC, thereby providing the evidence for the formation of the passivation layer. In addition, the P-O peak at 533.5 eV observed in the O 1s spectra in addition to an obvious phosphate peak in the P 2p spectra demonstrates that TFEP did indeed decompose to form a polyphosphoester-based CEI.



Figure S27. Schematic illustrations of the ring-opening polymerization of TFEP for formation of the cathode electrolyte interphase (CEI) on the surface of NMC622 cathode.

Based on our experimental results and previous publications^{1, 5}, we propose the following CEI formation mechanism. The phosphorus center of the cyclic phosphate was first underwent nucleophilic attack by oxygen atoms on the M-O rich surface (Figure S15), the subsequent proton transfer then initiates the polymerization of TFEP via a ring-opening reaction, which leads to the formation of polyphosphoesters on the NMC surface.

ElectrolyteCompositionSimulation ell size0.95 M LiFSI in
TFEP/FEMC60LiFSI, 114TFEP, 366FEMC $46.85 \text{ Å} \times 46.85 \text{ Å} \times 46.85 \text{ Å}$ 0.93 M LiFSI in
TFEP/FEMC/HFE60LiFSI, 95TFEP, 304FEMC,
82HFE $47.69 \text{ Å} \times 47.69 \text{ Å} \times 47.69 \text{ Å}$

Table S3. Compositions and simulation cell sizes for MD simulations.



Figure S28. Structures and atom names of electrolyte molecules and ions used in MD simulations.

atom name	ε [kcal/mol]	<i>r</i> [Å]	charge [e]
P1	0.200	2.100	0.991
O1	0.210	1.661	-0.519
02, 03	0.170	1.684	-0.357
O4	0.170	1.684	-0.311
C1, C2	0.109	1.910	0.045
C3	0.109	1.910	-0.092
C4	0.109	1.910	0.538
F1, F2, F3	0.061	1.750	-0.182
H1, H2, H3, H4	0.016	1.387	0.081
H5, H6	0.016	1.387	0.119

Table S4. Lennard-Jones parameters and partial atomic charges of TFEP.

atom name	ε [kcal/mol]	r [Å]	charge [e]
01	0.210	1.661	-0.542
02, 03	0.170	1.684	-0.378
C1	0.109	1.910	0.906
C2	0.109	1.910	0.019
C3	0.109	1.910	0.017
C4	0.109	1.910	0.541
F1, F2, F3	0.061	1.750	-0.182
H1, H2, H3	0.016	1.387	0.070
H4, H5	0.016	1.387	0.076

Table S5. Lennard-Jones parameters and partial atomic charges of FEMC.

atom name	ε [kcal/mol]	r [Å]	charge [e]
01	0.170	1.684	-0.365
C1	0.109	1.910	-0.059
C2	0.109	1.910	0.555
C3	0.109	1.910	-0.080
C4	0.109	1.910	0.651
C5	0.109	1.910	0.049
H1, H2	0.016	1.387	0.088
F1, F2	0.061	1.750	-0.192
F3, F4	0.061	1.750	-0.029
F5, F6	0.061	1.750	-0.206
F7, F8	0.061	1.750	-0.036

 Table S6.
 Lennard-Jones parameters and partial atomic charges of HFE.

atom name	ε [kcal/mol]	<i>r</i> [Å]	charge [e]
N1	0.170	1.824	-0.595
S1, S2	0.250	2.000	1.048
01, 02, 03, 04	0.210	1.661	-0.490
F1, F2	0.061	1.750	-0.271
Li ⁺	0.018	1.137	1.000

 Table S7. Lennard-Jones parameters and partial atomic charges of LiFSI.

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