

Supporting Information:

Fluoroethylene Carbonate as a Directing Agent in Amorphous Silicon Anodes - Electrolyte Interface Structure Probed by Sum Frequency Vibrational Spectroscopy and Ab-initio Molecular Dynamics

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Sum Frequency Generation Vibrational Spectroscopy – fitting model

The operational principle of SFG vibrational spectroscopy (SFGVS) technique relies on a second-order nonlinear optical process which involves the mixing of an infrared (ω_{IR}) and visible light (ω_{VIS}) to produce light at frequency which is the sum of the two: $\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{VIS}}$. Figure S1 shows an energy level diagram and an illustration of an optical transition for SFGVS, as well as a schematic representation of the experimental setup for SFGVS. Basically, two laser beams are spatially and temporally overlapped on a sample's surface and their SFG signal is reflected to a photon multiplier tube (PMT).

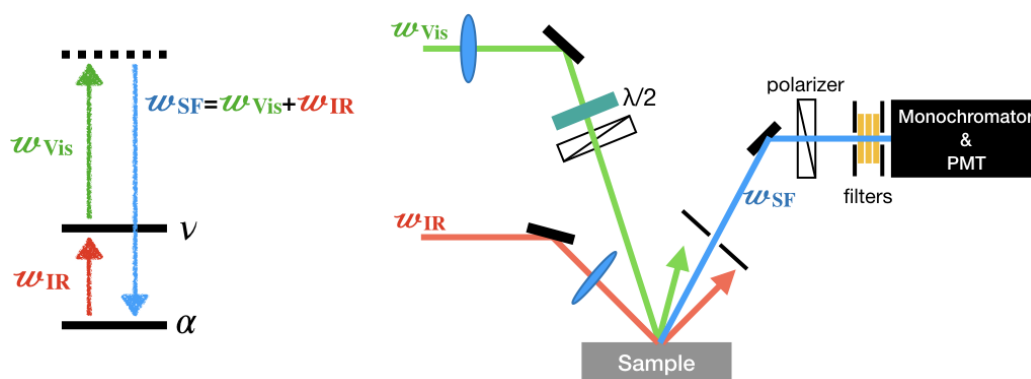


Figure S1. *Left* - an energy level diagram and optical transition for SFGVS. *Right* - a schematic of SFGVS system, which probes the vibrational signatures of adsorbed species on the surface.

For a vibrational mode to be SFG active it must be both IR and Raman active. Although, this is forbidden in a media with an inversion symmetry (e.g., bulk, rule of mutual exclusion) under the electric-dipole (ED) approximation, SFG is allowed at surfaces or interfaces where the inversion symmetry is essentially broken. Hence, SFG is highly surface specific except for specific cases in which an additional electric field generated by an external source exists in the bulk. As described elsewhere in detail,¹ the SFG output intensity, can be described by the following equation:

$$S_{SFG} \propto \left| \left[\vec{L}(\omega_{SFG}) \cdot \hat{e}_{SFG} \right] \cdot \vec{\chi}_s^{(2)} : \left[\hat{e}_{VIS} \cdot \vec{L}(\omega_{VIS}) \right] \left[\hat{e}_{IR} \cdot \vec{L}(\omega_{IR}) \right] \right|^2 I_{vis} I_{IR} = \left| \vec{\chi}_{eff}^{(2)} \right|^2 I_{vis} I_{IR} \quad (1)$$

Where I_{VIS} and I_{IR} are the input beam intensities at ω_{VIS} and ω_{IR} . $\vec{L}(\omega_i)$ and \hat{e}_i denote the Fresnel transmission coefficient tensor and unit polarization vector at ω_i respectively. Local field factors can be calculated based on angles and polarizations of beams, refractive index of the medium, etc. In the present SFG measurement, SFG spectrum of z-cut quartz at the same experimental setup was used to normalize the SFG spectrum of sample. The SFG data has to be processed so that we can deduce the surface nonlinear susceptibility, $\left| \vec{\chi}_s^{(2)} \right|$ from the SFG signal amplitude. We first remove geometric factors and Fresnel coefficients, and so find the signal's amplitude. This gives us, $\left| \vec{\chi}_s^{(2)} \right|$ that in turn leads to the information of the adsorbate's molecular structure such as orientation and ordering.²

The surface nonlinear susceptibility can be expressed as:

$$\vec{\chi}_{s,ijk}^{(2)} = \vec{\chi}_{NR}^{(2)} + \sum_q \frac{A_{q,ijk}}{\omega_{IR} - \omega_q + i\Gamma_q} \quad (2)$$

$\vec{\chi}_{NR}^{(2)}$ denotes the nonresonant contribution and $A_{q,ijk}$ is the amplitude of the q^{th} vibrational mode at frequency ω_q with damping constant Γ_q .

The basic idea of using SFG vibrational spectroscopy to study the C=O stretching mode from the ethylene carbonate (EC) or fluoroethylene carbonate (FEC) a-Si anode surface is quite straightforward. The C=O stretching mode can be regarded as $C_{\infty v}$ symmetry group on an azimuthally isotropic surface because of the polycrystalline domain structure. In the present SFG measurement with the SSP and SPS polarization combinations, $\chi_{ijk}^{(2)}$ can be reduced to non-zero component $\chi_{yyz}^{(2)} = \chi_{xxz}^{(2)}$ and $\chi_{yzy}^{(2)} = \chi_{xzx}^{(2)}$ respectively, where $\chi_{ijk}^{(2)} = N_s \sum_{abc} \langle (\hat{i} \cdot \hat{a})(\hat{j} \cdot \hat{b})(\hat{k} \cdot$

$\hat{c})\rangle \alpha_{abc}^{(2)}$. a, b and c represent the molecular coordinates as described in Figure 2S, $\alpha_{abc}^{(2)}$ is the molecular hyperpolarizability and is related to the infrared dipole and Raman polarizability of a vibrational mode. We consider the Z axis to be along the surface normal and the X and Y axis, to lie in parallel to the surface. For the stretching mode of C=O,

$$x_{yyz}^{(2)} = \frac{1}{2} N_s \alpha_{ccc} [\langle \cos \theta \rangle (1 + R) - \langle \cos^3 \theta \rangle (1 - R)] \quad (3)$$

$$x_{yzy}^{(2)} = -\frac{1}{2} N_s \alpha_{ccc} [\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle] (1 - R) \quad (4)$$

with θ denoting the tilt angle of C=O with respect to the z-axis. R is hyperpolarizability ratio of α_{acc} and α_{ccc} , R was adopted as 0.16 in the present work. The angle brackets represent the ensemble average over $f(\theta)$, the polar orientation distribution of the C=O bonds in the tilt angle θ ($0 \leq \theta \leq \pi/2$) from the surface normal. From the normalized intensity ratio deduced from the ssp and sps spectra, the average θ can be determined.

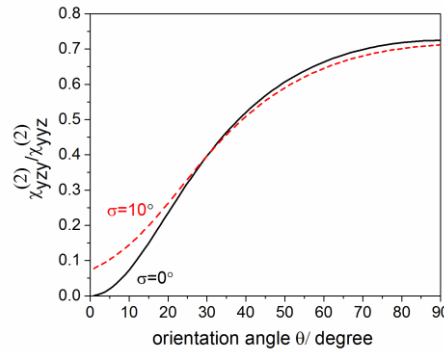
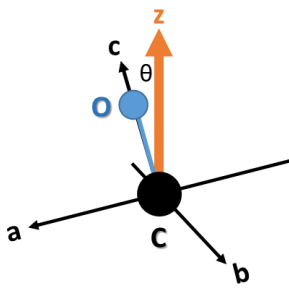


Figure S2.
Left: The molecular coordinates of a carbonyl (C=O) group. Right:

ratio of $x_{yzy}^{(2)}$ to $x_{yyz}^{(2)}$ in regards to average angle θ . Black and red lines are for the ratio of $x_{yzy}^{(2)}$ to $x_{yyz}^{(2)}$ which is calculated with Gaussian distribution function and angle distribution of 0 and 10 degree, respectively.

In our study, we normalized the raw SFG spectra that was acquired after 10 consecutive scans, with a 2.5 wavenumber step and 200 shots per step with a reference SFG spectra taken with a Z-cut quartz sample under the same experimental configuration. In Figure S3, we show one example of our raw SFG spectra of EC / FEC: 8:2 (20% FEC, *wt/wt* ratio) mixture under SSP polarization combination. The standard deviation is displayed as the gray bars.

In order to validate our SFG peak assignment we carried out model fitting that is expressed in Eq. S2. We assume, based on previous and current experimental data and published work that our amorphous silicon has a constant isotropic background. The peak assignments as well as their amplitude and line width are list in Table S1.

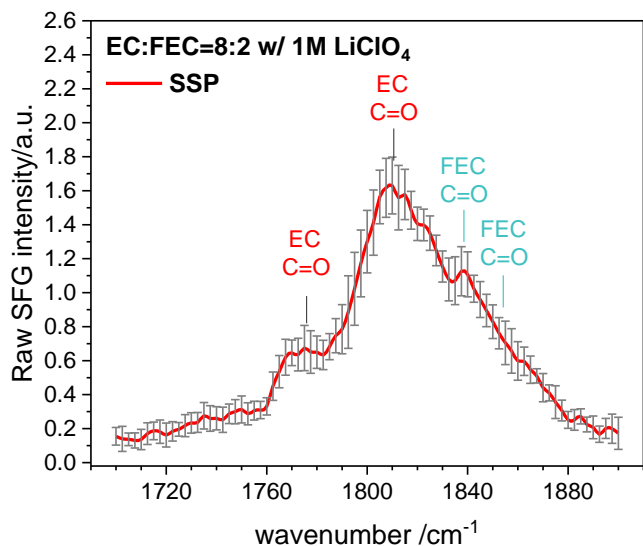


Figure S3. One example of raw SFG spectra of mixtures in *wt/wt* ratio of EC / FEC: 8:2 (20 wt % FEC) under SSP polarization combination. The gray bars represent the standard deviation.

Table S1. Physical properties (peak frequency, amplitude and width) derived from SFG spectra at SSP and SPS polarizations.

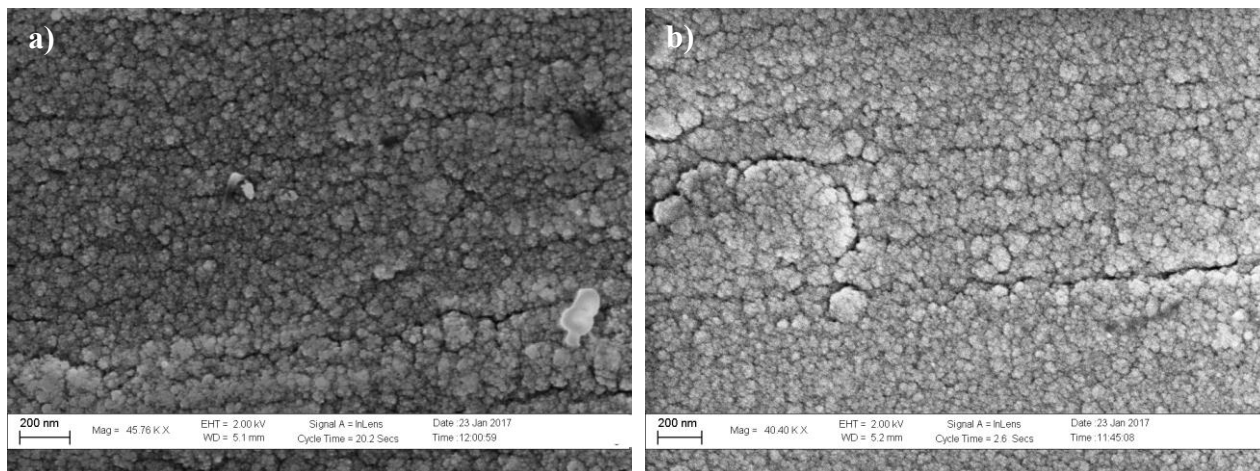
			EC	20 wt % FEC	30 wt % FEC	50 wt % FEC	FEC
SSP	C=O ^a	Amp	1.8	0.8	1.2	2.0	
		Freq	1778	1773	1781	1792	
		width	10	6	7	8	
	C=O ^b	Amp	2.1	18.5	14.2	21.1	
		Freq	1814	1813	1814	1823	
		width	12	18	20	22	
	C=O ^c	Amp		17.0	6.4	3.0	-0.5
		Freq		1839	1837	1845	1827
		width		17	17	8	6
	C=O ^d	Amp		2.5	2.7	8.4	9.3
		Freq		1857	1855	1860	1862
		width		11	14	13	18
SPS	C=O ^a	Amp	1.0	0.7	-0.1	0.0	
		Freq	1779	1777	1781	1782	
		width	8	10	11	8	
	C=O ^b	Amp	5.9	2.6	-2.0	0.2	
		Freq	1815	1811	1814	1823	
		width	14	20	19	10	
	C=O ^c	Amp		0.7	-1.3	0.0	-0.9
		Freq		1838	1837	1840	1840
		width		20	20	8	22
	C=O ^d	Amp		-0.1	0.4	0.1	0.9
		Freq		1852	1855	1860	1857
		width		12	22	13	6

a, b, c, d used to assign peaks in SFG spectra.

Scanning electron microscopy (SEM)

In Figure S3 we compare ex situ SEM scans of amorphous silicon substrates held under inert conditions or in contact (soaked) with an electrolyte solution. The soaked sample was rinsed in dimethyl ether (DME) before it was scanned. The reduction of the electrolyte to form the SEI will result in different surface morphology.^{3, 4} The samples were attached by short copper foils to an in-house built sample holder in order to ensure electric conductivity. The scanning properties used in the Zeiss Gemini Ultra-55 Analytical Field Emission Scanning Electron Microscope (SEM) are noted in Figure S3a-b.

In Figure S3a we show the scan of an a-Si anode that was held under inert atmosphere. In Figure S3b we present the scan of an a-Si anode that was soaked in 1M LiClO₄:EC:FEC 7:3 (w/w) solution for a week. The SEM scans show that no change occurred in the



soaked a-Si.

Figure S4. Ex situ SEM scans of: a) Pristine a-Si anode held under inert conditions b) Soaked a-Si anode that was in contact with 1M LiClO₄:EC:FEC 7:3 (w/w) solution for a week.

Atomic force microscopy (AFM) of a-Si anode surface

In order to verify that no SFG signal arises from the a-Si substrate we have carried out ex situ AFM (Asylum MFP-3D Atomic Force Microscope) measurements in tapping mode on two a-Si samples (kindly refer to Figure S4a,b). The first was an anode that was not in contact with the

electrolyte solution and the second was an anode that we frequently used in our open circuit potential experiments. We have calculated⁵ the surface roughness (RMS) and average height of these a-Si anodes. In the case of the clean a-Si the roughness is 2.878 and the average height is 7.046 nm. For the a-Si anode used in our OCP experiments the roughness is 6.094 and the average height is 15.11 nm. The height distributions are presented in Figure S4c,d.

Our conclusion from these AFM scans is that the a-Si anode does not have any features in the SFG spectra.

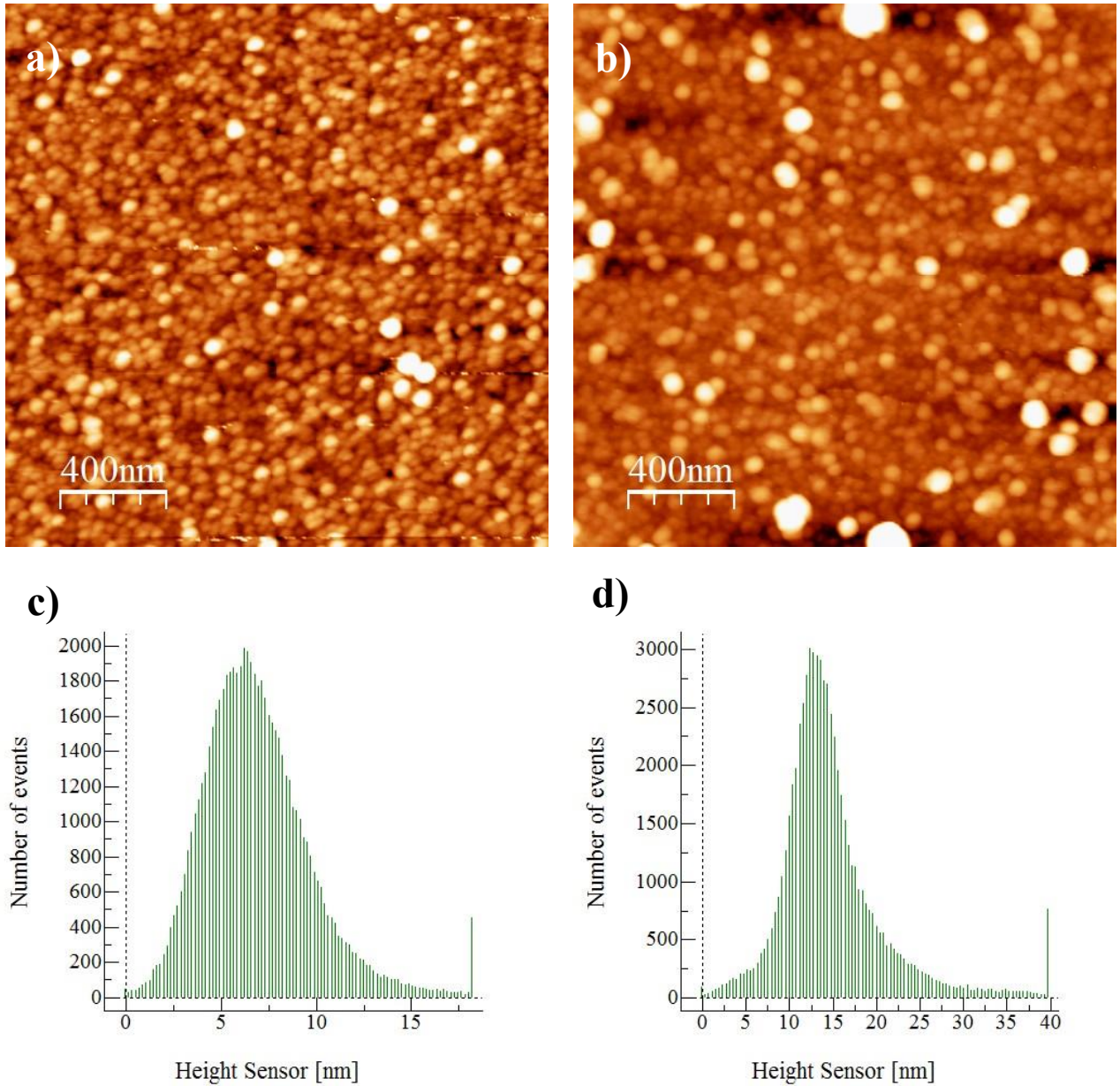


Figure S5. AFM scans ($2 \times 2 \mu\text{m}^2$) of two a-Si anodes, the unused (a) and after being in contact with 1M LiClO₄:EC:FEC 7:3 (w/w) solution for a week at open circuit potential conditions (b). The corresponding height distribution histograms of the unused a-Si (c) and used (d).

X-ray photoelectron spectroscopy (XPS)

We have carried out ex situ XPS (PHI 5400 X-ray Photoelectron Spectroscopy System) with a conventional (non-monochromatic) Al X-ray source ($K\alpha = 1486.7 \text{ eV}$) operated at 350 W. We carried out the XPS scans in order to verify that no lithium alloying took place as well as possible fluoroethylene carbonate dissociation at open circuit potential (no applied potential) conditions after seven days in contact with the amorphous silicon anode. The samples were attached to a home built sample holder by conductive carbon tape. For each sample: pristine, soaked for a week and cycled 10 times (2.8 V to 0.1 V at 0.1 mV/sec), we have scanned for fluorine (F 1s) and lithium (Li 1s), as well as for silicon (Si 2p). After which, we have divided the F 1s and Li 1s spectra from each sample with its corresponding Si 2p area. By dividing each element spectra with the substrate's background, we can assume abundance of Li and F on each sample's surface. Only after cycling did we notice a peak for fluorine at about 685 eV and another for lithium at 55.6 eV both associated with the compound LiF.^{3, 6}

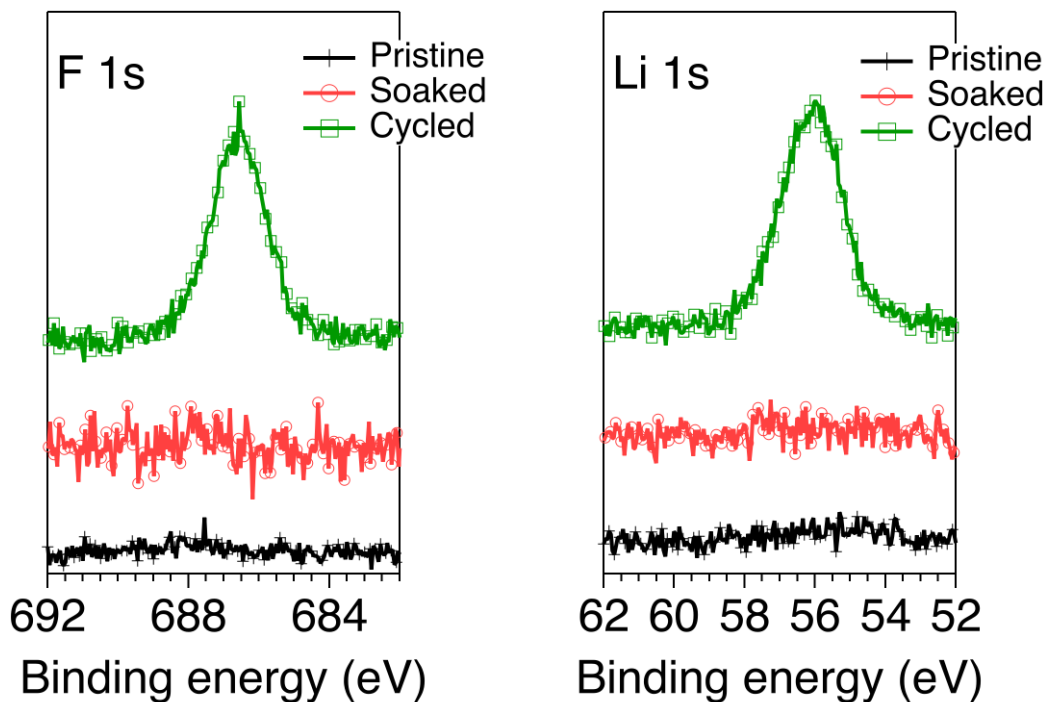


Figure S6. XPS scans of fluorine (F 1s) and lithium (Li 1s) from the three sample silicon anodes: pristine, soaked for a week and cycled 10 times. The spectra were divided by their corresponding silicon (Si 2p) area.

Ab-initio molecular dynamics simulations of time evolution of Si-O and C-O bonds

In the pure FEC model, after 50 ps of simulation time three FEC molecules are adsorbed at the surface. A fourth FEC molecule is not yet adsorbed at the surface but it is close and most likely as the system evolves it will adsorb at the surface. The Si-O bond distance of the FEC molecule that gets closer to the a-Si fluctuates between 2.78 and 6.60 Å, and on average this distance is 4.08 Å

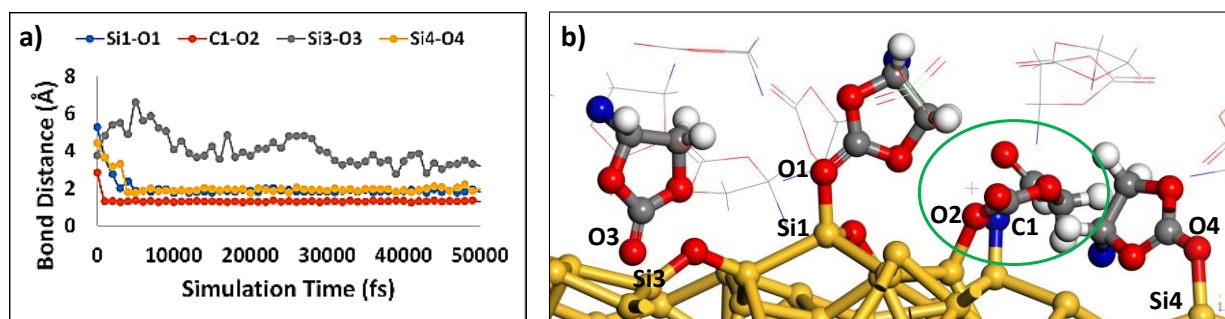


Figure S7. a) Time evolution of Si-O and C-O bonds involved in the FEC adsorption at the a-Si surface for the pure FEC model and b) snapshot at the 50 ps frame showing the adsorption and position of FEC relative to the a-Si slab. The decomposed FEC molecule is shown within a green ellipse. The color code is as follows: yellow, red, gray, white and dark blue spheres represent Si, O, C, H and F atoms, respectively. For clarity, some solvents are removed from the snapshots and solvents and salt not interacting with the Si surface are shown in a line display style.

A note on the effect of silicon oxygen (SiO_x) composition on EC and FEC adsorption

Indeed, all silicon surfaces are reactive with oxygen and form silicon oxides (SiO_x). Yet, the exact composition of the SiO_x is dependent on the synthesis conditions. Moreover, the role of the silicon oxide in active material performance is still poorly understood, with many conflicting accounts in the literature.⁷ To add the effect of oxygen, we simulated surfaces of composition SiO_{0.09}. One may speculate that the presence of oxygen atoms would have a repulsive effect on the solvent molecules. However, this is not the case as shown by the adsorption of solvent evidenced also by the SFG results. So, even if there is a higher O concentration on the surface, the molecules should attach forming O-Si bonds as shown by the AIMD simulations. To test this, we ran an AIMD simulation for the pure FEC (1 M LiClO₄) model in contact with a SiO₂ (001) surface slab as shown in the figure below. After 2.8 ps of simulation time, one FEC molecule is adsorbed at the SiO₂ (001) surface slab via its O atom of the CO group. The Si-O bond length (2.07 Å) is comparable to the Si-O bond distances found in the amorphous Si models. Therefore,

we conclude that the amount of O content at the surface of the amorphous Si slab will not change the adsorption mode of the solvent molecules.

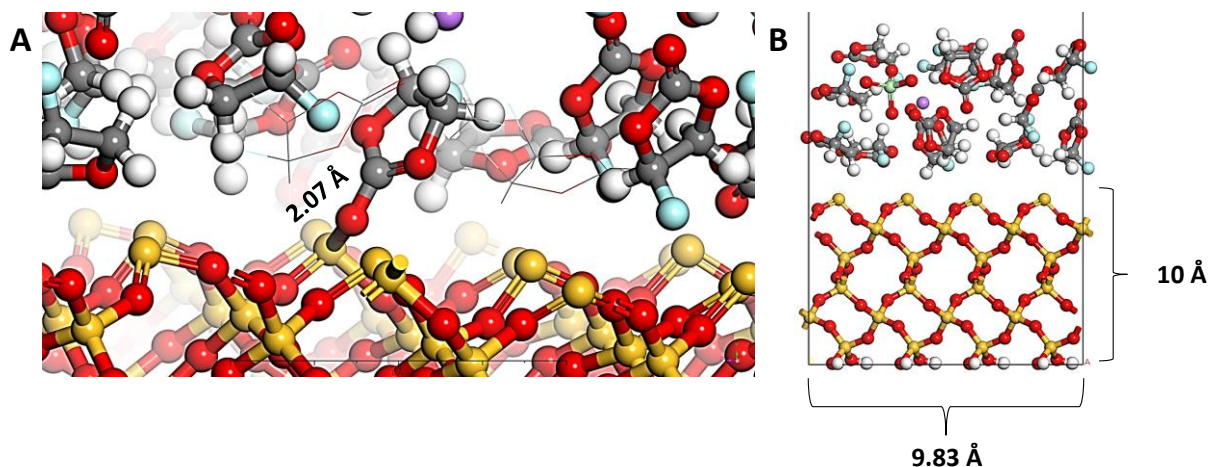


Figure S8. Panel A shows a snapshot at 2.8 ps of simulation time of the pure FEC model. The FEC molecules are in contact with a SiO₂ (001) surface slab. Panel A shows one adsorbed FEC molecule at the SiO₂ surface via its O atom of the carbonyl group. The adsorption results in a Si-O bond with a 2.07 Å distance that is comparable to the amorphous Si models. Panel B shows the initial configuration for the model. Here, a 1 M LiClO₄ salt is dissolved in the FEC solvent. H atoms passivate the bottom O atoms and all atoms were allowed to move during the simulation. For clarity, solvent molecules near the adsorbed FEC are shown in a line display style. Color code is as follows: white, red, yellow, light blue, purple, green and grey spheres represent H, O, Si, F, Li, Cl and C atoms, respectively.

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