Supporting Information

Direct *Operando* **Observation of Double Layer Charging and Early SEI Formation in Li-Ion Battery Electrolytes**

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S1. Experimental details

Raman measurements and *operando* **SERS.** All chemicals were stored and manipulated inside an argon filled MBRAUN glovebox. LP40 electrolyte was purchased from Sigma-Aldrich (14 ppm H₂O as determined by Karl Fischer Titration). The Au SERS substrates were purchased from Silmeco company. The *operando* measurements were performed in a custom-made spectroelectrochemical cell (figure S1). The cell was assembled in the coin cell configuration with an Au SERS substrate as the working electrode, two glass fibre separators soaked with 200 μ L of LP40 electrolyte and a lithium foil as the counter electrode. An additional glass fibre separator with a hole in the middle, surrounding the Au SERS substrate, was employed in order to ensure the electrolyte mass transport to the substrate gold side. The laser beam hits the Au substrate from the back side of the cell, that is opposite to the counter electrode. This configuration certainly results in a more complex mass transport phenomena and an increased overall cell IR drop, which is however a very common issue for the most spectroelectrochemical cells and is acceptable for the model systems studies. In order to compensate for the backward cell configuration, the induced electrode potential changes were performed at a slow rate to leave time for ion transport.

Electrochemical measurements were performed with a portable Biologic SP-240 potentiostat.

Raman measurement were performed on a Renishaw Raman spectrometer using 785 nm laser, 1200 grating, 50x lens magnification, 0.5% laser power with 100 s acquisition time.



Figure S1. Cross section schematic representation of the custom-made *operando* Raman spectroelectrochemical cell: 1) PTFE O-ring; 2) stainless steel mesh; 3) working electrode (SERS substrate); 4) glass fiber separator; 5) counter electrode (lithium foil); 6) insulating cylinder 7) HDPE ring.

EQCM. The solid electrolyte interphase mass change on a gold electrode was captured by EQCM. General information about the experimental setup and procedure are described elsewhere¹. Here, a 5 MHz gold coated QCM-sensor (Biolin Scientific AB, Sweden) was polarized versus a Li metal counter electrode between 3.0 and 0.5 V vs. Li⁺/Li with 0.1 mV/s scan rate in LP40 electrolyte (1 M LiPF₆ in EC: DEC 1:1), using glass fibre separator. The sensor resonance frequency and dissipation of the 1st to 13th odd harmonic overtone where simultaneously captured by the Q-Sense E1 module (Biolin Scientific AB). Relatively low dissipation values and overlapping normalized resonance frequency curves indicate the formation of a homogeneous and rigid interphase during the experiment. Therefore, the SEI mass is calculated by the Sauerbrey equation. The interphase forming mechanisms is analysed by calculating the gold electrode mass change per mole of electrons transferred (mpe-value).

OEMS. The online electrochemical mass spectrometry (OEMS) system consists of a 316L steel custom-made semi-closed electrochemical cell with headspace sampling. The temperature and pressure in the cell are monitored using a high precision pressure transducer (Keller-Druck). The electrochemical cell is connected to a mass spectrometer (Pfeiffer PrismaPlus QME220) via an injection system and fused silica capillary tube (Trajan). The mass spectrometer is calibrated using calibration gasses. The mass spectrometer injection system consists of miniature high-speed pressure valves (series 99, Parker) and Swagelok VCR connections for leak-proof connections. The injection system with Ar gas and vacuum pumping (ACP15 root pump, Pfeiffer) before each measurement. Every 10 minutes the headspace of the electrochemical cell is sampled while simultaneously refilled with pure Ar (Air liquide, 99.9999% purity).

The electrochemical cell was prepared with a Li metal counter electrode (15 mm in diameter), two glass fiber separators (20 mm in diameter, Whatman), gold coated Celgard (17 mm in diameter), and 200 μ L LP40 (Sigma Aldrich). Gold coated Celgard was prepared by coating a slurry consisting of 90% Au powder (Gold \geq 99.96% (metals basis), spherical powder APS 0,8-1,5 μ m, VWR) and 10% PVDF, that was followed by vacuum drying at 80°C overnight. The cell rested at OCP for 30 minutes before the potential was held at 3.0 V for 3.5 hours. A linear sweep from 3.0 V to 0.5V with a scan rate of 0.069 mV/s was used.

S2. Raman spectra of electrolyte and individual components

In figure S2, normal Raman spectra of the LP40 electrolyte and its components in the wavenumber interval 600-1900 cm⁻¹ are presented. Detailed Raman band assignment based on the literature are presented in table S1. Ethylene carbonate and LiPF₆ peak assignments are described in the main text. The 902 cm⁻¹ band belongs to the DEC component and can be assigned to the O-C-O vibration. Two bands, at 1092 and 1121 cm⁻¹, both arise from DEC and could be assigned to O-C-O symmetric stretching and CH₃ rocking. The bands in the interval of 1450-1500 cm⁻¹ are characteristic for CH bending modes and correspond to CH₃ groups of DEC at 1454 cm⁻¹ and CH₂ groups of EC at 1487 cm⁻¹. Finally, the higher wavenumber bands at 1700-1800 cm⁻¹ are typical for C=O stretching vibrations and come from DEC at 1745 cm⁻¹ and EC at 1775 cm⁻¹ and 1800 cm⁻¹.

Reference Raman spectra of potential inorganic SEI components are shown in figure S3.



Figure S2. Normal Raman spectra of LP40 electrolyte and its individual components in the wavenumber range 600-1900 cm⁻¹.

Wavenumber, cm ⁻¹	Assignment	Compound
717	ring breathing/O-C-O bending	EC
729	EC ring breathing/bending mode coordinated with	EC with Li ⁺
	Li ⁺	
742	Symmetric v P-F	PF ₆ -
893	Ring breathing	EC
902	0-C-0	DEC
904	EC ring breathing coordinated with Li ⁺	EC with Li ⁺
973	C-C	EC
1073	C-C and C-O stretching	EC
1092	vO-C-O symmetric stretching	DEC
1121	δCH ₃ rocking	DEC
1225	CH ₂ twist	EC
1454	δCH ₃ asymmetric	DEC
1487	CH ₂ bending	EC
1745	C=O stretching	DEC
1775	C=O stretching	EC
1800	C=O stretching	EC

Table S1. Raman bands assignment for components of LP40 electrolyte in the wavenumber interval 600-1900 cm⁻¹, based on the literature^{2–5}.



Figure S3. Normal Raman spectra of reference compounds: $LiOH*H_2O$, Li_2CO_3 , Li_2O_2 and LiF.



Figure S4. H₂ gas evolution from porous Au in LP40 as measured by OEMS during CV 3.0 – 0.5 V vs. Li⁺/Li at 0,069 mV/s sweep rate. Gas evolution maxima tentatively assigned to HF (2.6-1.8 V) and H₂O (1.8-1.0 V) reduction. Electrolyte reduction (<1 V), but exact electrochemical mechanism unknown.</p>

S3. Concentration of lithium ion at the surface

The ratio between solvated and free EC peaks can be used to determine the Li⁺ concentration on the Au surface. Calculation of the Li⁺ concentration is based on the ratio between the 717 and 729 cm⁻¹ Raman peaks and is performed by using the equation provided by Yang et al.² (figure 7 in their manuscript):

Rec s = -2.9 $\chi_{Li^+}^2$ + 3.81 χ_{Li^+}

where Rec s = $A_s/(A_s+A_u)$, A_s and A_u are the integrated band areas of coordinated and noncoordinated EC at 729 and 717 cm⁻¹, respectively.

Peak fitting was performed using MATLAB software. Results are presented in graph S5. Please note that at very low voltages (below 1V), the peaks intensity to noise ration decreases significantly, thus lowering the precision of peak area fitting and concentration calculation procedure. Therefore, we attribute the very low concentration value of 0.4M below 1 V to a data-processing artefact, rather than the actual concentration value.



Figure S5. Li⁺ surface concentrations.

References

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