

Supplementary Information

Carbonate Swollen Lithiated Nafion Electrolyte for Quasi-Solid-State Lithium-Sulfur Batteries

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Dynamic Mechanical Analysis (DMA) of SLIC-SPE membranes

The mechanical properties of the Nafion SLIC membranes were investigated by dynamic mechanical analysis (DMA), in dry and in EC/PC swollen state, in order to investigate the effect of swelling on the mechanical resistance of the polymer films in a wide temperature range from room temperature to 300 °C. Comparison between protonated (H⁺-form) and lithiated (Li⁺-form) Nafion membranes have been performed. Figure S1a report the evolution of the elastic (Yang) modulus, E', in the temperature sweep tests. The swelling in the organic solvents produces a plasticizing effect on the electrolyte membrane, which is softer and consequently lowering the moduli. However, as we can observe, Yang modulus of lithiated Nafion membranes swelled and unswelled is the same at low temperature, while it differs greatly at high temperature. Since the DMA measurements were conducted in air, the membrane certainly absorbs humidity (being an extremely hydrophilic membrane), especially during the initial phase in which the sample is mounted on the grips. The swelled EC/PC membrane may also absorb some moisture, but we expect it to be minimal. This assumption is corroborated by the gradual increase of E' by heating from 40 °C to 90 °C, attributable to the evaporation of absorbed water (which also has a plasticizing effect).

A clear sigmoid trend of E' emerges with an inflection point which indicates the glass transition state. This high temperature (α) transition, related to the T_g of the ionic clusters for the Nafion, is most evident by the damping factor (tan δ) plot of Figure S1b, where we find the peak is at about 225 °C for the Li⁺-Nafion swelled membrane, while it is at about 260 °C for the dry membrane. Typically, the α -transition for the protonated Nafion is at ~ 120 °C, as we can also see from the measurement reported in the graphs, therefore, the lithium ions trigger a greater degree of cross-linking within the ionic clusters of the polymer, likely changing the local meso-morphology.

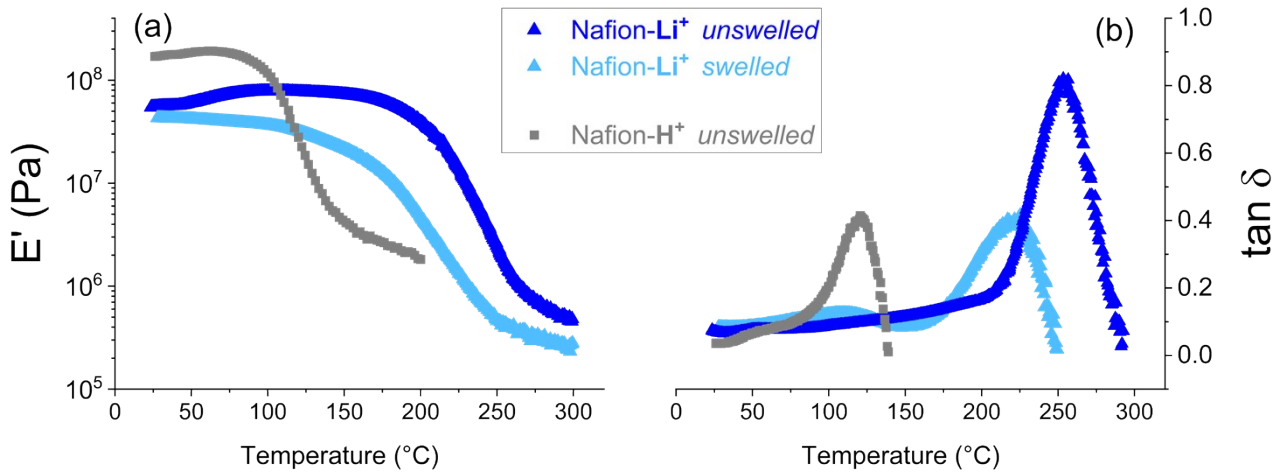


Figure S 1 Figure S1 DMA from 20 °C up to 300 °C, of the lithiated Nafion membranes, both unswelled and swelled in the EC/PC mixtures: (a) Yang modulus (E') vs. T and (b) $\tan \delta$ vs. T. Protonated Nafion membrane is reported for comparison in unswelled state.

Transport mechanism in SLIC-SPEs

The simplest model to describe mobility of charges in any electrolyte is the so-called Nernst-Einstein (NE) approximation where there is not any correlation in the motion of ions. Within this approximation, ionic conductivities can be easily obtained directly from the diffusion coefficients of charge carriers under the assumption of completely uncorrelated motions of anions and cations. This implies the absence of any relevant anion-anion, cation-cation and anion-cation thermodynamic interaction within the electrolyte. Thus, the transference number (T_+) of cations (or anions) can be directly related to their diffusion coefficients (D_+ and D_- , respectively) through the relation:

$$T_+ = \frac{D_+}{D_+ + D_-} \quad 1$$

In a polyelectrolyte (i.e. polymeric electrolyte with a single ion conductor, swelled or non-swelled in a liquid solvent) with immobilized anions (polymer- A^-) and mobile cations (C^+), the motion of negative charges can be assumed smaller by orders of magnitude compared to the motion of positive charges and therefore, under the NE approximation, $D_- \rightarrow 0$ and $T_+ \rightarrow 1$. This is a drastic approximation and neglects a realistic representation of the local coordination environments of cations/anions in the polyelectrolytes, thus providing an unrealistic model for the motions of ions.

SLIC-SPEs, like lithiated Nafion membranes swelled in organic carbonates or ethers, are polyelectrolytes constituted by anions ($-\text{CF}_2\text{SO}_3^-$), immobilized on the hydrophobic backbone of the polymeric matrix, and mobile cations (Li^+). The membrane swelling with polar solvent molecules leads to a partial solvation of Li^+ ions and the corresponding charge shielding of the anions, both surrounded by a coordination shell.

The fraction of unpaired ions in the swelled polyelectrolyte can vary depending by the balancing between the $(-\text{CF}_2\text{SO}_3^-)-(\text{Li}^+)$ Gibbs energy of ion pairing, the (solvent)-(solvent) Gibbs energy of solvent self-solvation as well as the $(\text{Li}^+)-(\text{solvent})$ and the $(-\text{CF}_2\text{SO}_3^-)-(\text{solvent})$ Gibbs energies of ionic solvation. These thermodynamic quantities are strongly dependent on the solvent physico-chemical properties, like the mean dielectric constant, the molecular electric dipole moment and the molecular polarizability. Thus, the relative amount of unpaired ions within any swelled membrane is closely related to the solvent properties.

In the SLIC-SPEs a net charge transport across the membrane is driven by two major mechanisms:

- (I) the free diffusion of unpaired cations coordinated by solvent molecules (e.g. bulk Li^+ diffusion in SLIC-SPEs);
- (II) the hopping of negative charges between vicinal neutral $(-\text{CF}_2\text{SO}_3^-)-(\text{Li}^+)$ and negatively charged sulphonic groups $(-\text{CF}_2\text{SO}_3^-)$ (i.e. Grotthuss-like anion diffusion).

Other mechanisms can also occur, like for example the hopping of positive charges between vicinal neutral $(-\text{CF}_2\text{SO}_3^-)-(\text{Li}^+)$ and positively charged sulphonic groups $(-\text{CF}_2\text{SO}_3^-)-(\text{Li}^+)_2$ (i.e. Grotthuss-like cation diffusion). Here, for the sake of simplicity, we discuss only the contributions from mechanism (I) and (II).

Going beyond the NE approximation, the ionic transport in any electrolyte, and therefore also in swelled polyelectrolytes, are impacted by correlations in the ion motion. As a consequence, equation 1 cannot represent correctly the transference number of positive charges.

Generally speaking several transport phenomena may compete: (a) cation self diffusion L_{self}^{++} ; (b) cation distinct diffusion $L_{distinct}^{++}$; (c) anion self diffusion L_{self}^{--} ; (d) anion distinct diffusion $L_{distinct}^{--}$; (e) anion-cation distinct diffusion $L_{distinct}^{+-}$.

The self-diffusion terms capture the motion of uncorrelated ionic species whereas the distinct terms represent the diffusion of correlated ions. Both uncorrelated and correlated terms contribute to the net motion of ions and, therefore, the diffusions of cations (L^{++}) and anions (L^{--}) are given by:

$$L^{++} = L_{self}^{++} + L_{distinct}^{++} - L_{distinct}^{+-} \quad 2$$

$$L^{--} = L_{self}^{--} + L_{distinct}^{--} - L_{distinct}^{+-} \quad 3$$

Thermodynamic considerations impose that whereas L_{self}^{++} and L_{self}^{--} must be positive, $L_{distinct}^{++}$ and $L_{distinct}^{--}$ can be either positive (correlated motions) or negative (anti-correlated motions), thus promoting or hindering the overall ion diffusions, respectively. The same applies also to the anion-cation distinct diffusion term, i.e. $L_{distinct}^{+-}$, that can be either positive (correlated motion between anions and cations, unlikely to occur in polarized electrolytes) or negative (anticorrelated motion between anion and cations, likely to occur in polarized electrolytes). Under this general approach the cation transference number is given by the following equation:

$$T_+ = \frac{L_{self}^{++} + L_{distinct}^{++} - L_{distinct}^{+-}}{L_{self}^{++} + L_{distinct}^{++} - 2L_{distinct}^{+-} + L_{self}^{--} + L_{distinct}^{--}} \quad 4$$

Under the NE approximation where all motions are uncorrelated (i.e. $L_{distinct}^{+-} = L_{distinct}^{--} = L_{distinct}^{++} = 0$), equation 4 reduces to:

$$T_+ = \frac{L_{self}^{++}}{L_{self}^{++} + L_{self}^{--}} = \frac{D_+}{D_+ + D_-} \quad 5$$

In the SLIC-SPEs the Grotthuss-like anion diffusion mechanism implies a strong anti-correlation between the motion of positive and negative charges, i.e. $L_{distinct}^{+-} < 0$, as previously observed by molecular dynamic calculations in the case of various polyelectrolyte phases.(1, 2)

Fong et al.(3) demonstrated that for polyelectrolyte with immobilized negative charges on extended polymer chains and mobile cations, the following relations apply:

$$(i) \quad L_{self}^{++} \gg L_{self}^{--}$$

$$(ii) \quad L_{distinct}^{++} > 0$$

(iii) $L_{distinct}^{--} = L_{intrachain}^{--} + L_{interchain}^{--} \geq 0$, being $(L_{intrachain}^{--} > 0)$ the correlation between negative charges on the same polymer chain (that are constrained to move together) and $(L_{interchain}^{--} < 0)$ the anti-correlation between negative charges on different polymer chains (that repel each other).

(iv) $L_{self}^{++} + L_{distinct}^{++} > L_{self}^{--} = \beta > 0$

(v) $L_{distinct}^{+-} < 0$

As a consequence:

(vi) $[L_{self}^{++} + L_{distinct}^{++} - (2L_{distinct}^{+-})] = (A + \alpha) > [L_{self}^{++} + L_{distinct}^{++} - (L_{distinct}^{+-})] = A > 0$

These considerations allow to reformulate equation 4

$$T_+ = \frac{A}{A + \alpha + \beta + (L_{intrachain}^{--} + L_{interchain}^{--})}$$

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Overall, being $(A, \alpha, \beta) > 0$ and $L_{intrachain}^{--} + L_{interchain}^{--} \geq 0$, T_+ falls below unity when $|\alpha + \beta + L_{intrachain}^{--}| > |L_{interchain}^{--}|$.

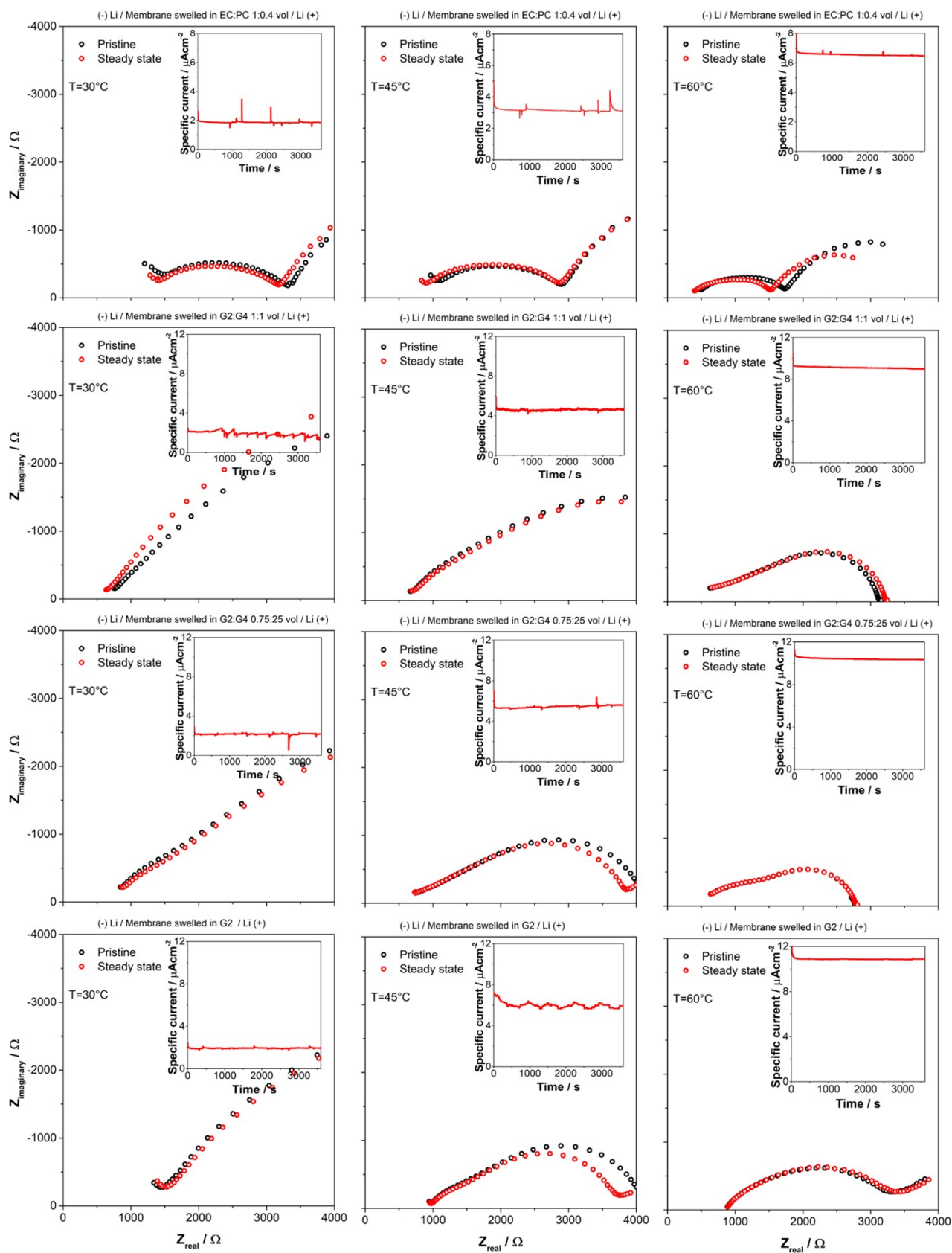


Figure S2 Chronoamperometric and impedance spectra of the Li/Li symmetric cells with swelled membranes for the transference number evaluation.

Electrochemical performance in Li-S cells

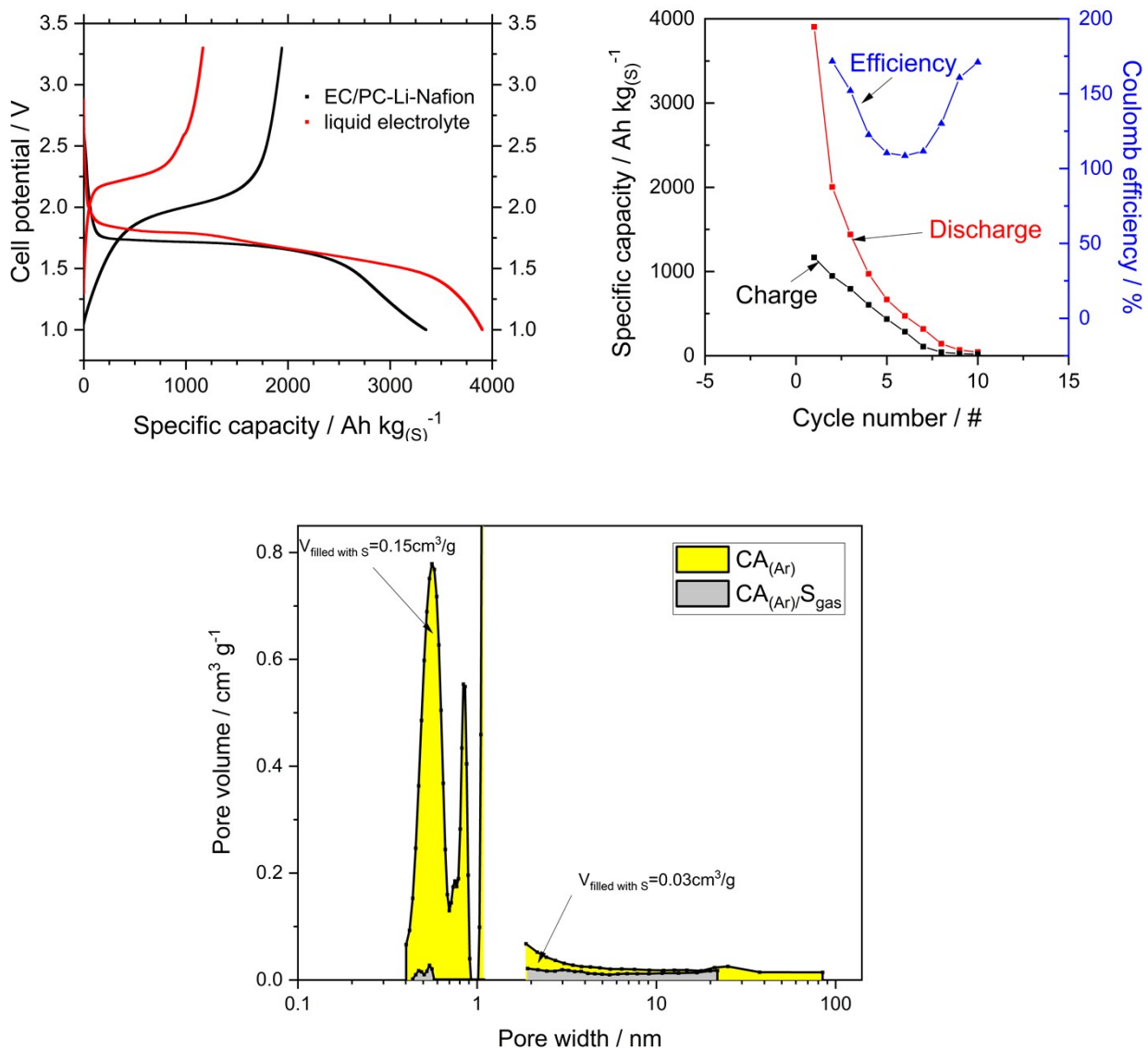


Figure S3 (a) First cycle charge-discharge profile at 30°C CA_(Ar)/S_{gas} cathode vs. lithium foil with EC/PC-Li-Nafion (black) and liquid electrolyte (red) at 83.5 A kg_(s)⁻¹ (0.05C), (b) specific capacity and coulomb efficiency over cycles with liquid electrolyte at 83.5 A kg_(s)⁻¹ (0.05C). (c) N₂-isotherms of CAs at 77 K.

Electrochemical performance in symmetrical lithium cell configuration

The quasi-solid-state Li|EC/PC-Li-Nafion|Li cells and the conventional electrolyte Li|liquid electrolyte|Li cells were fabricated and evolution of AC impedance was monitored during 24 h equilibration in open circuit potential. Afterward the cells were subjected to a typical stripping-plating of Li electrode at a current density of 0.2 mA cm^{-2} at $25 \text{ }^\circ\text{C}$. Afterwards the AC impedance was measured again.

Figure S4(a-b) displays the OCV impedance data and fitted data with the used equivalent circuits. The electrolyte resistance of both systems emerges in the high frequency domain. For the quasi-solid-state Li|EC/PC-Li-Nafion|Li cell, electrolyte/bulk resistance R_{ion} is modelled within a $(RQ)_{\text{bulk}}$ circuit with the geometrical/bulk constant phase element Q_{bulk} in parallel whereas for the liquid electrolyte system a series resistance R_{el} is used in concordance with the models used for fitting of Li-S cells. The Li|EC/PC-Li-Nafion|Li cell arises a stable electrolyte resistance of $54 \text{ } \Omega$, while the cell with liquid electrolyte provides a lower electrolyte resistance of $3 \text{ } \Omega$. The subsequent semi-circle that arises in the low frequency area of both electrolyte systems can be attributed to the solid electrolyte interphase (SEI) at the interface between electrolyte/lithium. This interface process is modelled with the resistance R_{film} in parallel to the constant phase element Q_{film} of its associated double layer capacitance. For both electrolyte systems, a growing film resistance can be observed during 24 h of resting, indicating an emerging surface layer. The resistance R_{film} of SEI of Li|EC/PC-Li-Nafion|Li cell immediately had a value of $95 \text{ } \Omega$, stabilizes after 12 h at $140 \text{ } \Omega$ and continues growing up to $160 \text{ } \Omega$ after 24 h at OCV. The resistance R_{film} of SEI of liquid electrolyte cell is slightly below, immediately had a value of $76 \text{ } \Omega$, stabilizes after 12 h at $116 \text{ } \Omega$ and continues growing up to $135 \text{ } \Omega$ after 24 h at OCV. Galvanostatic stripping/plating behaviour of both cells is shown in Figure S4c, where the liquid cell shows a stable overpotential of 60 mV over 100 cycles at a current density of 0.2 mA cm^{-2} . The Li|EC/PC-Li-Nafion|Li cell initially had an overpotential of 100 mV corresponding to its higher cell resistance. During stripping/plating its overpotential continuously raises up to 300 mV and its AC impedance after stripping/plating reveals a 2.6-fold higher cell resistance, shown in Figure S4(d-e). Fitted resistances before and after galvanostatic cycling are summarized in Figure S4e and show stable values for liquid electrolyte cell, while electrolyte resistance R_{bulk} of Li|EC/PC-Li-Nafion|Li cell raises from $54 \text{ } \Omega$ to $64 \text{ } \Omega$ and the SEI resistance R_{film} raises from $160 \text{ } \Omega$ to $520 \text{ } \Omega$. Indicating reactivity between swollen Nafion membrane and lithium metal anode leading to an increasing resistive layer at the interface and a drying of membrane. This is in accordance with findings of others.(4) For liquid cell, showing constant overpotential during cycling, comparable resistance was fitted before and after cycling.

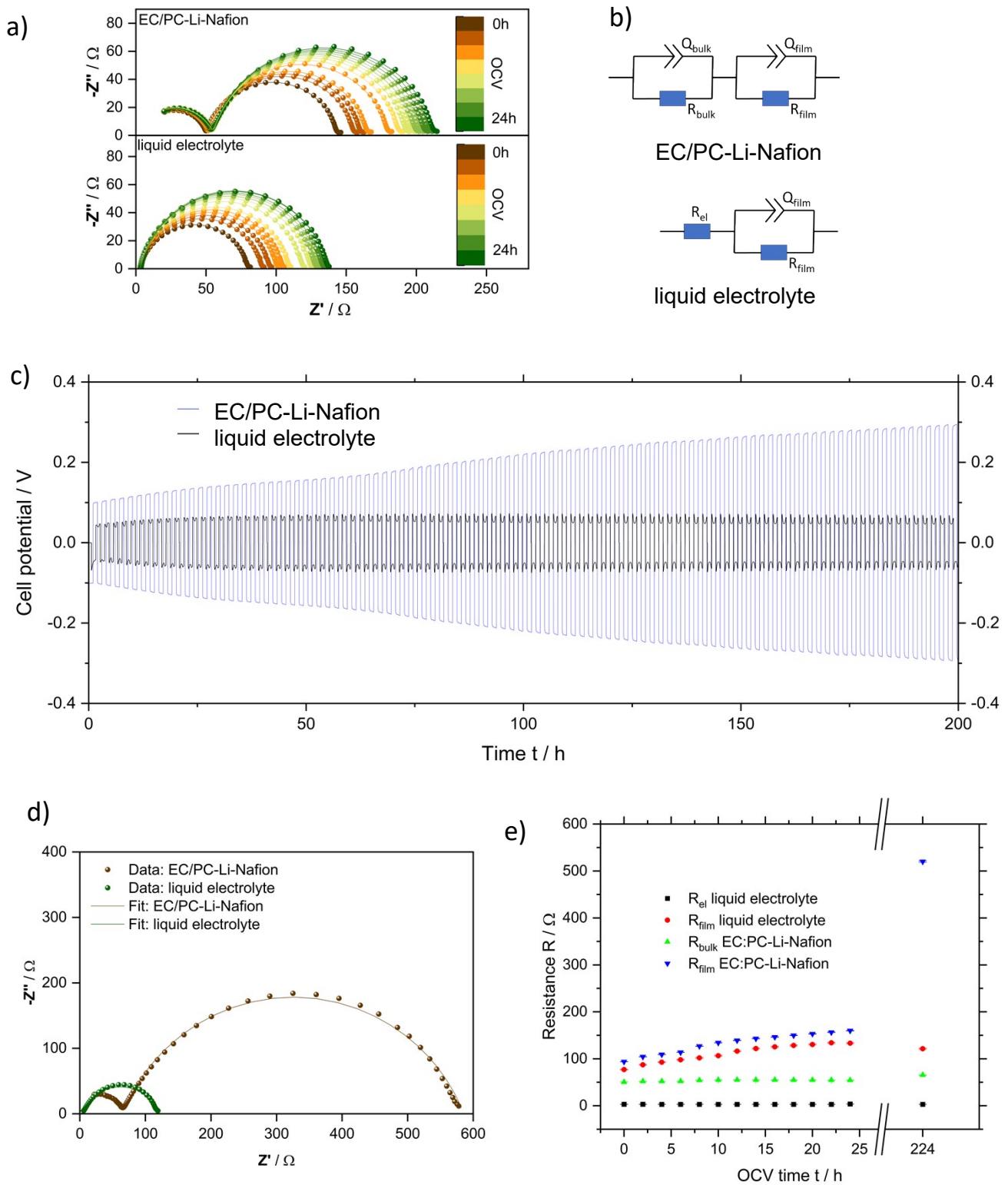


Figure S4 (a) Evolution of AC impedance at 25°C during 24 h OCV of Li|EC/PC-Li-Nafion|Li and Li|liquid electrolyte|Li cells with (b) used equivalent circuits for fitting, (d) stripping/plating 100 cycles at 25°C and 0.2 mA cm² and (d) corresponding AC impedance at 25°C after stripping/plating, (e) summary of fitted resistances during OCV and after stripping/plating

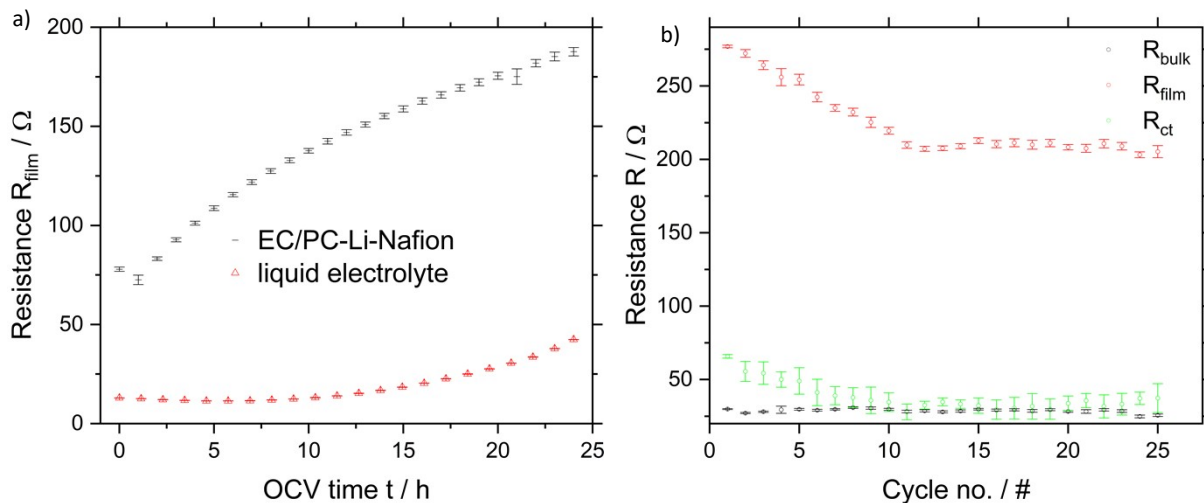


Figure S5 Summary of (a) fitted resistances R_{film} during 24 h equilibration time in OCV of Li-S full cells and (b) of fitted resistances after discharge in EC/PC-Li-Nafion full cell.

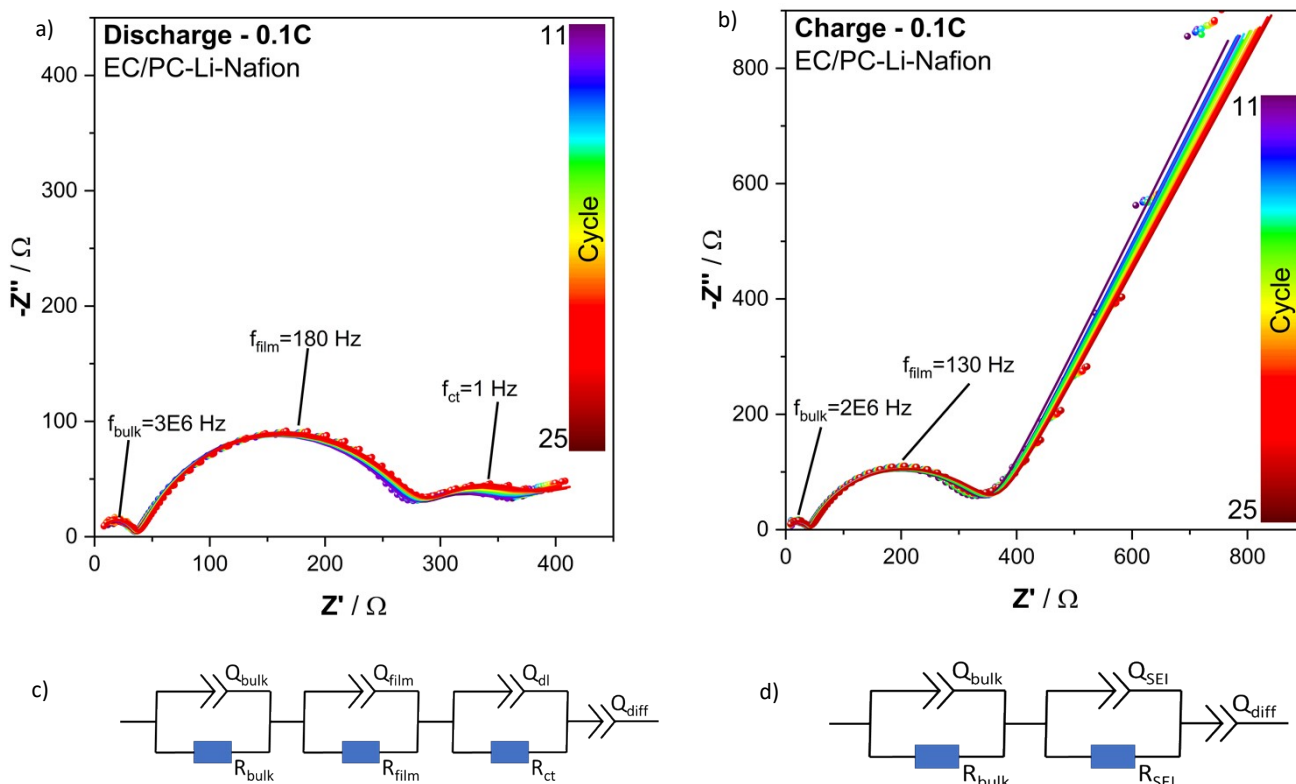


Figure S6 Evolution of AC impedance at 30°C of $\text{CA}_{(\text{Ar})}/\text{S}_{\text{gas}}$ cathode vs. lithium foil full cells with EC/PC-Li-Nafion with used equivalent circuits for fitting: (a)+(c) 10 discharge cycles at 0.1C; (b)+(d) 10 charge cycles at 0.1C

References

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