

Supporting Information

Ion Transport and Growth Behavior of Solid Electrolyte Interphases on Li and Na with Liquid Electrolytes Based on Impedance Analysis

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I. Experimental section

i) Material preparation

Li rods (99.9%, trace metals basis) and Na cubes stored in mineral oil (99.9%, trace metals basis) were purchased from Sigma Aldrich and stored in a glovebox under Ar atmosphere ($O_2 < 0.1$ ppm and $H_2O < 0.1$ ppm). Liquid electrolytes were prepared by dissolving $LiCF_3SO_3$ (LiTf, 98%, Sigma Aldrich) and $NaCF_3SO_3$ (NaTf, 99.5%, Solvionic) into triethylene glycol dimethyl ether (triglyme, 99%, Alfa Aesar) and the mixture of ethylene carbonate (EC, 98%, Sigma Aldrich) and dimethyl carbonate (DMC, 98%, Sigma Aldrich) (EC/DMC=50/50 in volume %) with a concentration of 1M. All procedures were done in the glovebox.

ii) Electrochemical cell assembly

CR2032-type coin cells made of stainless steel were assembled for electrochemical measurement. Due to the high reactivity of Li and Na even under Ar condition, Li rods and Na cubes were cut freshly with stainless steel blades each time right before the cell assembly. Subsequently, Li/Na electrodes were sandwiched between two Celgard separators (thickness: 20 μ m, H2013) and pressed with stainless-steel roller to the thickness of 0.15 mm, and cut into discs with a diameter of 10 mm. Two symmetric Li/Na electrodes were separated by the Celgard separators and two types of electrolyte (1M LiTf/NaTf in triglyme and 1M LiTf/NaTf in EC/DMC) were added in an amount of 20 μ L for each cell. All the procedures of cell assembly were performed in the glovebox. Ionic conductivity of the electrolytes was measured with the homemade cell made of gold-coated brass.

iii) Electrochemical impedance spectroscopy (EIS) measurements

EIS was measured in the frequency range of $10^6 \sim 1$ Hz with an amplitude of 10 mV at 0 V in the potentiostatic mode. Solatron 1260 was used and analysis of the impedance spectra was carried

out with ZView software (Scribner Associates, version 3.5c). Temperature-dependent EIS measurements were performed in the temperature starting from 80 °C to 0 °C for 1 hour for each temperature using an external thermostat (Lauda RC6CP).

II. Impedance spectra of symmetric Li and Na cells with glyme- and carbonate-based electrolytes

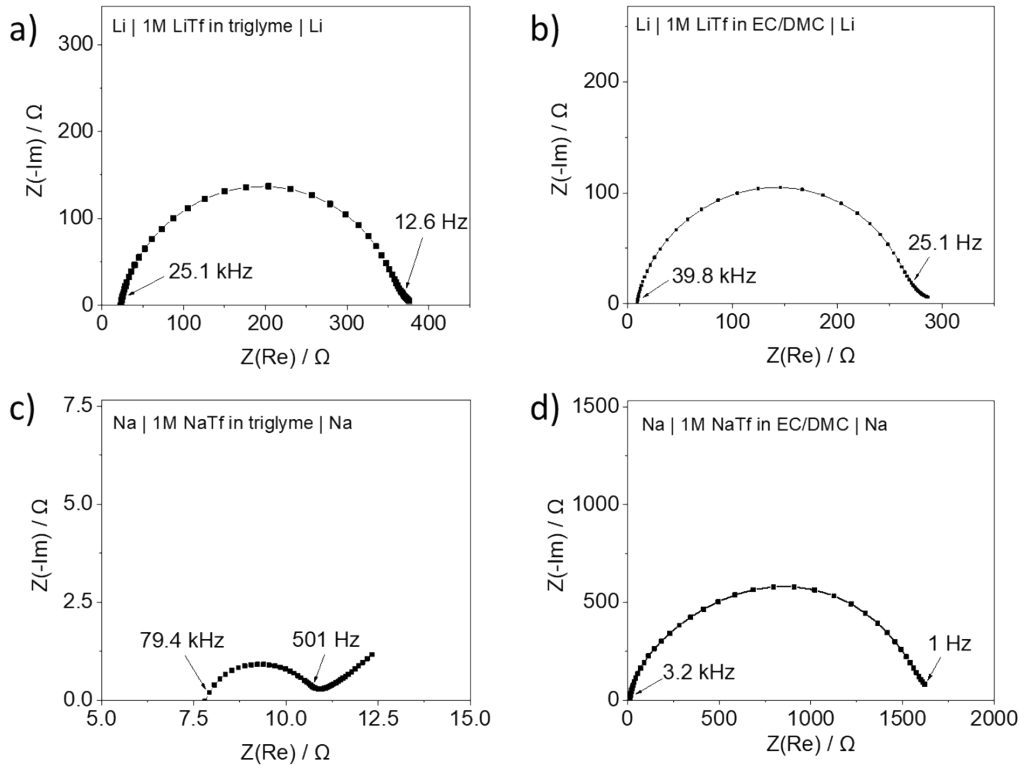


Figure S1. Impedance spectra of symmetric Li and Na cells with glyme- and carbonate-based electrolytes.

Given by the ionic conductivity of the liquid electrolyte that was measured ($\sim 10^{-3} \text{ S cm}^{-1}$), the frequency range where ion conduction in bulk liquid electrolyte occurs is higher than 60 MHz (

$$f_{peak} = \frac{1}{2\pi RC} = \frac{\sigma_{liquid}}{2\pi\epsilon_0\epsilon_{liquid}}, \sigma_{liquid} > 10^{-3} \text{ S cm}^{-1} \quad \text{and} \quad \epsilon_{liquid,pore} < 30^{1,2}).$$

Also, the frequency range at which concentration polarization in the bulk liquid electrolyte should be observed is smaller than

0.03 Hz ($f_{peak} = \frac{D}{L^2}$, where D and L are taken from reference³). Even though the concentration gradient forms in the pores, its influence on the impedance spectrum is negligible as the blocking electrode is still the counter electrode. Therefore, the observed impedance signals are from neither ion conduction in bulk liquid nor concentration polarization in bulk liquid. The ionic conductivity follows the Arrhenius equation, allowing for determination of the activation energy from temperature-dependent EIS measurements, E_a through $\sigma T = A \exp(-E_a/(k_B T))$, where A is the Arrhenius prefactor at infinite temperature, and k_B is the Boltzmann constant.

III. Summary of ionic conductivities and activation energies of inorganic Li/Na SEI compounds

Table S1. Summary of ionic conductivity () and activation energy of ionic transport (E_a) of Li SEI compounds

Compound	$\sigma_{ion} / S\text{ cm}^{-1}$ (at room temperature)	E_a / eV	Reference	Notes
LiF	$\sim 10^{-13}$	0.88	C. Li <i>et al.</i> , <i>Adv. Funct. Mater.</i> 21 (15), 2901 (2011)	Extrapolated from 250 °C, 333 nm-thick-thin film
Li ₂ S	$\sim 10^{-11}$	0.90	S. Lorgier <i>et al.</i> , <i>Adv. Funct. Mater.</i> 29 (6), 1807688 (2018)	
Li ₂ CO ₃	$\sim 10^{-13}$	1.09	J. Mizusaki <i>et al.</i> , <i>Solid State Ionics</i> 53-56 , 791 (1992)	Extrapolated from 300 °C
Li alkyl carbonates (C ₁ Li-C ₈ Li)	$\sim 10^{-13}$	0.72	L. Schafzahl <i>et al.</i> , <i>Chem. Mater.</i> 30 3338 (2018)	Extrapolated from 40 °C
LiOH	$\sim 10^{-13}$	0.90	R.T. Johnson <i>et al.</i> , <i>Mater. Res. Bull.</i> 12 (6), 577 (1977)	Extrapolated from 120 °C
Li ₂ O	$\sim 10^{-12}$	0.86	S. Lorgier <i>et al.</i> , <i>J. Electrochem. Soc.</i> 166 (10) A2215 (2019)	

Electrolyte	$\sigma_{ion} / S\text{ cm}^{-1}$ (at room temperature)	E_a / eV	Reference	Notes
1M LiTf in triglyme	1.03×10^{-3}	0.15	K. Lim <i>et al.</i> , <i>ACS Appl. Mater. Interfaces</i> 13 (43) 51767 (2021)	
1M LiTf in EC/DMC	2.74×10^{-3}	0.16	K. Lim <i>et al.</i> , <i>ACS Appl. Mater. Interfaces</i> 13 (43) 51767 (2021)	

Table S 2. Summary of ionic conductivity () and activation energy of ionic transport (E_a) of Na SEI compounds

Compound	$\sigma_{ion} / S\ cm^{-1}$ (at room temperature)	E_a / eV	Reference	Notes
NaF	$\sim 10^{-16}$	2.38	C.F. Bauer <i>et al.</i> , <i>Phys. Stat. Sol.</i> 37 , 585 (1970)	Extrapolated from 496 °C
Na ₂ S	$\sim 10^{-10}$	0.59	B. Bertheville <i>et al.</i> , <i>J. Phys. Chem. Sol.</i> 58 (10), 1569 (1997)	
Na ₂ CO ₃	10^{-13} to 10^{-10}	0.74	P. Cerisier <i>et al.</i> , <i>J. Sol. State Chem.</i> 22 , 245 (1977)	Extrapolated from 315 °C
Na alkyl carbonates (C ₁ Na-C ₈ Na)	$< 10^{-14}$	> 1.40	L. Schafzahl <i>et al.</i> , <i>Chem. Mater.</i> 30 3338 (2018)	Extrapolated from 72 °C
NaOH	$\sim 10^{-15}$	1.10	M. Spaeth <i>et al.</i> , <i>Solid State Ionics</i> 97 291 (1997)	Extrapolated from 144 °C, most likely H ⁺ conduction

Electrolyte	$\sigma_{ion} / S\ cm^{-1}$ (at room temperature)	E_a / eV	Reference	Notes
1M NaTf in triglyme	2.02×10^{-3}	0.15	K. Lim <i>et al.</i> , <i>ACS Appl. Mater. Interfaces</i> 13 (43) 51767 (2021)	
1M NaTf in EC/DMC	5.07×10^{-3}	0.16	K. Lim <i>et al.</i> , <i>ACS Appl. Mater. Interfaces</i> 13 (43) 51767 (2021)	

IV. Reasons for neglecting $R_{solid,channel}$ and $C_{solid,channel}$ for the case 1 ($E_a(SEI) \sim E_a(liquid)$)

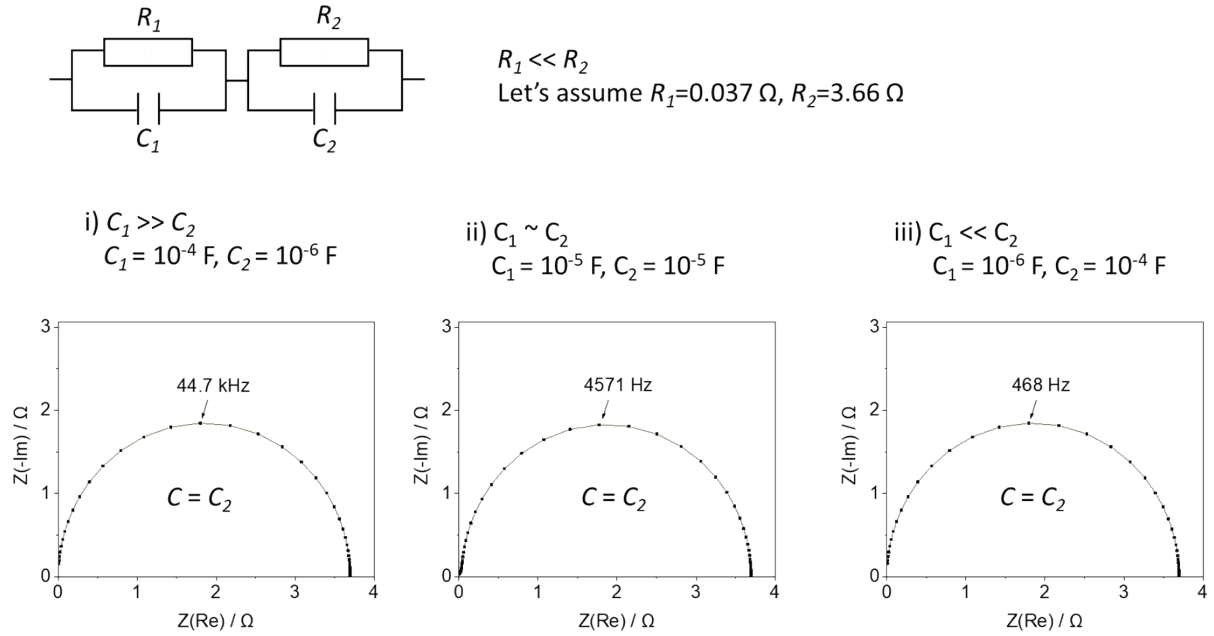


Figure S2. Simulated impedance spectra of two RC parallel circuits in series with three different condition of capacitance values. In Na symmetric cells with glyme-based electrolyte, R_{SEI} is 3.67Ω , so that $R_1 = 0.037 \Omega$ and $R_2 = 3.66 \Omega$ were assumed. The simulation shows that no matter how large the C_1 and C_2 values are, the whole impedance spectra and the measured effective capacitance is always dominated by the R_2 - C_2 parallel element.

V. TEM studies of SEI on Li upon contact with carbonate-based electrolyte

The sample (collected from Li|1M LiTf|Li in EC/DMC after sever hours of contact under open circuit condition and dried in the glovebox, corresponding to Fig. 3c, d) was prepared for TEM investigation and measured by Julia Deuschle and Tobias Heil at the Stuttgart Center for Electron Microscopy (StEM). For the preparation a FEI Scios focused ion beam scanning electron microscope (FIB-SEM) was utilized and the TEM investigation was conducted with a probe-corrected JEOL ARM200F microscope, operating with an acceleration voltage of 200kV.

We cannot observe any SEI porosity even in images with a higher resolution (Fig. S5), but since the lamella thickness in beam direction is about 400 nm, a system of small sizes pores (below 10 nm each) may be present but not observable due to the overlap. Thinner lamella samples could not be prepared with the available FIB-SEM due to a lack of a cryo option.

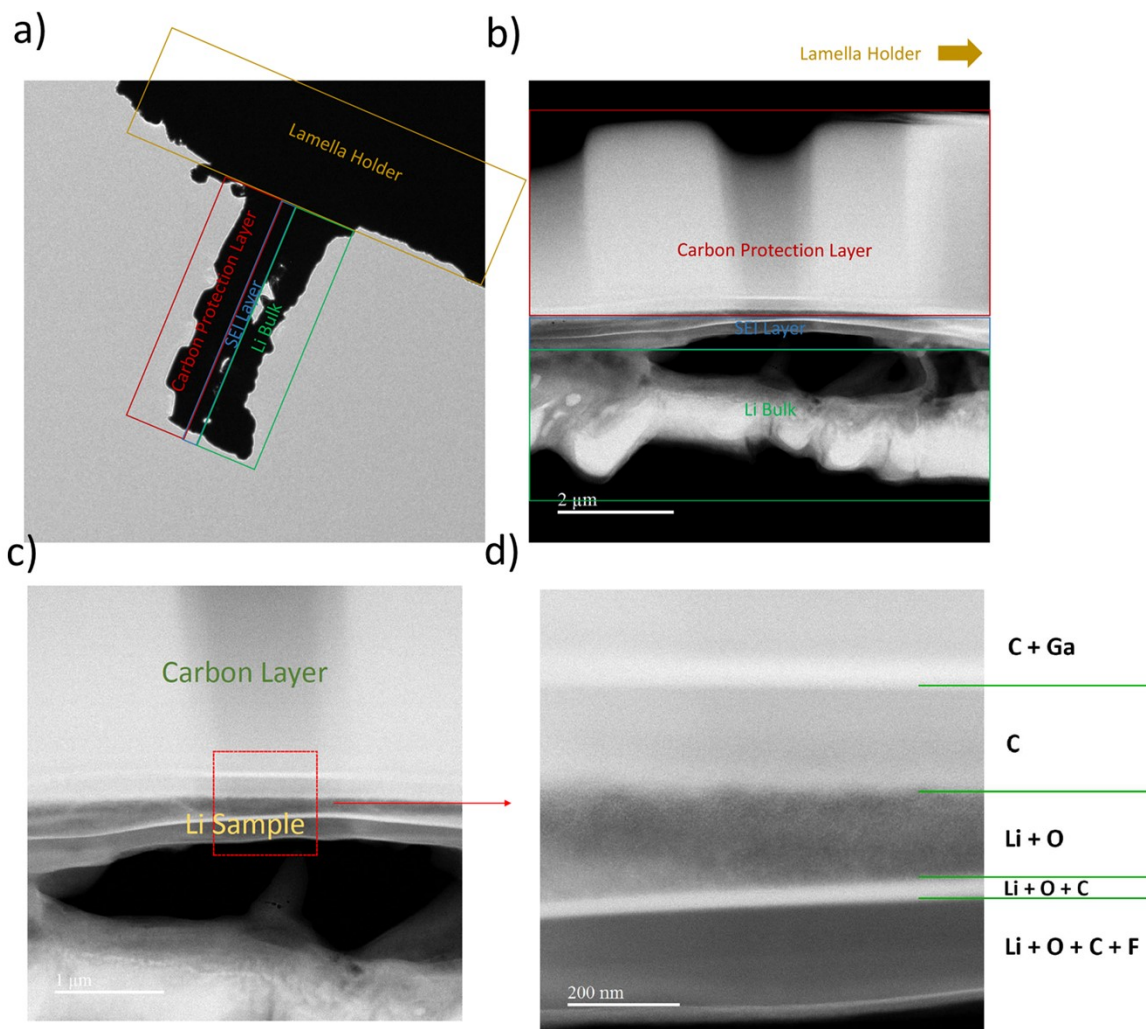


Figure S3. TEM images of Li covered with SEI upon contact with carbonate-based electrolyte. a) Overview showing the lamella holder, Li bulk, SEI and carbon protection layer. The holes between Li bulk and the SEI layer appear upon FIB-cutting and become bigger under the electron beam. b, c) Higher magnification images showing the cross-section upon FIB-SEM cutting. d) Higher magnification image showing several SEI layers including the likely elemental composition derived from Energy Dispersive X-Ray Spectroscopy (EDS) measurements (SEI1: Li+O, SEI2: Li+O+C, SEI3: Li+O+C+F).

VI. Dependence of the thickness of the solid in liquid channel ($d_{solid,channel}$) on the corresponding activation energy of transport ($E_a(solid,channel)$) and its ionic conductivity ($\sigma_{solid,channel}$)

From the equation (3) in the main text, $E_a(channel)=E_a(SEI)$ was first assumed. The values of $E_a(SEI)$, $E_a(liquid,channel)$ and $\sigma_{liquid,channel}$ were taken from our previous publication³ (also listed in Table 1, Table S1 and Table S2). The values of $\sigma_{solid,channel}$ and $E_a(solid,channel)$ were assessed to be in the range of $10^{-11} \text{ S cm}^{-1} < \sigma_{solid,channel} < 10^{-5} \text{ S cm}^{-1}$ and $0.3 \text{ eV} < E_a(solid,channel) < 1.1 \text{ eV}$, based on the σ_{ion} and E_a values of the Li/Na inorganic SEI compounds (Table S1 and Table S2, SI). Figure S3 displays the dependence of the thickness ratio ($\frac{d_{liquid,channel}}{d_{solid,channel}}$) on both $\sigma_{solid,channel}$ and $E_a(solid,channel)$.

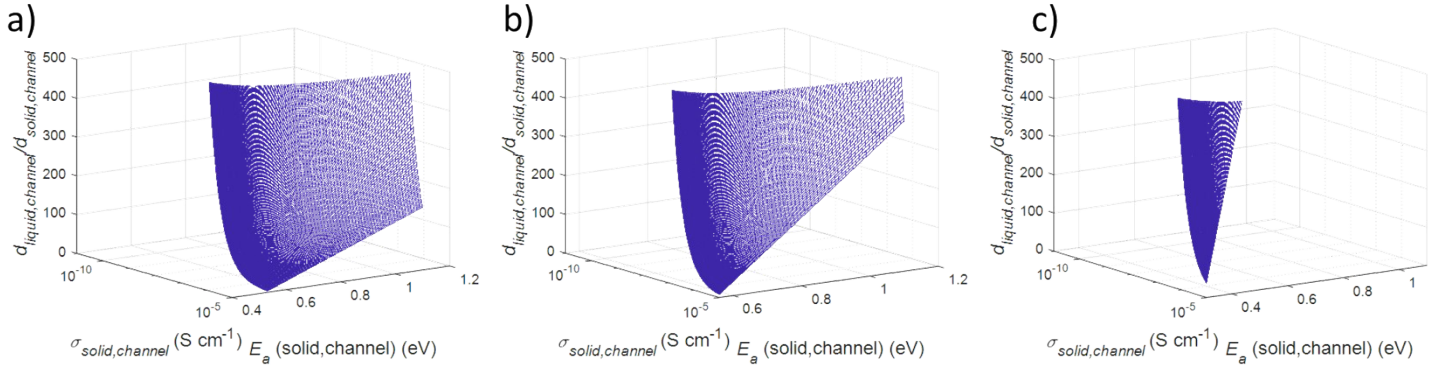


Figure S4. Dependence of the thickness ratio of the solid part and the liquid part in the channel ($d_{liquid,channel}/d_{solid,channel}$) on the corresponding activation energy of transport ($E_a(solid,channel)$) and its ionic conductivity ($\sigma_{solid,channel}$) according to the equation (3) in the main text. (a) Li|1M LiTf in triglyme|Li, (b) Li|1M LiTf in EC/DMC and (c) Na|1M NaTf in EC/DMC.

VII. R_{SEI} changes over time under open-circuit in six Na-glyme symmetric cells

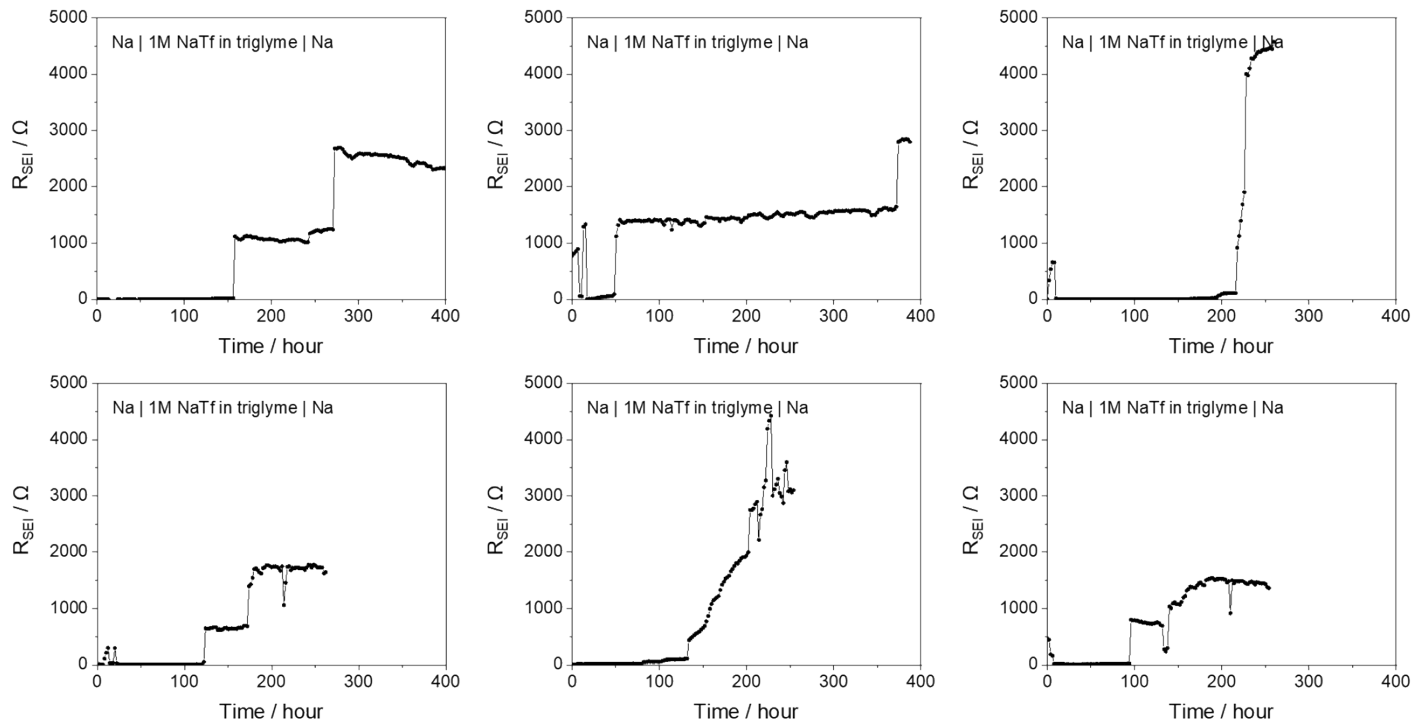


Figure S5. R_{SEI} changes over time under open-circuit in six Na-glyme systems. All six cells were assembled under the same experimental condition as was done for the sample in Figure 2e for reproducibility check.

VIII. Modeling of SEI growth for negative reaction volume

Modeling of the “self-similar” growth described in the main text (see Eq. (4b)). The parameters are obvious from the program.

```

r1=1E-5;
c1=r1*2500;
c2=r2*3300*1E4;
Rp=2800;
phi=linspace(0,1,1000);
R1=phi;
R2=R1;
R3=R1;
for i=1:1000
    R1(i)=c1/(phi(i)*r1+(1-phi(i)));
end
%plot(phi,R1);

for i=1:1000
    R2(i)=2500+(phi(i)*200);
end
R2(1000)=300;
for i=1:1000
    R3(i)=c2*Rp/(Rp*(phi(i)*r1+(1-phi(i)))+c2);
end
%plot(phi+3,R2+400,phi+2,R3,phi+1,R2,phi,R1,color='black');
xlabel('time');
ylabel('R_{SEI} / \Omega');

R_Phi2_Figure(phi(1:500)+4.2,R2(1:500)+300,phi*.5+3.7,R3,phi+2.7,R2,phi*2.7,R1);

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For simplicity purposes we set the series contribution to zero and used constant $\sigma_{solid}/\sigma_{liquid}$.

IX. Comparison of Pilling-Bedworth ratios (R_{PB}) of Li SEI compounds vs. Na SEI compounds

Table S3. Comparison of Piling-Bedworth ratios (R_{PB}) of inorganic Li/Na SEI compounds.

Li SEI compounds		Na SEI compounds	
Compound name	R_{PB}	Compound name	R_{PB}
LiF	0.76	NaF	0.69
Li ₂ O	0.57	Na ₂ O	0.58
Li ₂ O ₂	0.76	Na ₂ O ₂	0.59
Li ₂ CO ₃	1.35	Na ₂ CO ₃	0.88
LiOH	1.26	NaOH	0.79
Li ₂ S	1.06	Na ₂ S	0.89
LiH	0.75	NaH	0.72

References

1. N. Yao, X. Chen, X. Shen, R. Zhang, Z.-H. Fu, X.-X. Ma, X.-Q. Zhang, B.-Q. Li and Q. Zhang, *Angewandte Chemie*, 2021, **60**, 21473-21478.

2. I. N. Daniels, Z. Wang and B. B. Laird, *The Journal of Physical Chemistry C*, 2017, **121**, 1025-1031.
3. K. Lim, B. Fenk, J. Popovic and J. Maier, *ACS Applied Materials & Interfaces*, 2021, **13**, 51767-51774.