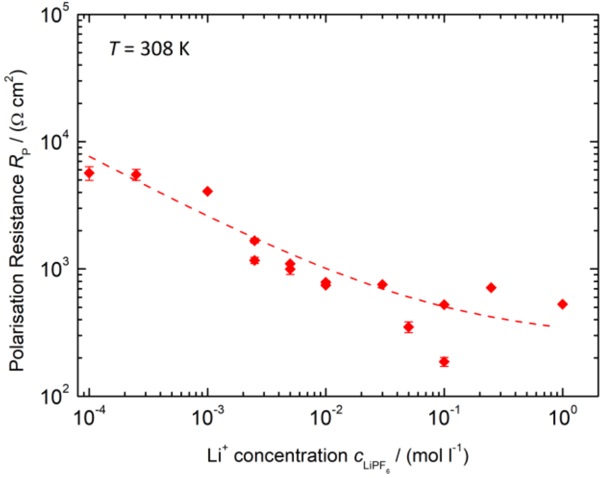
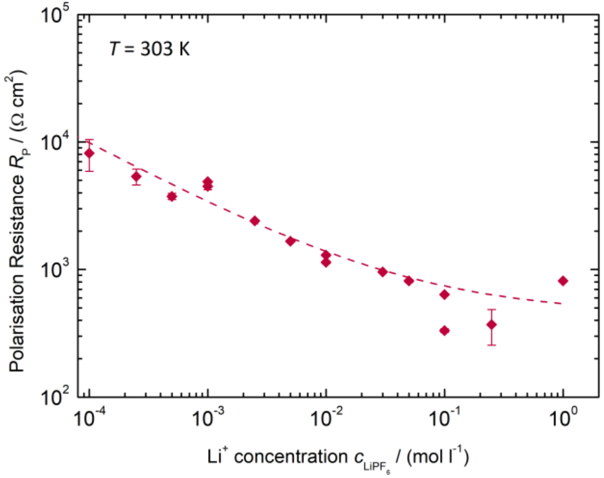
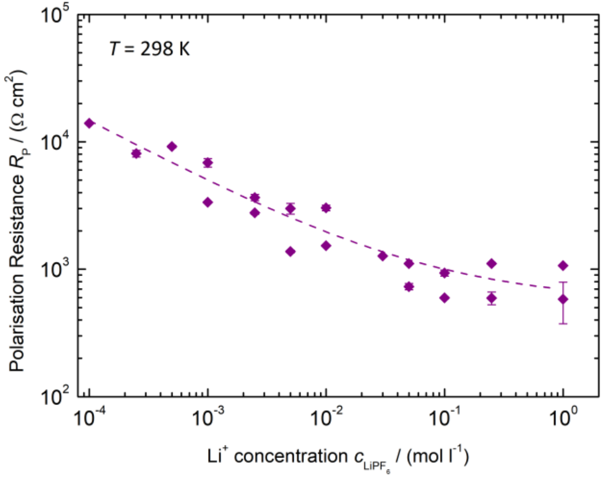
Supplemental Material

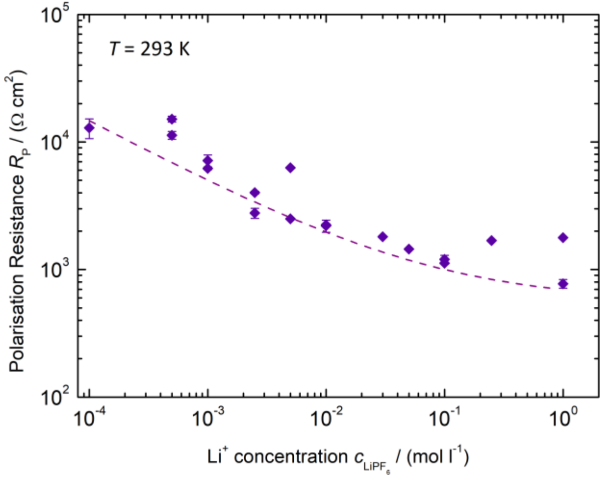
S1: Temperature dependent measurement of the (areal) polarisation resistance R_P, LLZO:Ta | EC/DMC + $LiPF_6$

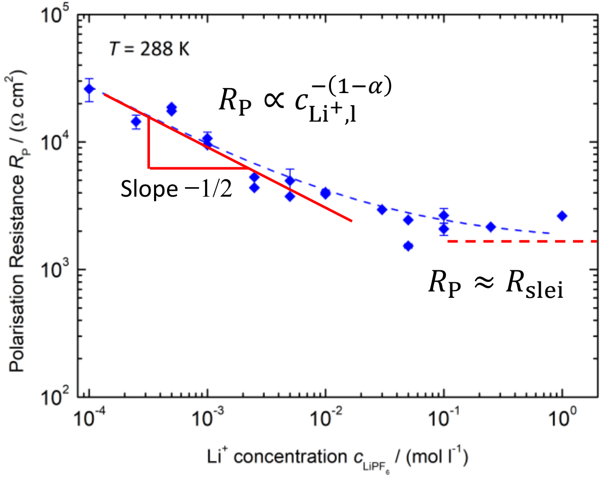
Polarisation resistance of all measured systems





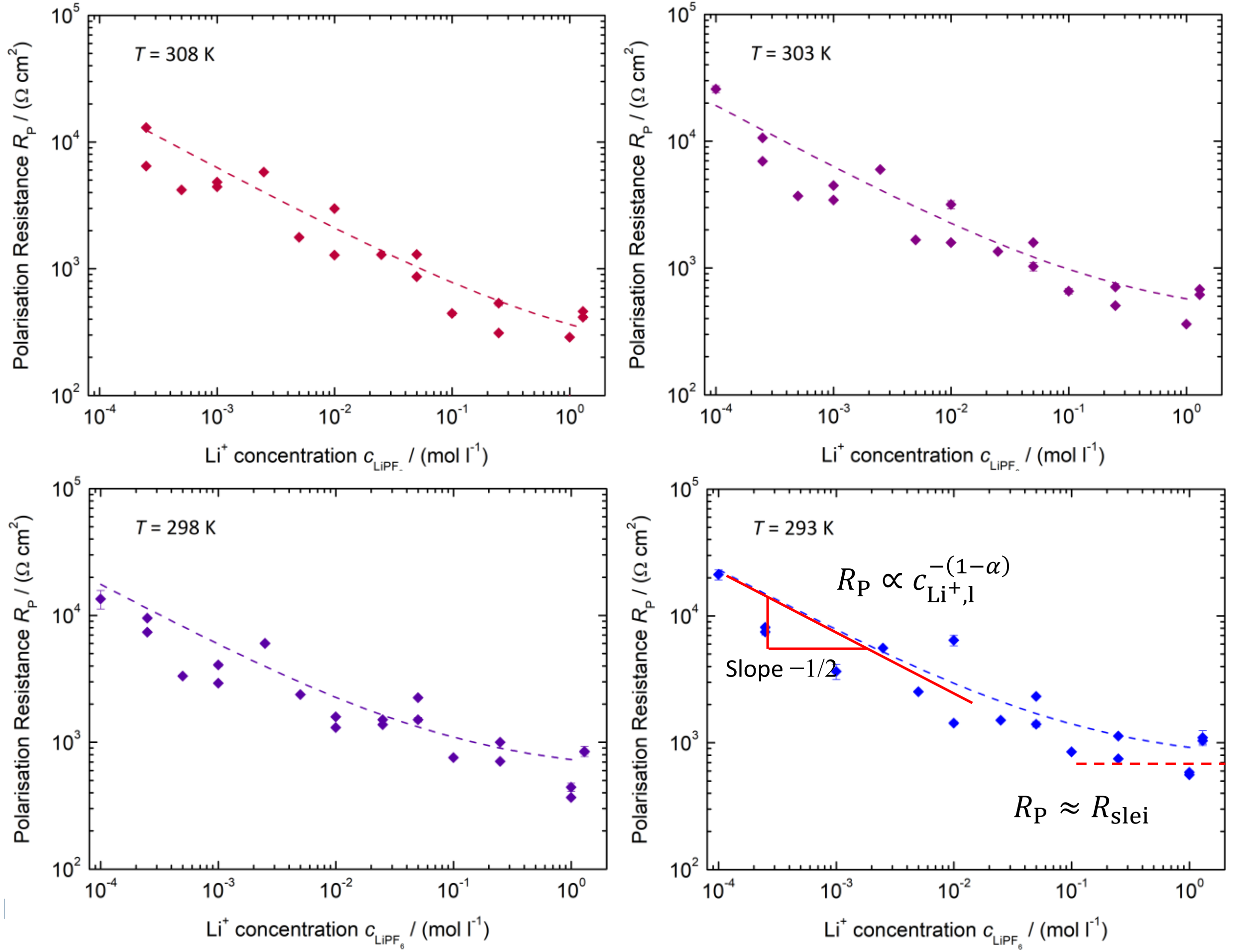




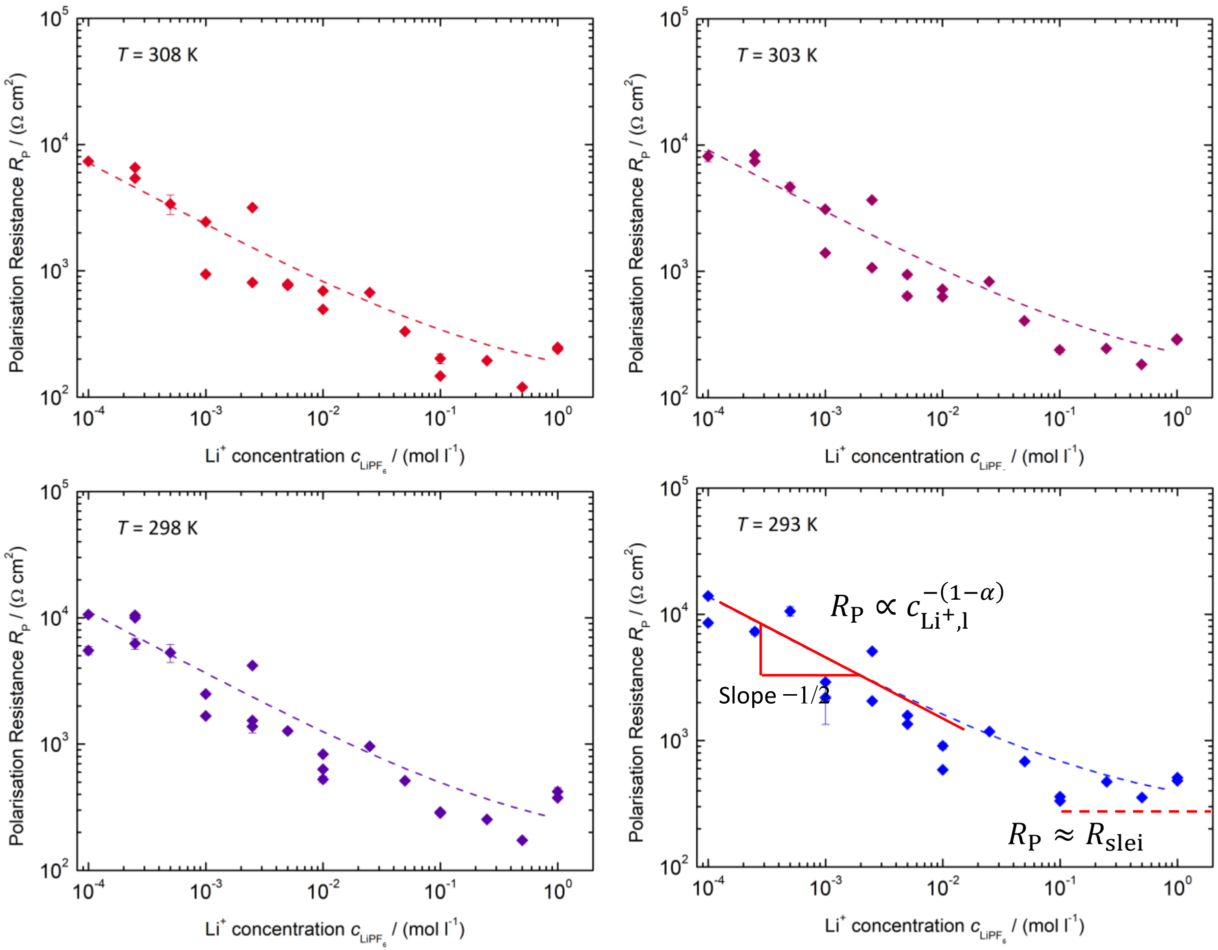


S2: Temperature dependent measurement of the (areal) polarisation resistance R_P, LLZO:Ta | DME/THF + LiBOB

Polarisation resistance of all measured systems



S3: Temperature dependent measurement of the (areal) polarisation resistance R_P, LATP | EC/DMC + $LiPF_6$



Polarisation resistance of all measured systems

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S4: Values for the areal resistance of the LE|SE interface layer R_{slei} and the Butler-Volmer-like rate constant $k_{ct}^{0\prime}$ at different temperatures T, obtained by fitting of the polarisation resistance R_p *vs.* Li^+ concentration curves in Fig. **S1** of the system LLZO:Ta | EC/DMC + $LiPF_6$

Temperature T / K	R_{slei} / (Ω cm^2)	$k_{ct}^{0\prime} \cdot 10^{-9}$/ (l$^{1/2}$ mol$^{1/2}$ s^{-1} cm^{-2})
288	1618 ± 215	1.06 ± 0.11
293	1060 ± 205	1.34 ± 0.20
298	559 ± 109	1.85 ± 0.22
303	443 ± 104	3.13 ± 0.46
308	284 ± 88	3.84 ± 0.74

$$\frac{T}{R_{slei}} = \frac{1}{(R_{slei})^*} \exp\left(-\frac{E_{a,slei}}{RT}\right)$$

$E_{a,slei}$ / (kJ mol^{-1})	$(R_{slei})^* \cdot 10^{-12}$ / Ω
67 ± 4	4.34 ± 7.79

$$k_{ct}^{0\prime} = (k_{ct}^{0\prime})^* \exp\left(-\frac{E_{a,ct}}{RT}\right)$$

$E_{a,ct}$ / (kJ mol^{-1})	$(k_{ct}^{0\prime})^*$ / (l$^{1/2}$ mol$^{1/2}$ s^{-1} cm^{-2})
51 ± 4	1.46 ± 2.59

S5: Values for the areal resistance of the LE|SE interface layer R_{slei} and the Butler-Volmer-like rate constant $k_{ct}^{0\prime}$ at different temperatures *T*, obtained by fitting of the polarisation resistance R_p *vs.* Li^+ concentration curves in Fig. **S2** of the system LLZO:Ta | DME/THF + LiBOB

Temperature T / K	R_{slei} / (Ω cm²)	$k_{ct}^{0\prime} \cdot 10^{-9}$/ ($l^{1/2}$ $mol^{1/2}$ s^{-1} cm^{-2})
293	695 ± 190	1.26 ± 0.22
298	560 ± 121	1.56 ± 0.20
303	384 ± 102	1.44 ± 0.18
308	172 ± 72	1.43 ± 0.19

$$\frac{T}{R_{slei}} = \frac{1}{(R_{slei})^*} \exp\left(-\frac{E_{a,slei}}{RT}\right)$$

$E_{a,slei}$ / (kJ mol^{-1})	$(R_{slei})^* \cdot 10^{-13}$ / Ω
71 ± 15	6.4 ± 38.3

$$k_{ct}^{0\prime} = (k_{ct}^{0\prime})^* \exp\left(-\frac{E_{a,ct}}{RT}\right)$$

$E_{a,ct}$ / (kJ mol^{-1})	$(k_{ct}^{0\prime})^* \cdot 10^{-8}$ / ($l^{1/2}$ $mol^{1/2}$ s^{-1} cm^{-2})
8 ± 9	3.7 ± 12.7

S6: Values for the areal resistance of the LE|SE interface layer R_{slei} and the Butler-Volmer-like rate constant $k_{ct}^{0\prime}$ at different temperatures *T*, obtained by fitting of the polarisation resistance R_p *vs.* Li^+ concentration curves in Fig. **S4** of the system LATP | EC/DMC + $LiPF_6$

Temperature T / K	R_{slei} / (Ω cm^2)	$k_{ct}^{0\prime} \cdot 10^{-9}$/ (l$^{1/2}$ mol$^{1/2}$ s^{-1} cm^{-2})
293	273 ± 92	2.14 ± 0.31
298	189 ± 71	2.40 ± 0.30
303	125 ± 53	2.82 ± 0.36
308	104 ± 44	3.73 ± 0.51

$$\frac{T}{R_{slei}} = \frac{1}{(R_{slei})^*} \exp\left(-\frac{E_{a,slei}}{RT}\right)$$

$$k_{ct}^{0\prime} = (k_{ct}^{0\prime})^* \exp\left(-\frac{E_{a,ct}}{RT}\right)$$

$E_{a,slei}$ / (kJ mol^{-1})	$(R_{slei})^* \cdot 10^{-10}$ / Ω
52 ± 5	4.22 ± 7.25

$E_{a,ct}$ / (kJ mol^{-1})	$(k_{ct}^{0\prime})^* \cdot 10^{-4}$ / (l$^{1/2}$ mol$^{1/2}$ s^{-1} cm^{-2})
27 ± 4	1.56 ± 2.69

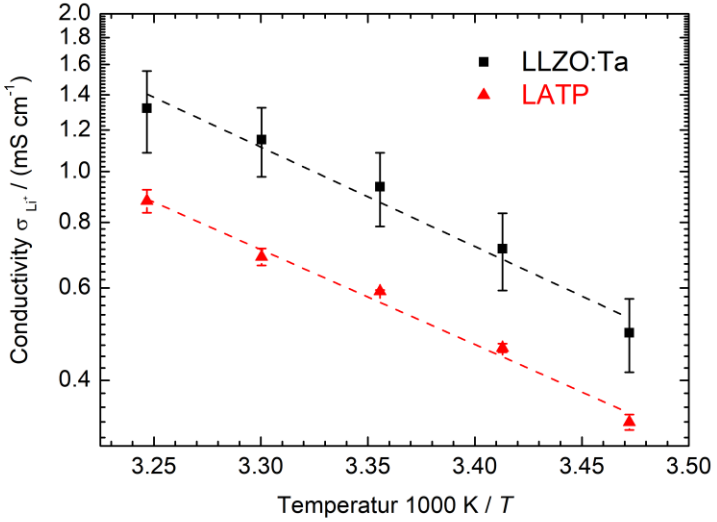
Li^+ conductivity of SEs

The potential drop $U_{p4} - U_{p3}$ between the probes p3 and p4 is equal to the electrochemical potential difference in the bulk of the SE. Its change as a function of the polarisation current density i is proportional to the bulk ionic conductivity σ_{Li^+}. The results for LLZO:Ta and LATP are depicted in Fig. S4 and S5.

$$\sigma_{Li^+} = F \frac{i\,\Delta x}{\Delta\tilde{\mu}_{Li^+}} = \frac{i\, d_{p4\ldots p3}}{U_{p4} - U_{p3}}$$

$d_{p4\ldots p3}$: Distance between the probes p3 and p4

S7: Ionic conductivity σ_{Li^+} of LLZO:Ta and LATP



S8: Ionic conductivity σ_{Li^+} of LLZO:Ta and LATP

	E_a / (kJ mol^{-1})
LLZO:Ta	36.3 ± 3.3
LATP	34.7 ± 2.1

$$T\sigma_{Li^+} = \sigma^*_{Li^+} \exp\left(-\frac{E_a}{RT}\right)$$

Comparison to a former study

S9: Polarisation resistance R_P of the system LLZO:Ta | EC/DMC + $LiPF_6$ at 298 K, data measured in this study (black squares) and data from M. Schleutker, J. Bahner, C.-L. Tsai and C. Korte, Phys. Chem. Chem. Phys., 2017, **19**, 26596–26605 (red diamonds) [19]