

# Supporting Information: Interplay of Structure and Dynamics in Solid Polymer Electrolytes: a Molecular Dynamics Study of LiPF<sub>6</sub>/polypropylene carbonate

Amaury Coste<sup>1</sup>, Thomas Meyer<sup>2</sup>, Claire Villevielle<sup>2</sup>, Fannie Alloin<sup>2</sup>,  
Stefano Mossa<sup>1</sup>, Benoit Coasne<sup>3,4</sup>

<sup>1</sup> Univ. Grenoble Alpes, CEA, IRIG-MEM-LSim, 38054 Grenoble, France

<sup>2</sup> Univ Grenoble Alpes, Univ Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, F-38000 Grenoble, France

<sup>3</sup>Univ. Grenoble Alpes, CNRS, LIPhy, Grenoble, 38000, France

<sup>4</sup>Institut Laue Langevin, 38042 Grenoble, France

amaury.coste@cea.fr; benoit.coasne@univ-grenoble-alpes.fr

## 1 Experimental Section

### 1.1 Polymer electrolyte elaboration

Polymer electrolytes elaboration was carried out in an argon-filled glovebox (H<sub>2</sub>O and O<sub>2</sub> < 0.1 ppm). There are made of poly(propylene carbonate) (Mn =50,000 by GPC, Sigma-Aldrich, store at -20 °C) and lithium hexafluorophosphate (LiPF<sub>6</sub>) (Tokyo Chemical Industry, purity > 97.0%, store under Ar). Three polymer electrolytes with various lithium content and a reference membrane without any lithium salt were prepared. Both, the polymer and the lithium salt, were dissolved in acetonitrile (Sigma-Aldrich, anhydrous, purity of 99.8%). After 2 h of magnetic agitation at 200 rpm at 80 °C, homogeneous solutions were casted in Petri dishes. Samples were dried at 60 °C under dynamic vacuum overnight.

### 1.2 Density Measurements

To estimate polymers density a Mettler Toledo 33360 density determination kit was used using the Archimedes method. Here, heptane (Sigma-Aldrich, purity ≥ 99.99%) was used because it is not dissolving the polymer electrolyte. Molecular sieve 0.3 nm was also use to obtain anhydrous heptane. Samples were weighted under argon and inside heptane. Experiments were performed in an argon-filled glovebox (H<sub>2</sub>O and O<sub>2</sub> < 0.1 ppm) at room temperature. Using Equation 1,

$$\rho_{\text{heptane}} = \rho_{\text{Ar}} \times \frac{m_{\text{sample in Ar}} - m_{\text{sample in heptane}}}{m_{\text{sample in Ar}}} \times (\rho_{\text{sample}} - \rho_{\text{Ar}}) \quad (1)$$

with  $\rho_i$  the density of  $i$  in g cm<sup>-3</sup> and  $m_i$  the mass of  $i$  in g. The  $\rho_{\text{argon}}$  is equal to 0.00178 at room temperature and the expected  $\rho_{\text{heptane}}$  is 0.6838 . The setup reliability was checked with samples made of either aluminum or inox with a known density of 2.71 and 7.8 , respectively.

## 2 Theoretical Section

### 2.1 Structural properties

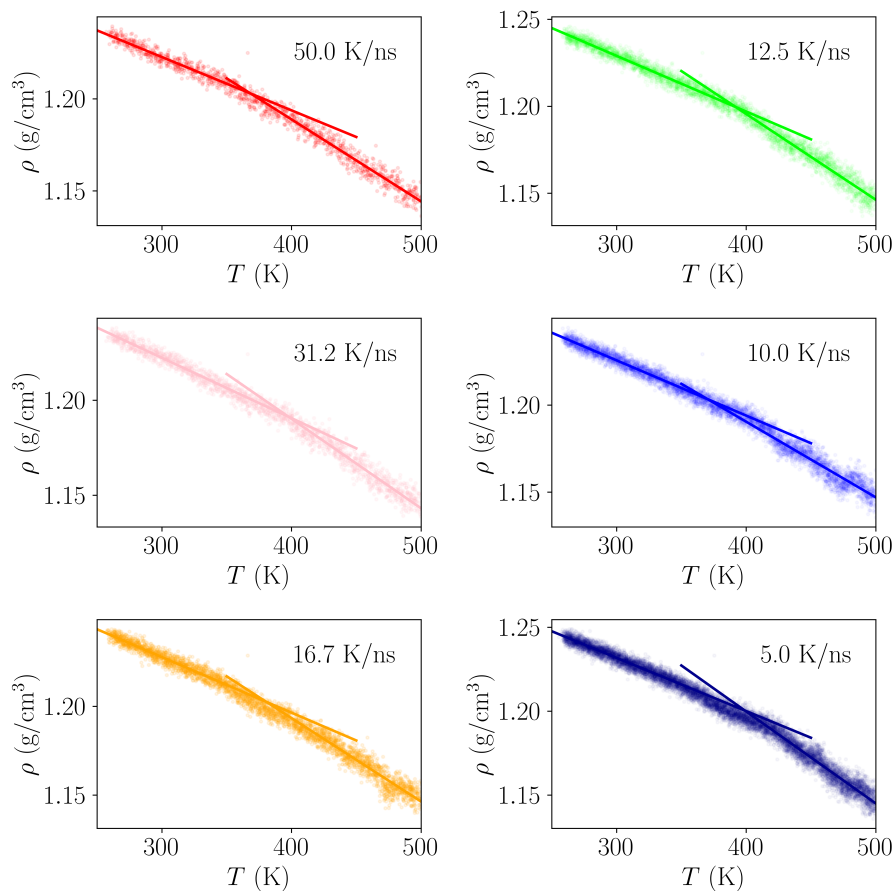


Fig. S1: Density–temperature profiles obtained from annealing simulations during cooling from 500 to 250 K at different cooling rates. Solid lines indicate fits to the two distinct regimes. The average glass transition temperature  $T_g$  is  $384 \pm 14$  K.

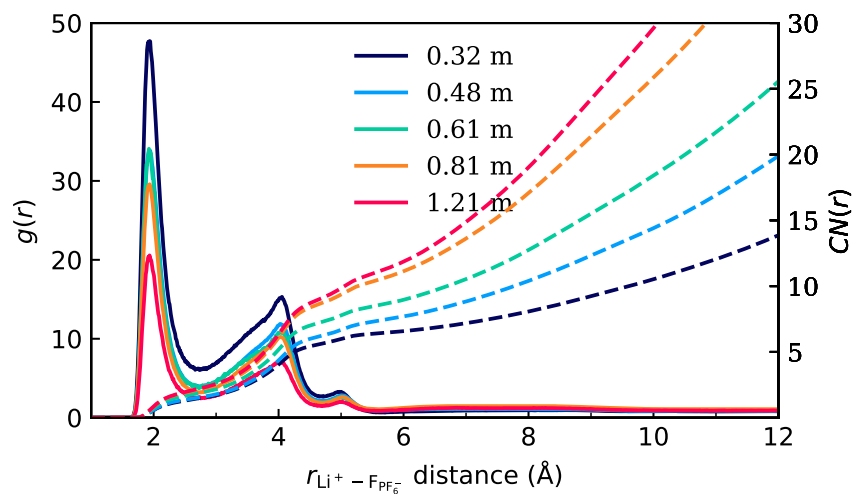


Fig. S2: Radial distribution function  $g(r)$  (solid lines) and associated coordination number  $CN(r)$  (dashed lines) for  $\text{Li}^+\text{-F}_{\text{PF}_6}^-$  interactions calculated at 353 K.

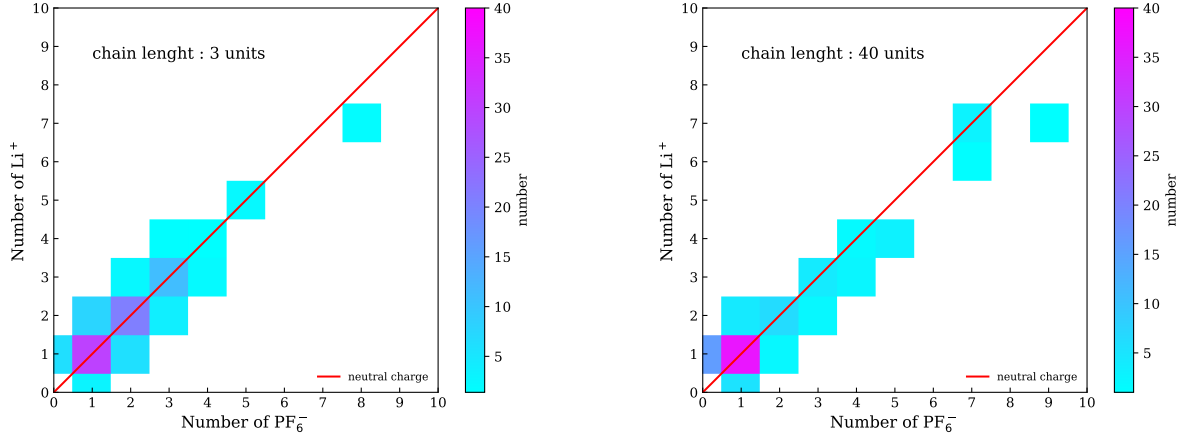


Fig. S3: Ion cluster  $[\text{Li}_x(\text{PF}_6)_y]^{x-y}$  population distribution for the solid polymer electrolyte with  $ratio_{\text{carbonate/salt}}$  equal to 8 at 353.15 K for the short chains (left panel) and the long chains (right panel) SPE. Ions belong to the same cluster if they formed a contact ion pair,  $r_{\text{Li-P}} \leq 5.1 \text{ \AA}$ . The red line show the equimolar clusters.

T (K)	$c_s$ (mol/kg)	Free ions (%)		ions in CIPs (%)		ions in clusters (%)	
		$\text{Li}^+$	$\text{PF}_6^-$	$\text{Li}^+$	$\text{PF}_6^-$	$\text{Li}^+$	$\text{PF}_6^-$
353	0.32	24	15	43	43	33	42
	0.48	15	6	43	43	42	51
	0.61	16	5	31	31	53	64
	0.81	13	3	23	23	64	74
	1.21	8	3	18	18	74	79
700	0.32	11	8	45	45	44	47
	0.48	11	7	37	37	52	56
	0.61	11	7	32	32	57	61
	0.81	10	6	26	26	64	68
	1.21	9	4	18	18	73	77
800	0.32	12	8	42	42	46	50
	0.48	11	8	35	35	54	57
	0.61	11	7	30	30	59	63
	0.81	10	6	24	24	66	70
	1.21	9	4	18	18	73	77

Table 1: Average distribution of  $\text{Li}^+$  cations and  $\text{PF}_6^-$  anions into their three different states : free ion, in contact ion pair  $\text{LiPF}_6$  and in cluster  $[\text{Li}_x(\text{PF}_6)_y]^{x-y}$  reported for different temperatures. Free ions are defined as ions with no counter ion in the first cation-anion coordination shell (radius 5.1  $\text{\AA}$ ), the rest of ions form CIPs or clusters.

## 2.2 Dynamics properties

### 2.2.1 Self diffusion coefficients of ions

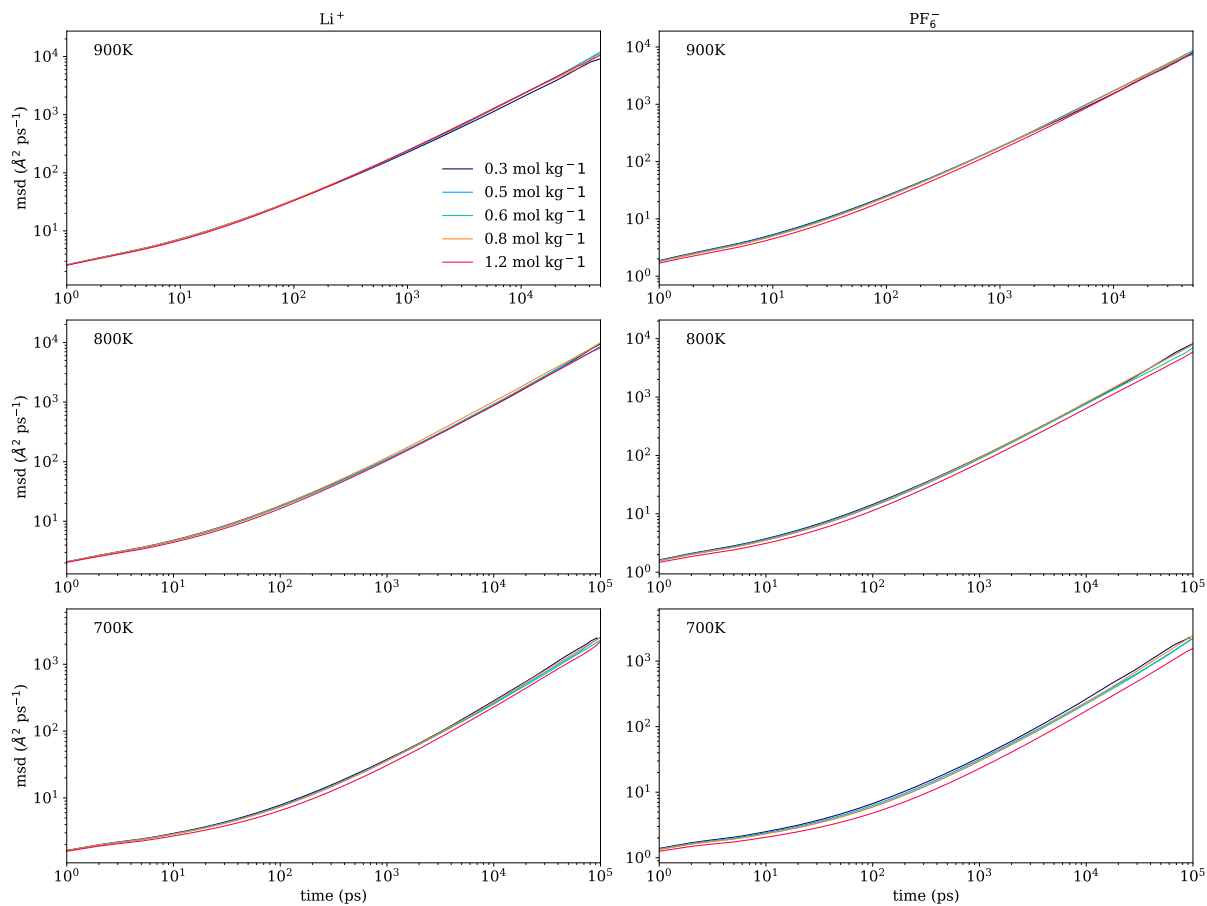


Fig. S4: Mean squared displacement for the  $\text{Li}^+$  cation and  $\text{PF}_6^-$  anion as a function of  $T$  and  $c_s$ .

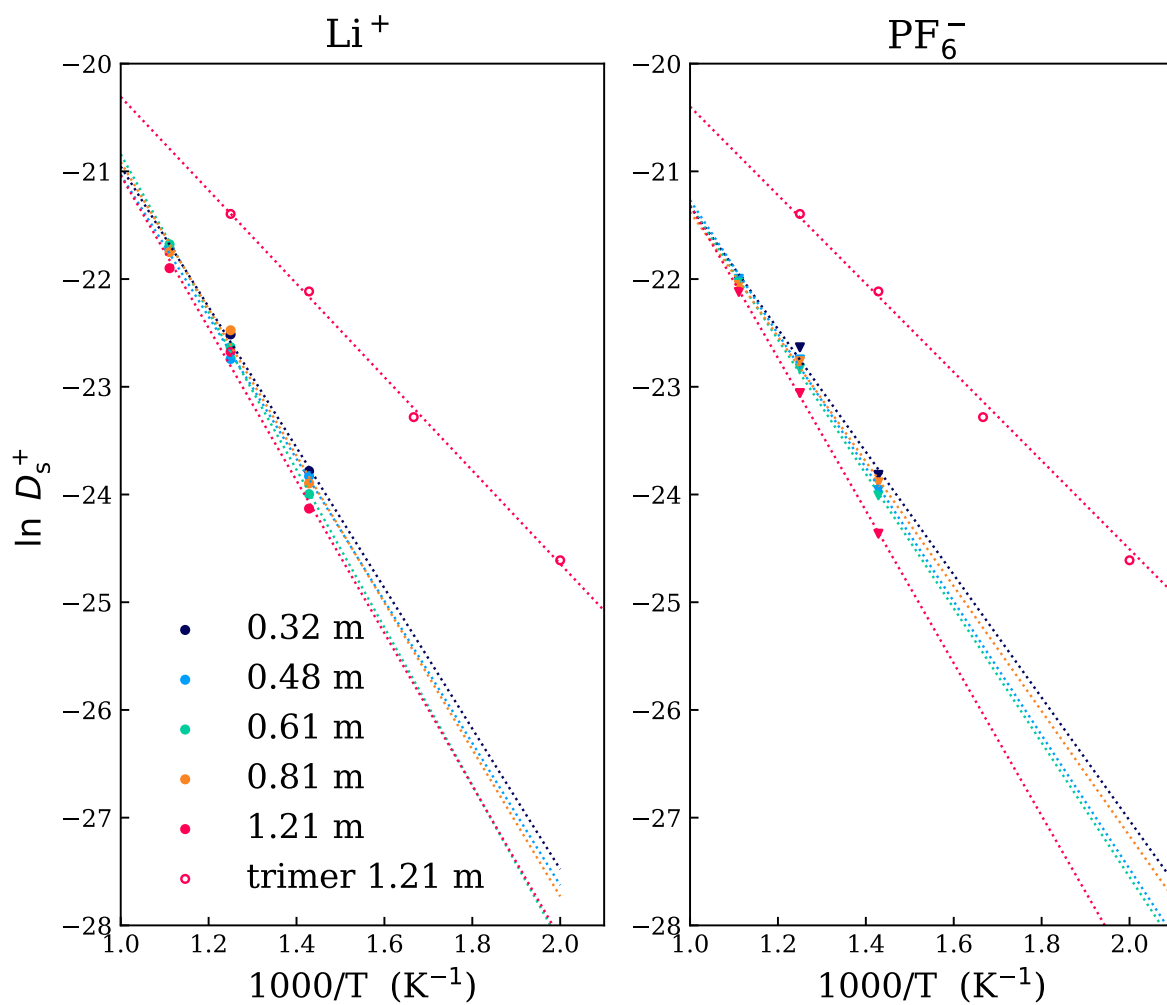


Fig. S5: Arrhenius plot for the self diffusion coefficients for  $\text{Li}^+$  cation and  $\text{PF}_6^-$  anion for the long (solid point) and short (empty point) chain polymer electrolytes solution with a salt concentration  $c_s$  ranging from 0.32 to 1.21 mol  $\text{kg}^{-1}$  (ratio carbonate/salt from 30 to 8).

## 2.2.2 Ionic conductivity

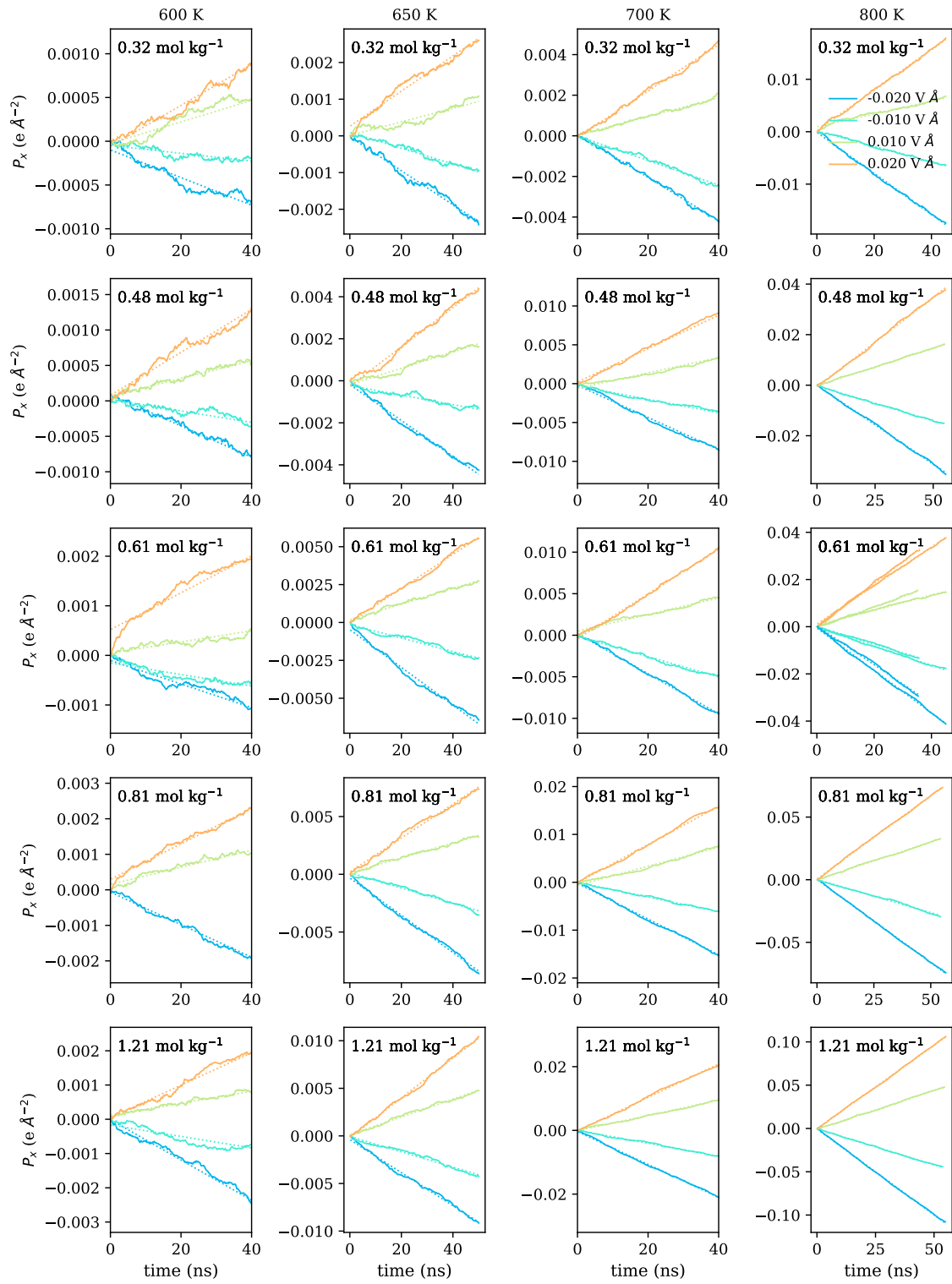


Fig. S6: Dipole as a function of time current for the the electric field  $E_x$  for the different temperatures  $T$  and salt concentration.

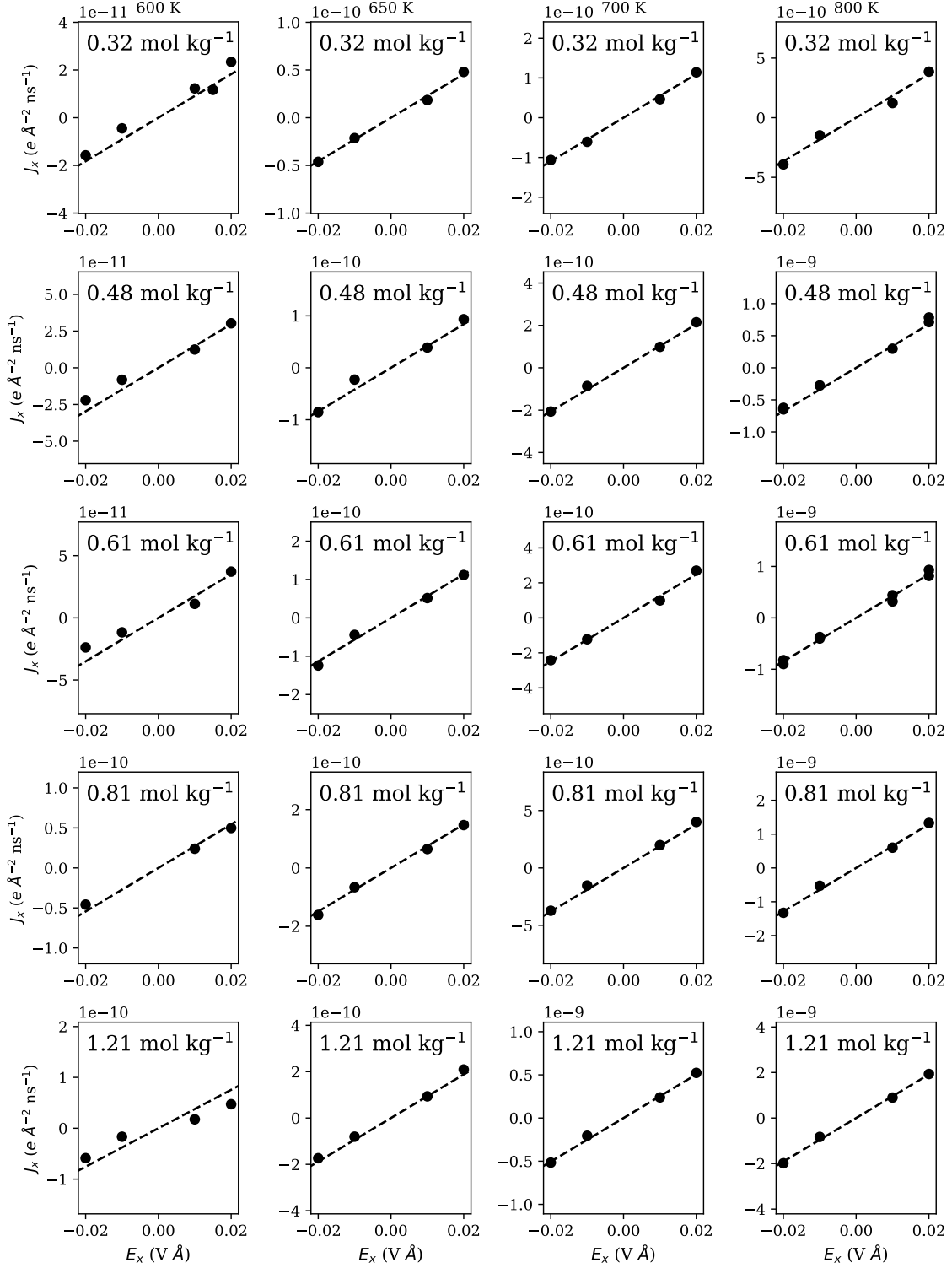


Fig. S7: Ionic current  $J_x$  as a function of electric field  $E_x$  for the different temperatures  $T$  and salt concentration.

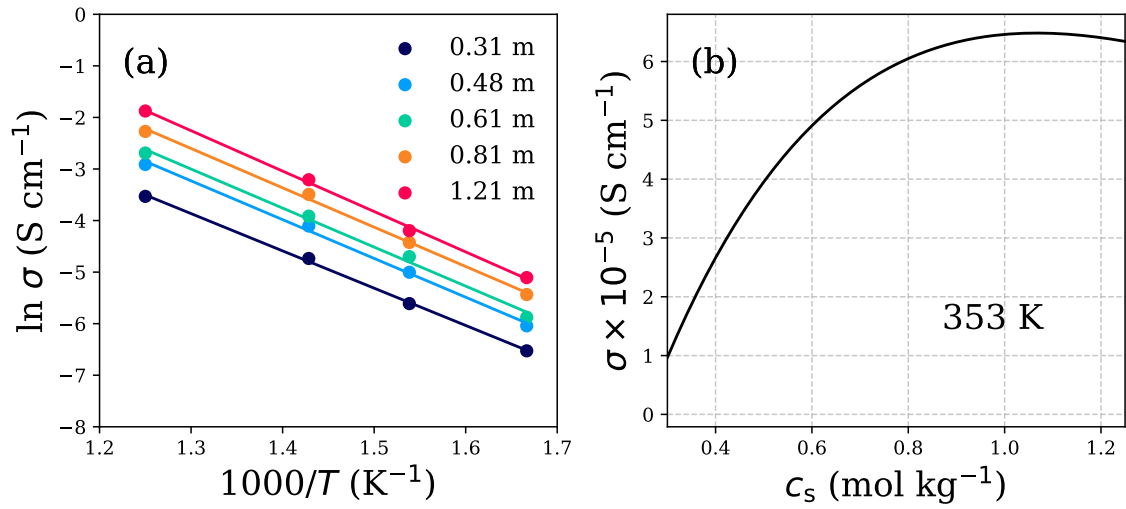


Fig. S8: (a) Arrhenius plot for  $\sigma$  for the different SPEs. (b) Electrical conductivity  $\sigma$  as a function of  $c_s$  at 353 K

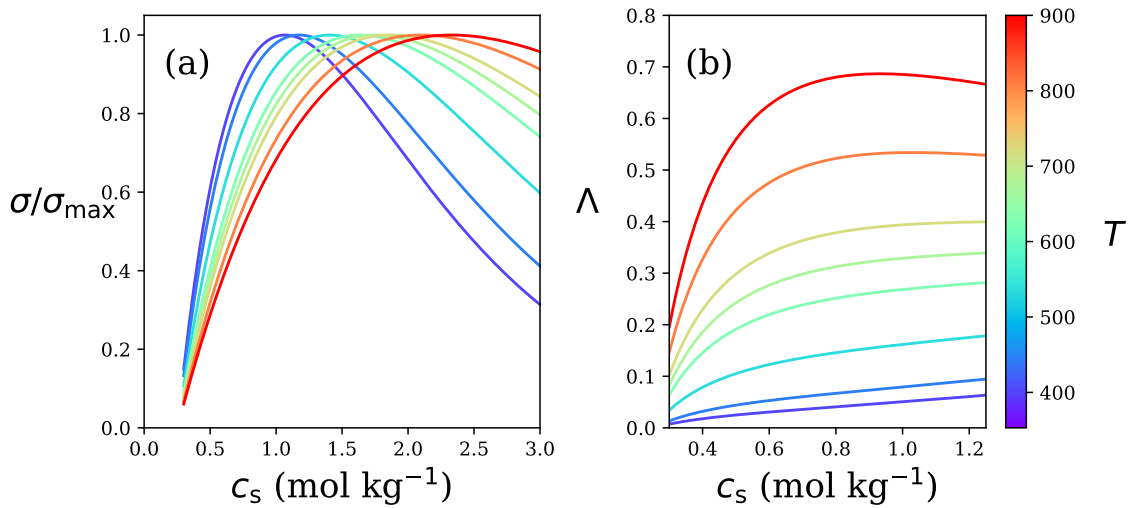


Fig. S9: Normalised ionic conductivity (a) and Ionicity  $\Lambda$  (b) predicted with Arrhenius models as a function of  $c_s$  and  $T$