Supplementary Information

Hybrid polymer-liquid electrolytes for lithium-ion batteries: effect of porosity on the ionic and molecular mobility.

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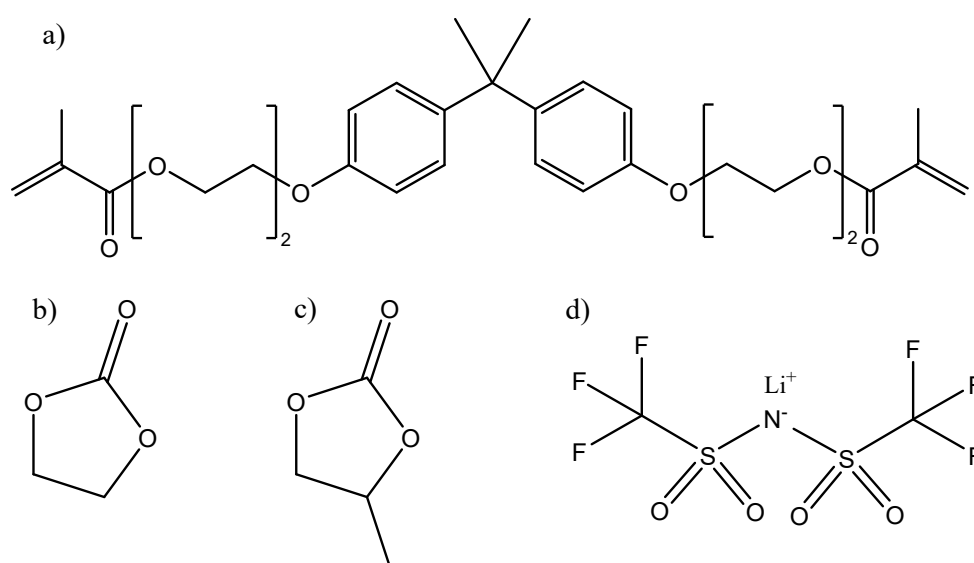
Figure S1: The chemical structure of the main chemicals used in this study: a) monomer Bisphenol A ethoxylate dimethacrylate (BPAMA), b) ethylene carbonate (EC), c) propylene carbonate (PC), d) LiTFSI salt.

- **Conversion calculation of the acrylate groups with FTIR analysis**

The conversions of the acrylate groups with FTIR for all the different formulations was calculated as following:

$$Conversion = \left(1 - \frac{A_{resin,\, C=O} * A_{film,\, C=C}}{A_{resin,\, C=C} * A_{film,\, C=O}}\right) * 100$$

where $A_{resin, C=O}$ is the absorbance area of the carbonyl peak of the ester group at 1715 cm^{-1} of the uncured resin, $A_{film, C=C}$ is the absorbance area of the vinyl peak at 1637 cm^{-1} of the cured film, $A_{resin, C=C}$ is the absorbance area of the vinyl peak at 1637 cm^{-1} of the uncured resin and $A_{film, C=O}$ is the absorbance area of the carbonyl peak of the ester group at 1715 cm^{-1} of the cured film.
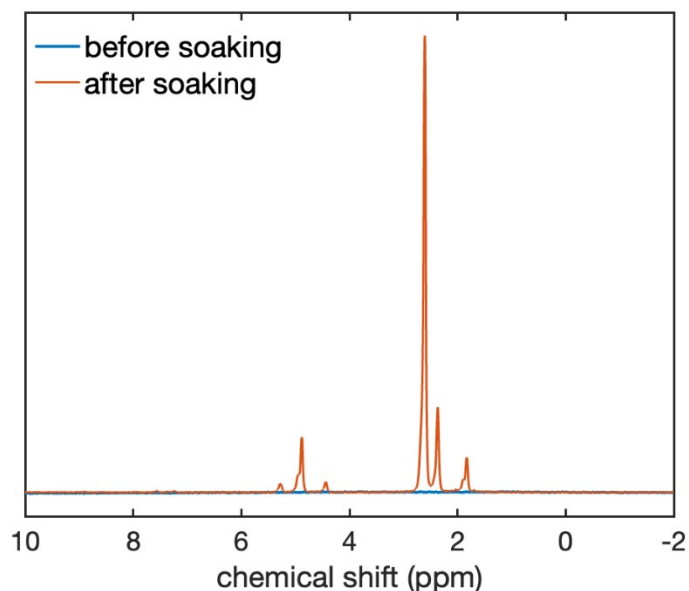
**Figure S2:** ^{1}H NMR spectra of the sample with pBPAMA as is (blue) and after having the pBPAMA soaked in acetonitrile (orange).
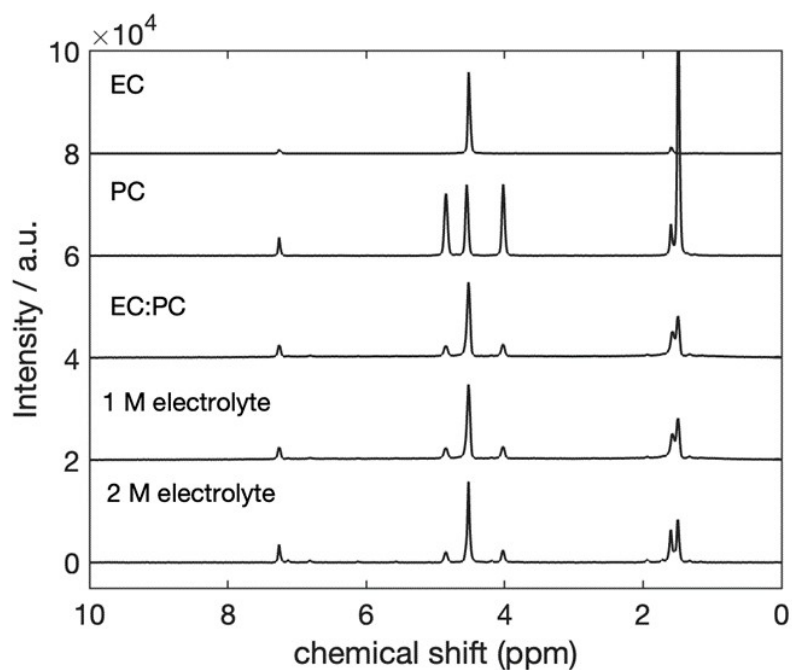

Figure S3: ^{1}H NMR spectra of pure EC, pure PC, a mixture of EC:PC (1:1 wt%), 1 M LiTFSI in EC:PC (1:1 wt%), 2M LiTFSI in EC:PC (1:1 wt%). In the EC:PC 1:1 wt%, the NMR peak at 4.52 ppm is contributed by EC and PC molecules at the molar ratio of 4.6:1.
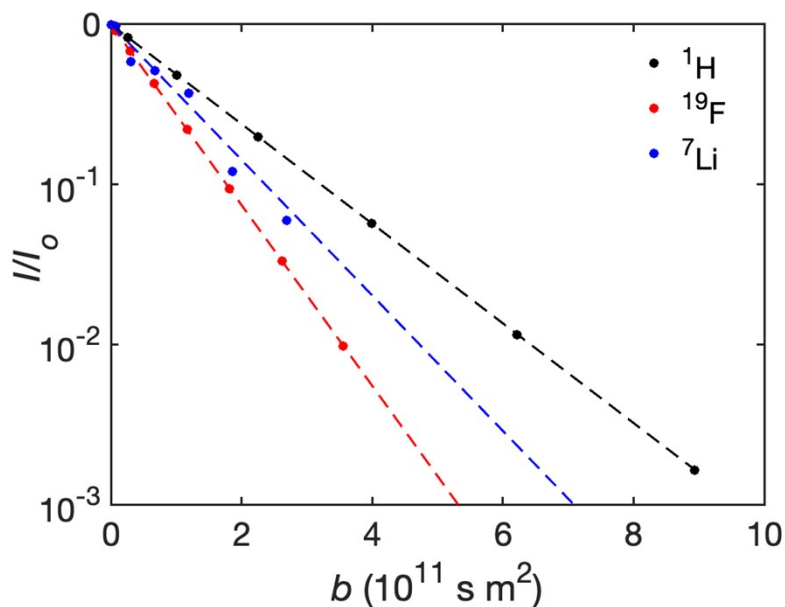
Figure S4: The diffusional decay obtained in different molecular components in the HE 50 wt% sample. [1]H signal is from the solvent (the peak at 4.52 ppm, methylene groups from both EC and PC, see Figure S2), the ^{19}F signal is from the anion and the [7]Li signal is from the cation. b is $\gamma^2\delta^2 g^2\left(\Delta - \dfrac{\delta}{3}\right)$. I and I_0 are the signal intensities with and without gradient, respectively.
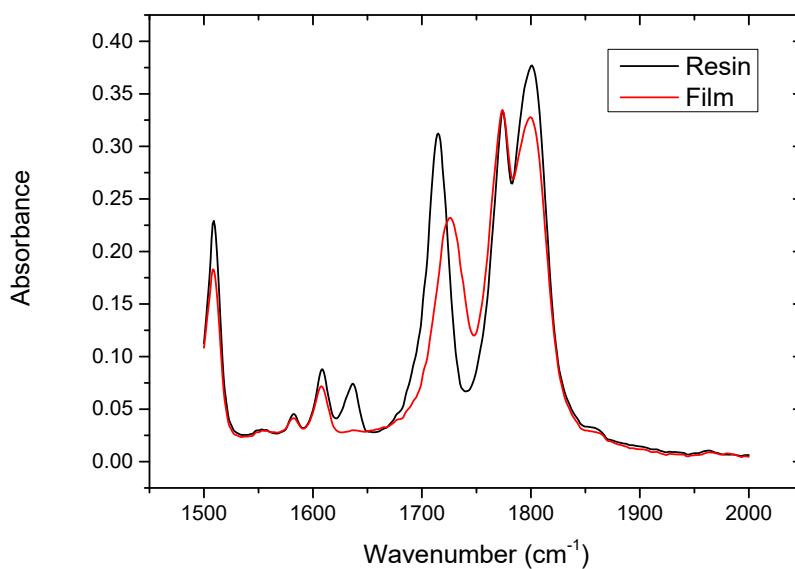
Figure S5: FTIR spectra of the resin (before curing) and of the film (after curing) showing the disappearance of the vinyl stretch peak at 1637 cm^{-1} for HE 40 wt%.
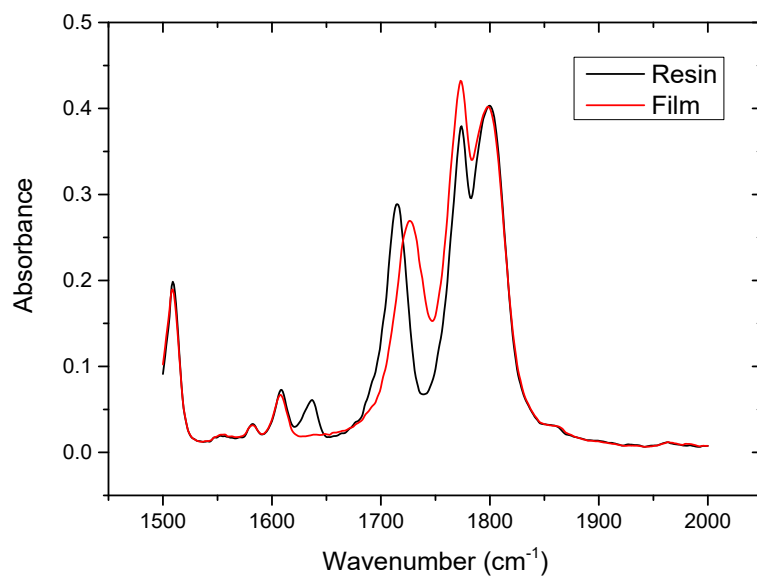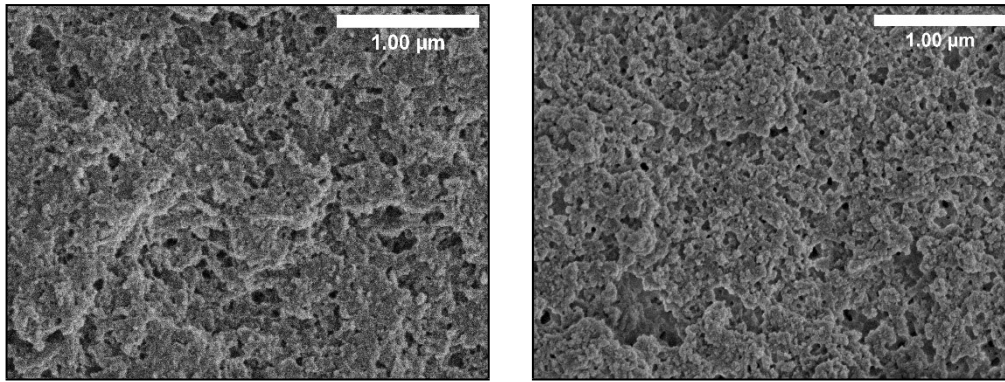
Figure S6: FTIR spectra of the resin (before curing) and of the film (after curing) showing the disappearance of the vinyl stretch peak at 1637 cm^{-1} for HE 45 wt%.
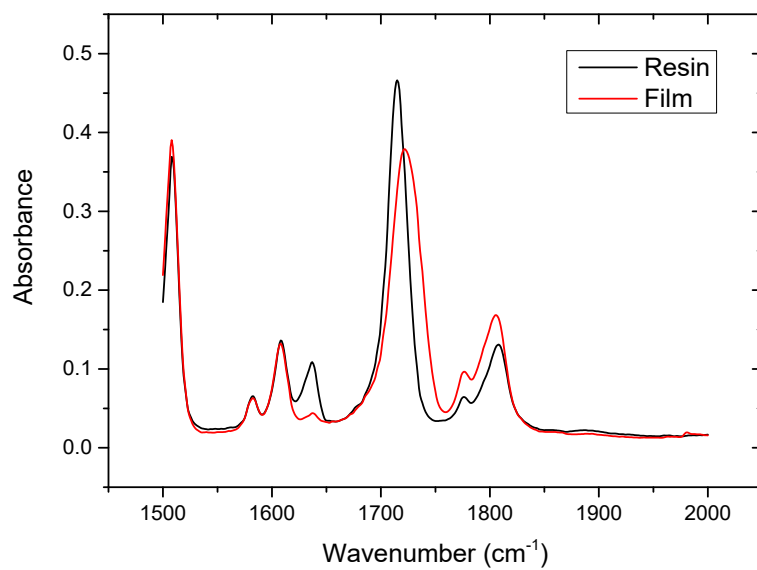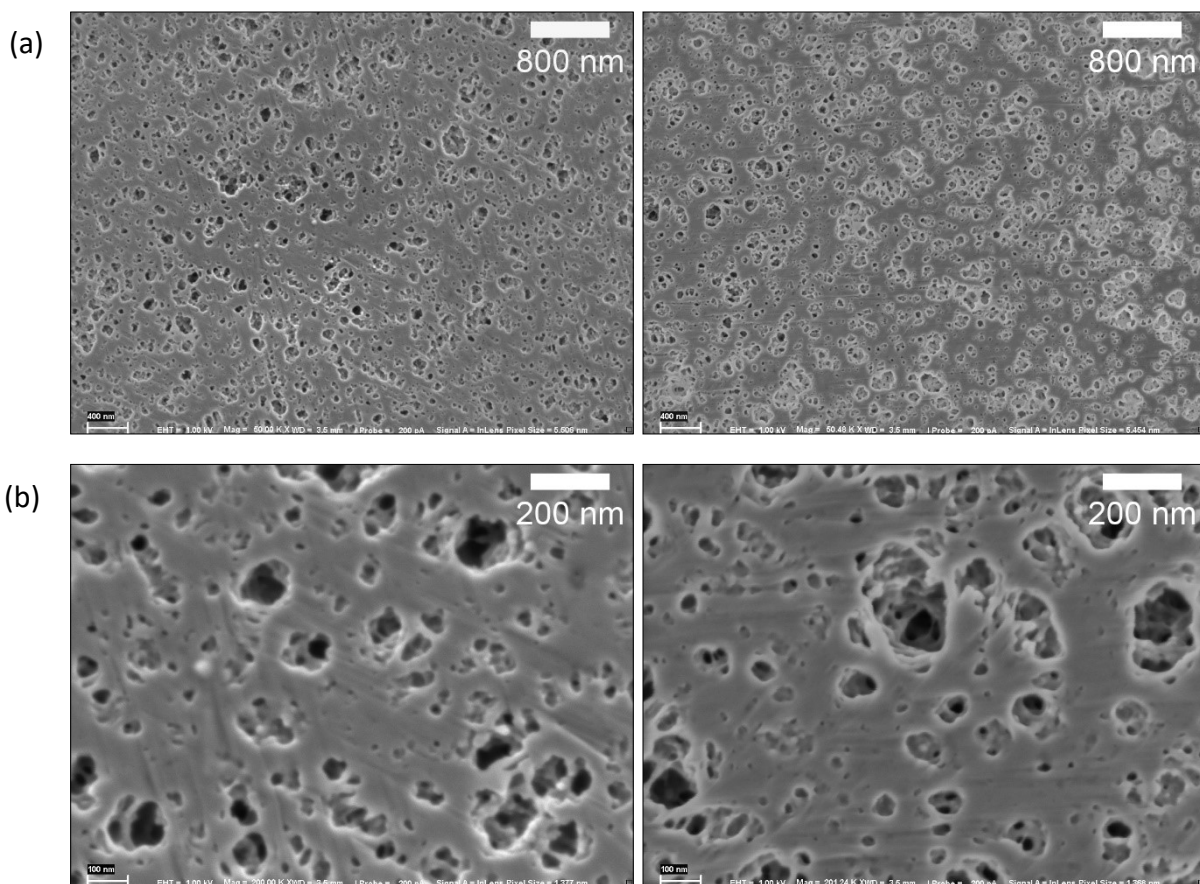

Figure S7: FTIR spectra of the resin (before curing) and of the film (after curing) showing the disappearance of the vinyl stretch peak at 1637 cm^{-1} for pBPAMA.

Figure S8: Cross-sectional SEM micrographs of cryo-fractured HE 45 wt% (left) and of HE 50 wt% (right). All samples were dried beforehand.

Figure S9: BIB-SEM images of HE 40 wt% (left) vs HE 50 wt% (right) electrolyte content HEs at different magnifications (a) 50k (b) 200 k.

- **Calculation of the absorbed LiTFSI in soaked pBPAMA**

The concentration of absorbed LiTFSI was calculated as following:

In Table 3 we detected 1.11 mg PC and 1.16 mg EC released from pBPAMA soaked in 1 M electrolytes. The density of PC:EC 50 /50 v/v was taken as 1.007 g/ml, thus the total volume of PC/EC mixture is

$$\frac{1.11 + 1.16}{1.0069} = 2.254\ \mu L$$

The LiTFSI released from the same sample was 0.21 mg (Table 3). The molecular weight of LiTFSI is 287.09 g/mol. Thus its concentration in the released PC/EC is $\frac{0.21 \times 10^{-3}}{287.09 \times 2.254 \times 10^{-6}} = 0.32\ M$.

Similarly, the concentration of absorbed LiTFSI in EC/PC for the pBPAMA soaked in 2M electrolytes was calculated as

$$\frac{1.20 + 1.22}{1.0069} = 2.403\ \mu L$$

$$\frac{0.16 \times 10^{-3}}{287.09 \times 2.403 \times 10^{-6}} = 0.23\ M$$
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Table S1: ^{1}H (solvent)[a], ^{19}F (anion) and ^{7}Li (cation) self-diffusion coefficients of the different electrolyte formulations

Samples	Average Conductivity (S*cm^{-1})	Diffusion coefficients (10^{-12} m^2/s)		
		^{1}H	^{19}F	^{7}Li
1 M LiTFSI	4.35*10^{-3}	241	153	108
HE 40 wt	3.66*10^{-5}	0.86	2.28	1.19
HE 45 wt%	1.36*10^{-4}	2.25	6.23	3.50
HE 50 wt%	2.94*10^{-4}	7.17	13.0	9.75

[a]The 4.52 ppm ^{1}H peak (see Figure S2) was used to follow the solvent behavior. In the 1:1 solvent mixture, the diffusion coefficient of PC obtained from the diffusional decay of the 1.5 ppm peak is 2.24×10^{-12} m^2/s. The overlapping EC/PC peak 4.52 ppm provides a diffusional decay that yields a diffusion coefficient of 2.44×10^{-12} m^2/s. Since this latter peak is contributed in intensity by roughly 80% by EC, the EC diffusion coefficient in the 1:1 mixture is roughly 2.5×10^{-12} m^2/s. Hence, the transport properties of the EC and PC molecules in the mixed solvent are roughly the same.