Cellulose nanofiber-reinforced solid polymer electrolytes with high ionic conductivity for lithium batteries – Supporting Information –

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Sample preparation



Figure S1: Flowchart for the preparation of a CNF-reinforced, LiTFSI salt-containing solid polymer electrolyte (SPE) composite using an EO–*co*–EPI statistical copolymer as the matrix.

Chemical characterisation

CNFs addition (Figure S2): Despite the overall similar spectra of the CNF-free, neat EO-*co*-EPI copolymer and the CNF-reinforced, neat EO-*co*-EPI copolymer composite, both spectra exhibit significantly reduced OH stretching bands in the region between 3500 cm⁻¹ and 3000 cm⁻¹ compared to the spectra of the CNFs, indicating the absence of free OH groups on the surface of the CNFs as a result of their interaction with the polymer matrix in the composite. In addition, the general systematic shift of peaks in the spectra of the EO-*co*-EPI copolymer compared to those of the CNF-containing EO-*co*-EPI composite further suggests efficient interactions between the CNFs and the matrix polymer.

LiTFSI addition (Figure S3): Analysis of the FTIR spectra of the LiTFSI salt-containing EO-co-EPI electrolyte compared to those of LiTFSI and EO-co-EPI allows evaluation of the salt-polymer interactions. For example, the observed S-N-S stretching band at around 1055 cm^{-1} in the spectra of LiTFSI and LiTFSI-doped EO-co-EPI clearly indicates the incorporation of the salt into the polymer matrix. In addition, the shift of the asymmetric CF_3



Figure S2: FTIR spectra of an EO–co–EPI composite reinforced with 10 % w/w CNFs and without added LiTFSI (top), a neat EO–co–EPI copolymer without added CNFs and without added LiTFSI (middle), and a CNF sample (bottom).

stretching band from 1194 cm^{-1} for LiTFSI to 1188 cm^{-1} for the LiTFSI-doped EO-*co*-EPI indicates interactions between the salt and the polymer matrix. Importantly, a similar shift observed for the C-O-C stretching band from 1092 cm^{-1} to 1089 cm^{-1} confirms the well-known complexation of the ether oxygens in EO-based polymers with Li⁺ ions.¹ In addition, a shift is observed for the C-H stretching band at 2867 cm⁻¹ for the neat EO-*co*-EPI to 2873 cm^{-1} band in the LiTFSI-doped EO-*co*-EPI, which also confirms polymer-salt interactions. Interestingly, while peaks are seen at 742 cm^{-1} for the neat EO-*co*-EPI characteristic of C-Cl stretching and at 746 cm^{-1} for LiTFSI attributed to S-N-S stretching, the spectra of the LiTFSI-doped EO-*co*-EPI shows a shifted peak at 740 cm^{-1} , suggesting interactions between the Cl atom of EO-*co*-EPI and LiTFSI.

Polymer composites (Figure S4): In analogy to the FTIR spectra of the LiTFSIdoped EO-*co*-EPI (Figure S3), for the CNF-reinforced, LiTFSI-doped EO-*co*-EPI (Figure S4) the S-N-S stretching band at 1056 cm⁻¹ and the (shifted) C-O-C stretching band at 1090 cm⁻¹ strongly confirm the successful incorporation of LiTFSI into the EO-*co*-EPI. The C-O-C stretching band appears at 1092 cm⁻¹ for the neat EO-*co*-EPI, slightly shifts up to 1093 cm⁻¹ for the CNF-reinforced EO-*co*-EPI (no LiTFSI), while it shifts down to 1089 cm⁻¹ for the LiTFSI-doped EO-*co*-EPI (no CNF). For the CNF-reinforced, LiTFSI-doped EO-*co*-EPI, the C-O-C stretching band is at 1090 cm⁻¹, which appears to be a result of both LiTFSI and CNF addition, reflecting that the ether oxygen in C-O-C can complex Li⁺ of LiTFSI, but also hydrogen bond to OH in CNFs.



Figure S3: FTIR spectra of an EO–co–EPI electrolyte with an LiTFSI concentration of r = 0.04 and without added CNFs (top), a neat EO–co–EPI copolymer without added LiTFSI and without CNFs (middle), and LiTFSI salt (bottom) with the chemical structures of EO–co–EPI and LiTFSI shown as insets.



Figure S4: FTIR spectra of an EO–co–EPI composite electrolyte with 10% w/w CNFs and an LiTFSI concentration r = 0.04 (top), an EO–co–EPI electrolyte without added CNFs and an LiTFSI concentration r = 0.04 (middle), and an EO–co–EPI composite with 10% w/w CNFs and without added LiTFSI (bottom).

Mechanical properties



Figure S5: Storage modulus E' vs temperature of EO–co–EPI composite electrolytes with different LiTFSI salt concentrations (r = 0.02, r = 0.04, r = 0.08) and 10% w/w CNFs.

Thermal properties



Figure S6: DSC curves of EO–co–EPI composite electrolytes with 10 % w/w CNFs and different LiTFSI salt concentrations r.

Characterisation of ionic conductivity



Figure S7: Comparison of the temperature–dependent ionic conductivities of the EO–co–EPI composite electrolytes reinforced with 10% w/w and 15% w/w CNFs and constant LiTFSI salt concentration of r = 0.04.



Figure S8: VTF fitting of the ionic conductivity of an LiTFSI-doped EO-co-EPI composite electrolyte without added CNFs as well as LiTFSI-doped EO-co-EPI composite electrolytes with 10% w/w CNFs and different salt concentrations r.

Electrochemical characterisation

The CV curve of an EO-*co*-EPI electrolyte with an LiTFSI concentration of r = 0.04 and without CNFs (Figure S9) agrees with previous work on similar systems.^{2,3} For the cathodic sweep, the peak at -0.5 V is characteristic of the Li deposition in Cu, while for the anodic scan, the small peak slightly below 4 V is due to the oxidation of PEO.^{4,5}



Figure S9: Cyclic voltammogram of an EO–*co*–EPI electrolyte with an LiTFSI concentration of r = 0.04 and without CNFs over a potential range of -0.5 V - 5.5 V, at a scan rate of 0.5 mV s^{-1} and a temperature of 70 °C.



Figure S10: Plots of the voltage versus total charge passed for symmetrical Li/Li using LiTFSI– doped EO–co–EPI composite electrolytes with a salt concentration of r = 0.04 a) without CNF reinforcement, and b) with 10% w/w CNFs. In both cases the last cycles before failure are shown.

References

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