

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

– Supporting Information –

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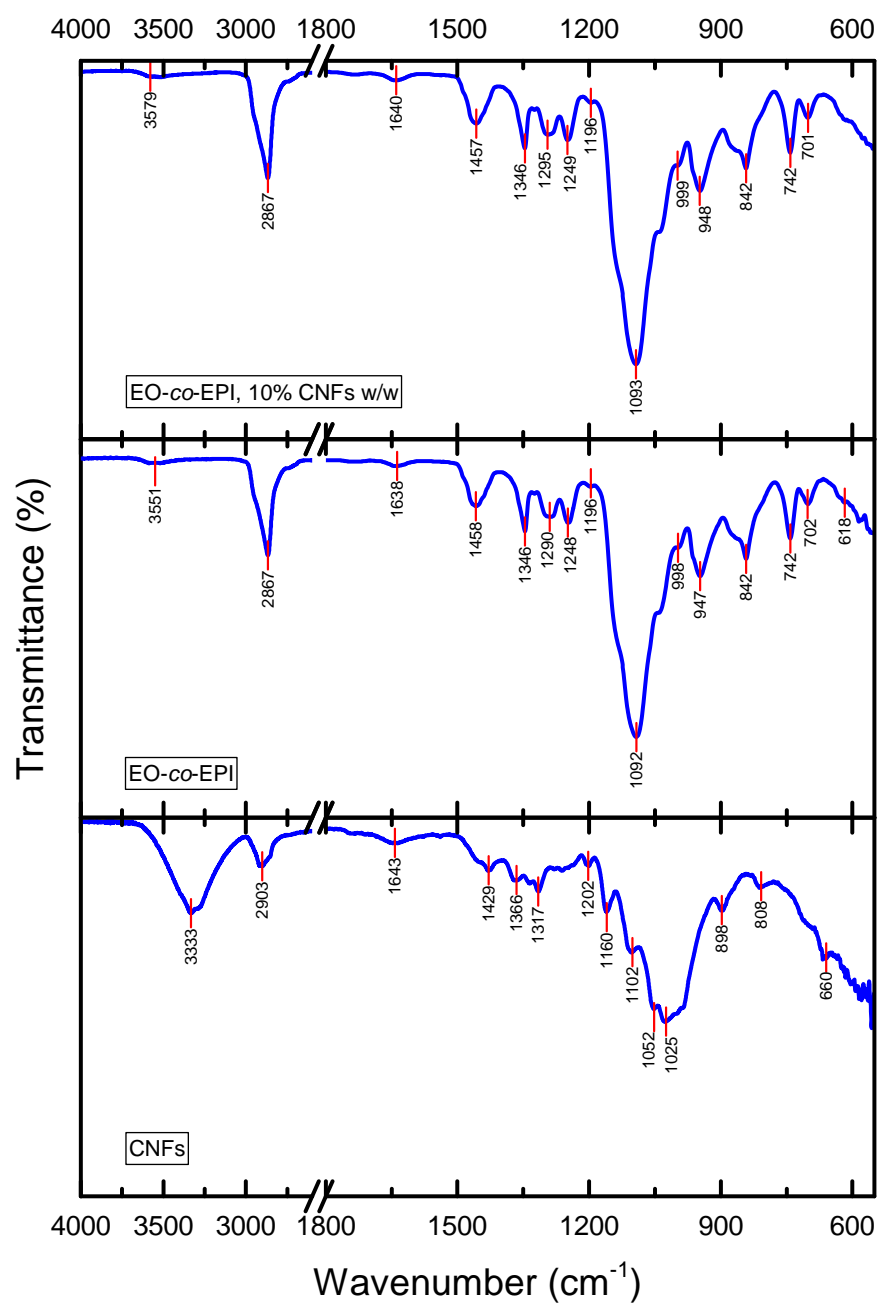


Figure S2: FTIR spectra of an EO-co-EPI composite reinforced with 10 % w/w CNFs and without added LiTFSI (*top*), a neat EO-co-EPI copolymer without added CNFs and without added LiTFSI (*middle*), and a CNF sample (*bottom*).

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 (FigureS4): In analogy to the FTIR spectra of the LiTFSI-doped EO-*co*-EPI (FigureS3), for the CNF-reinforced, LiTFSI-doped EO-*co*-EPI (FigureS4) 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.

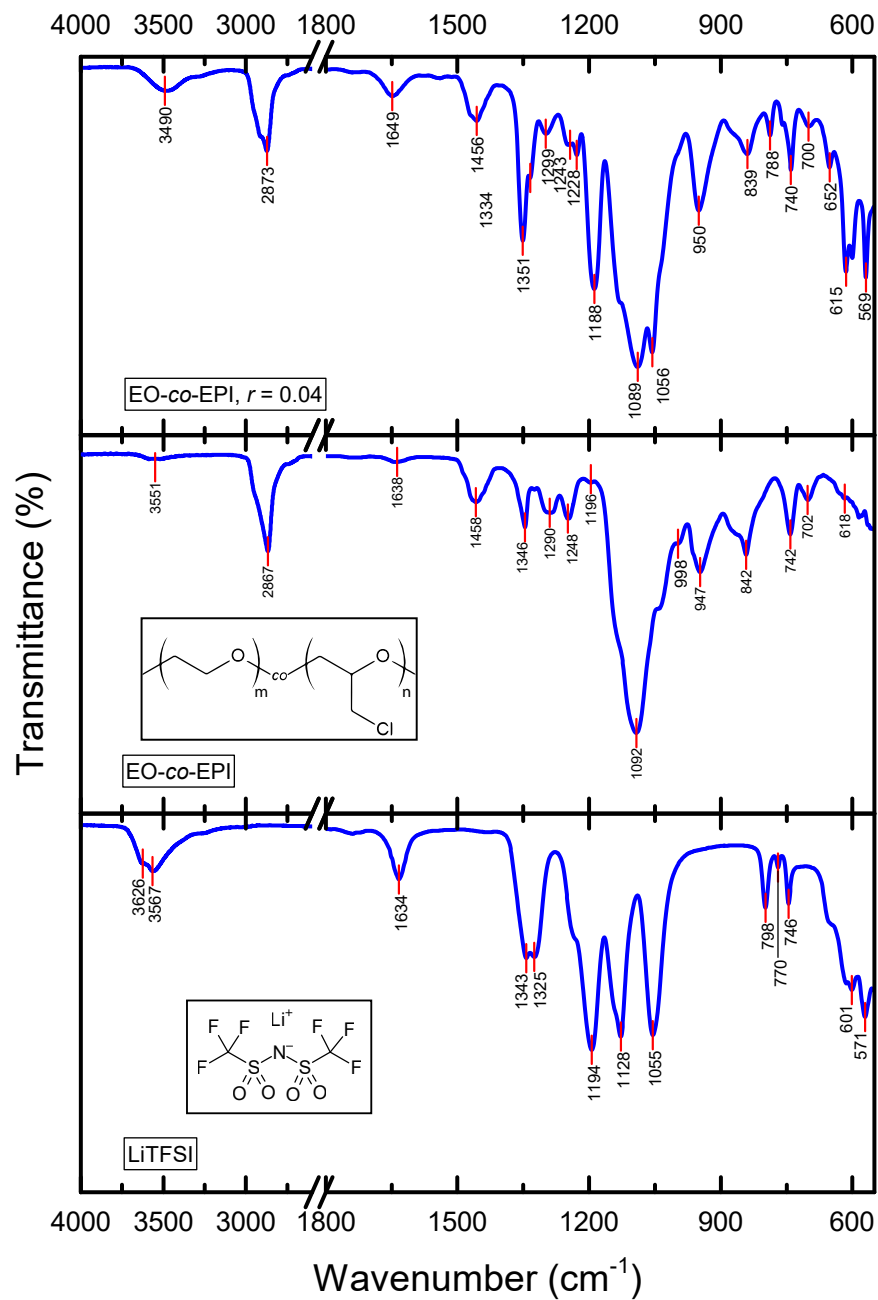


Figure S3: FTIR spectra of an EO-co-EPI electrolyte with an LiTFSI concentration of $r = 0.04$ and without added CNFs (*top*), a neat EO-co-EPI copolymer without added LiTFSI and without CNFs (*middle*), and LiTFSI salt (*bottom*) with the chemical structures of EO-co-EPI and LiTFSI shown as insets.

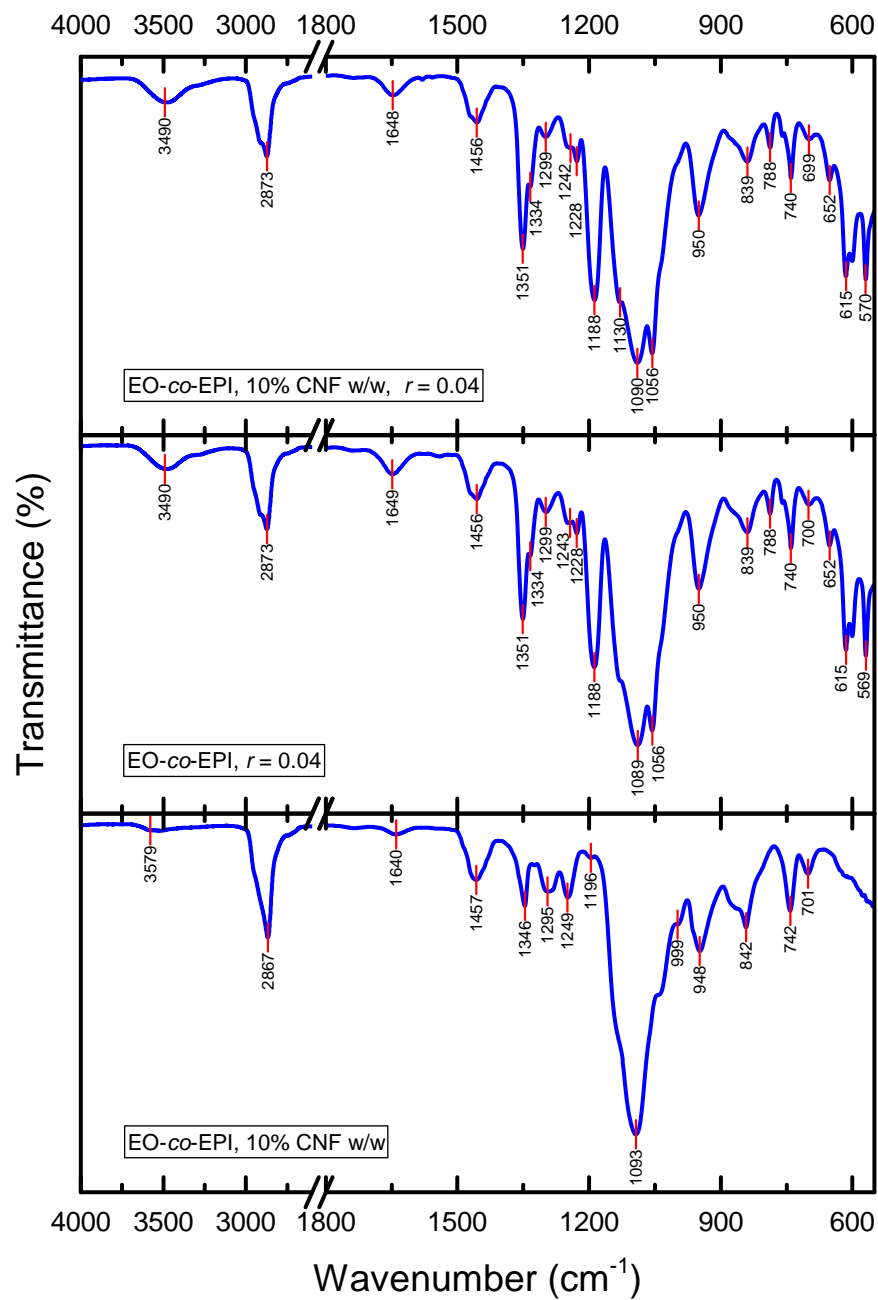


Figure S4: FTIR spectra of an EO-co-EPI composite electrolyte with 10% w/w CNFs and an LiTFSI concentration $r = 0.04$ (top), an EO-co-EPI electrolyte without added CNFs and an LiTFSI concentration $r = 0.04$ (middle), and an EO-co-EPI composite with 10% w/w CNFs and without added LiTFSI (bottom).

Mechanical properties

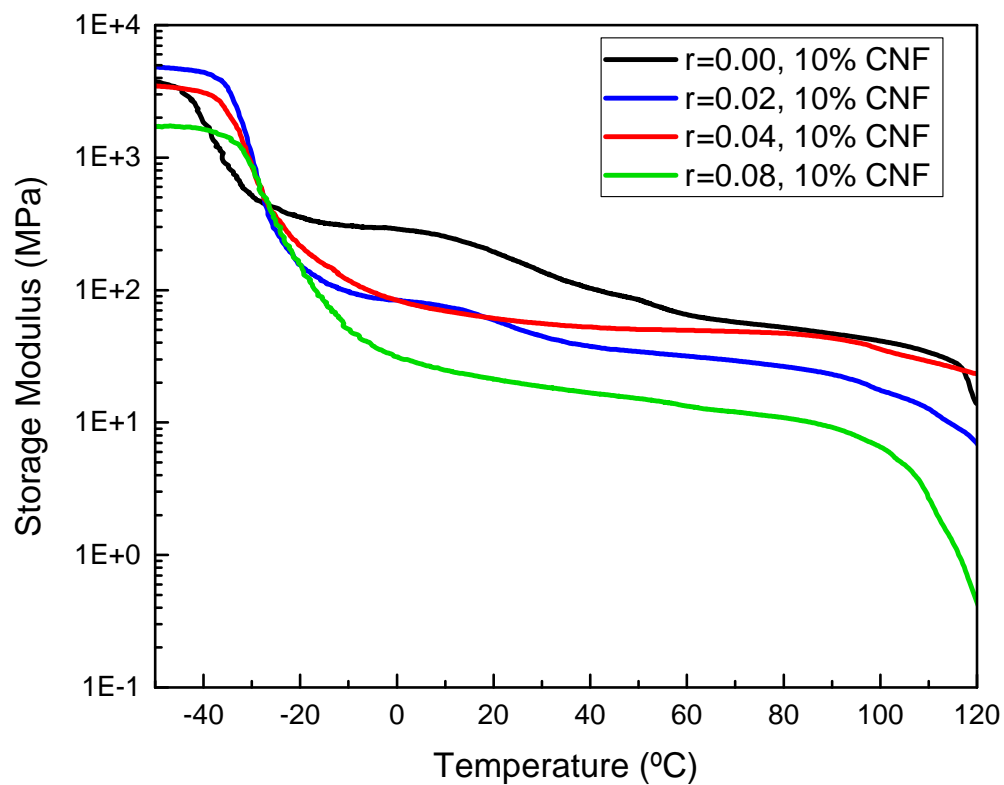


Figure S5: Storage modulus E' vs temperature of EO-co-EPI composite electrolytes with different LiTFSI salt concentrations ($r = 0.02$, $r = 0.04$, $r = 0.08$) and 10% w/w CNFs.

Thermal properties

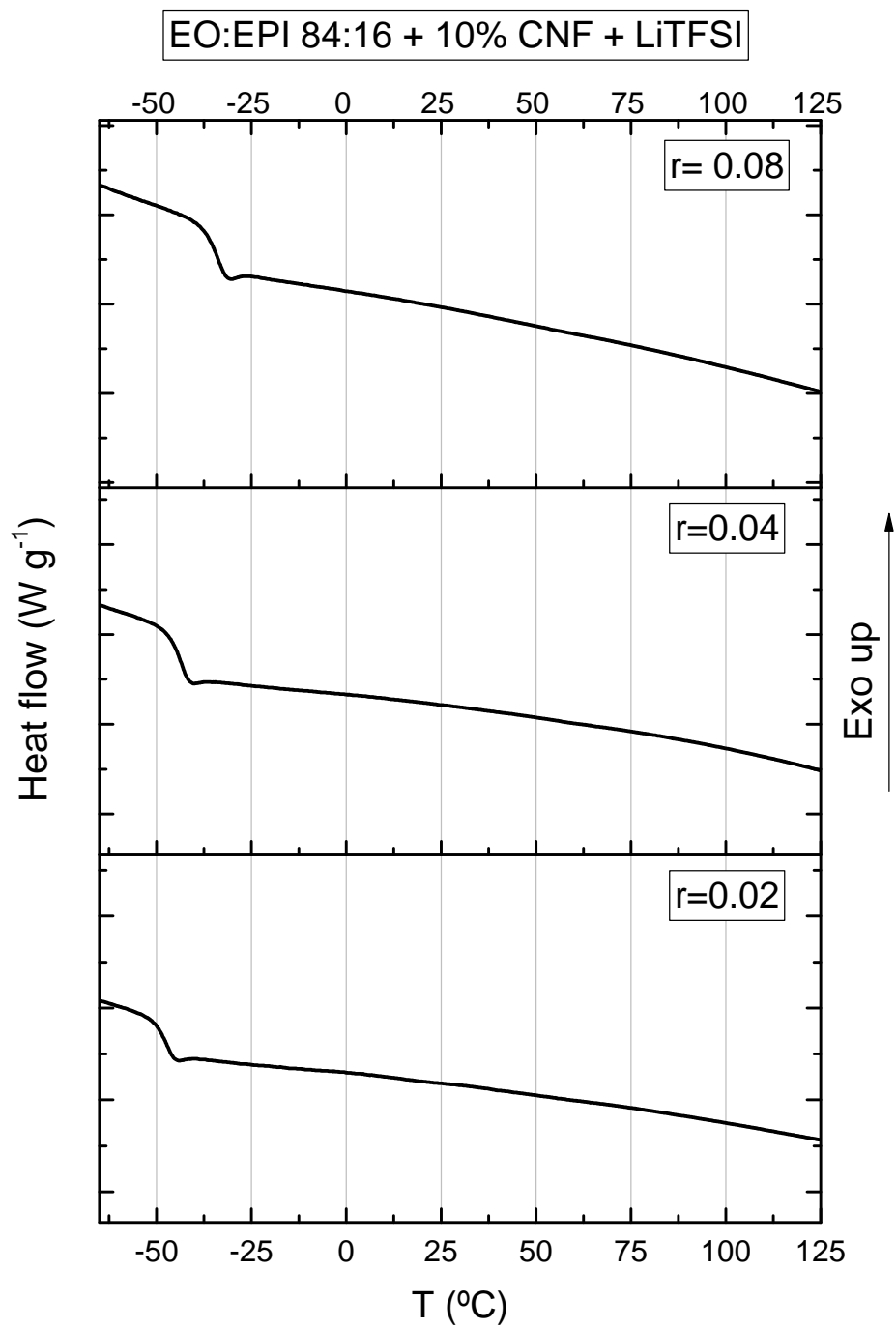


Figure S6: DSC curves of EO-co-EPI composite electrolytes with 10% w/w CNFs and different LiTFSI salt concentrations r .

Characterisation of ionic conductivity

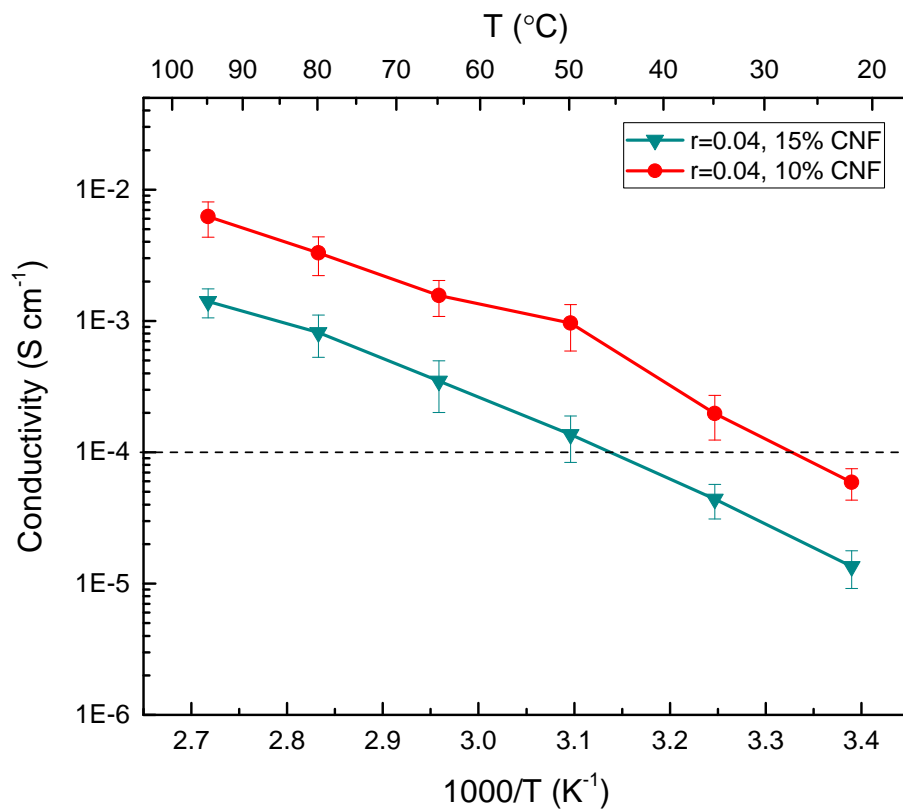


Figure S7: Comparison of the temperature-dependent ionic conductivities of the EO-co-EPI composite electrolytes reinforced with 10% w/w and 15% w/w CNFs and constant LiTFSI salt concentration of $r = 0.04$.

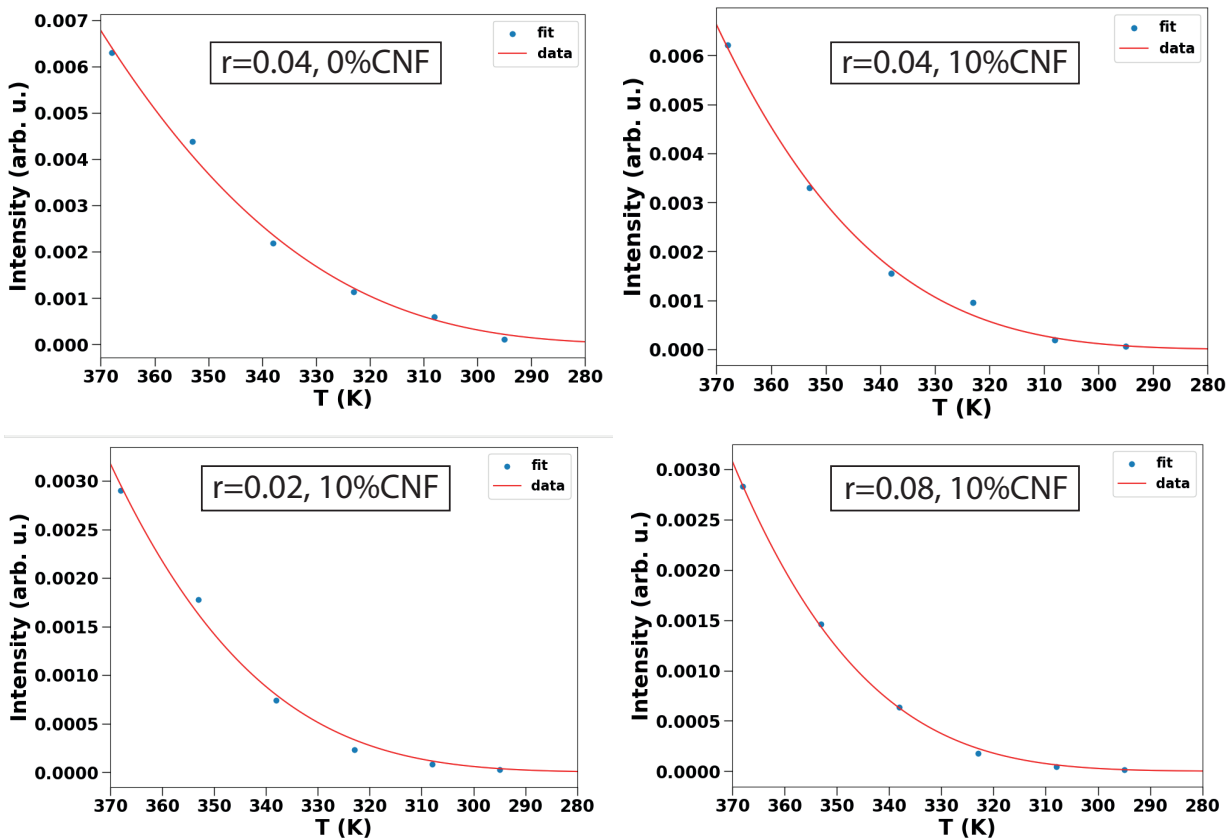


Figure S8: VTF fitting of the ionic conductivity of an LiTFSI-doped EO-co-EPI composite electrolyte without added CNFs as well as LiTFSI-doped EO-co-EPI composite electrolytes with 10% w/w CNFs and different salt concentrations r .

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}

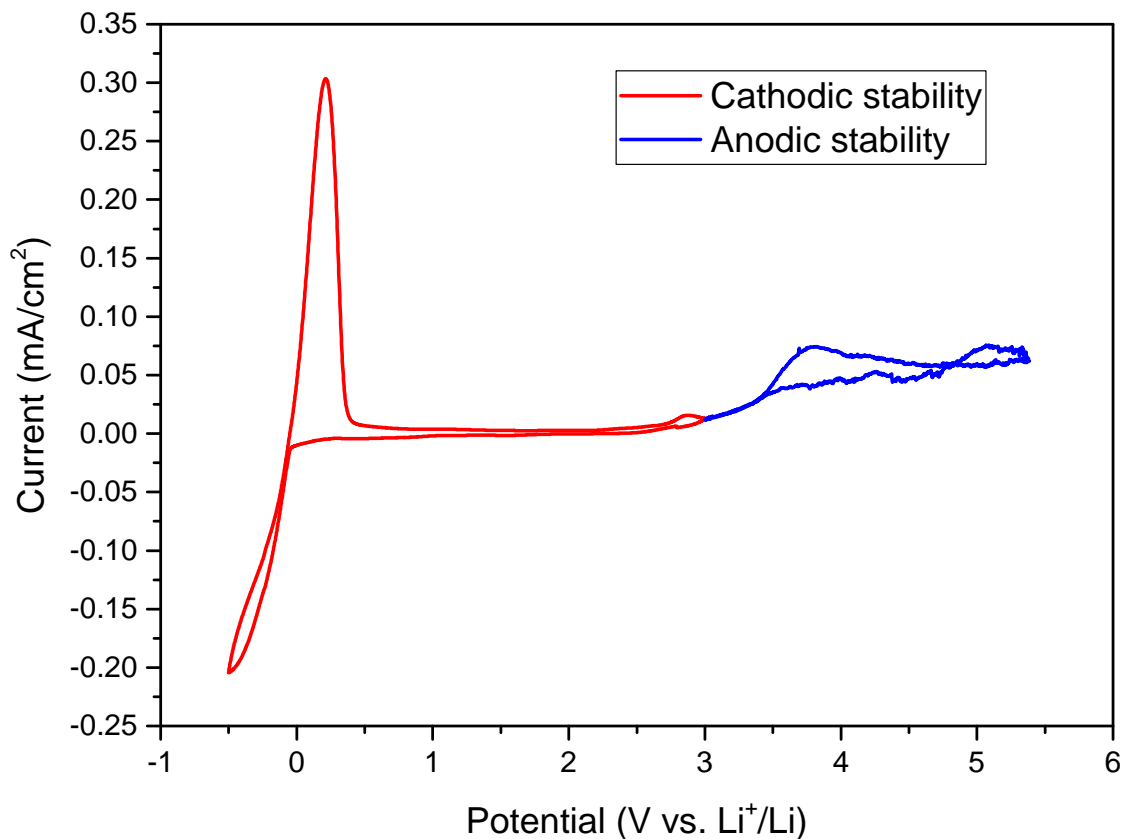


Figure S9: Cyclic voltammogram of an EO-*co*-EPI electrolyte with an LiTFSI concentration of $r = 0.04$ and without CNFs over a potential range of $-0.5 \text{ V} - 5.5 \text{ V}$, at a scan rate of 0.5 mV s^{-1} and a temperature of 70°C .

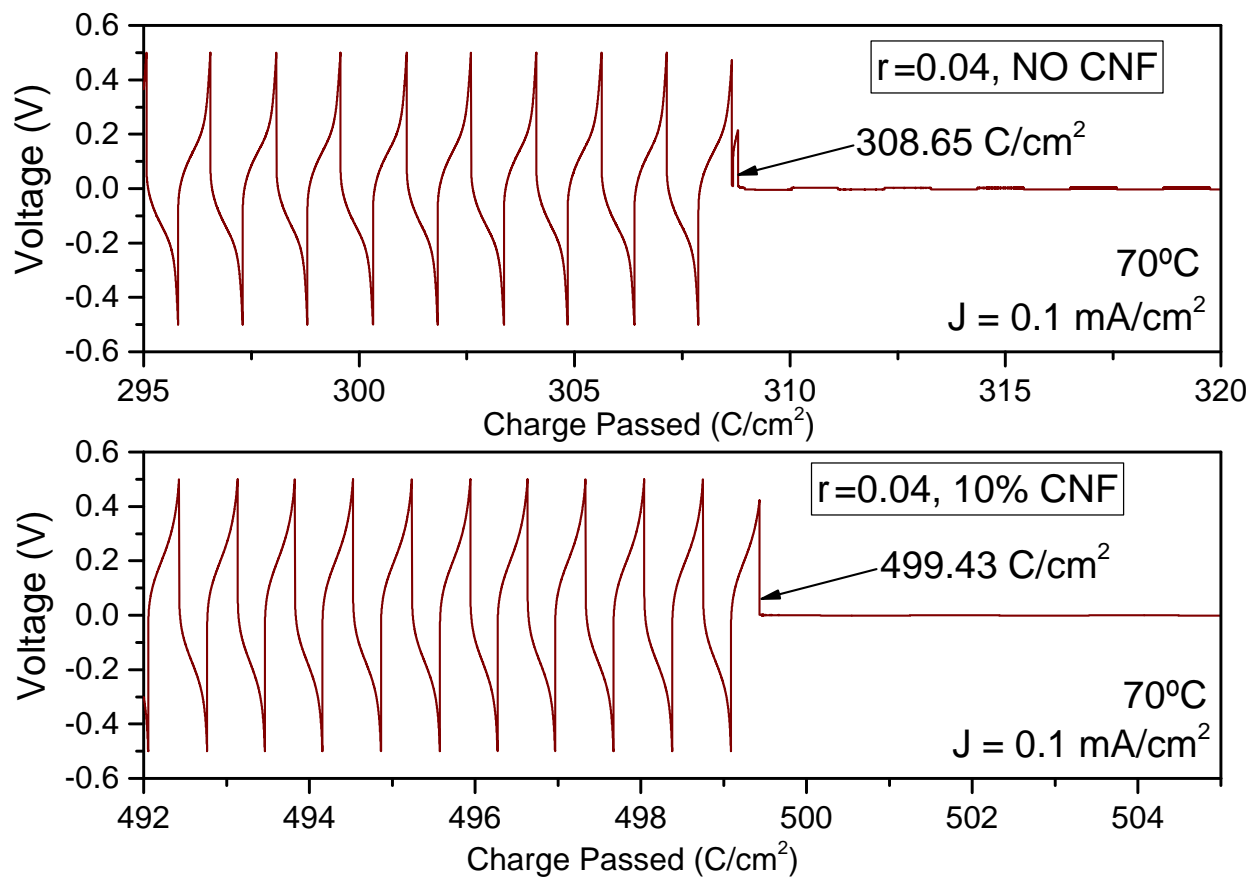


Figure S10: Plots of the voltage versus total charge passed for symmetrical Li/Li using LiTFSI-doped EO-co-EPI composite electrolytes with a salt concentration of $r = 0.04$ a) without CNF reinforcement, and b) with 10% w/w CNFs. In both cases the last cycles before failure are shown.

References

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