Amine-Functionalized Lignin Hydrogels for High-Performance N-Type Ionic Thermoelectric Materials

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Supplementary information†

In this study, we systematically optimized key experimental parameters to achieve the desired performance characteristics of the aminated lignin-based hydrogels. The hydrogel network was established by carefully controlling the lignin-to-crosslinker ratio (5 %, v/v) of the epichlorohydrin) to balance mechanical strength and efficient ionic transport, crucial for optimal ion migration. Following the synthesis of the crosslinked hydrogel, we investigated the impact of the amination reaction time by testing durations of 24 h, 48 h, and 72 h. Our findings revealed that a functionalization period of 72 h yielded the highest negative Seebeck coefficient (−7.48 mV/K) and ionic conductivity (39.9 mS/cm). Subsequently, we evaluated the performance of our functionalized samples (FLH-72h) using various electrolytes, including NaCl, KCl, and H_2SO_4, to identify the most suitable electrolyte based on the negative Seebeck coefficient and ionic conductivity. The results indicated that KCl was the most suitable electrolyte. Further optimization of the alkali electrolyte concentration (KCl) was then tested ranging from 0.5 M to 4 M, identifying 1 M KCl as the optimal condition for maximizing the power factor (223.52 μW/m·K^2).

Cross-linked (CLH) and functionalized hydrogel (FLH-24h, FLH-48h, FLH-72h)

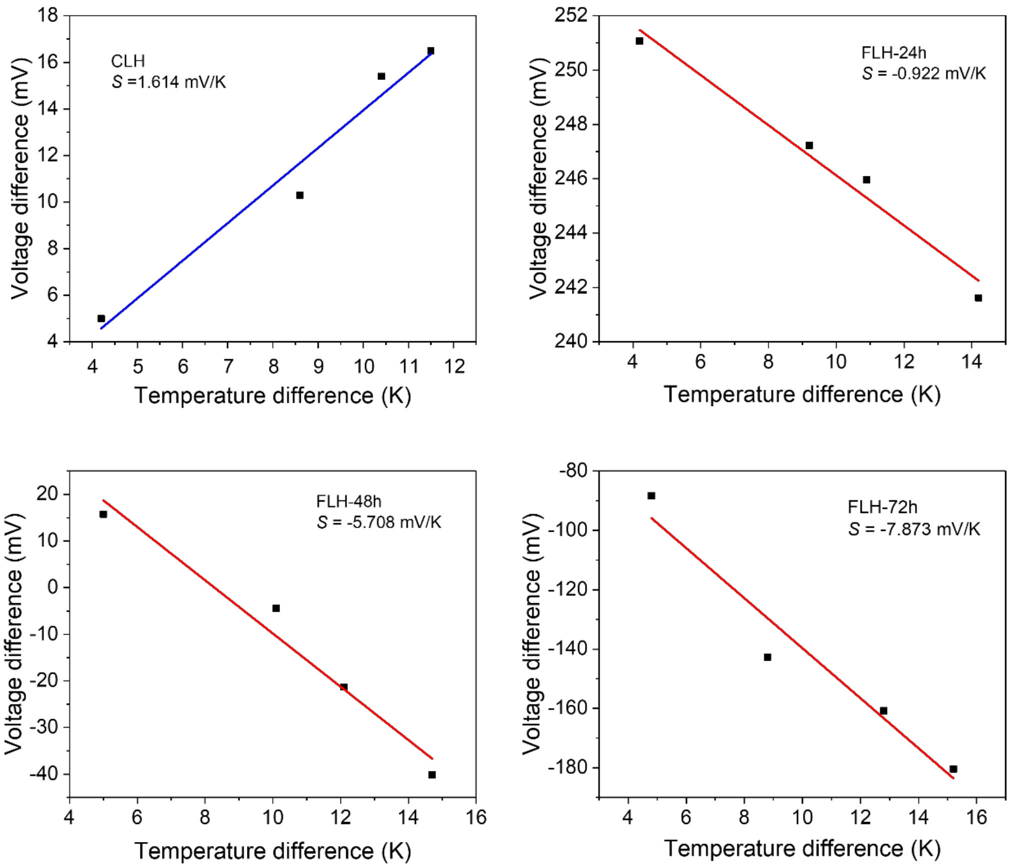

Fig. S1 linear fit of the open circuit voltage vs. temperature difference for CLH and FLH hydrogel samples.

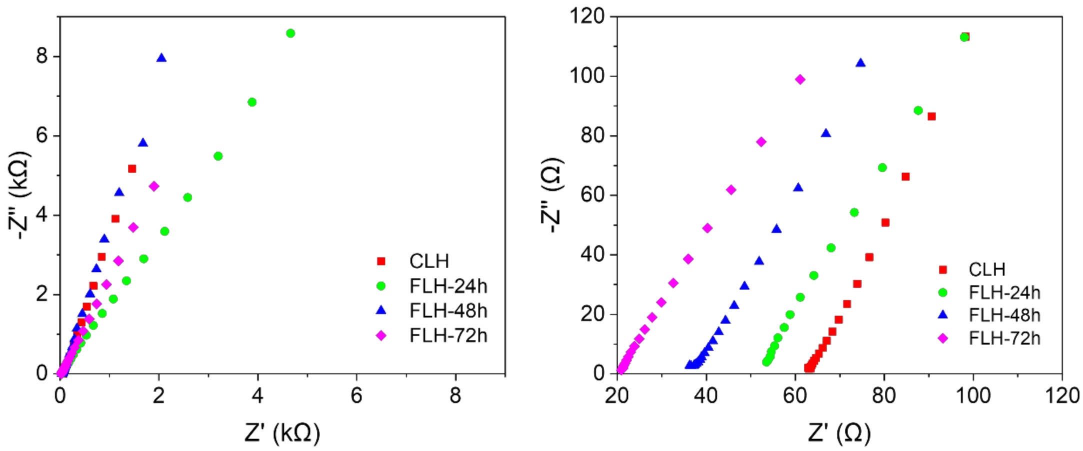

Fig. S2 Nyquist plots of crosslinked hydrogel (CLH) and functionalized hydrogel (FLH-42h, FLH-48h, FLH-72h) (left: full plot; right: zoomed plot)

FLH-72h infiltrated with various 1M electrolyte

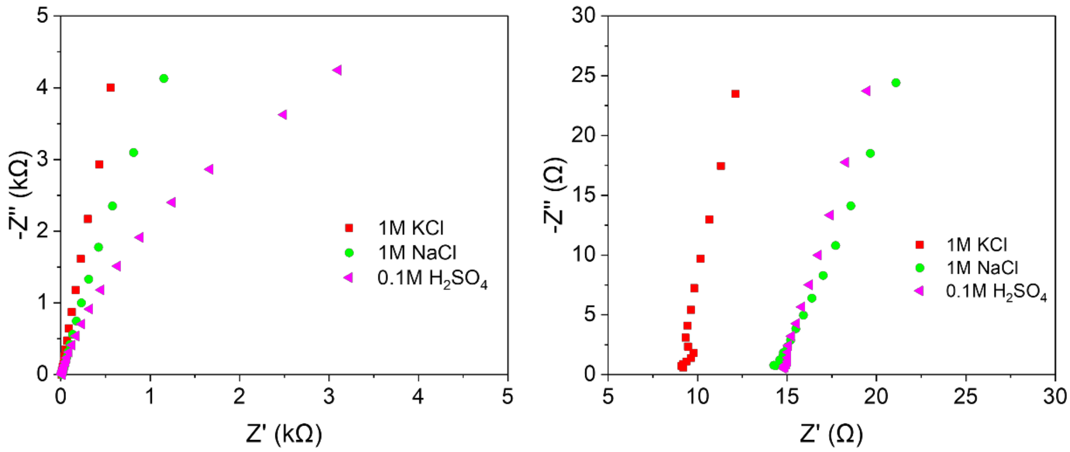

Fig. S3 Nyquist plots of functionalized hydrogels (FLH-72h) infiltrated with various electrolytes (1 M) (left: full plot; right: zoomed plot)

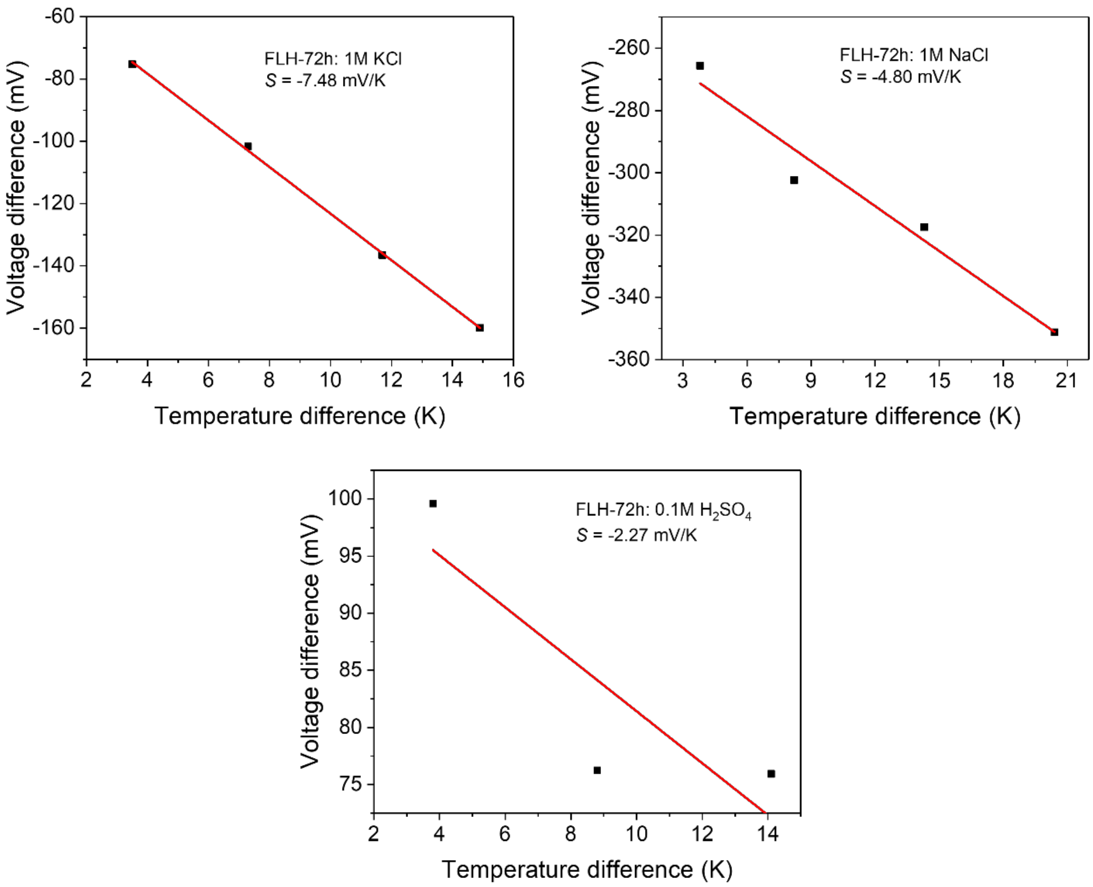

Fig. S4 linear fit of the open circuit voltage vs. temperature difference for all FLH-72h hydrogel samples infiltrated with various electrolytes.

FLH-72h infiltrated with various concentrations of KCl electrolyte

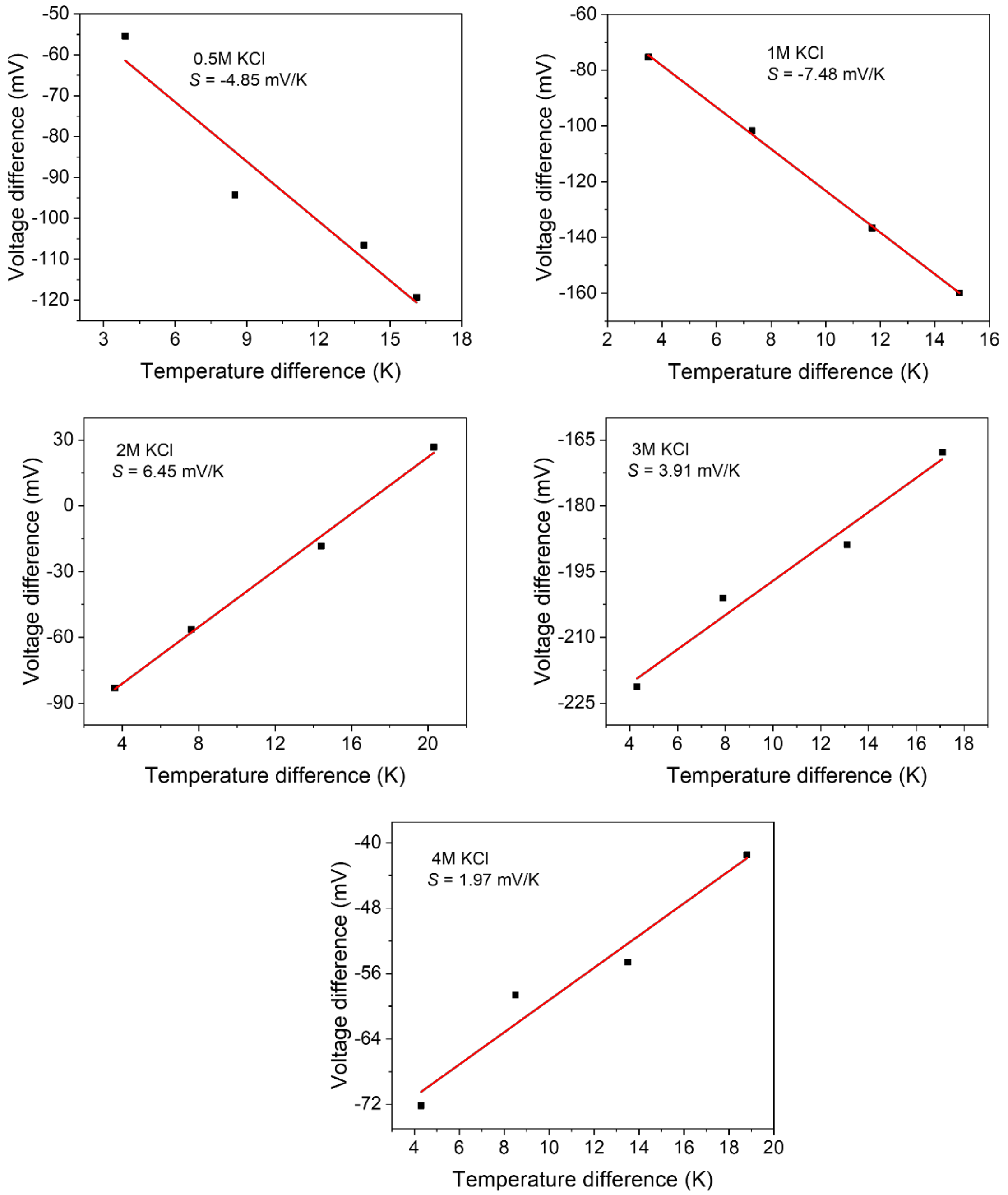

Fig. S5 linear fit of the open circuit voltage vs. temperature difference for all FLH-72h hydrogel samples infiltrated with various concentration of KCl electrolyte.

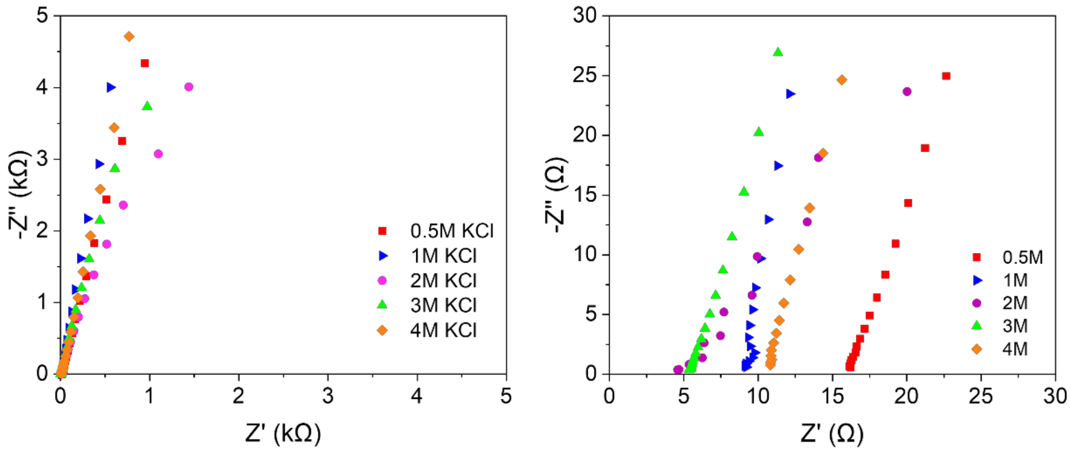

Fig. S6 Nyquist plots of functionalized hydrogels (FLH-72h) infiltrated with various KCl concentrations (0.5M – 4.0 M) (left: full plot; right: zoomed plot)

Stability investigation of FLH-72h infiltrated with 1 M KCl electrolyte

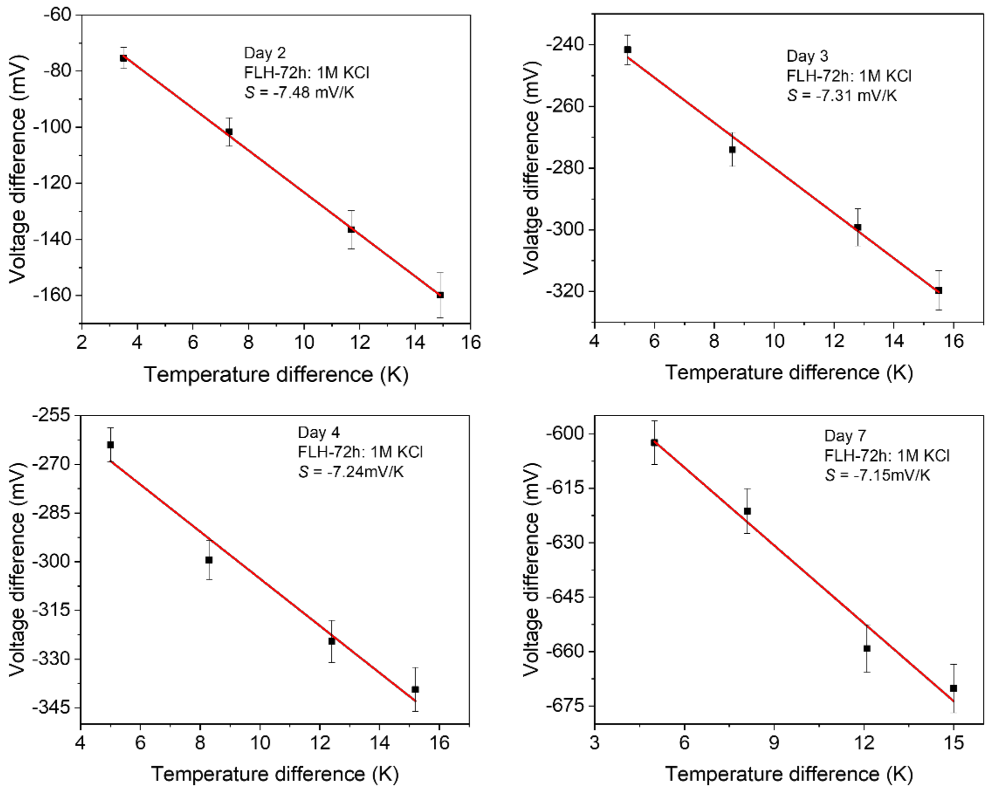

Fig. S7 linear fit of the open circuit voltage vs. temperature difference for all FLH-72h hydrogel samples infiltrated with 1 M KCl electrolyte over seven days period.

The fabricated ionic thermoelectric samples (FLH-72h: 1M KCl) were evaluated for their capacitive behavior using Electrochemical Impedance Spectroscopy (EIS) and Cyclic

Voltammetry (CV) with an IVIUM potentiostat. EIS was performed by applying a 10 mV AC signal and sweeping the frequency from 100 kHz to 10 mHz (Fig. S8†a-b). Cyclic voltammetry (CV) was performed with a scan rate of 10 mV/sec along a 0-0.2V voltage range (Fig. S8†c). The quasi-rectangular shape of the CV curve further confirms the capacitive characteristics of the hydrogel.

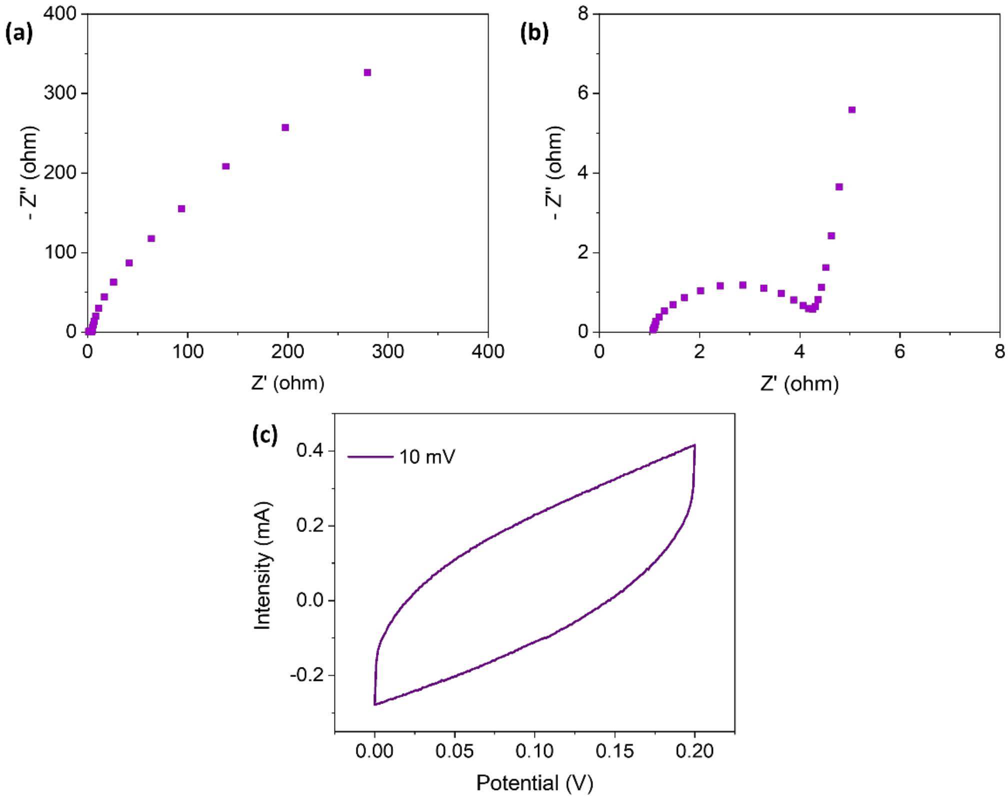

Fig. S8 Characterization of ionic thermoelectric materails. (a-b) Nyquist plot (left: full plot; right: zoomed plot). (c) Cyclic voltammetry.