Supporting Information

Ion-Selective Transport in Surface-Modified Cellulose Membranes for Aqueous Ionic Thermoelectrics

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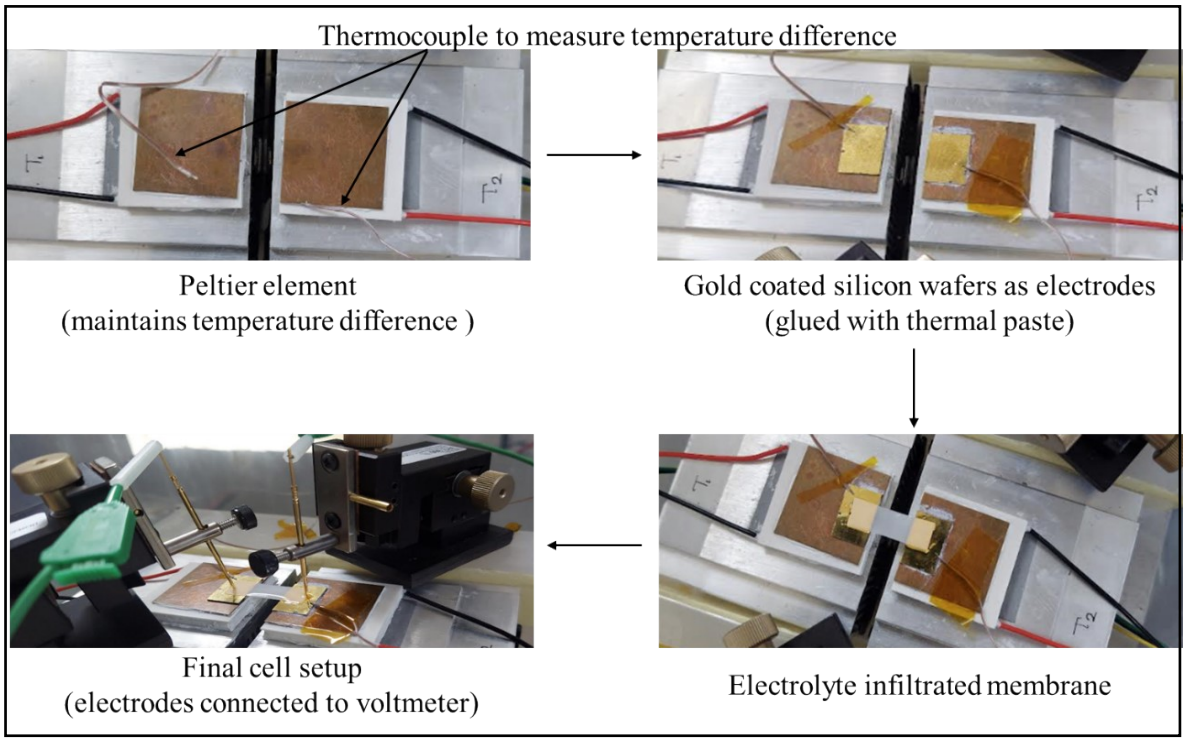


Figure S1. Assembly of the perpendicular thermoelectric measurement setup used to characterise RC membranes. RC membranes were placed between two gold-coated silicon wafers to ensure uniform electrical contact (top left) and secured with Kapton tape for thermal and mechanical stability (top right). Micromanipulator probes were used to establish electrical contact with the electrodes (bottom left), and thermocouples (T_1 and T_2) were positioned on either side of the setup to monitor the temperature gradient. The final configuration (bottom right) integrates all thermal and electrical connections, enabling the accurate measurement of the thermovoltage along the membrane.

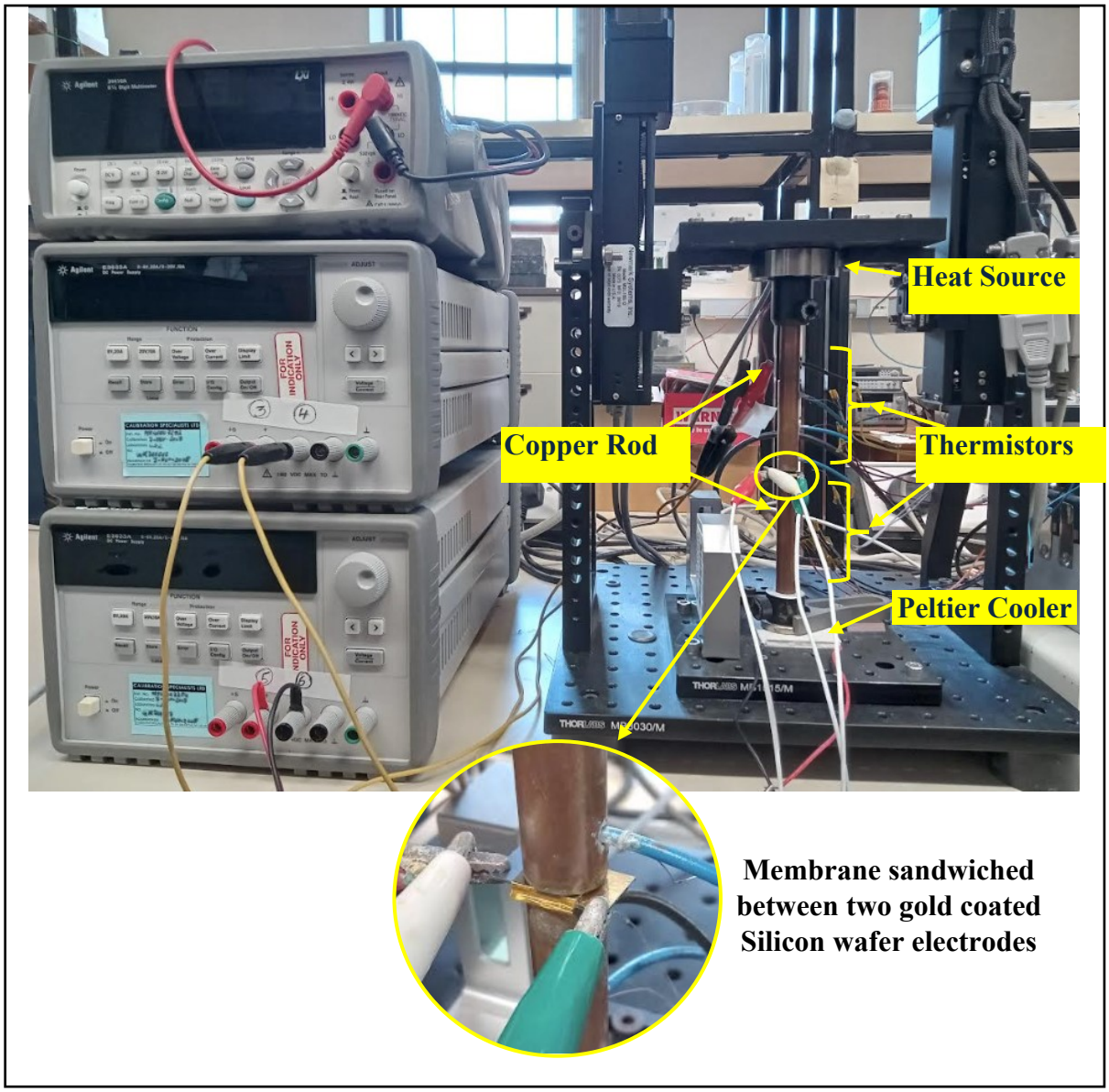


Figure S2. Modified ASTM 5470-06 based device setup to measure the cross-sectional ionic thermoelectric properties of stacked RC membranes. The apparatus consists of Agilent B2912A source-measure units used to control the temperature gradient and record electrical signals, integrated with a Thorlabs vertical test stage that enables precise positioning of heating and cooling blocks across the membrane sample. Electrical and thermal contacts are established using insulated leads and thermocouples. The close-up image shows the membrane positioned between two gold-coated silicon wafers, clamped between copper blocks, with thermocouple and voltage leads attached to measure local temperature and thermovoltage across the membrane.

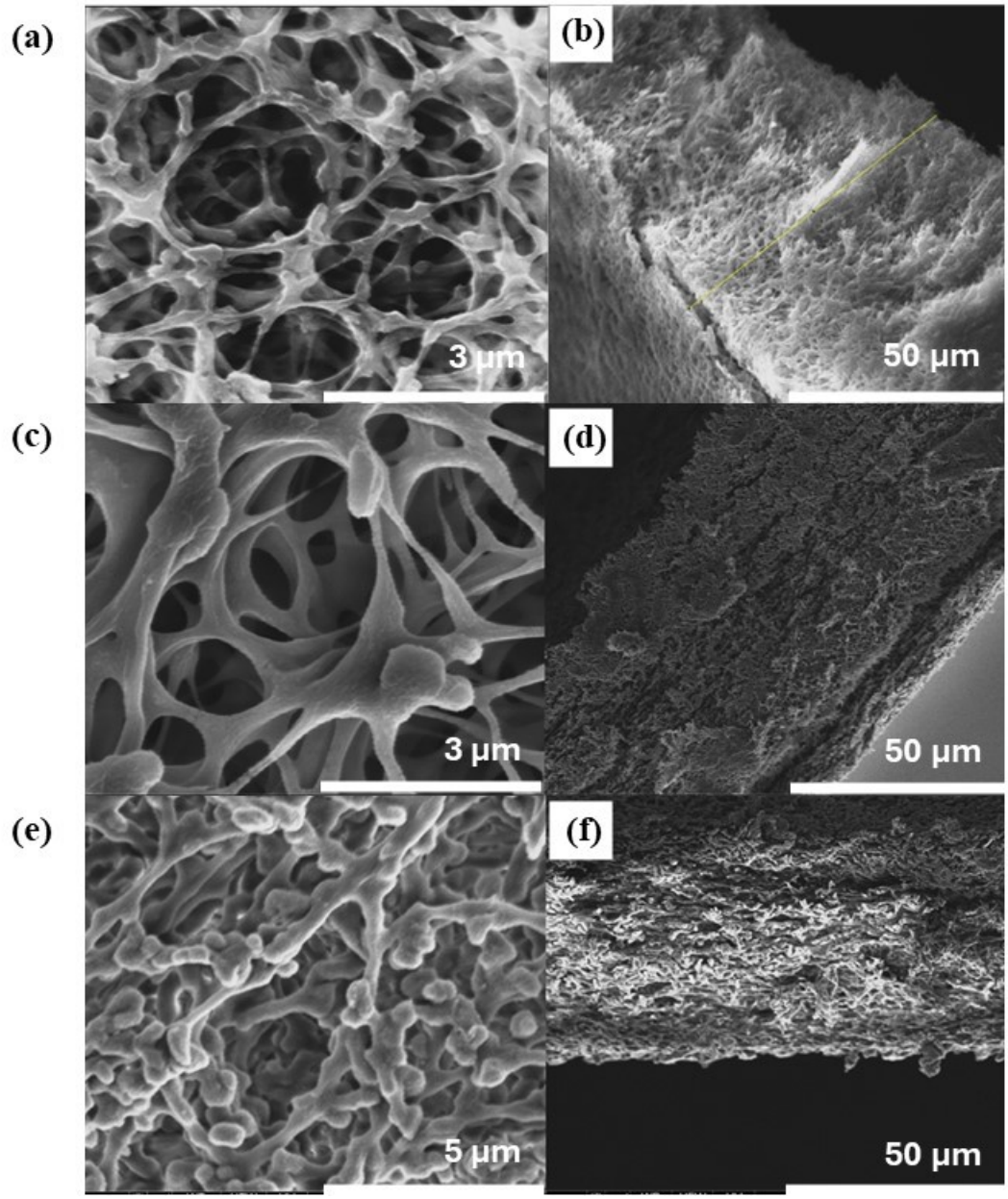


Figure S3. Scanning electron microscopy (SEM) images of RC membranes. (a) Surface morphology of RC-200 (scale bar: 3 μm), (b) cross-sectional view of RC-200 (scale bar: 20 μm), (c) surface of RC-450 (scale bar: 3 μm), (d) cross-section of RC-450 (scale bar: 50 μm), (e) surface of RC-1k (scale bar: 5 μm), and (f) cross-section of RC-1k (scale bar: 50 μm).

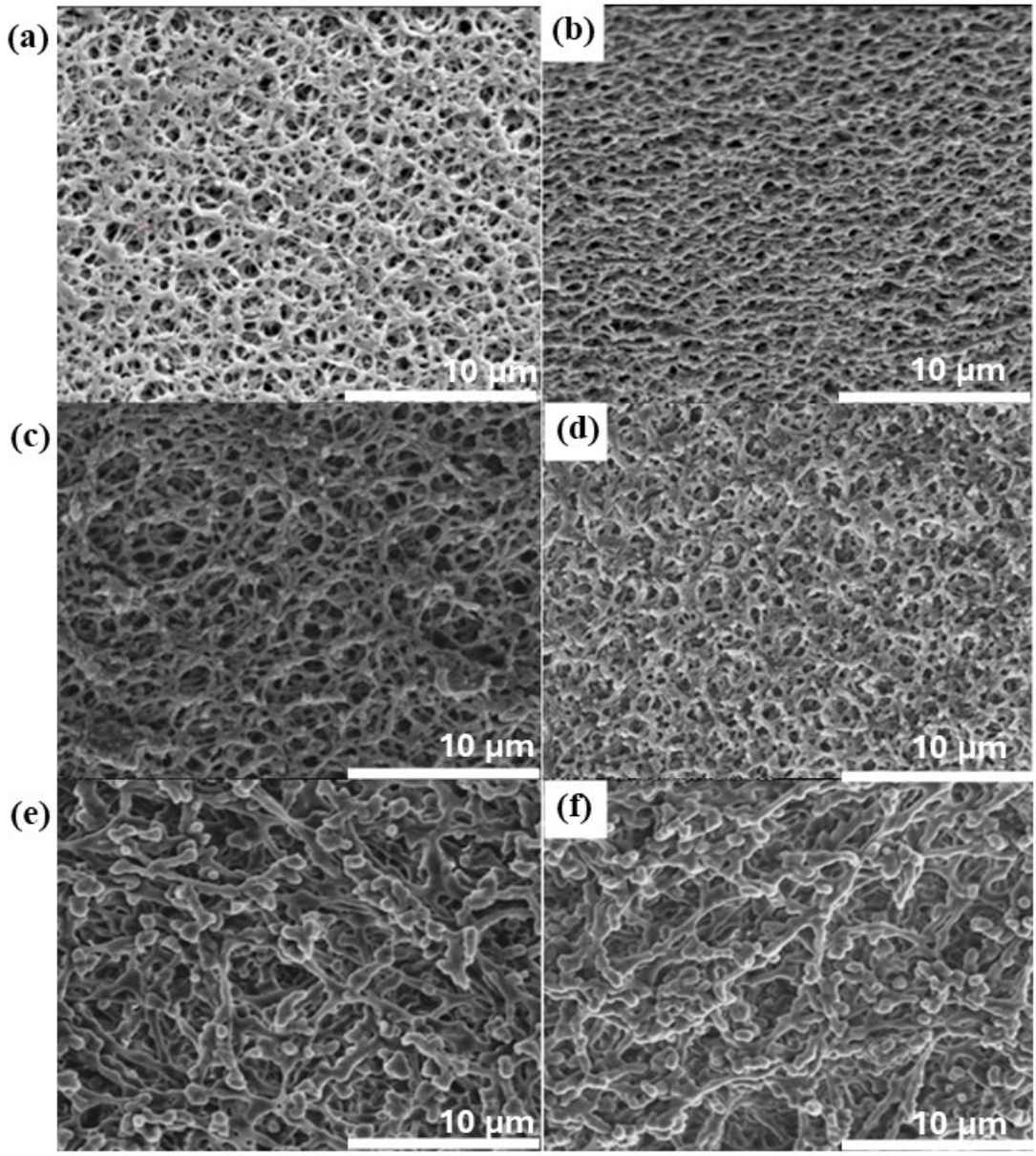
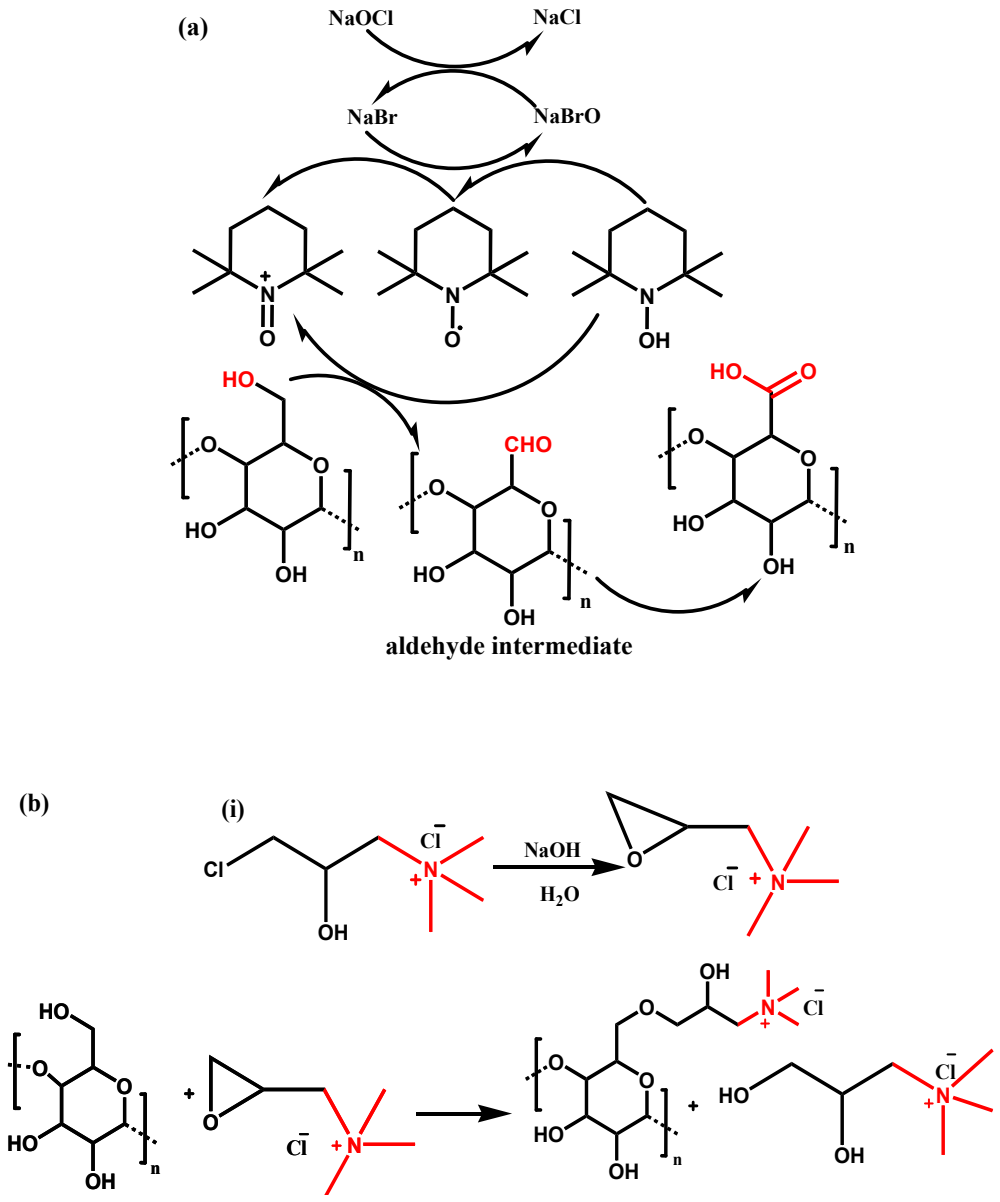


Figure S4. Surface scanning electron microscopy (SEM) images of functionalised RC membranes. (a) TEMPO-functionalised RC-200, (b) CHMAC-functionalised RC-200, (c) TEMPO-RC-450, (d) CHMAC-RC-450, (e) TEMPO-RC-1k, and (f) CHMAC-RC-1k. All images share a scale bar of 10 µm.



Scheme S1. Reaction pathways for the surface functionalisation of RC membranes: (a) TEMPO-mediated oxidation of surface hydroxyl groups to carboxyl groups, and (b) CHMAC-mediated etherification introducing quaternary ammonium groups.

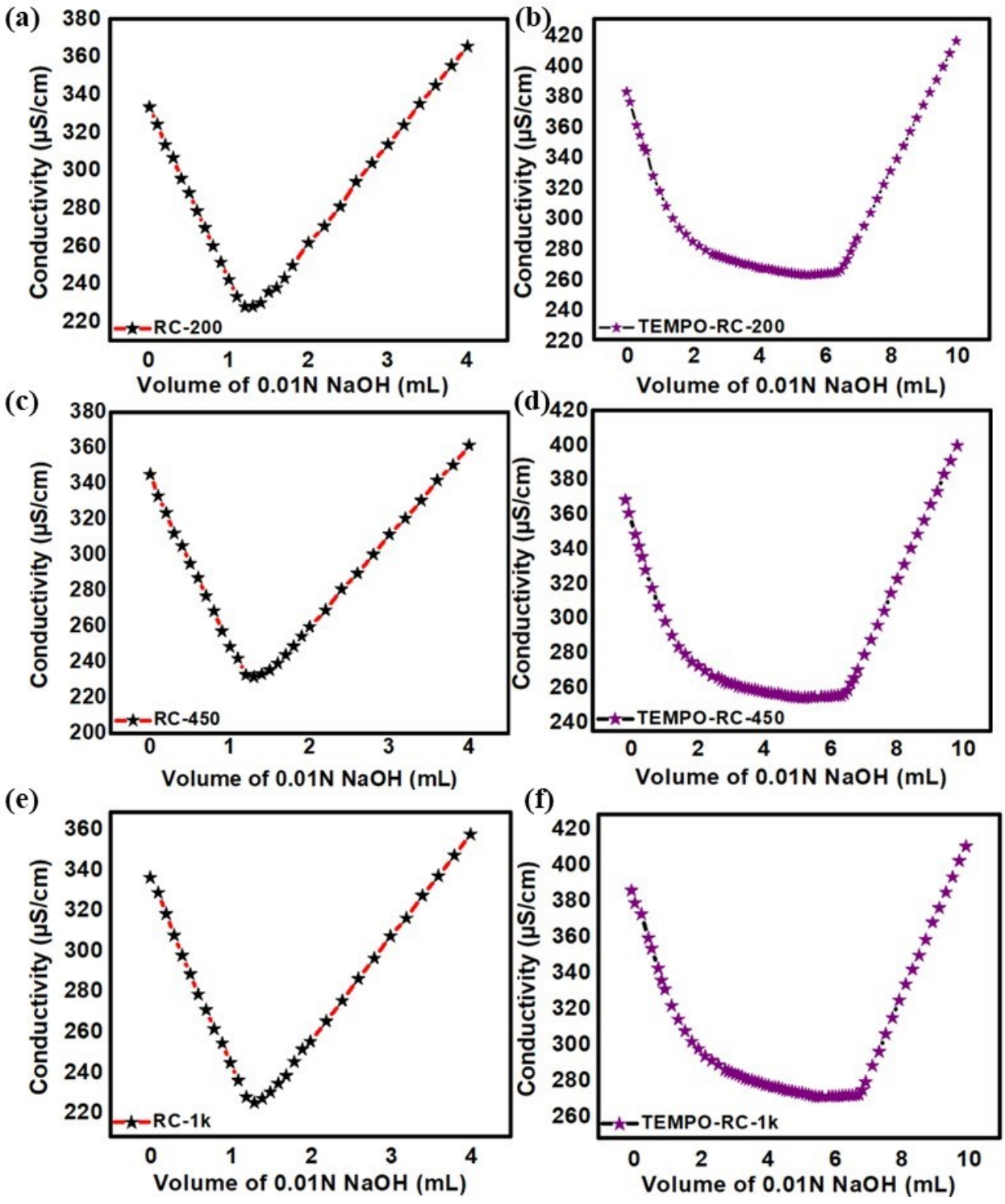


Figure S5. Conductometric titration curves of pristine and TEMPO-functionalised RC membranes with 0.01 M NaOH: (a) RC-200, (b) TEMPO-RC-200, (c) RC-450, (d) TEMPO-RC-450, (e) RC-1k, and (f) TEMPO-RC-1k.

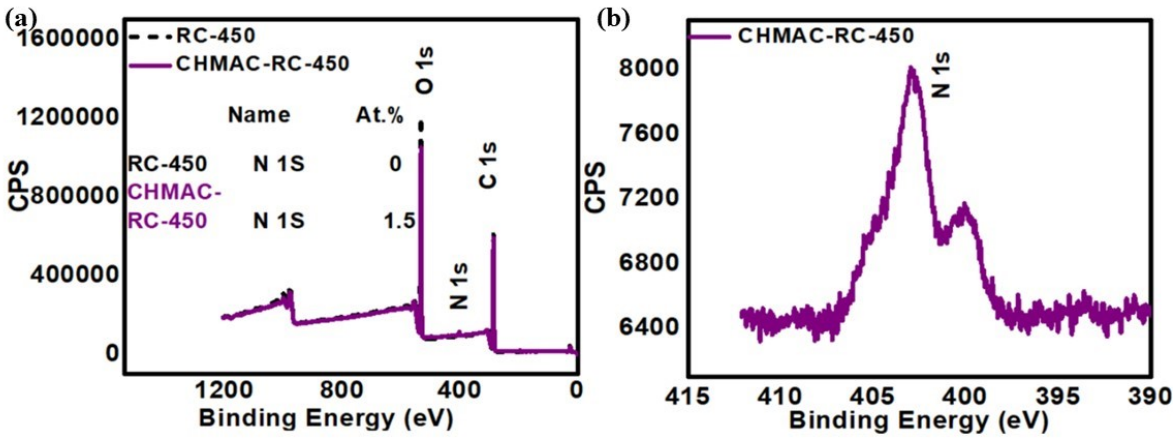


Figure S6. (a) XPS survey spectra of RC-450 membranes before and after CHMAC functionalisation, including quantified N 1s atomic percentages. (b) High-resolution XPS spectra in the 390-415 eV region highlighting the N 1s peak.

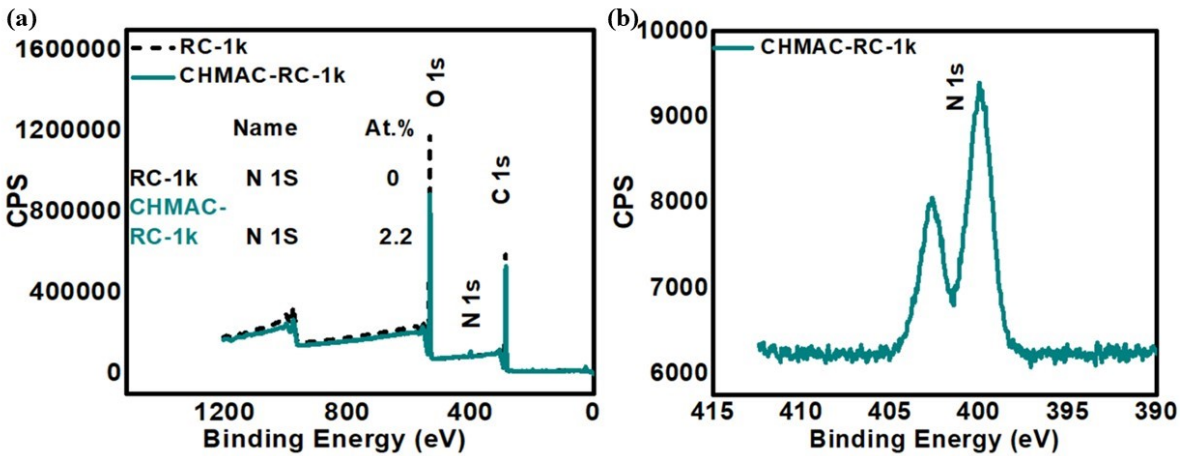


Figure S7. (a) XPS survey spectra of RC-1k membranes before and after CHMAC functionalisation, with corresponding N 1s atomic percentage quantification. (b) High-resolution XPS spectra in the 390–415 eV region showing the N 1s peak.

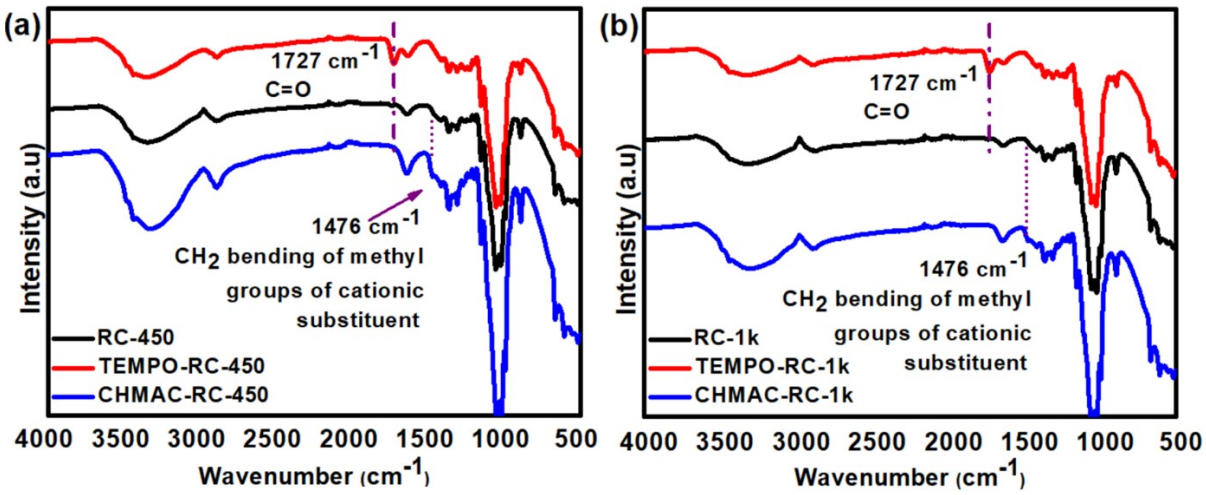


Figure S8. FTIR spectra showing structural characterisation of pristine (black), TEMPO-functionalised (red), and CHMAC-functionalised (blue) RC membranes: (a) RC-450 and (b) RC-1k.

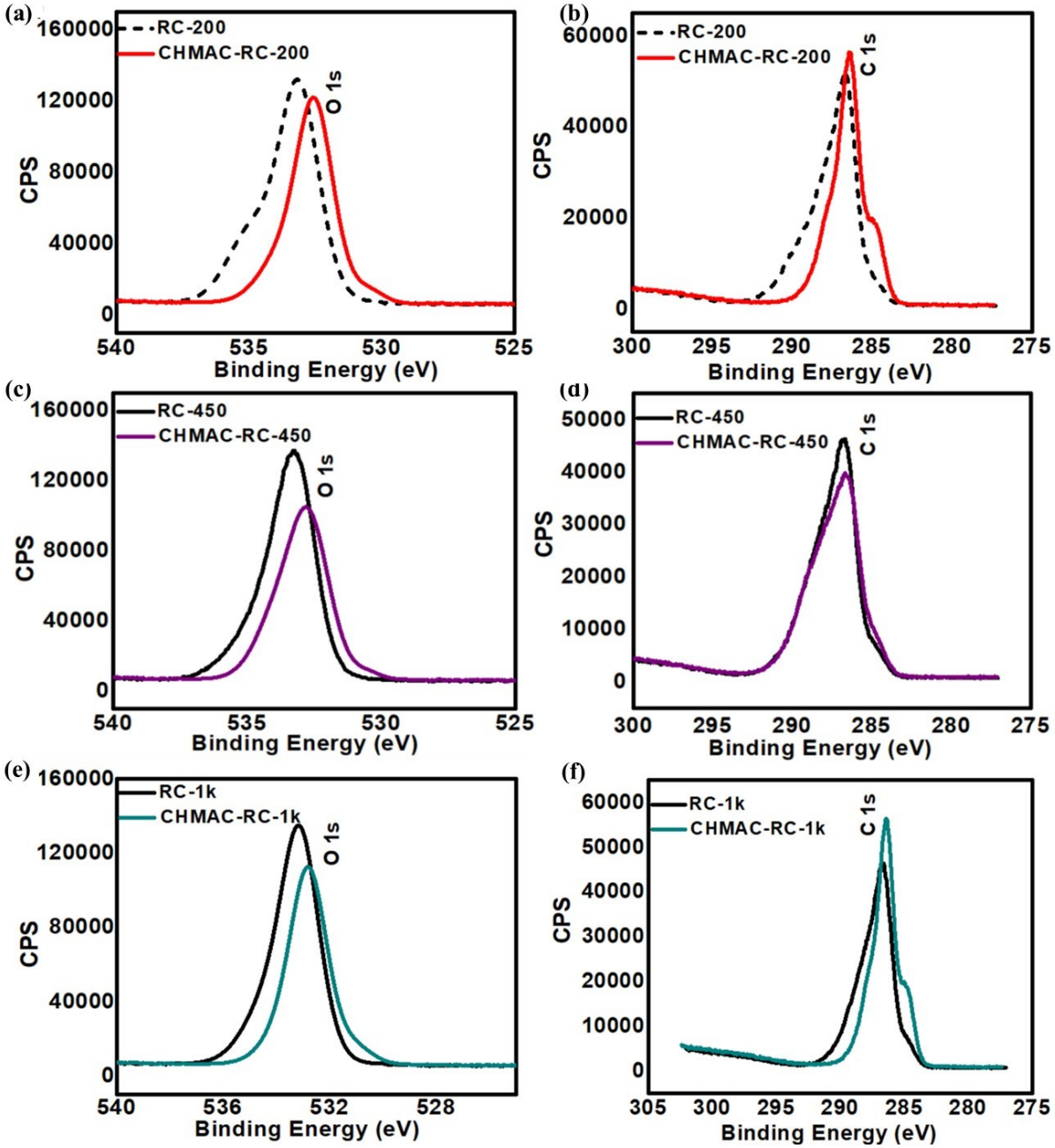


Figure S9. High-resolution XPS spectra highlighting the O 1s peak (525-540 eV) and C 1s peak (275-300 eV) for: (a–b) RC-200, (c–d) RC-450, and (e–f) RC-1k membranes.

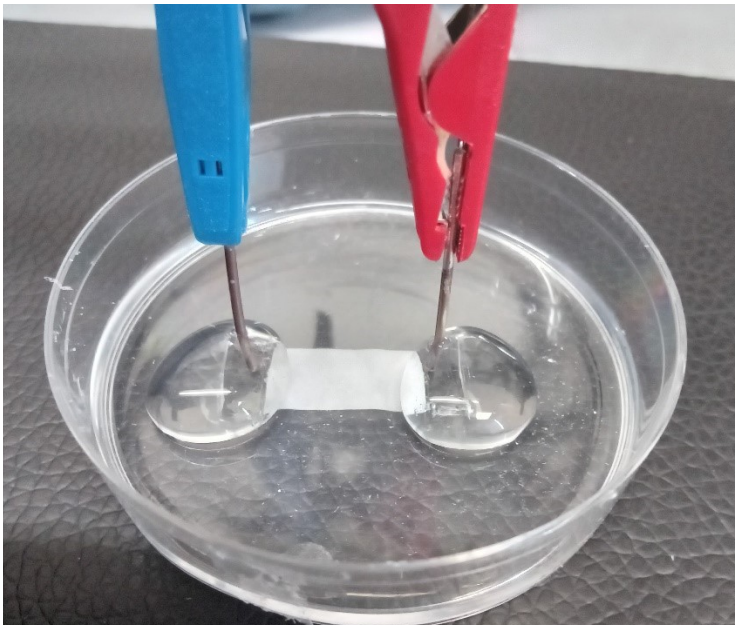


Figure S10. Photo of the membrane-based nanofluidic testing device. A cellulosic membrane is embedded in SYLGARD-184 silicone elastomer. After curing, two reservoirs were created to expose both membrane ends to the electrolyte solution. Ag/AgCl electrodes were used for electrochemical measurements.

Table S1. Electrokinetic Properties of Functionalised RC Membranes Compared to Literature

Membrane	pH	Zeta Potential (mV)	Effective Surface Charge Density (mC/m^2)	Average Pore Diameter (nm)	Source / Notes
RC-200	4.1	-4.6	-0.0042	200	This work
TEMPO-RC-200	4.0	-21.0	-0.0221	200	This work
CHMAC-RC-200	4.0	+13.4	+0.0139	200	This work
RC-450	4.1	+1.78	+0.0016	450	This work
TEMPO-RC-450	4.0	-18.1	-0.0189	450	This work
CHMAC-RC-450	4.4	+13.2	+0.0156	450	This work
RC-1k	4.1	-1.43	-0.0013	1000	This work
TEMPO-RC-1k	4.0	-18.0	-0.0188	1000	This work
CHMAC-RC-1k	4.0	+14.4	+0.0150	1000	This work
CHMAC-BC (Bacterial Cell.)	6.0	+45	+3.1	3.37 nm height	Wu et al. 2021[1]
Silica Nanochannels	3.6	-45	-0.87	40 nm height	D C Martins et al.[2]

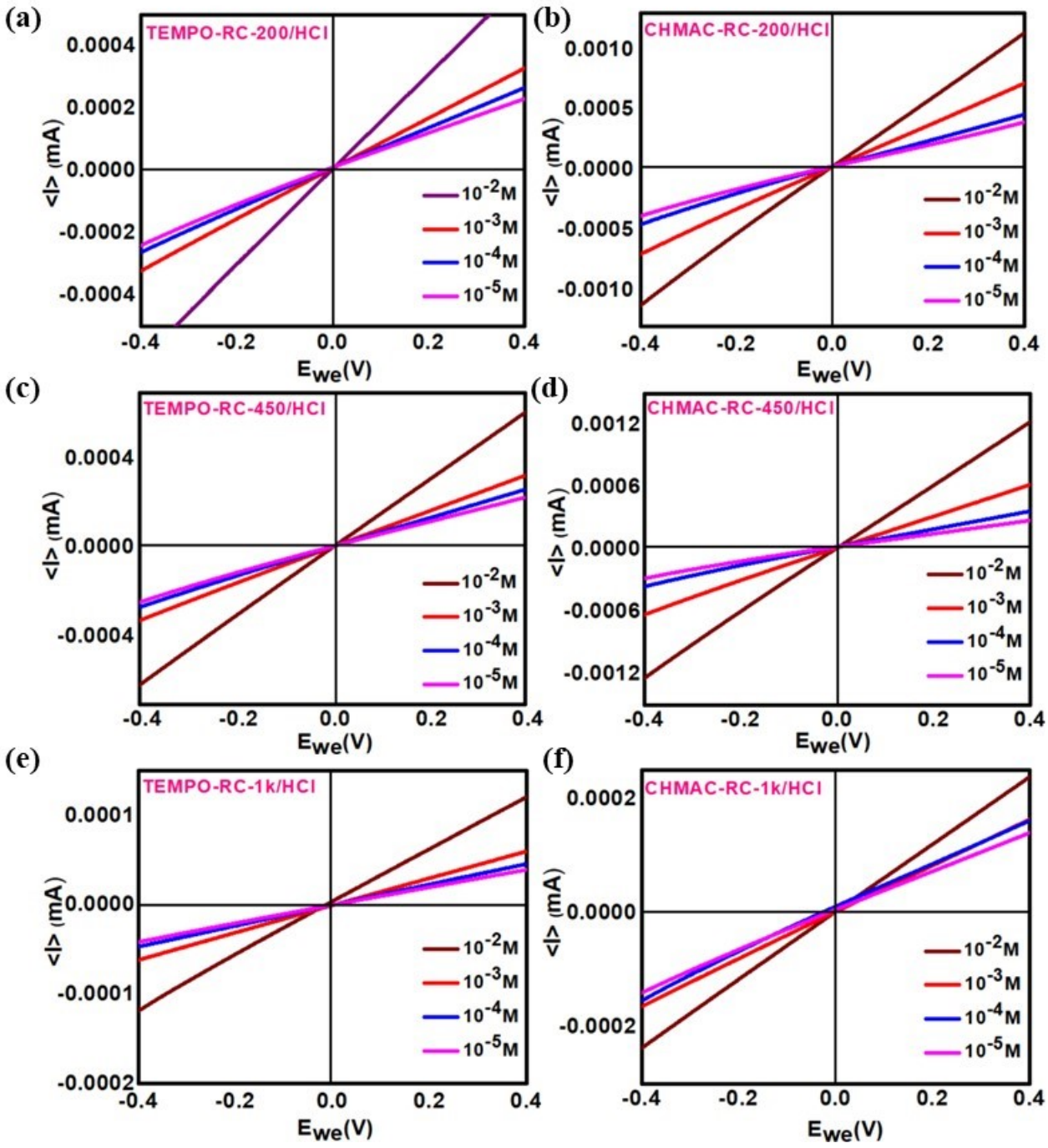


Figure S11. *I-V* curves of TEMPO- and CHMAC-functionalised RC membranes measured in HCl solutions with concentrations from 10^{-5} M to 10^{-2} M: (a) TEMPO-RC-200, (b) CHMAC-RC-200, (c) TEMPO-RC-450, (d) CHMAC-RC-450, (e) TEMPO-RC-1k, and (f) CHMAC-RC-1k.

Electrochemical Impedance Spectroscopy

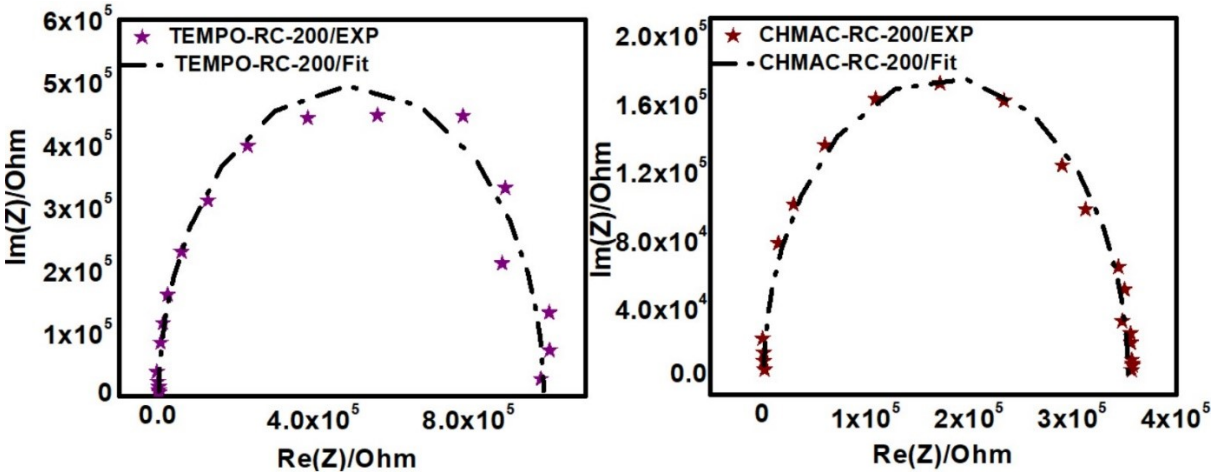


Figure S12. EIS curves of nanofluidic devices containing functionalised RC-200 membranes infiltrated with 10^{-4} M HCl.

Electrochemical impedance spectroscopy (EIS) was employed to validate the ionic transport characteristics of CHMAC- and TEMPO-functionalised regenerated cellulose (RC-200) membranes immersed in 10^{-4} M HCl. The data were analysed using a two-time-constant equivalent circuit model, R1+(C2||R2), which allowed for the differentiation between bulk resistance (R1) and interfacial charge transfer contributions (R2). The CHMAC-RC-200 membrane demonstrated a lower charge transfer resistance R2 of 351.5 kΩ, in contrast to 990.9 kΩ for TEMPO-RC-200. This nearly threefold decrease indicates improved ion exchange at the CHMAC membrane-electrolyte interface, likely attributed to the positive surface charge from quaternary ammonium groups that facilitate Cl^- transport. The ionic conductivities derived from R2 were 1.64 mS cm^{-1} for CHMAC-RC-200 and 0.58 mS cm^{-1} for TEMPO-RC-200, highlighting a significant enhancement in charge transport due to CHMAC functionalisation. The increased conductivity of CHMAC-RC-200 is linked to surface-bound ammonium groups that enhance Cl^- conduction and promote efficient charge transfer at the electrode. Conversely, the TEMPO-functionalised membrane, which has carboxyl groups,

favors H^+ transport but is more prone to electrode polarisation. Both membranes display comparable interfacial capacitance values (C2 at around 20 pF), suggesting that capacitance is not the limiting factor; instead, the differences in surface charge type and density primarily influence the variations in conductivity observed. Table 1 summarises the parameters obtained from LSV and EIS for RC-200.

Table S2. Ionic conductivity of functionalised RC-200 membranes, from EIS and LSV techniques for 10^{-4} M HCl.

Membranes	Ionic Conductivity (mS/cm) - EIS	Ionic Conductivity (mS/cm) - LSV
TEMPO-RC-200	0.58	0.51
CHMAC-RC-200	1.64	1.19

Together, the EIS and LSV results provide a comprehensive understanding of the membranes' electrochemical behaviour: EIS offers mechanistic insight into interfacial transport processes, while LSV captures conductivity under practical operating conditions. The enhanced performance of CHMAC-functionalised membranes highlights the significance of surface charge engineering in improving ionic conductivity and thermoelectric efficiency.

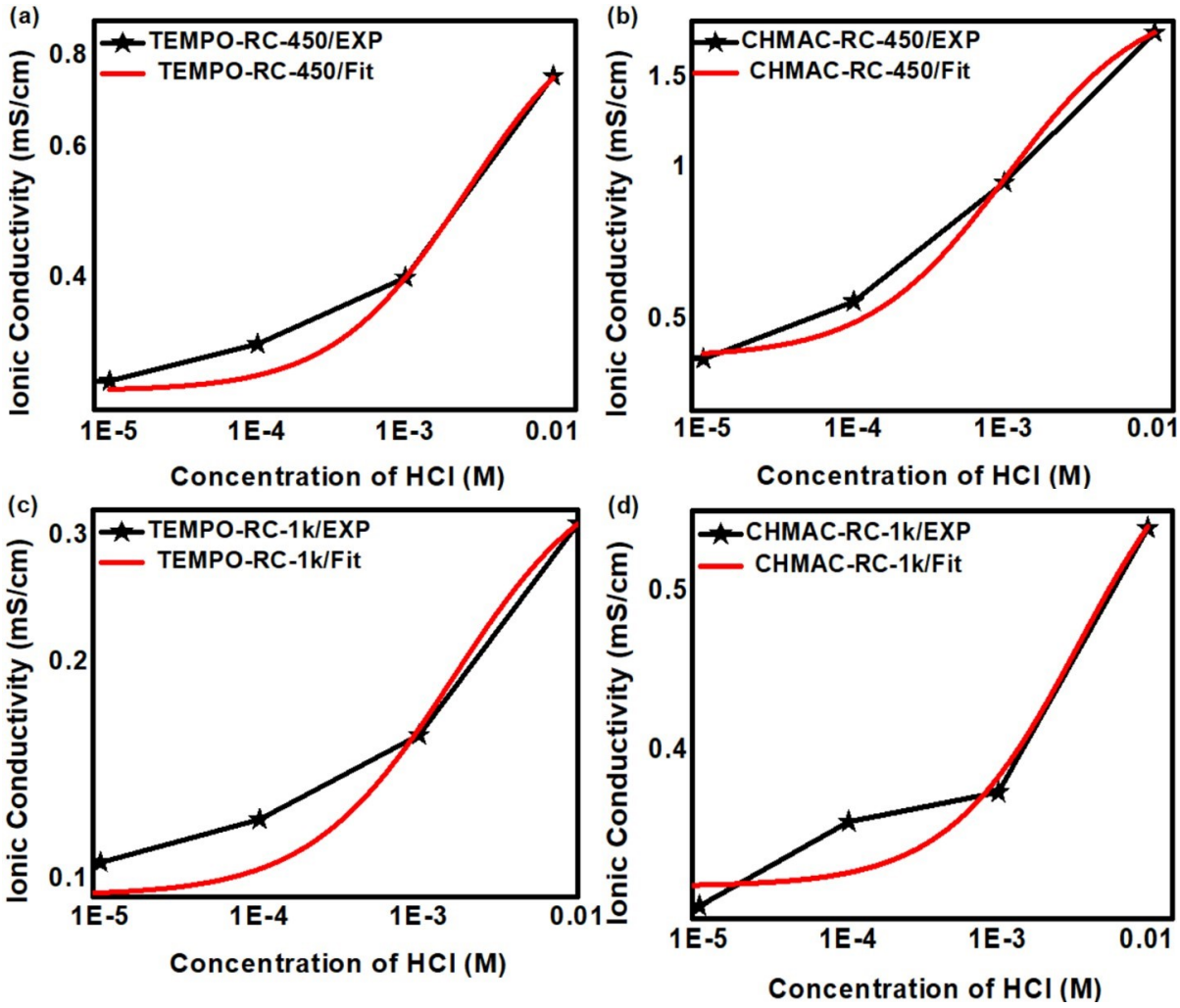


Figure S13. Ionic conductivity of functionalised RC membranes as a function of HCl concentration (10^{-5} to 10^{-2} M), measured experimentally using a nanofluidic device and fitted using an ionic conductivity model: (a) TEMPO-RC-450, (b) CHMAC-RC-450, (c) TEMPO-RC-1k, and (d) CHMAC-RC-1k.

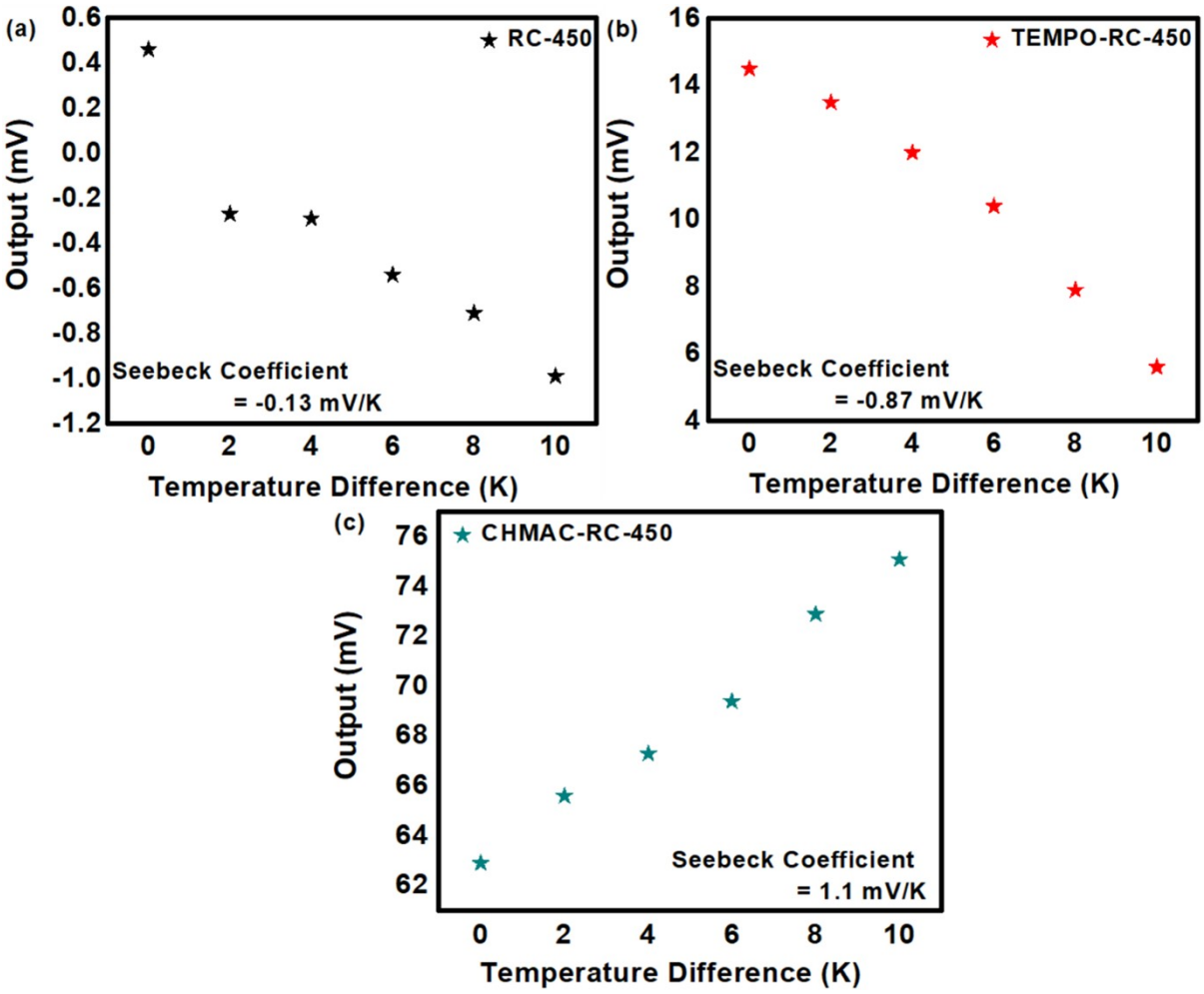


Figure S14. Thermal charging plots for RC-450 membranes: (a) pristine, and (b–c) functionalised variants, with temperature increased in 2 °C increments from room temperature.

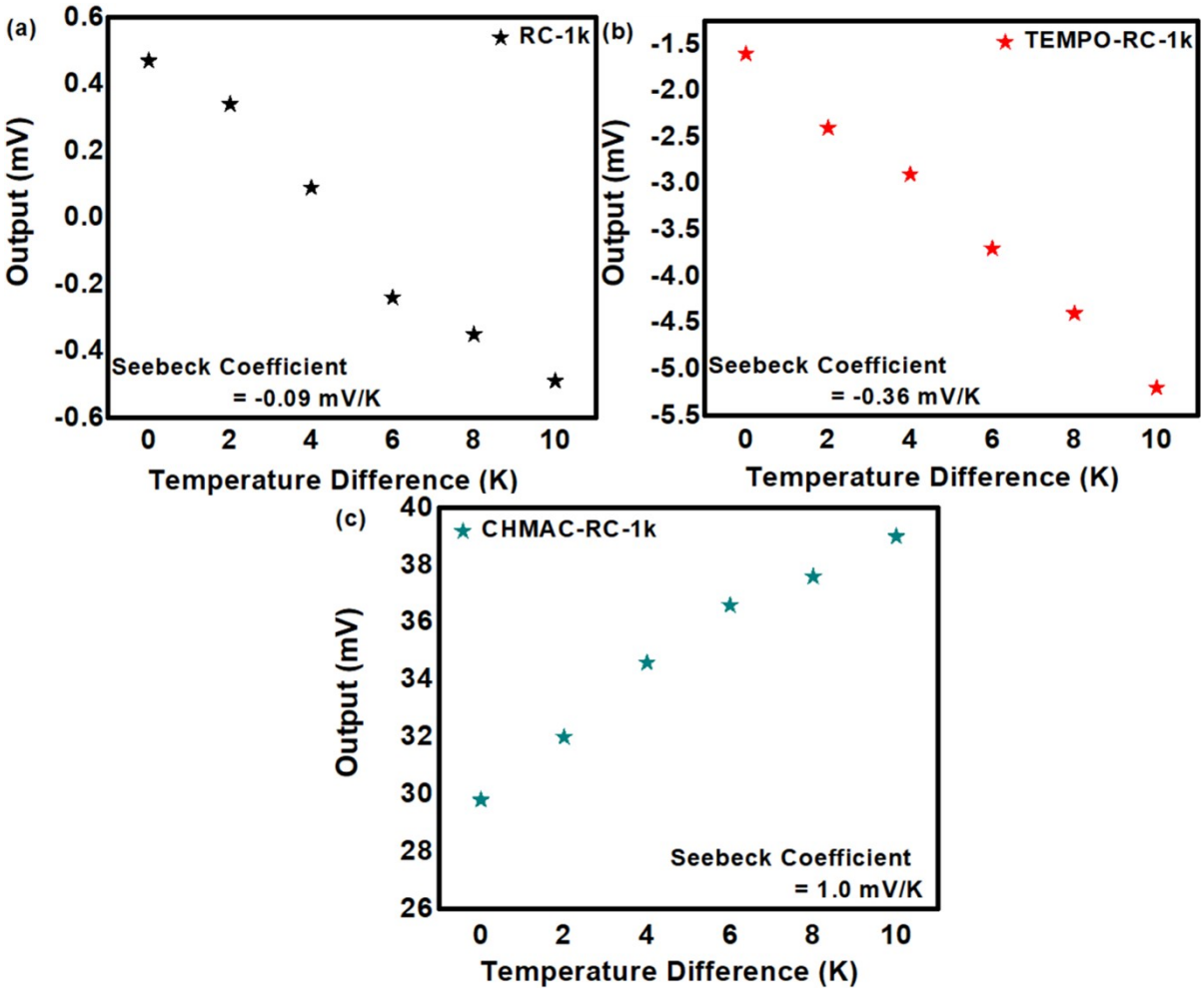


Figure S15. Thermal charging plots for RC-1k membranes: (a) pristine, and (b–c) functionalised samples, with temperature increased in 2 °C increments from room temperature.

References

1. Z. Wu, P. Ji, B. Wang, N. Sheng, M. Zhang, S. Chen and H. Wang, *Nano energy*, 2021, **80**, 105554.
2. D. C. Martins, V. Chu, J. P. Conde, *Biomicrofluidics,* 2013, **7**, 034111.