Supporting Information

Complexation-Driven Ion-Exchange Polymer Inclusion Membranes for Separation of Cobalt and Nickel ions from Lithium ion via Proton Pumping

Babafemi Adigun[a, b], Bishnu P. Thapaliya[c*], Huimin Luo[d*], Sheng Dai[a, b, c*]

[a] Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996, United States

[b] Institute of Advanced Materials & Manufacturing, Knoxville, Tennessee 37920, United States

[c] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Email: prasadthapab@ornl.gov, dais@ornl.gov

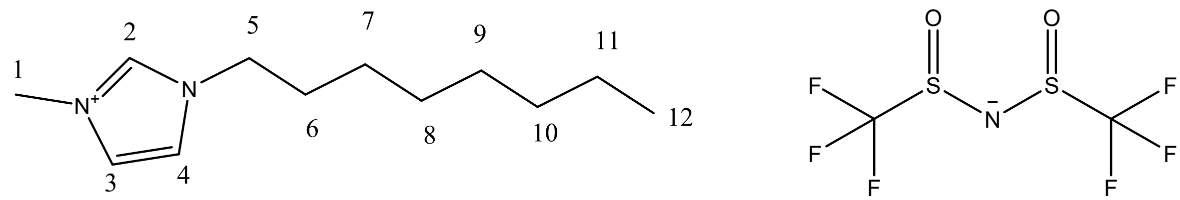
[d] Manufacturing Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Email: luoh@ornl.gov

KEYWORDS: *Ion-Exchange Polymer Inclusion Membrane (IEPIM), ionic liquids, membrane separation, membrane stability.*

Synthesis of Ionic Liquids

Ionic liquid 1-Octyl-3-methylImidalozium bis(trifluoromethanesulfonimide) (OMIm-NTf_2) was synthesized by modified procedure from the literature.[1]



^{1}H NMR (400 MHz, DMSO-D6) δ 9.38 – 8.91 (s, 1H, H_2), 7.72 (d, J = 1.9 Hz, 1H, H_4), 7.65 (d, J = 1.7 Hz, 1H, H_3), 4.19 – 4.04 (t, J = 7.2 Hz, 2H, H_5), 3.80 (s, 3H, H_1), 1.92 – 1.51 (m, J = 7.2 Hz, 2H, H_6), 1.42 – 0.92 (m, J = 8.8 Hz, 10H, H_{11}, H_{10}, H_9, H_8, H_7), 0.87 – 0.46 (t, J = 6.7 Hz, 3H, H_{12}).

^{13}C NMR (101 MHz, DMSO-D6) δ 137.02 (C_2), 124.14 (C_4), 122.79 (C_3), 120.02 (q, J = 322.0 Hz) (CF_3), 49.30 (C_5), 36.25 (C_1), 31.68 (C_6), 29.90 (C_7), 29.00 (C_8), 28.85 (C_9), 26.01 (C_{10}), 22.58 (C_{11}), 14.43 (C_{12}).

Membrane Characterization

Infrared (IR) spectroscopy was conducted on a Nicolet IS50 FT-IR (ATR) spectrometer in the range of 4000-500 cm^{-1}. The surface morphology of the IEPIM and PVDF-HFP was investigated on a Zeiss Auriga Crossbeam scanning electron microscopy (SEM).

FTIR Spectra of Cyanex 301

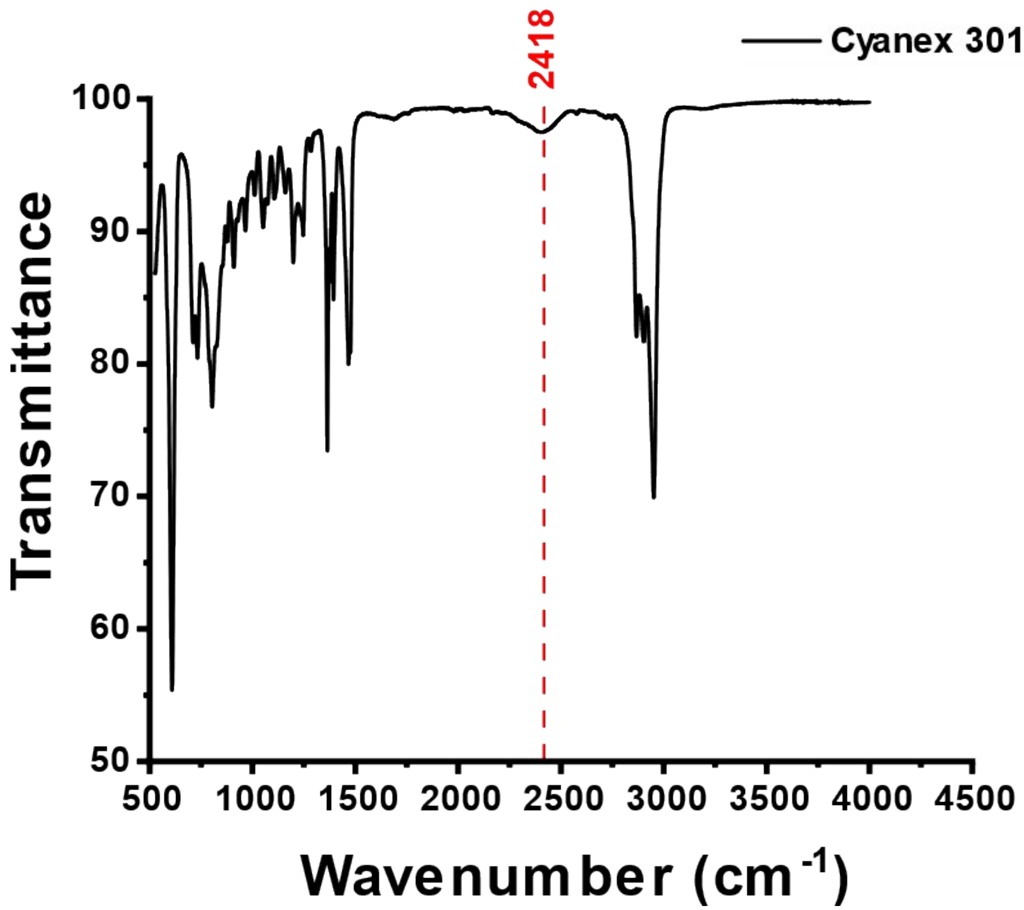


Figure S1: FTIR Spectra of Cyanex 301 showing the peak corresponding to S—H stretching bonds.

Transport of Co^{2+}, Ni^{2+} and Ni across IEPIM at different weight compositions.

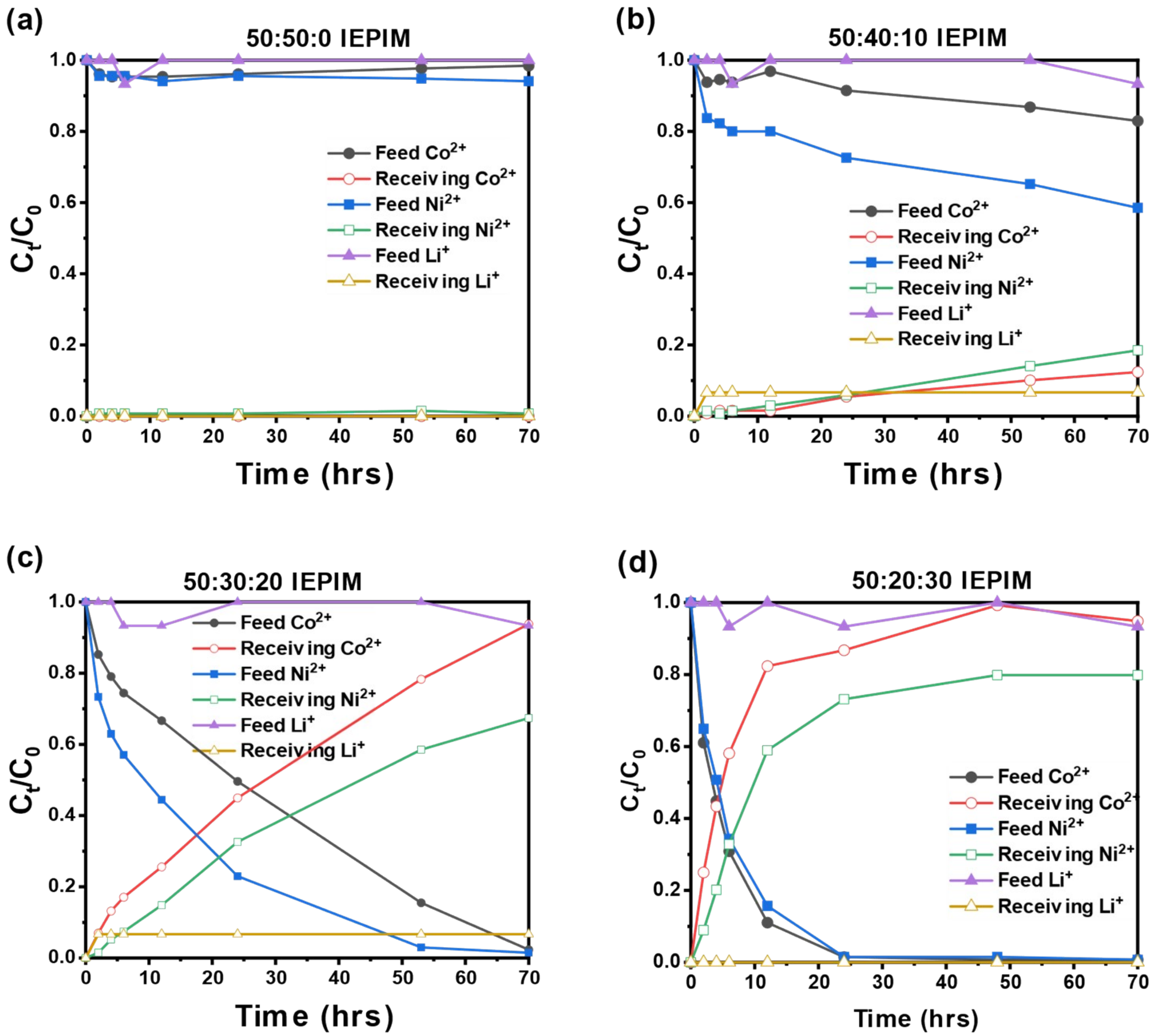


Figure S2: Co^{2+}, Ni^{2+} and Li^{+} transport across IEPIM at varying weight percent composition (a) 0% wt. composition (b) 10% wt. composition (c) 20% wt. composition and (d) 30% wt. composition.

Effect of Membrane Thickness on Transport of ions

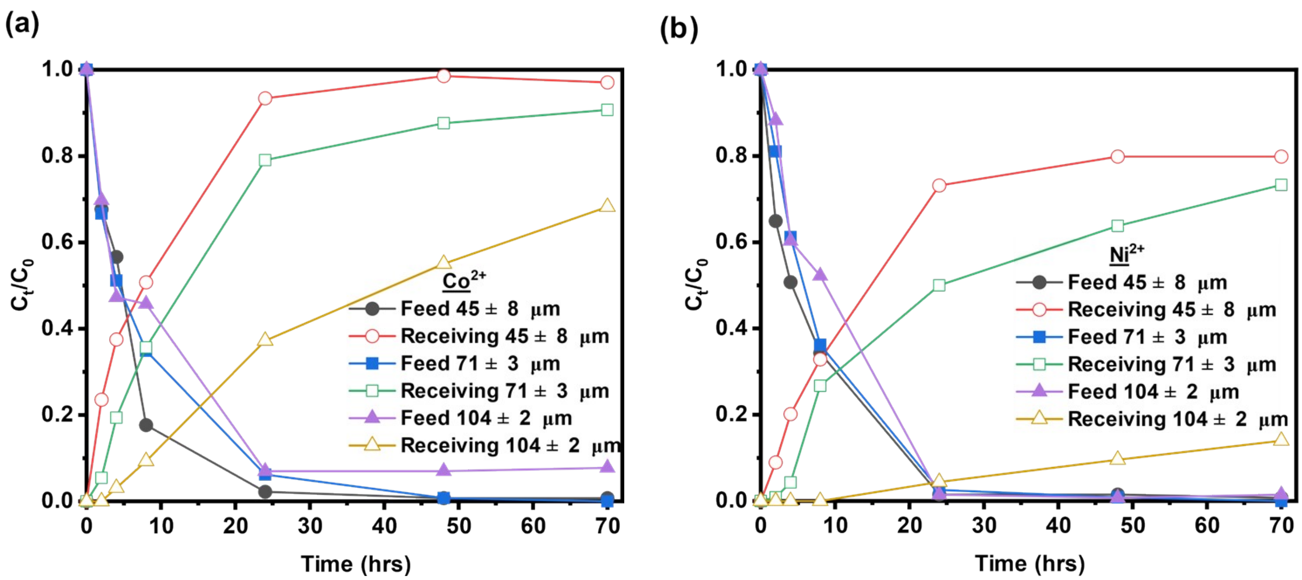


Figure S3: (a) Transport of Co^{2+} (b) Transport of Ni^{2+} across an IEPIM at different thickness. The concentration of the feed solution decreased over time, showing that IEPIM was able to extract Co^{2+} and Ni^{2+} from the feed solution.

Stability of IEPIM for Transport of Co^{2+} and Ni^{2+}

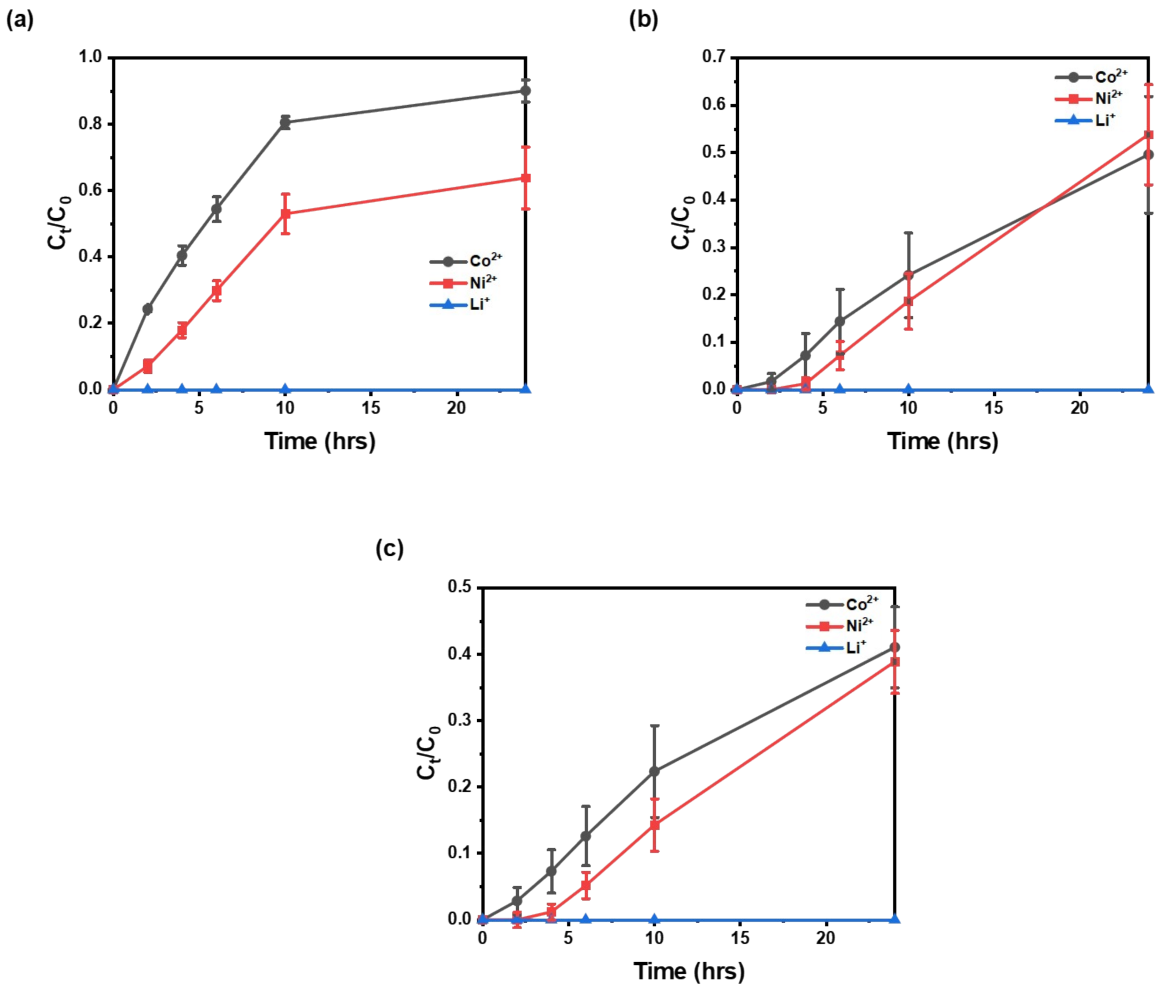


Figure S4: Transport of Co^{2+} , Ni^{2+} and Li^{+} after 24 hours across IEPIM for three cycles: (a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle.

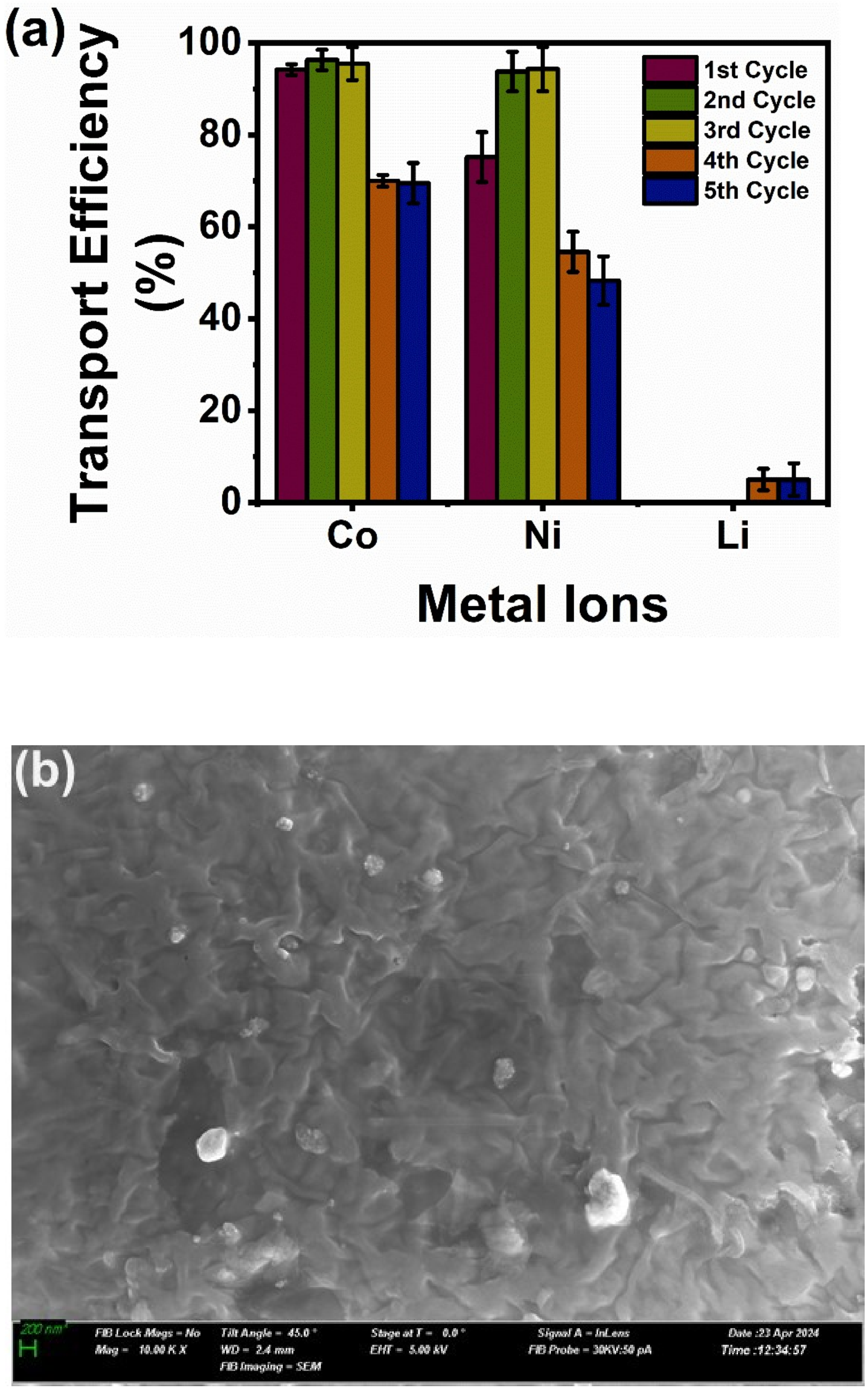


Figure S5: (a) Transport efficiency of 5 transport cycles. Feed solution: 100 mL of 0.1 mM Li^+, Co^{2+}, and Ni^{2+}. Receiving Solution: 2M HCl. (b) SEM image of the IEPIM after 5 transport cycles.

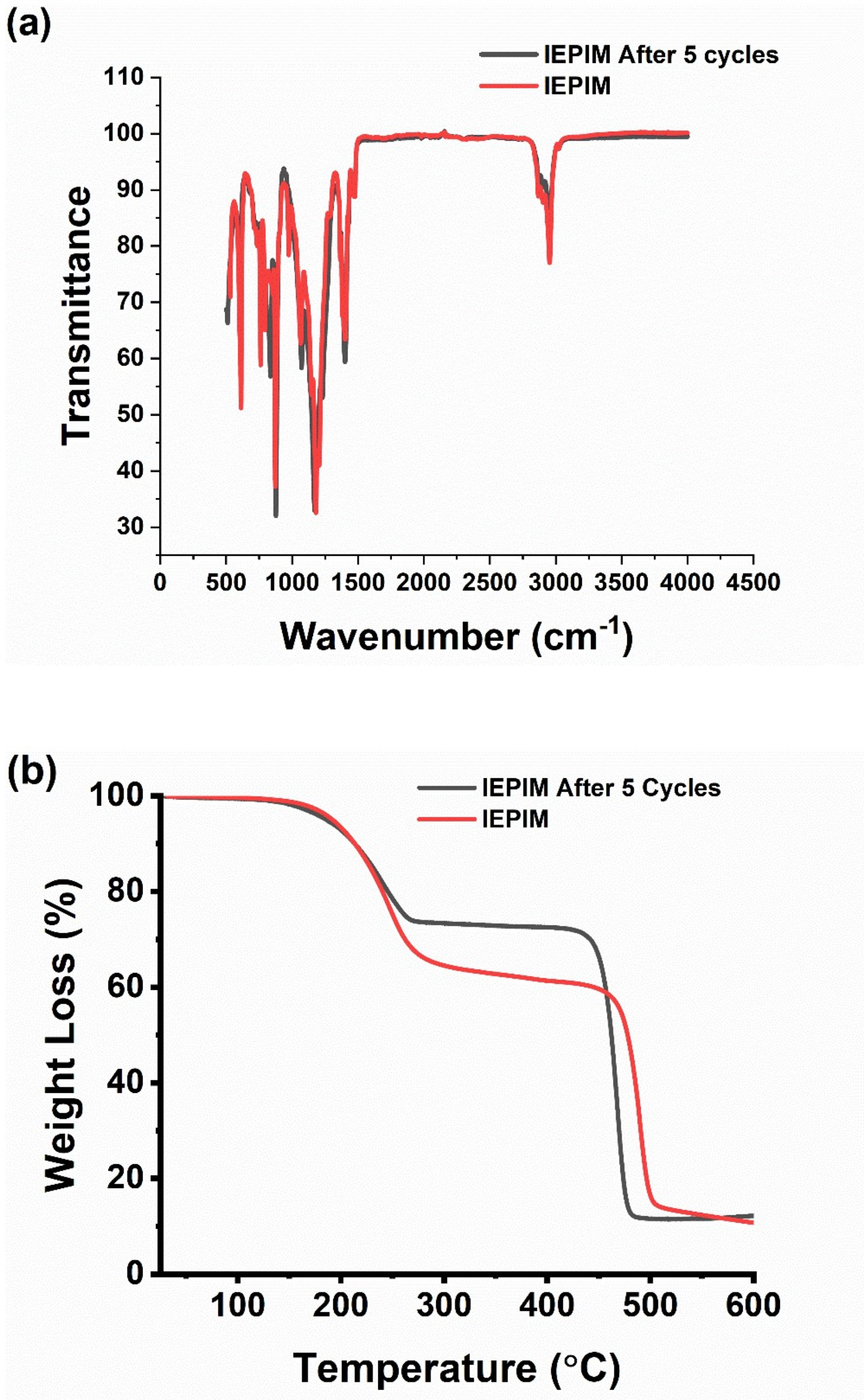


Figure S6: (a) FTIR (b) TGA of IEPIM after 5 transport cycle of experiments under N_2 at a scan rate of 10°C/min

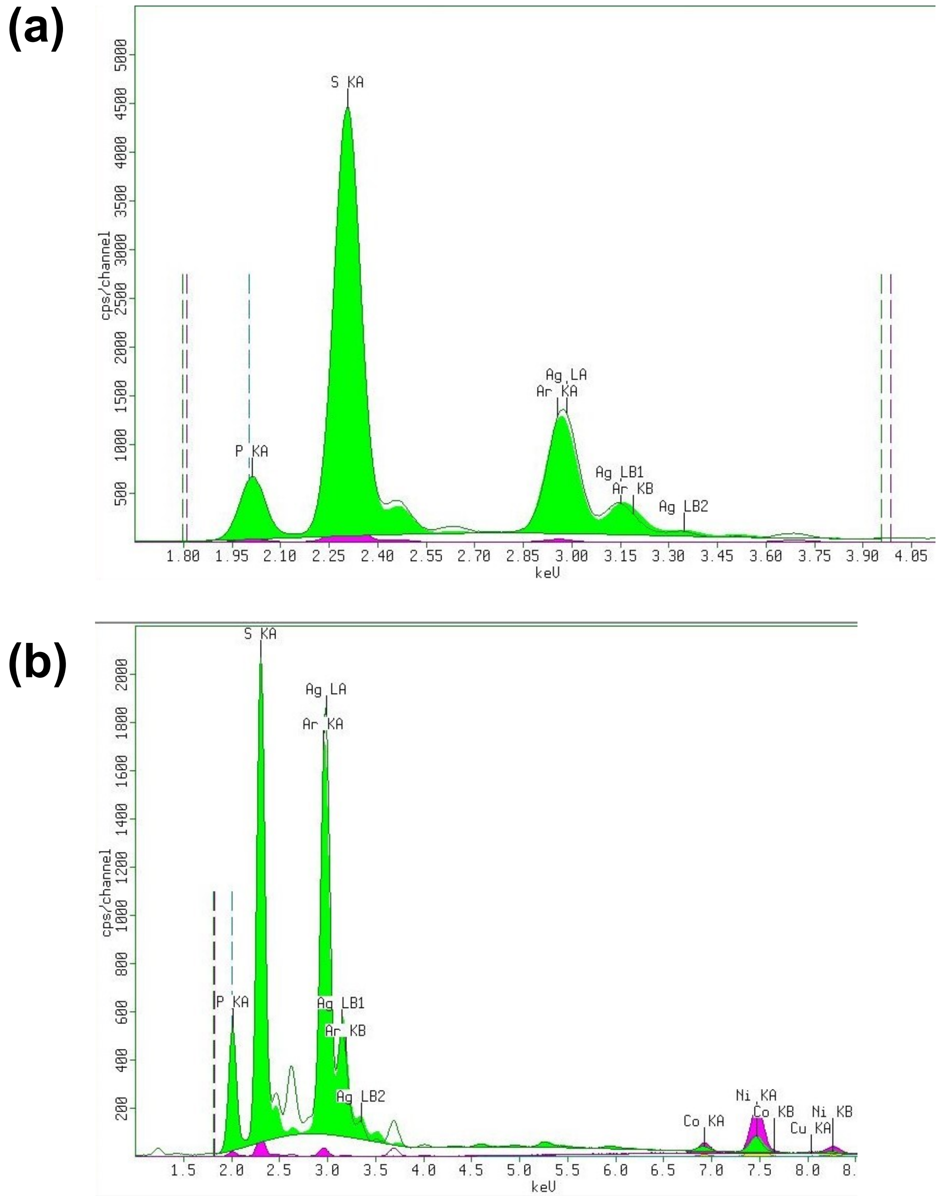


Figure S7: EDXRF spectra of the IEPIM (a) before transport experiment (b) after 5 cycles of experiment showing the presence of cobalt and nickel in the membrane.

REFERENCES

(1) Bonhote, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. Hydrophobic, highly conductive ambient-temperature molten salts. *Inorganic chemistry* **1996**, *35* (5), 1168-1178.