Supporting Information

Expanding Metal Cation Options in Polymeric Anion Exchange Membranes

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Contents

I. Materials and Instrumentation

All chemicals were purchased from Sigma-Aldrich, Acros Organics, Fisher Scientific, and Alpha Aesar and were used as received, unless otherwise stated. The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker 500 MHz Ascend retrofitted with a cryo-probe with all J-values given in Hz. FTIR was performed using a PerkinElmer Spectrum 100 FTIR spectrometer with a Universal ATR sampling accessory. Mass spectroscopy was recorded using a Bruker MicrOTOF ESI-TOF Mass Spectrometer at the University of Massachusetts, Mass Spectroscopy Facility. Mechanical properties were obtained using dynamic mechanical analysis (DMA) on a TA Instruments DMA Q800. Conductivity data was obtained using a custom system that multiplexes the impedance analyzer to temperature-calibrated positions within an ESPEC SH-241 bench-top type temperature and humidity chamber.

II. Experimental Procedures

Synthesis of compound P1. P1 was synthesized as an adaption of a previous report.[1] *Exo*-5-nobornene-2-carboxylic acid (1.0 g, 7.2 mmol), was dissolved in THF (22.5 mL) and cooled in an ice bath. Lithium aluminum hydride solution in THF (2.4 M, 2.26 mL) was added dropwise to the solution, the flask was removed from the ice bath and the reaction was stirred overnight at room temperature. The flask was then cooled in an ice bath and quenched with RO water. The precipitated salt was filtered and the THF was removed *in vacuo*. The remaining oil was diluted

with water and the product was extracted with chloroform. The chloroform was dried over Na_2SO_4 and removed *in vacuo* providing precursor monomer, **P1**, (0.863 g, 96 %) as a clear liquid product. δH (500 MHz, $CDCl_3$) 6.10 (2H, m), 3.71 (1H, m), 3.55 (1H, m), 2.83 (1H, s), 2.76 (1H, s), 1.62 (1H, m), 1.37-1.20 (3H, m), 1.12 (1H, m).

Synthesis of compound P2. P2 was synthesized as an adaption of a previous report.[1] **P1** (2.0 g, 0.016 mol) was added to a flask containing KOH (2.6 g, 0.046 mol) in DMSO (40 mL) and was heated at 75 °C for 2 hours. 4'-chloro-2,2':6',2"-terpyridine (2.16 g, 0.0081 mol) dissolved in DMSO (40 mL) was heated at 75 °C for 2 hours then poured into the flask containing **P1**. The mixture was stirred for 48 hours at 80 °C. Once cooled, the mixture was poured into cold RO water and the product extracted with ethyl acetate. The ethyl acetate was dried over Na_2SO_4 and removed *in vacuo*. Pure **P2** (2.43 g, 86 %), was recrystallized from methanol and obtained as off-white crystals. δH (500 MHz, $CDCl_3$) 8.76 (4H, br), 8.15 (2H, br), 7.99 (2H, br), 7.45 (2H, br), 6.15 (2H, m), 4.38 (1H, m), 4.21 (1H, m), 2.91 (2H, d), 1.97 (1H, m), 1.39 (4H, m).

Synthesis of compound M1. M1 was synthesized following a previously reported procedure.[1] **P2** (1.0 g, 2.8 mmol) in methanol (200 mL) was stirred under reflux. $RuCl_3$-$3H_2O$ (0.736 g, 2.8 mmol) was then added and the solution was stirred under reflux overnight. It was then cooled to -20 °C and the resulting brown precipitate was filtered and washed with ice cold RO water and ethyl ether to yield the intermediate complex (1.4 g, 88%). That was then dissolved in methanol (400 mL) with 2,2':6',2"-terpyridine (0.5 g, 2.1 mmol) and stirred under reflux for 30 minutes. *N*-ethylmorpholine (0.544 mL, 4.3 mmol) was then added and the solution was stirred under reflux overnight. Solvent was removed *in vacuo* and the resulting solid was partitioned between RO water and chloroform. The aqueous layer was washed with chloroform, removed *in vacuo* and then dried under vacuum. **M1** (1.6 g, 82 %) was obtained as a red powder. IR ν_{max}/cm^{-1} 3362, 3056, 2400, 1612, 1547, 1465, 1442, 1387, 1360, 1284, 1217, 1163, 1109, 1089, 1042, 1006, 919, 861**.** δH (500 MHz, D_2O) 8.72 (2H, d, 8.2), 8.46 (2H, d, 8.2), 8.40 (2H, d, 7.9), 8.32 (3H, s), 7.84 (4H, q, 8.3) 7.42 (2H, d, 5.5), 7.33 (2H, d, 5.2), 7.13 (2H, t, 6.6), 7.06 (2H, t, 6.4), 6.24 (2H, m), 4.59 (1H, m), 4.46 (1H, m), 3.18 (3H, m), 3.00 (1H, s), 2.96 (1H, s) 2.07 (1H, m), 1.51 (1H, br), 1.43 (3H, br), 1.28 (3H, t, 7.3). δC (126 MHz; CD_3OD) 168.87, 158.36, 155.92, 152.03, 151.77, 137.92, 137.80, 136.93, 135.89, 135.27, 127.52, 127.44, 124.53, 124.27, 123.54, 111.01, 74.29, 63.77, 52.22, 51.26, 44.65, 43.72, 41.64, 38.50, 29.18, 7.92. ESI-MS m/z 345.1497 (M^{2+}, 82%), 377.2359 (M^+, 9.0), 725.2613 (M^+, 9.0).

Synthesis of compound M2. P2 (0.5 g, 1.4 mmol) and $RuCl_3$-$3H_2O$ (0.175 g, 0.67 mmol) were dissolved in methanol (125 mL) and stirred under reflux for 2 hours. *N*-ethylmorpholine (0.147 mL, 1.1 mmol) was added and the solution was stirred under reflux overnight. The solution turned a deep red/brown color as the reaction went. The methanol was removed *in vacuo* and the resulting powder was dried under vacuum. **M2** (0.43 g, 79 %) was obtained as a red powder and used as is with no further purification. IR ν_{max}/cm^{-1} 3343, 2963, 1606, 1542, 1466, 1417, 1396, 1358, 1339, 1283, 1207, 1158, 1114, 1040, 1022, 1001, 982, 902, 859, 787, 758, 712, 696**.** δH (500 MHz, CD_3OD) 8.72 (4H, d, 8.2), 8.63 (4H, s), 7.98 (4H, t, 7.8), 7.51 (4H, d, 5.2), 7.26 (4H, t, 6.6), 6.26 (4H, m), 4.67 (2H, m), 4.52 (2H, t, 9.2), 3.08 (2H, s), 3.02 (2H, s), 2.17 (2H, m), 1.63 (2H, d, 8.5), 1.55 (6H, m). δC (126 MHz; CD_3OD) 166.39, 158.57, 156.42, 151.95, 137.64, 136.92, 135.87, 127.40, 124.34, 110.85, 74.17, 44.63, 43.71, 41.63, 38.50, 29.18. ESI-MS m/z 267.2377 (M^+, 12%), 362.1364 (M^{2+}, 16), 406.2014 (M^{2+}, 72).

Synthesis of compound M3. P2 (0.5 g, 1.4 mmol) dissolved in DCM (5 mL) was added to $NiCl_2$-$6H_2O$ (0.167 g, 0.702 mmol) dissolved in methanol (5 mL) in a round bottom flask with stir bar. The methanol solution changed from a green to brown color very quickly as **P2** was added. The solution was stirred at room temperature overnight. The solvent was removed *in vacuo* and the resulting solid was dried under vacuum. **M3** was obtained in quantitative yield as a tan colored solid and was used as-is with no further purification. IR v_{max}/cm^{-1} 2963, 1600, 1558, 1472, 1437, 1365, 1220, 1159, 1054, 1033, 1014, 1002, 859, 793. ESI-MS m/z 340.1472 (M^{2+}, 26%), 384.2060 (M^{2+}, 62), 803.3941 ($M^{2+} + Cl^-$, 12).

Synthesis of compound M4. P2 (0.5 g, 1.4 mmol) dissolved in DCM (5 mL) was added to $CoCl_2$-$6H_2O$ (0.167 g, 0.702 mmol) dissolved in methanol (5 mL) in a round bottom flask with stir bar. The methanol solution changed from a blue/violet to deep brown color very quickly as **P2** was added. The solution was stirred at room temperature overnight. The solvent was removed *in vacuo* and the resulting solid was dried under vacuum. **M4** was obtained in quantitative yield as a red/brown solid and was used as-is with no further purification. IR v_{max}/cm^{-1} 3303, 2961, 1600, 1554, 1472, 1438, 1364, 1254, 1219, 1159, 1054, 1029, 1000, 859, 792**.** ESI-MS m/z 340.6440 (M^{2+}, 34%), 384.7001 (M^{2+}, 49), 716.2576 ($M^+ + Cl^-$, 4) 804.3863 ($M^+ + Cl^-$, 13).

General AEM synthesis. All AEMs were synthesized following an adaption of a previously reported procedure.[1] The required monomer, dicyclopentadiene, and norbornene (for **M2-M4**), were dissolved in a methanol/chloroform mixture. A solution of Grubb's 2nd generation catalyst (G2) in chloroform was added and the solution was stirred vigorously for up to one minute. The solution was transferred to a pre-heated (40 °C) aluminum pan (diameter of ~7 cm and depth of ~1.5 cm) on a hot plate set to 40 °C. The pan was then covered by a glass jar (diameter of ~7.5 cm and depth of ~9 cm) to slow down evaporation of the solvent. After one hour, the cover was removed and the temperature remained at 40 °C. After another hour, the temperature was raised to 70°C. The membrane was then cooled and transferred to a glass jar. It was then swelled in 100% methanol, followed by 70% aqueous methanol, and then 30% aqueous methanol for at least 6 hours each. Finally the membrane was swelled in 100% RO water for at least 12 hours and the resulting membrane was stored in fresh RO water at all time unless otherwise stated.

Synthesis of AEM 1. M1 (0.15 g, 0.16 mmol) and dicyclopentadiene (0.114 mL, 0.84 mmol) were dissolved in a chloroform/methanol co-solvent (2.03 mL/0.225 mL, respectively). G2 (2.9 mg, 0.0034 mmol) was dissolved in chloroform (0.225 mL), added to the monomers and stirred vigorously. The resulting red, translucent membrane was generated as stated above. The associated N-ethylmorpholinium chloride byproduct associated with ruthenium complexes is not shown in Scheme 2 since its presence is well documented and its thorough removal was performed as described previously.[1,2]

Synthesis of AEM 2. M2 (0.15 g, 0.15 mmol), norbornene (0.0135 g, 0.14 mmol) and dicyclopentadiene (0.078 mL, 0.58 mmol) were dissolved in a chloroform/methanol co-solvent (2.03 mL/0.225 mL, respectively). G2 (2.9 mg, 0.0034 mmol) was dissolved in chloroform (0.225 mL), added to the monomers and stirred vigorously. The resulting deep red, translucent membrane was generated as stated above. The associated N-ethylmorpholinium chloride byproduct associated with ruthenium complexes is not shown in Scheme 2 since its presence is well documented and its thorough removal was performed as described previously.[1,2]

Synthesis of AEM 3. M3 (0.15 g, 0.18 mmol), norbornene (0.0165 g, 0.18 mmol) and dicyclopentadiene (0.096 mL, 0.71 mmol) were dissolved in a chloroform/methanol co-solvent

(2.03 mL/0.225 mL, respectively). G2 (2.9 mg, 0.0034 mmol) was dissolved in chloroform (0.225 mL), added to the monomers and stirred vigorously. The resulting brown, translucent membrane was generated as stated above.

Synthesis of AEM 4. M4 (0.15 g, 0.18 mmol), norbornene (0.0165 g, 0.18 mmol) and dicyclopentadiene (0.096 mL, 0.71 mmol) were dissolved in a chloroform/methanol co-solvent (2.03 mL/0.225 mL, respectively). G2 (2.9 mg, 0.0034 mmol) was dissolved in chloroform (0.225 mL), added to the monomers and stirred vigorously. The resulting red/brown, translucent membrane was generated as stated above.

III. Redox Potentials

Table S1. Redox potentials for an AEMFC and all three metals studied. [a]At PH 14. [b]Coordinated to two equivalents of terpyridine.

Metal	Redox Potential (V)	Source of redox Potential
AEMFC Electrodes.[3,4, a]	+0.4 +0.83	Reduction of oxygen at cathode Oxidation of hydrogen at anode
Ruthenium[5–8, b]	-0.98 to -1.08 -1.41	Oxidation wave Reduction wave
Cobalt[9, b]	+0.26 -0.77	+3/+2 transition +2/+1 transition
Nickel[10, b]	-1.07 -1.36	First wave Second wave

IV. AEM Characterizations

1. Measurement of Water Uptake. Liquid water uptake was determined for all AEMs in the chloride form at room temperature. The fully hydrated AEM was removed from liquid water and the surface was blotted to remove surface water not absorbed into the membrane. The mass of the AEM was then recorded immediately and the membrane placed back into water for 5-10 minutes. This process of weighing the hydrated membrane was repeated 3-5 times until consistent masses were obtained. They were then dried for 24 hours in vacuum at 50 °C and the dried AEM was weighed for its dehydrated mass. The percent water uptake was calculated using:

$$\boldsymbol{wu} = \frac{\boldsymbol{m_{hyd} - m_{dry}}}{\boldsymbol{m_{dry}}} \times \mathbf{100}\% \qquad \textbf{(1)}$$

where *wu* is the water uptake in percent, m_{hyd} is the hydrated mass and m_{dry} is the dry mass. The water uptake for AEMs **1**, **2**, **3**, and **4** were 231%, 28%, 36% and 29%, respectively.

To demonstrate that the water uptake differences observed between AEM **1** and AEMs **2-4** is due to the water solubility of the initial monomers **M1-M4**, UV-vis spectra for each monomer dissolved in DI water was taken. Each monomer was added to 10 mL of DI water at a concentration of 0.219 mM. At this concentration only **M1** fully dissolved, all other monomer solutions were saturated. The UV-vis spectra for each is shown in Figure S1 where only **M1** showed a strong absorbance in the UV region.

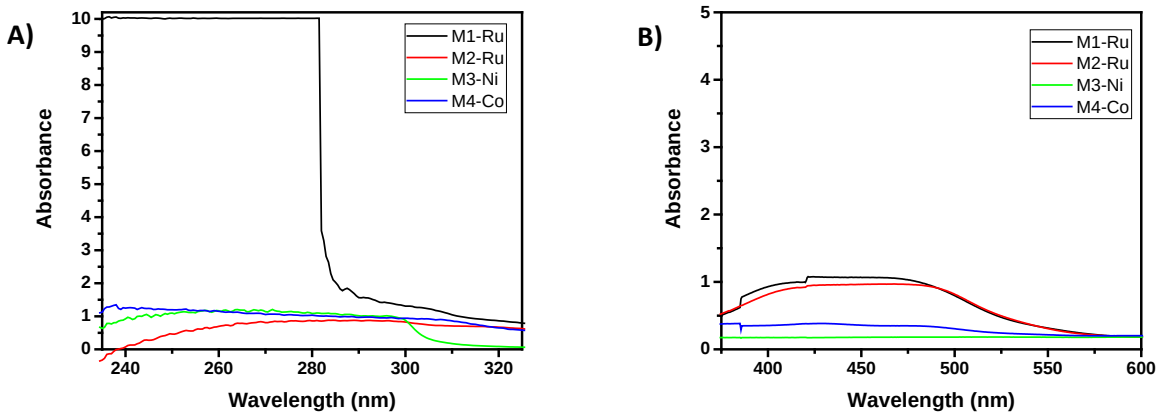

Figure S1. UV-vis spectra for monomers in DI water at a concentration of 0.219 mM A) in the UV region and B) in the visible region.

2. Measurement of AEM Mass Stability. All AEMs were tested in the same way. The AEM in the chloride form was converted to the hydroxide form by ion exchange in an aqueous 1 M KOH solution for 1 hour. The membrane was then washed with RO water to remove excess ions and dried for 24 hours at 50 °C under vacuum. The dried membrane was weighed, and then placed in an aqueous 2 M KOH solution at 80 °C. The AEM was removed from the solution after either 6, 24 or 48 hours, washed with RO water to remove excess ions and then dried under vacuum at 50 °C for 24 hours. The percentage of mass remaining after 48 hours was calculated to be 72%, 94%, 98% and 99% for AEM **1**, **2**, **3**, and **4**, respectively. Mass remaining for each time point can be seen in Figure 3. Due to the high mass loss seen in AEM **1** as compared to previous reports,[1] the procedure from that report was performed. AEM **1** was converted to the hydroxide form by immersion in 1 M KOH for one hour. It was then dried for 24 hours at 50 °C under vacuum, weighed and placed in a 1 M NaOH solution at 80°C for either 6, 24 or 48 hours. After the required time, the membrane was removed from solution, washed with RO water and dried for 24 hours at 50 °C under vacuum. The dried membrane was then weighed and compared to immersion in 2 M KOH, as shown in Figure S2. Both 1 M NaOH and 2 M KOH showed a mass percent remaining of 70-72% after 48 hours.

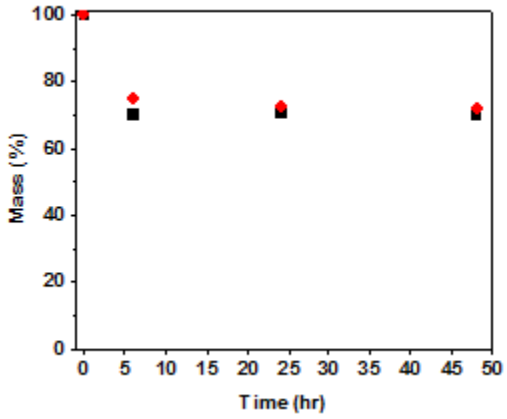

Figure S2. Percentage of mass remaining for AEM **1** comparing between 1 M NaOH (black squares) and 2 M KOH (red circles) after 48 total hours.

In order to test whether the mass loss and observed leveling off was due to a degradation equilibrium, AEM **1** samples, after an initial immersion for 6, 24 or 48 hours in 2 M KOH at 80 °C followed by drying and weighing of the sample (Figure S3), were immersed in a new solution of 2 M KOH at 80 °C for an additional 24 hours. The sample was then washed with RO water and dried at 50 °C for 24 hours under vacuum. Figure S4 shows the mass percentage remaining after the second incubation of 24 hours. While the first incubation showed a mass percent remaining of 72% after 48 hours, after subsequent immersion in 2 M KOH the AEM showed no further loss of mass. All of the sample's post-incubation mass remained after the second incubation, indicating that the mass loss was more likely due to loss of sol fraction, since additional mass loss would be expected in the case of AEM degradation.

Finally, the gel fraction of each membrane was determined in order to support that the mass loss was due to sol fraction and not degradation. Each AEM was synthesized as described previously, but instead of the standard work-up, they were instead placed in methanol and heated at 70°C overnight. The samples were then dried in vacuum at 50°C and weighed. The results can be seen in Table S2. As can be seen, AEM **1** had a much lower gel fraction than 2-4, thus supporting that the mass loss observed is most likely related to the sol fraction and not actual degradation.

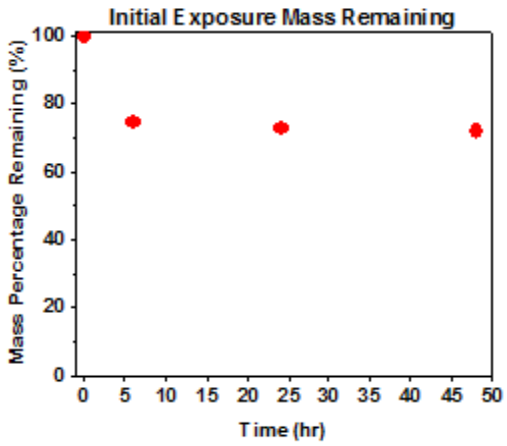

Figure S3. Percentage of mass remaining after AEM **1** was immersed in 2 M KOH solution at 80 °C for various times.

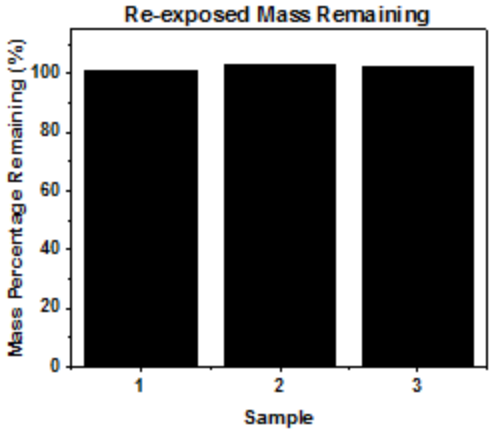

Figure S4. Percentage of mass remaining after a second incubation of AEM **1** in 2 M KOH at 80 °C for 24 hours after an initial incubation of 6 hours (sample 1), 24 hours (sample 2), or 48 hours (sample 3).

Table S2. Experimental IEC and gel fraction for AEMs **1-4**.

Sample	Gel Fraction
1	65%
2	93%
3	79%
4	76%

3. Experimental IEC. The experimental IEC was determined for each AEM through back titration. All samples were dried overnight in vacuum at 50°C to obtain the dry mass. They were then re-swelled in DI water for 24 hours. After fully re-hydrated, each sample was converted to the OH^- form, washed thoroughly with DI water to remove excess KOH, and placed in 10 mL of a 0.01 M HCl solution and stirred for 24 hours along with a control solution not containing a membrane. After stirring for 24 hours, all five samples were titrated with 0.0107 M aqueous KOH solution until a pH of 7 was reached. The experimental IEC was then calculated using equation 2 with values shown in Table 1.

$$IEC_{exp} = \frac{(V_c - V_s)c_{KOH} * 1000}{m_s} \quad \textbf{(2)}$$

Where V_c is the volume of the KOH solution used for the control sample, V_s is the volume of the KOH solution used for the AEM sample, c_{KOH} is the concentration of the KOH solution and m_s is the dried mass of the sample.

4. Measurement of Mechanical Properties. The mechanical properties of all AEMs were tested using DMA while in the chloride form. All samples were cut into rectangular films 3-6 mm wide and 15-20 mm long, and then dried for 24 hours at 50 °C under vacuum. The test was run with a preload force of 0.001 N followed by a force ramp of 1 N/min. The test was run until the sample broke, giving the stress and strain at break. The results of trial one can be seen in Figure 4, while trial 2 and 3 can be seen in Figure S5A and Figure S5B, respectively.

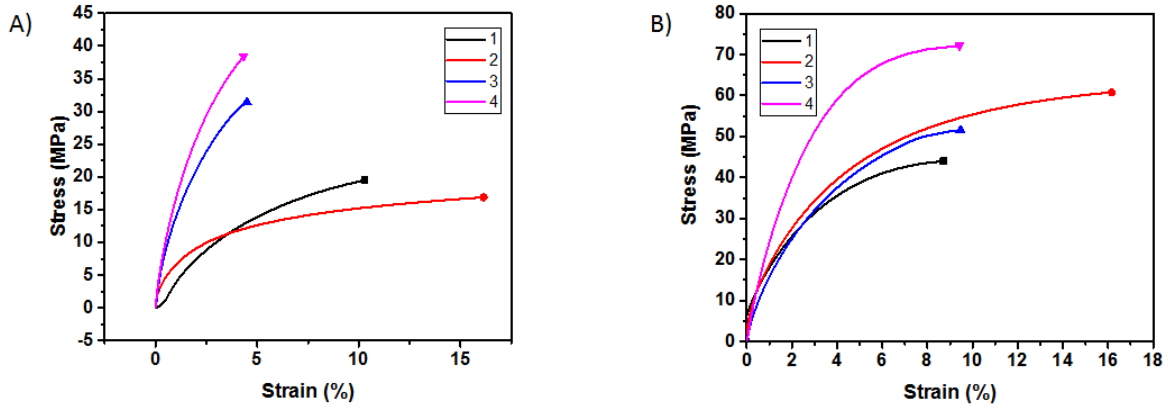

Figure S5. DMA results for all four AEMs for A) trial 2 and B) trial 3.

5. Measurement of Ionic Conductivity. Conductivity of samples in the chloride form was performed using an electrochemical impedance spectrometer (EIS). For the measurements, aluminum mounts were first sputter coated with gold using a Cressington 108 sputter coater. Samples were first measured for their thickness, in centimeters, and then placed into a sample holder containing two electrodes, with the sample in between the two electrodes. The holder was then loaded into a custom system that multiplexes the impedance analyzer to one of eight temperature-calibrated positions within an ESPEC SH-241 bench-top type temperature and humidity chamber. Samples were then heated at 95% relative humidity to 30 °C for 7200 seconds. Impedance spectra in the frequency range of 10 MHz-0.1 Hz were recorded for each sample at repeated time intervals of 1800 seconds, totaling four spectra per temperature. This was then repeated at 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 70 °C, 60 °C, 50 °C, 40 °C, and 30 °C, in that order. The temperature was ramped up and then back down to ensure consistency at both the beginning and end of the experiment. The bulk resistance to ion conduction, R, was then determined by fitting a constant function to the first plateau of the impedance magnitude occurring at high frequencies. The conductivity was then calculated from the known sample area, A = 0.074 cm^2, and the measured sample thickness, d, as $\sigma = d/(AR)$. The chloride conductivity for AEMs **1**, **2**, **3**, and **4** were 4.2 mS/cm, 1.09 mS/cm, 3.24 mS/cm and 0.405 mS/cm, respectively

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