## Supporting Information: On the stability of anion exchange membrane fuel cells incorporating polyimidazolium ionene (Aemion+<sup>®</sup>) membranes and ionomers

Qiliang Wei, <sup>a</sup> Xinzhi Cao, <sup>a</sup> Philipp Veh, <sup>b</sup> Anastasiia Konovalova, <sup>a</sup> Peter Mardle, <sup>a</sup> Philip Overton, <sup>a</sup> Simon Cassegrain, <sup>a</sup> Severin Vierrath, <sup>b,c</sup> Matthias Breitwieser, <sup>b</sup> and Steven Holdcroft. <sup>a</sup>

<sup>a</sup> Holdcroft Research Group, Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby BC V5A 1S6, Canada

<sup>b</sup> Electrochemical Energy Systems, IMTEK, Department of Microsystems Engineering, University of Freiburg, Georges-Koehler-Allee 103, 79110 Freiburg, Germany

<sup>c</sup> Freiburg Center for Interactive Materials and Bioinspired Technologies, FIT, University of Freiburg, Georges-Köhler-Allee 105, 79110 Freiburg, Germany



**Figure S1: (a)** Example of fitting the EIS spectra for ex-situ conductivity measurements. Fitting was conducted with the equivalent circuit **(b).** R1 is taken as the resistance for ionic conduction within the AEM.



**Figure S2:** In-plane (solid) and through-plane (dashed) Cl<sup>-</sup> conductivity for all AEMs tested at 60 (black), 70 (red) and 80 (blue) °C.



**Figure S3:** DVS for all three temperatures and AEMs investigated in the AEMFC study. Thicker variants were used for direct comparison with the ex-situ conductivity measurements. All isotherms were acquired in the desorption direction (high RH to low). Materials characterized are: Aemion<sup>®</sup>, 50  $\mu$ m (A/50) • Aemion+<sup>®</sup>, 50  $\mu$ m (A+/50) • Aemion<sup>®</sup>+, 40  $\mu$ m, reinforced (A+/40-r).



**Figure S4**: (a) In-plane conductance for AEMs in their Cl<sup>-</sup> form at 70 °C and (b) through-plane area specific resistance focused on the monolithic AEMs. Materials characterized are: Aemion<sup>®</sup>, 50 μm

(A/50) • Aemion+<sup>®</sup>, 50  $\mu$ m (A+/50)  $\bigcirc$  Aemion<sup>®</sup>+, 40  $\mu$ m, reinforced (A+/40-r) and  $\diamondsuit$  Aemion+<sup>®</sup>, 10  $\mu$ m, reinforced (A+/10-r).



**Figure S5: (a)** LLP and **(b)** LVP where the water flux on the y-axis is normalized for the wet thickness of the AEM. The slope therefore corresponds to the permeability. Materials characterized are: Aemion<sup>®</sup>, 25  $\mu$ m (A/25)  $\clubsuit$  Aemion+<sup>®</sup>, 10  $\mu$ m (A+/10) and  $\diamondsuit$  Aemion+<sup>®</sup>, 10  $\mu$ m, reinforced (A+/10-r).





**Figure S6:** ATR-FTIR of AEMs in their Cl<sup>-</sup> form. Before (pristine) and after degradation by submerging in 3 M KOH<sub>(aq)</sub> for 7 days at 80 °C. **(a)** Aemion<sup>®</sup>, 25  $\mu$ m, **(b)** Reinforced Aemion+<sup>®</sup>, 10  $\mu$ m, **(c)** Aemion+<sup>®</sup>, 10  $\mu$ m. Transmittance is normalized between 1-0.

	Tensile Strength / MPa	Elongation at break /%	Young's Modulus / MPa
Aemion+® (10 μm)	28 ± 4	40 ± 14	443 ± 58
Aemion+® (10 μm, reinforced)	29 ± 10	61 ± 24	403 ± 132

**Table S1:** Mechanical strength tests of AEMs in their Cl<sup>-</sup> form, atmospheric conditions after degradation in 3M KOH<sub>(aq)</sub> for 7 days at 80 °C. Aemion<sup>®</sup> was too brittle after the degradation test to be measured.



**Figure S7**. Polarization curves and power density curves of single cells between OCP and 0.3 V using TKK Pt/C as cathode and PtRu/C as anode with a Pt loading of 0.5 mg<sub>Pt</sub> cm<sup>-2</sup> on both cathode and anode. The H<sub>2</sub> and O<sub>2</sub> flows are set to 0.5 slpm. The cell temperature was 60 °C. The effect of anode and cathode RH on an MEA with Aemion+<sup>®</sup> (10  $\mu$ m, reinforced) is shown.



**Figure S8**. Polarization curves and power density curves of single cells between OCP and 0.3 V using TKK Pt/C as cathode and PtRu/C as anode with a Pt loading of 0.5 mg<sub>Pt</sub> cm<sup>-2</sup> on both cathode and anode. The H<sub>2</sub> and O<sub>2</sub> flows are set to 0.5 slpm. The RH at the anode and cathode was 90%. The effect of cell temperature on an MEA with Aemion+<sup>®</sup> (10  $\mu$ m, reinforced) is shown.



**Figure S9:** EIS in the frequency range 10 kHz - 0.1 Hz at 0.8 V with amplitude 10 mV. AEMFC conditions are the same as in **Figure 2a**.



**Figure S10:** ATR-FTIR spectrums and matching active area surface SEM images of membranes after AEMFC test: **(a)-(b)** Aemion<sup>®</sup> (25  $\mu$ m); **(c)-(d)** Aemion<sup>®</sup>+ (10  $\mu$ m); **(e)-(f)** Aemion<sup>®</sup>+ (10  $\mu$ m, reinforced). Transmittance is normalized between 1-0.



Figure S11: Active area surface SEM images of the reinforced Aemion<sup>®</sup> + membrane: (a) Anode side;
(b) Cathode side; (c) Side B magnification.



Figure S12: SEM image of the MEA cross-section of the DMD-based AEM fuel cell, showing the thin total membrane thickness of only 5  $\mu$ m.



**Figure S13: (a)** Voltage decay and, **(b)** ASR increase of single cells with TKK Pt/C as cathode and PtRu/C as anode with a Pt loading of 0.5 mg<sub>Pt</sub> cm<sup>-2</sup> on both cathode and anode. The H<sub>2</sub> and O<sub>2</sub> flows are set to 0.5 slpm. The RH at the anode and cathode was 90%. The cell temperature was 70 °C and the current density was 600 mA cm<sup>-2</sup>. Aemion+<sup>®</sup> (10  $\mu$ m, reinforced) was used as the AEM.