

Supplementary Information: The effect of ionomer content in catalyst layers in anion-exchange membrane water electrolyzers prepared with reinforced membranes (Aemion+™)

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Loading investigation

Due to the significant ink instabilities and variation in the thickness of the anode catalyst layers seen in FIB/SEM cross sections the real loading of the anode catalyst was investigated post-processing. During fabrication the loading was determined using a microgram resolution scale to weigh metal plates and the loading was calculated from the fraction of solids expected for the catalyst from the mixing ratios in the ink. Due to the ink instabilities this loading is likely distorted, since metal particles and ionomer may sediment with different time constants and the ratio may vary over the spraying process (even if the ink is continuously stirred). The metal plates were thus measured using X-Ray Fluorescence spectrometer (Bruker Tornado μ XRF) and an analysis method using Brukers XMethod software was used to acquire a quantitative amount of Iridium from the XRF spectra. The real Ir content as determined by this method was not calibrated, so values should only be analyzed as a relative comparison between samples and not taken as the real quantitative loading. A calibration using a mass spectrometry technique or thermogravimetric analysis should be employed to determine real quantitative values and get the real ionomer:catalyst ratio. This was however beyond the scope of this study.

Fig. S 1 shows the loading as determined by XRF using different ionomer contents in the anode catalyst layer, showing a variation between 0.84 mg/cm² and 1.1 mg/cm², which is significantly smaller than the variations of layer thickness observed in FIB/SEM cross-sectional images.

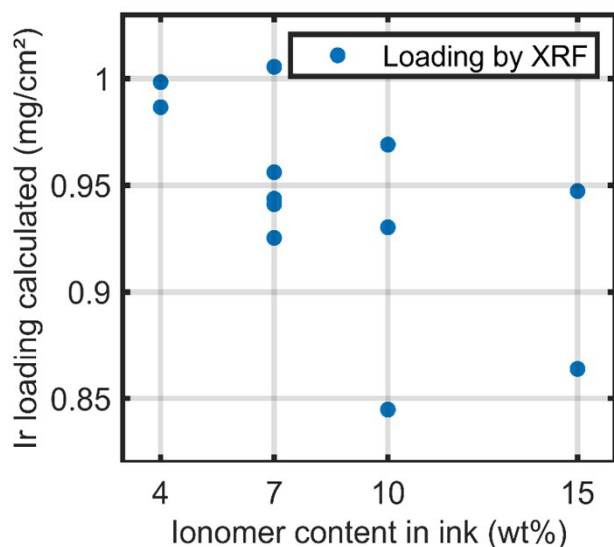


Fig. S 1 Iridium loading as determined by X-Ray Fluorescence images of metal plates used to check the loading during CCM spray coating.

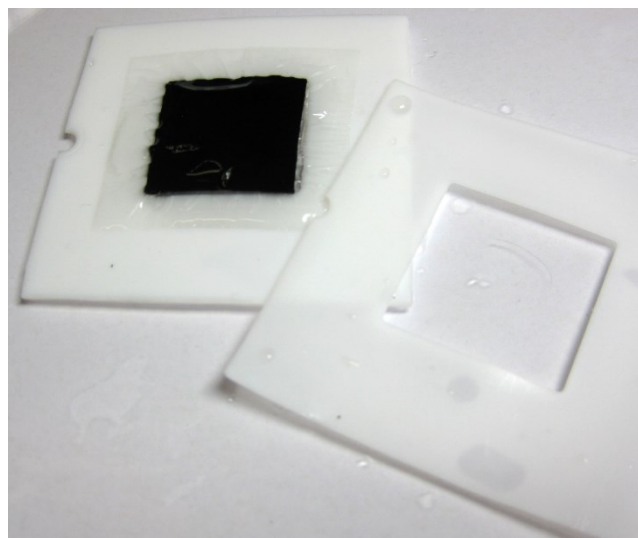
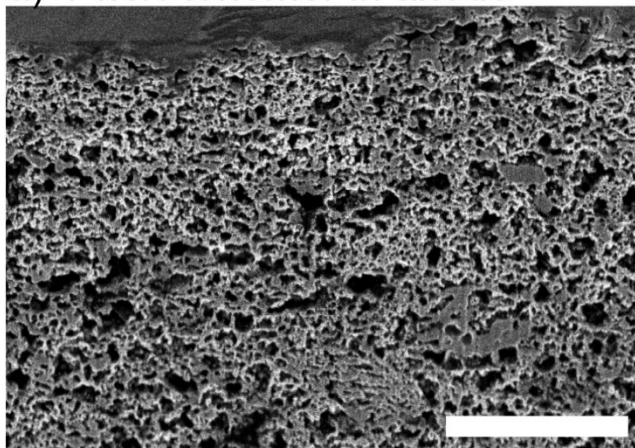


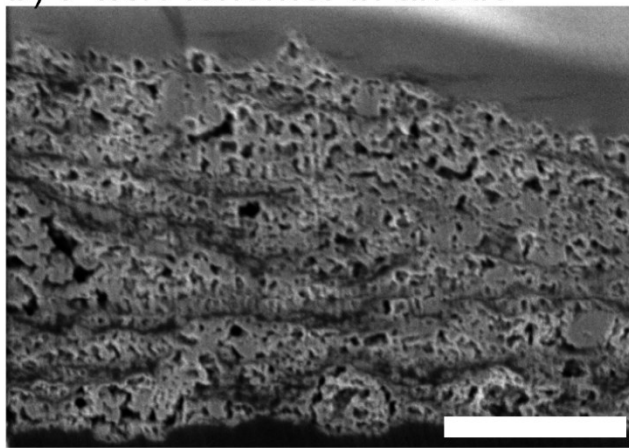
Fig. S 2 The CCM is fixed between PTFE-templates to prevent curling during ion exchange and facilitate the subsequent assembly.

Additional morphology data

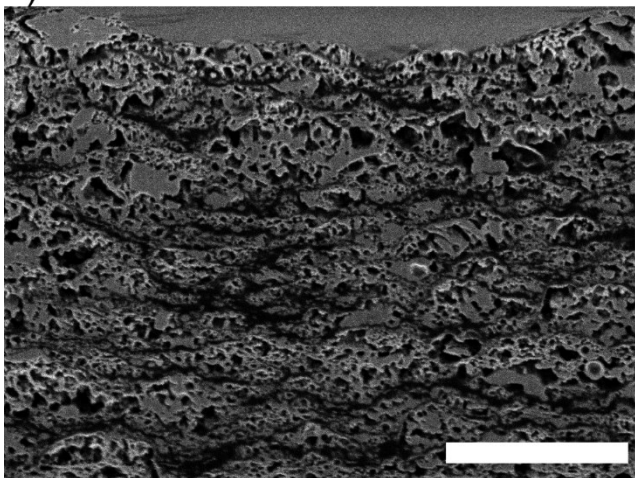
a) 4 wt% ionomer in anode



b) 7 wt% ionomer in anode



c) 10 wt% ionomer in anode



d) 15 wt% ionomer in anode

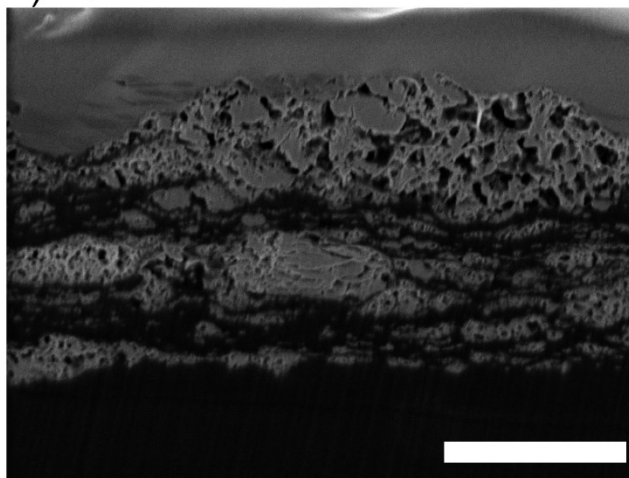


Fig. S 3 SEM images of FIB/SEM cross sections of anode catalyst layers including different ionomer contents, the magnification allows a visual distinction between ionomer rich areas and void spaces due to their shape and apparent texture. Scalebar represents 2 μm .

Additional performance data

Additional traces for the polarization data are shown here. No iR-free data is shown to here. In Fig. S 4 multiple cells with cathode ionomer content variation show that there is no clear, reproducible trend in performance dependence. Faid *et al.*¹⁸ saw a ranked performance for 10 wt%, 20 wt%, and then on the same level 30 wt% and 40 wt% ionomer content in Ni/C based cathodes, which

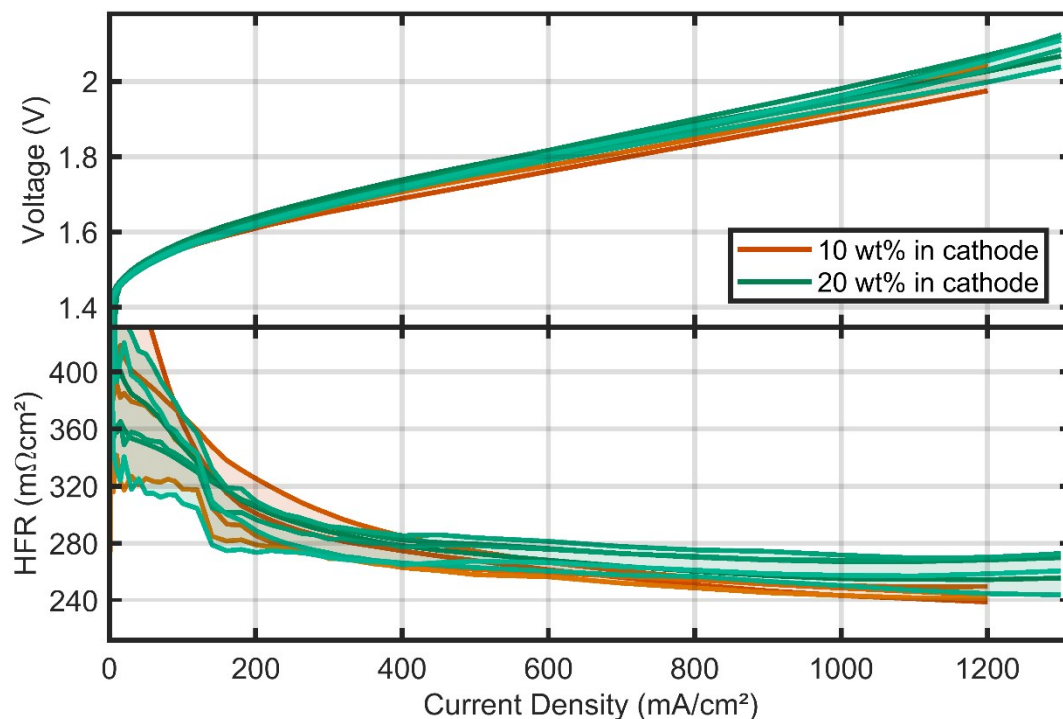


Fig. S 4 All polarization curves (top) and and HFR values (bottom) for the cathode ionomer variation (using 7 wt% ionomer in the anode), showing an overlap in overall performances.

was not seen here. This is likely due to the different ionomer (Fumion vs. Aemion+) and catalyst loading ($5 \text{ mg}/\text{cm}^2$ vs. $0.5 \text{ mg}/\text{cm}^2$) used.

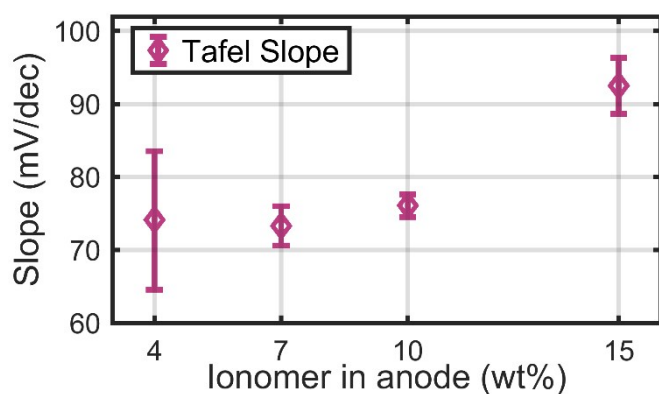


Fig. S 5 Tafel Slope extracted from the polarization curves of at least three samples for each ionomer content variation in the anode catalyst layer. The Tafel Slope was extracted from a linear fit to the iR-free voltage over the logarithmic current density in the range of 10 to 80 mA/cm^2 .

Fig. S 6 shows the various traces used to extract HFR and Tafel parameters for multiple cells with a variation in the ionomer content on the anode side. Showing at least a clear separation for the 15 wt% ionomer. The medians of the extracted Tafel slopes are shown in Fig. S 5.

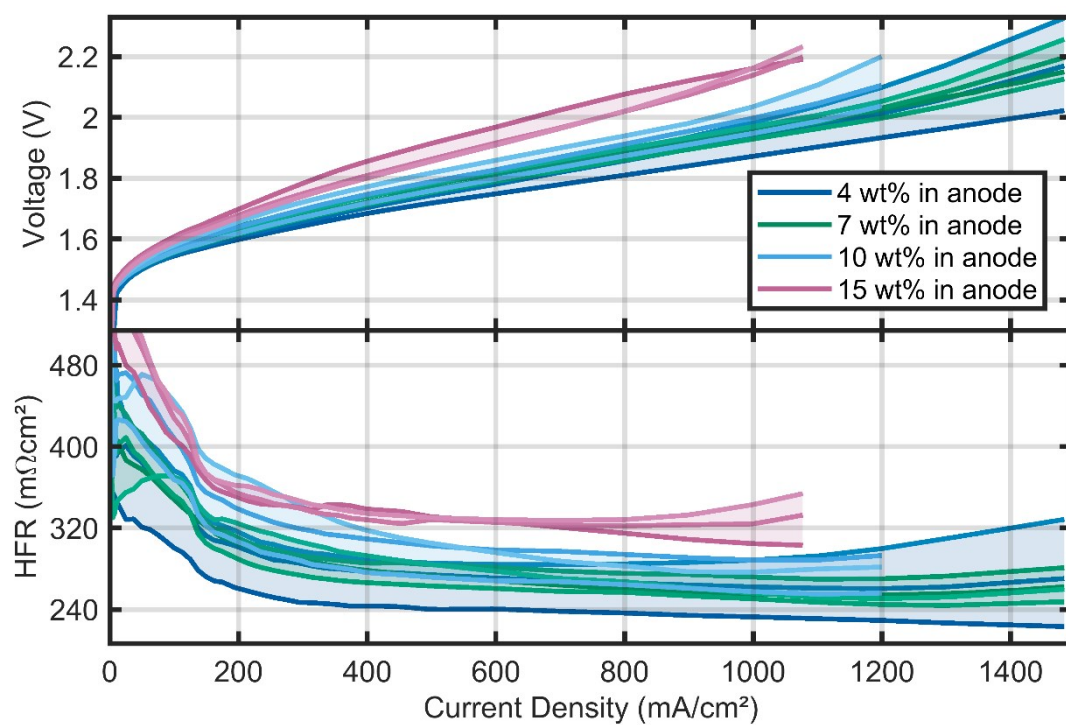


Fig. S 6 All polarization curves (top) and HFR values (bottom) for the anode ionomer variation (using 20 wt% ionomer in the cathode), which were included in the parameter summaries in the main text.

Additional degradation data and catalyst loss investigation

During a 1 Acm⁻² current hold, the voltage response was measured to extract short-term degradation parameters. Fig. S 7 shows the short-term degradation traces during current holds of multiple cells at 1 Acm⁻² for a maximum of 5 hours (measured twice in succession if possible). The shaded area corresponds to the range of all measured samples, while the line is their median.

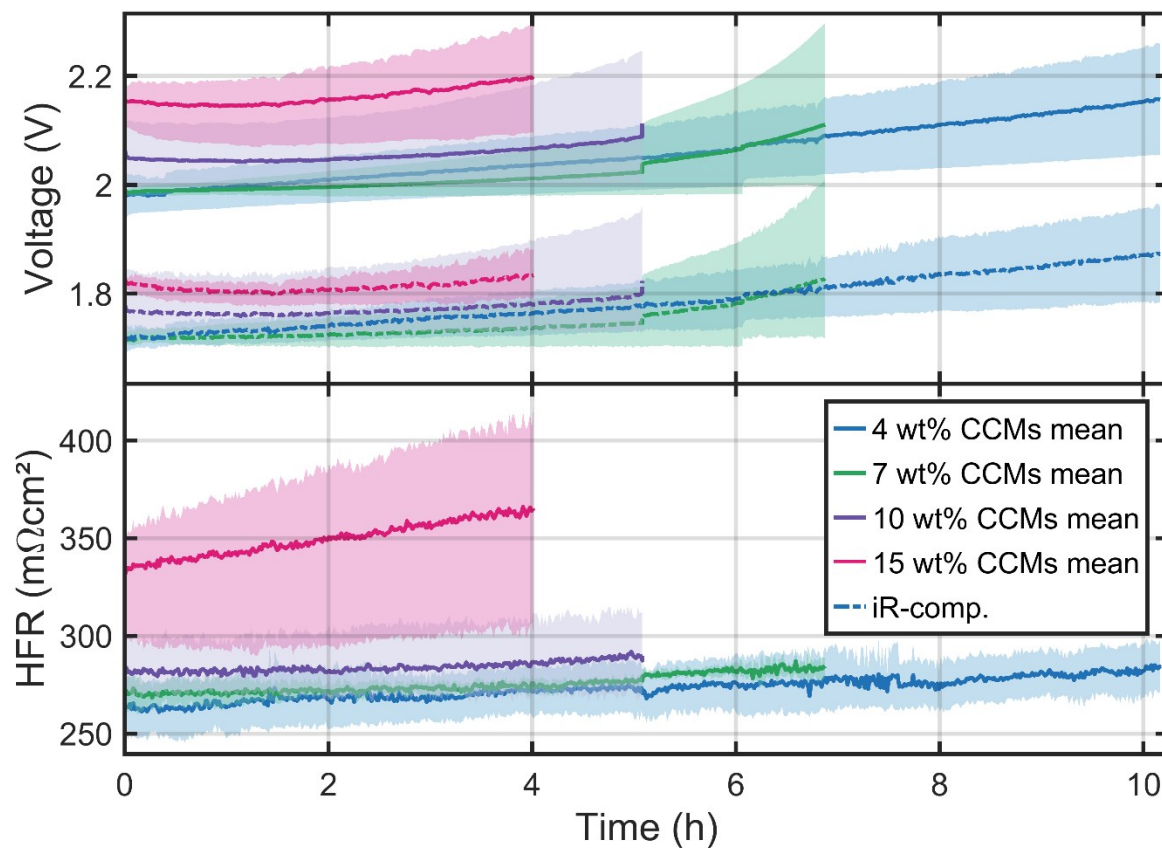


Fig. S 7 Short-term degradation of multiple cells summarized for different ionomer contents in the anode catalyst layer. The shaded area marks the range of all measured samples, while the line shows the mean of the measured traces. Data is only shown as long as at least two samples stayed under the set cut-off potential of 2.3 V at the applied current of 1 A/cm².

To confirm catalyst loss as one origin of the observed voltage loss during short-term degradation tests (Fig. S 7) the Ir loading was determined using XRF on the anode side of a CCM and a pristine Ti felt used as porous transport layer and at the end of test (EOT) as seen in Fig. S 8. The anode catalyst layer contained 7 wt% ionomer. A significant amount of catalyst is transferred to the Ti felt, which only happens after testing in AEMWE and not directly after cell assembly (this was tested by additional XRF measurements not shown here). In this particular case 44 % of the Ir is transferred to the Ti felt by the end of AEMWE measurements, while

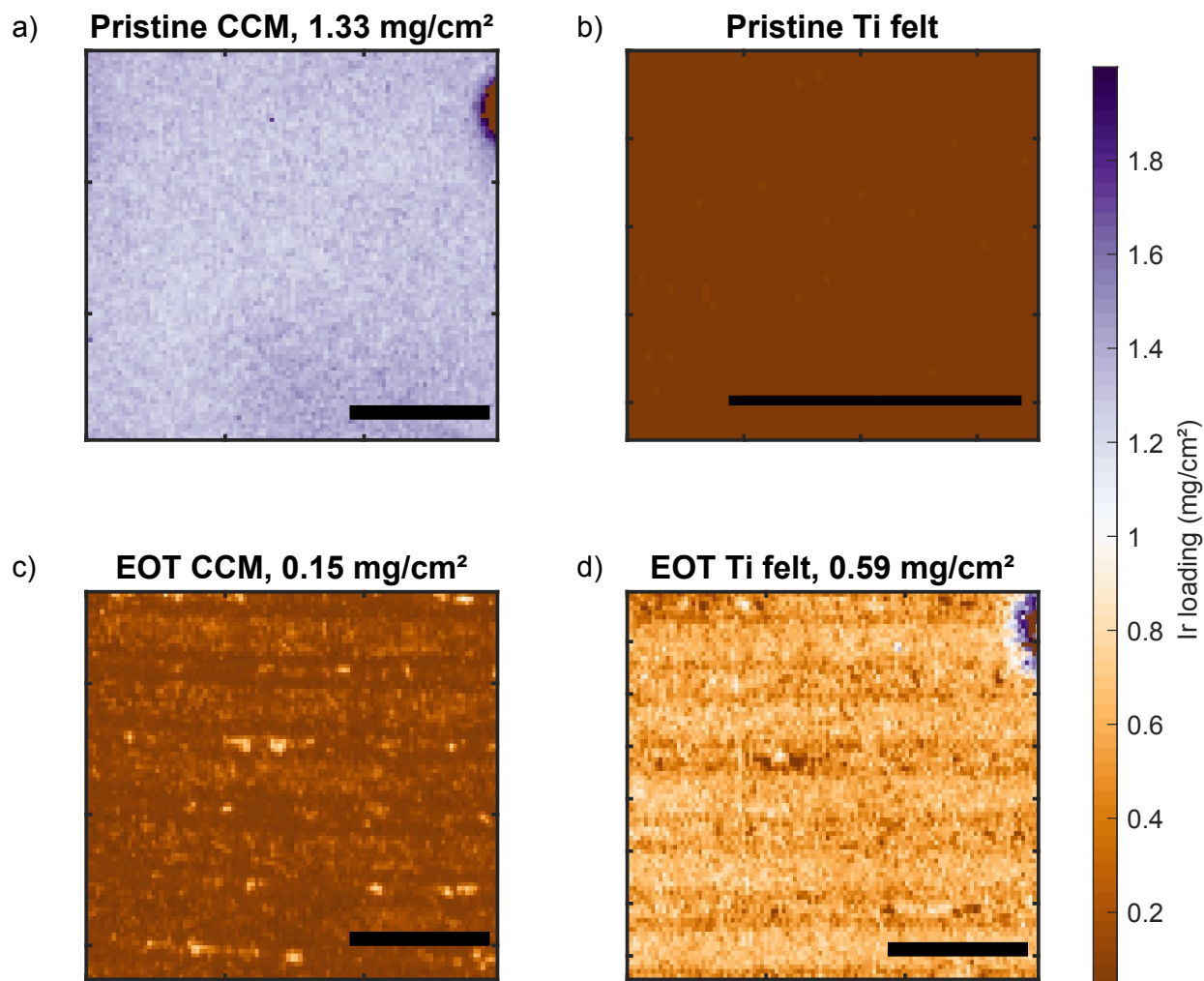


Fig. S 8 Ir loading as extracted from X-Ray Fluorescence measurements of a) a pristine CCM after spraying, b) a pristine, clean Titanium felt (to decrease measurement time only a smaller section was measured), c) CCM from a) after measuring, at the end of test (EOT) and d) Titanium felt after usage as the anode porous transport layer during the measurement of the CCM from a) and c). Summing up the measured values the Ir loading reduces from $1.33 \text{ mg}/\text{cm}^2$ to a sum of $0.75 \text{ mg}/\text{cm}^2$, which taking into account the error of $0.04 \text{ mg}/\text{cm}^2$ (estimated from the clean Ti felt, which should be free of Ir), shows a clear loss of at least $0.5 \text{ mg}/\text{cm}^2$. All scalebars represent 0.5 mm.

another 56 % are lost during operation and assumed to be suspended in the feed solution.

Additional data for varying feed solution concentrations

Multiple cells measured with different feed solution concentrations are shown in Fig. S 9 and the median values of all extracted

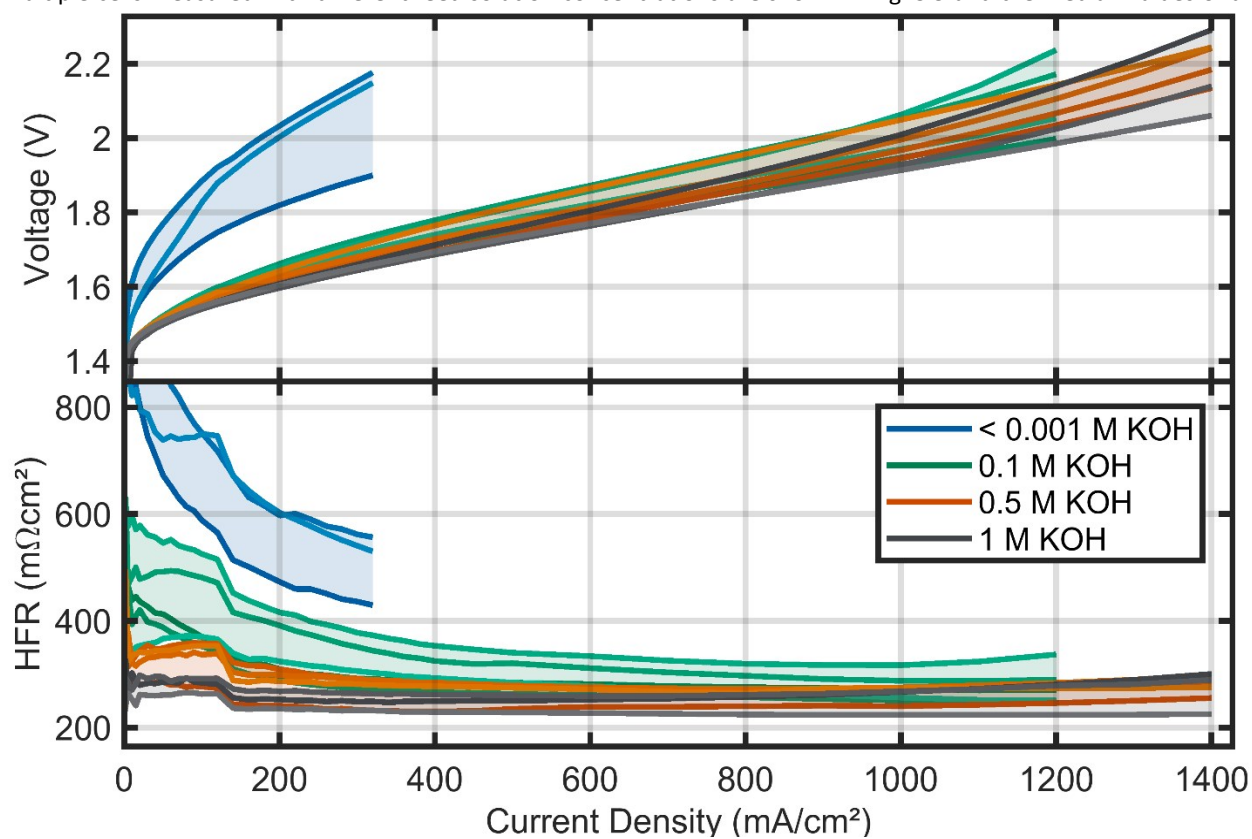


Fig. S 9 All cells measured with different molarity of KOH in the feed solution.

performance and degradation parameters are shown in Fig. S 10.

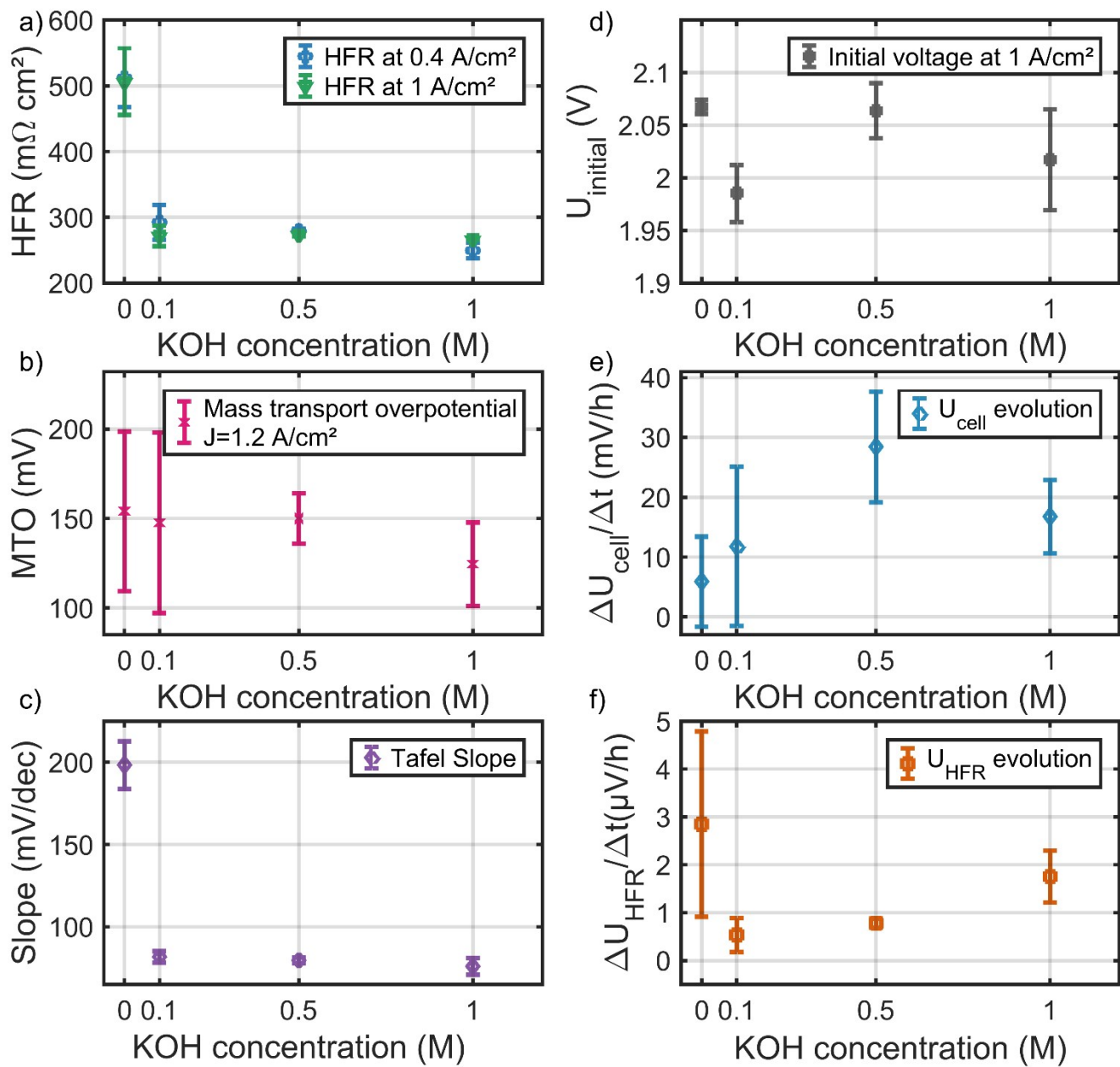


Fig. S 10 Performance and degradation parameters extracted from at least three cells measured for each variation of the feed solution concentration.