Supporting information

Improving the efficiency of fully hydrocarbon-based proton-exchange membrane fuel cells by ionomer content gradients in cathode catalyst layers

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Figure S1 shows that the MEAs with IPA:H_2O = 1:1 w/w vs MeOH:H_2O = 3:1 w/w in the anode (I/C = 0.2) show no significant difference in performance.

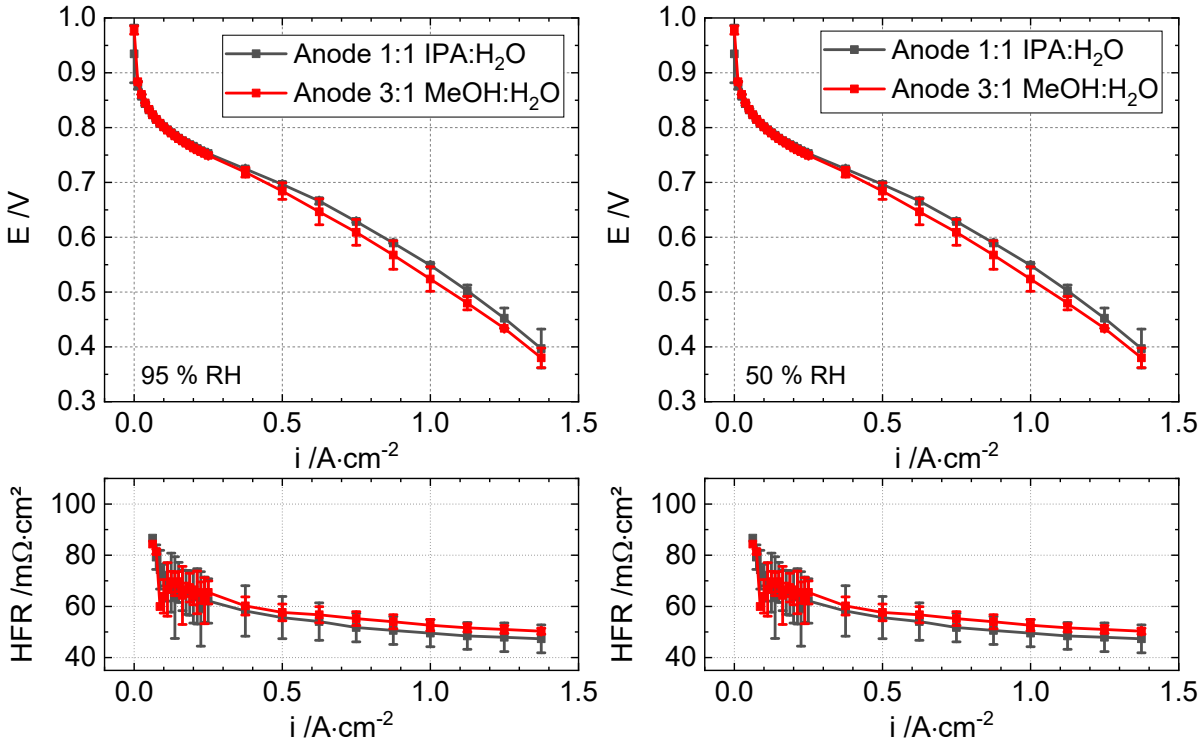

Figure S1: Performance of MEAs with different anode dispersion media (MeOH:H_2O = 3:1 w/w vs IPA:H_2O = 1:1 w/w). Testing conditions: H_2/air, 80 °C, 250 kPa_{abs} and 95 % RH (left) or 50 % RH (right).

The cyclic voltammograms (CVs) of all samples presented in this work (pure I/Cs and graded cathode I/C) are shown in Figure S2, indicating that neither the I/C nor the dual-layer approach causes any change in the ECSA or the form of the CVs.

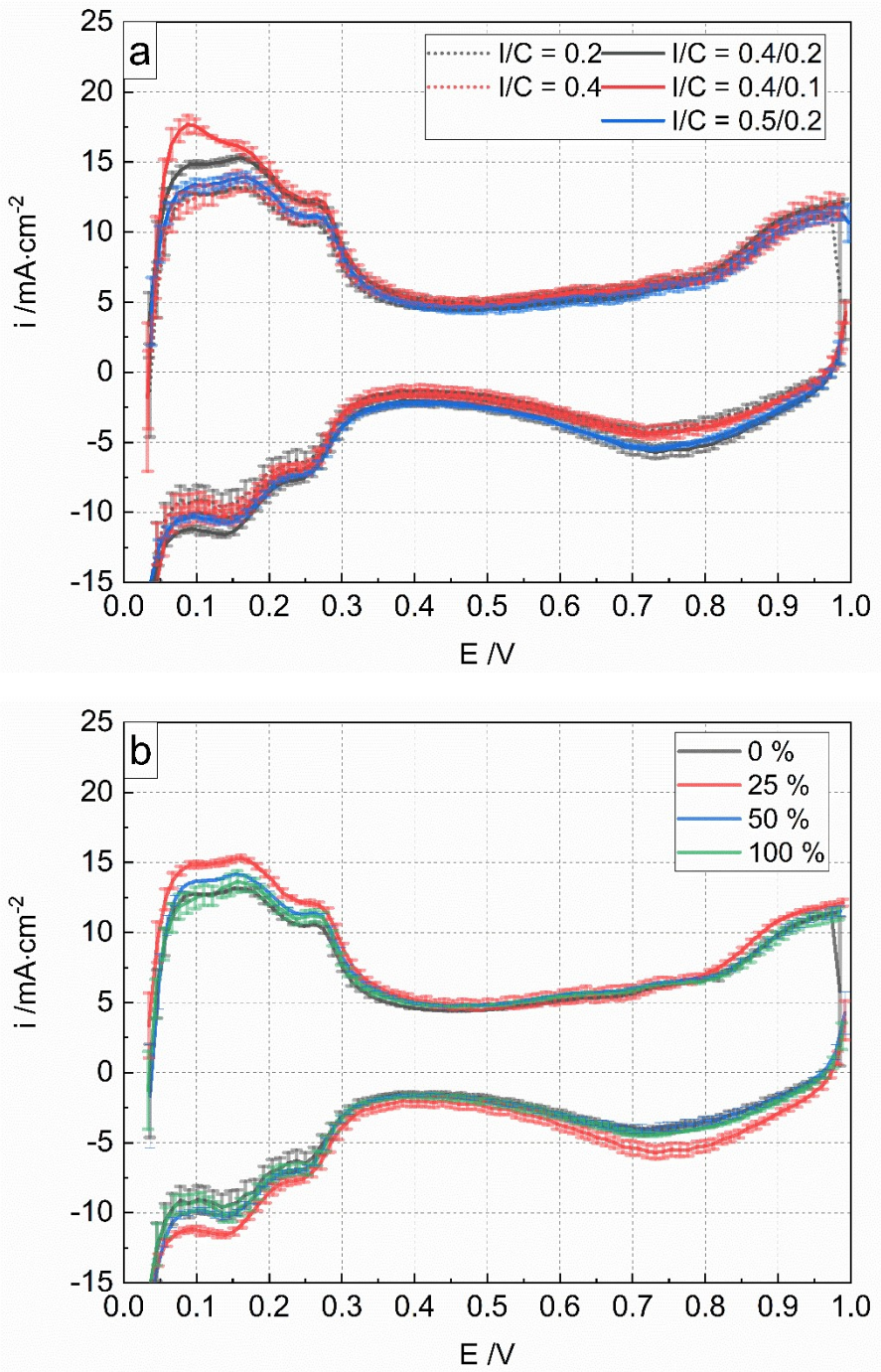

Figure S2: Cyclic voltammograms (CVs) of MEAs with homogeneous and graded ionomer content in the cathode catalyst layer (a) and CVs of an increasing proportion of I/C = 0.4 in the cathode sub-layer I (b): 0 % of I/C = 0.4 corresponds to the I/C ratio in sub-layer II = 0.2). Testing conditions: 35 °C, 96 % RH, ambient pressure.

The Tafel plot and the mass-specific current density i_m of the MEAs with different pure and graded cathode I/Cs are shown in Figure S3. It can be seen that the Tafel slopes of all MEAs are in the same range and normalized current density with Pt loading, *i.e.* mass-specific current density i_m *vs* $E_{HFR\text{-}free}$. The data for each cathode I/C (pure and graded) fall onto a straight line in this semi-logarithmic plot over the entire current density range of 30 – 100 mA cm^{-2}, indicating no change in the ORR kinetics with varying I/C in the pure and the graded cathode CLs.

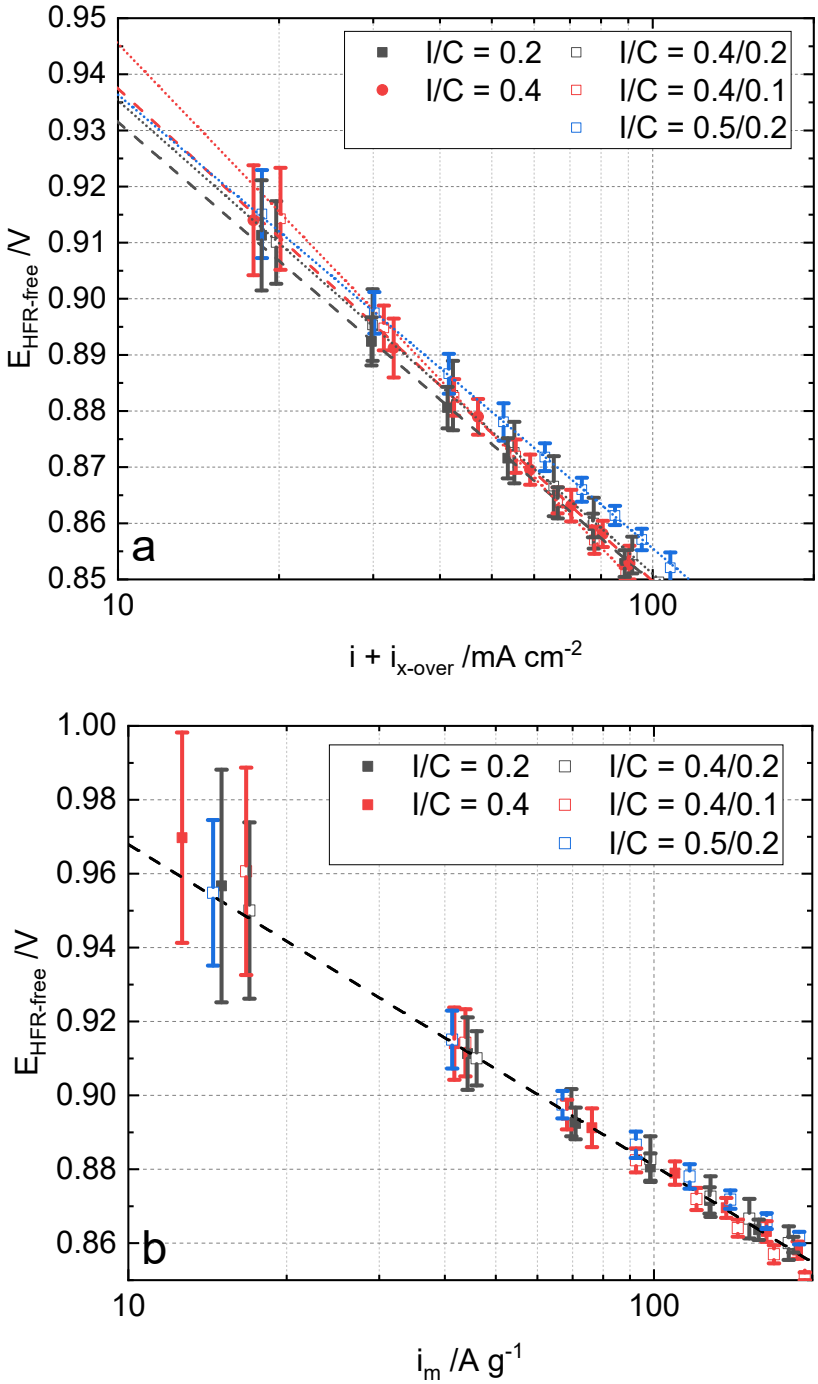

Figure S3: Tafel plot (a) and mass-specific current density vs the HFR-corrected cell voltage $E_{HFR\text{-}free}$ (b) of the MEAs with varied I/C in the sub-layer I and II. Test conditions: 80 °C, 96 % RH, 150 kPa_{abs}.

Similar to Figure S3, Figure S4 shows the Tafel plot and the mass-specific current density i_m of the MEAs with different proportions of /C = 0.4 in the cathode catalyst layers, with 0 % of the cathode I/C = 0.4 being an I/C of 0.2. It can also be seen here that the data for each proportion fall onto a straight line in this semi-logarithmic plot over the entire current density range of 30 – 100 mA cm^{-2}, indicating no change in the ORR kinetics via the dual-layer approach.

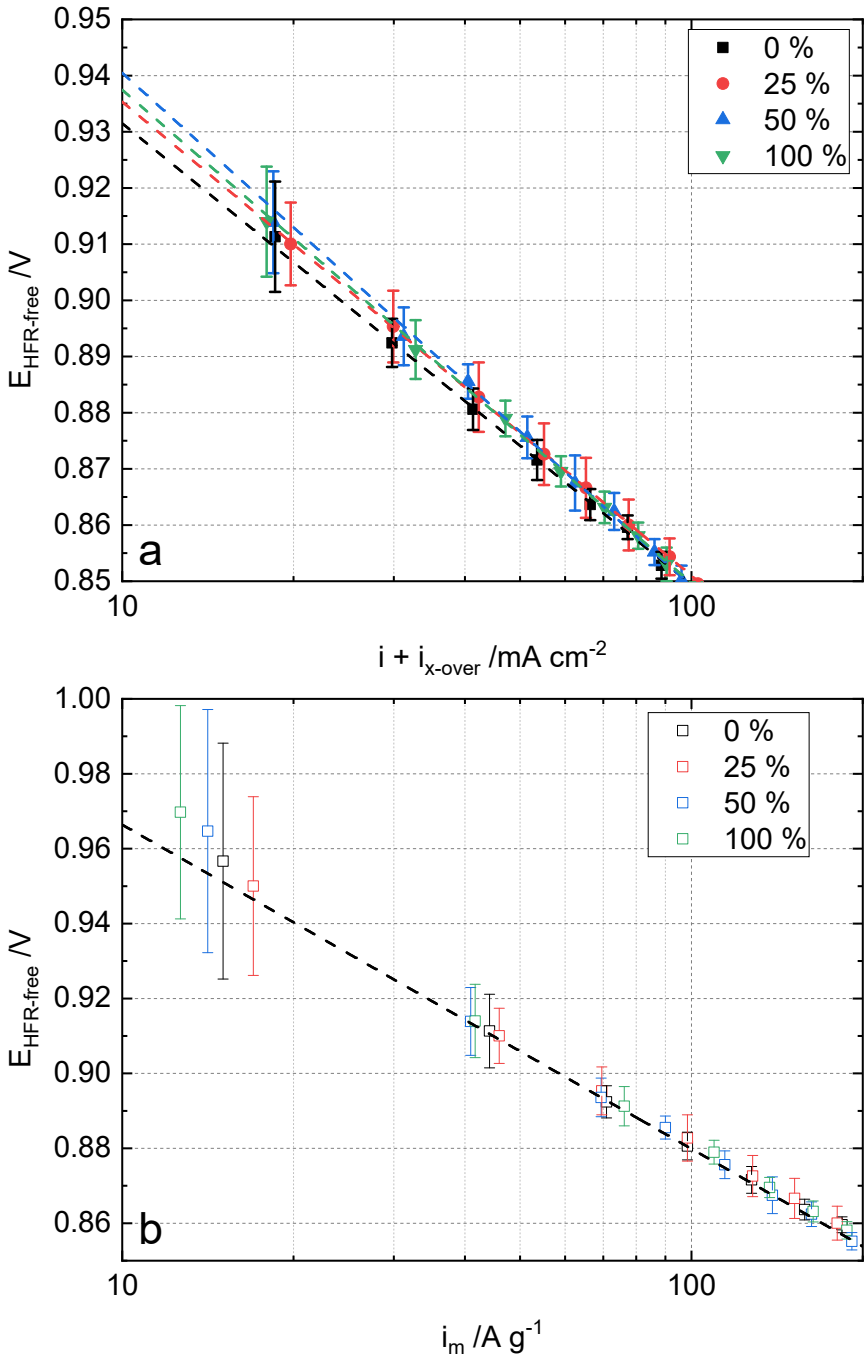

Figure S4: Tafel plot (a) and mass-specific current density vs the HFR-corrected cell voltage $E_{HFR\text{-}free}$ (b) of the MEAs with varied proportion of I/C = 0.4 in the sub-layer I and II (0 % of I/C = 0.4 corresponds to a cathode I/C = 0.2). Test conditions: 80 °C, 96 % RH, 150 kPa_{abs}.

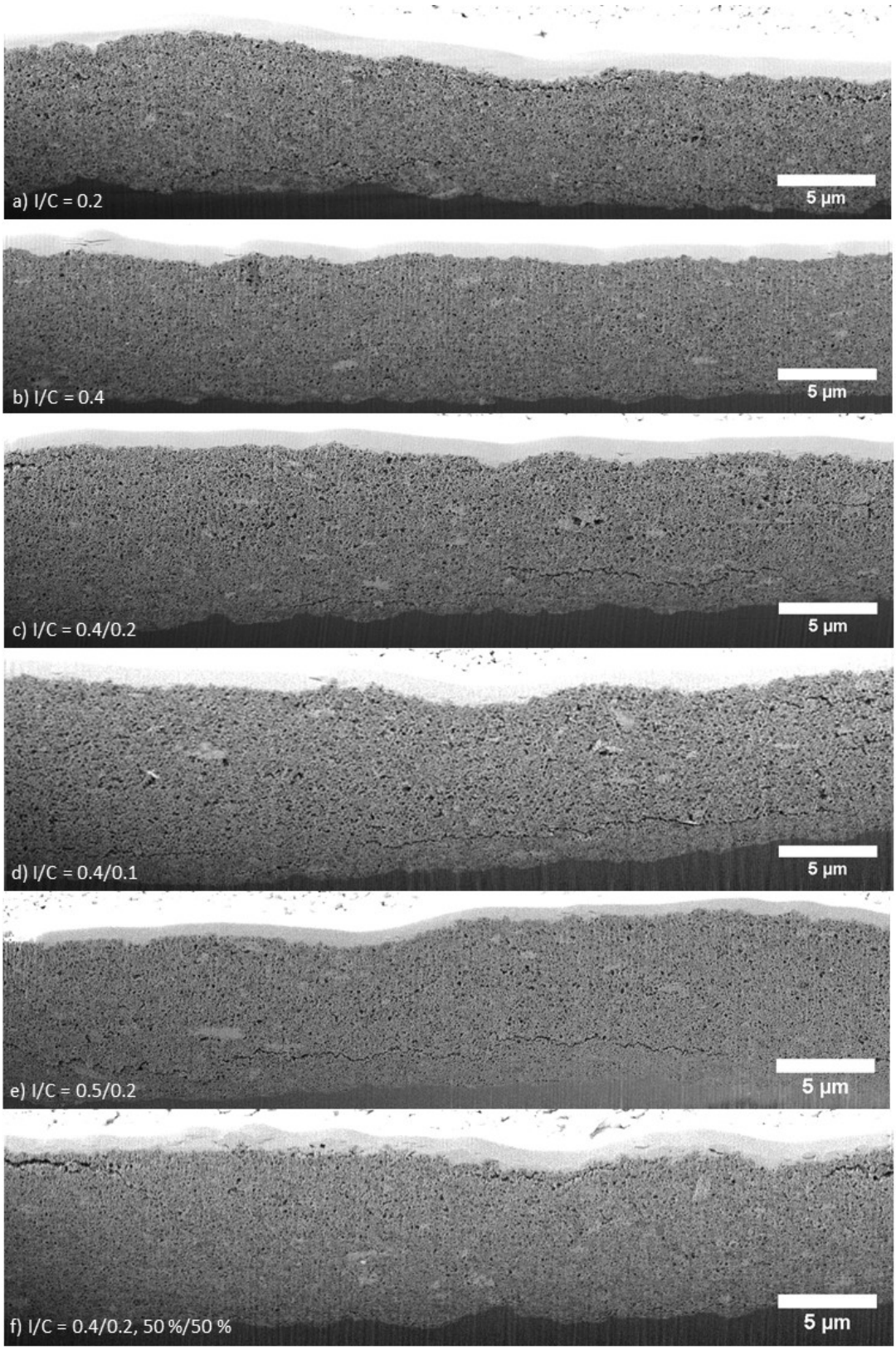

Figure S5a-f: Representative cross-sections of MEAs with varying graded ionomer content. No representative physical instability was observed within or on top of the gradient ionomer CL before or after the electrochemical tests.

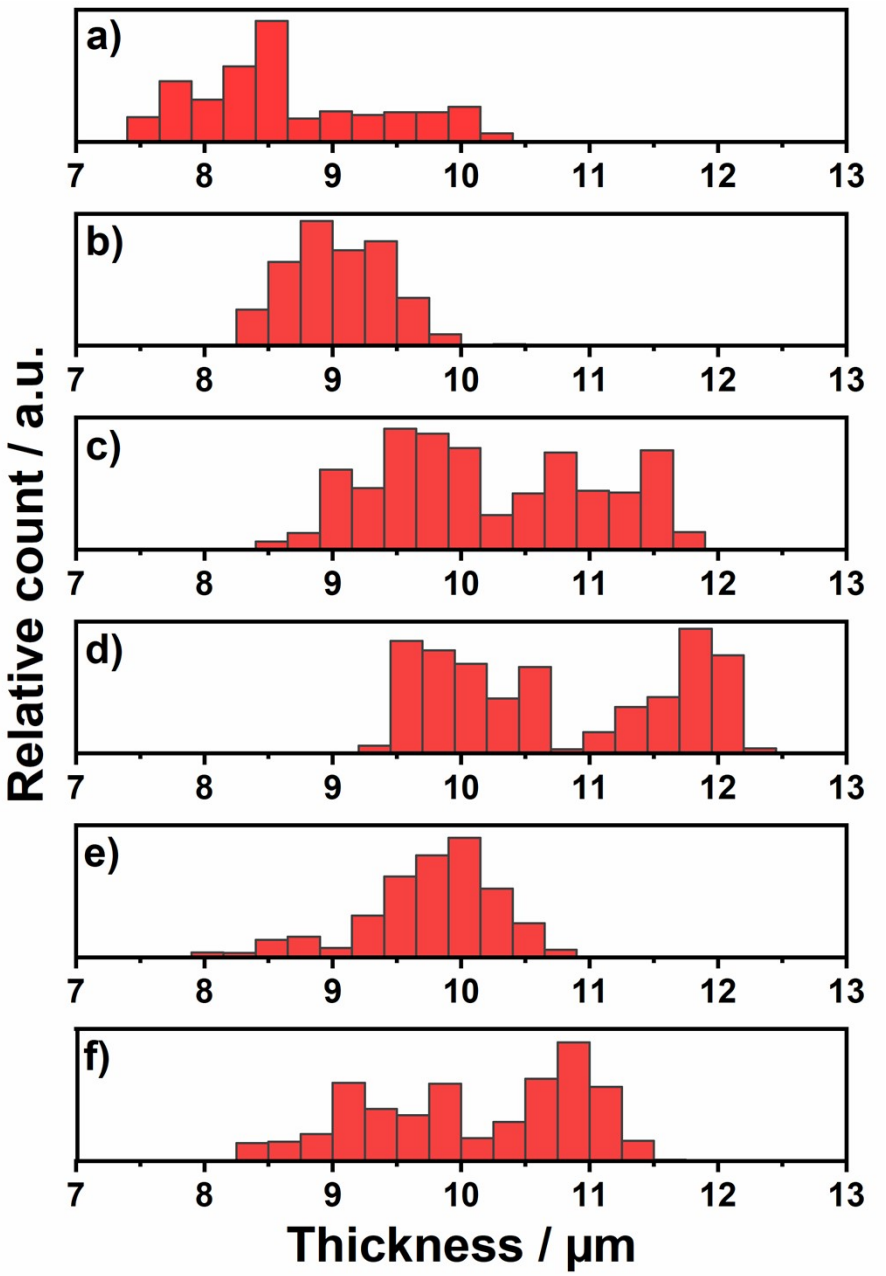

Figure S6a-f: Histograms of the layer thicknesses obtained from the FIB cross sections from Fig. S5a-f.

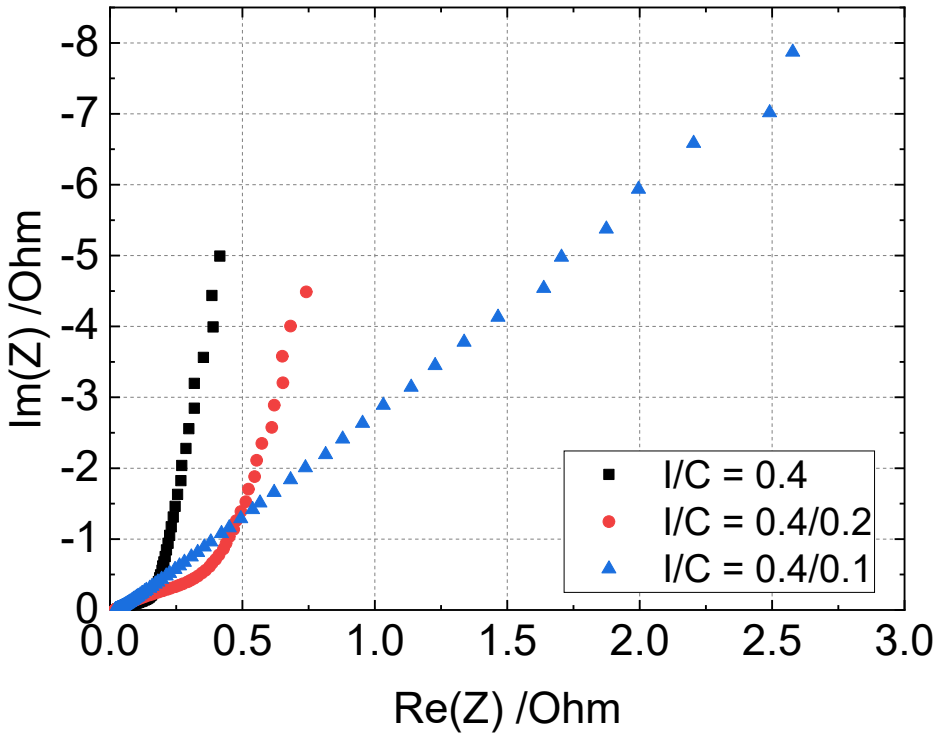

Figure S7: Nyquist plot of MEAs with different outer cathode I/Cs. Testing conditions: 80 °C, 50 % RH and 150 kPa_{abs}.

Figure S8 shows the Nafion cell with an I/C of 0.6, corresponding to 25 wt % ionomer content in the CL, has the most balanced performance at operation-relevant potential (e.g. E = 0.6 – 0.7 V) and peak power density under H_2/air, 95 °C, 50 % RH and 80 % RH, 250 kPa_{abs}.

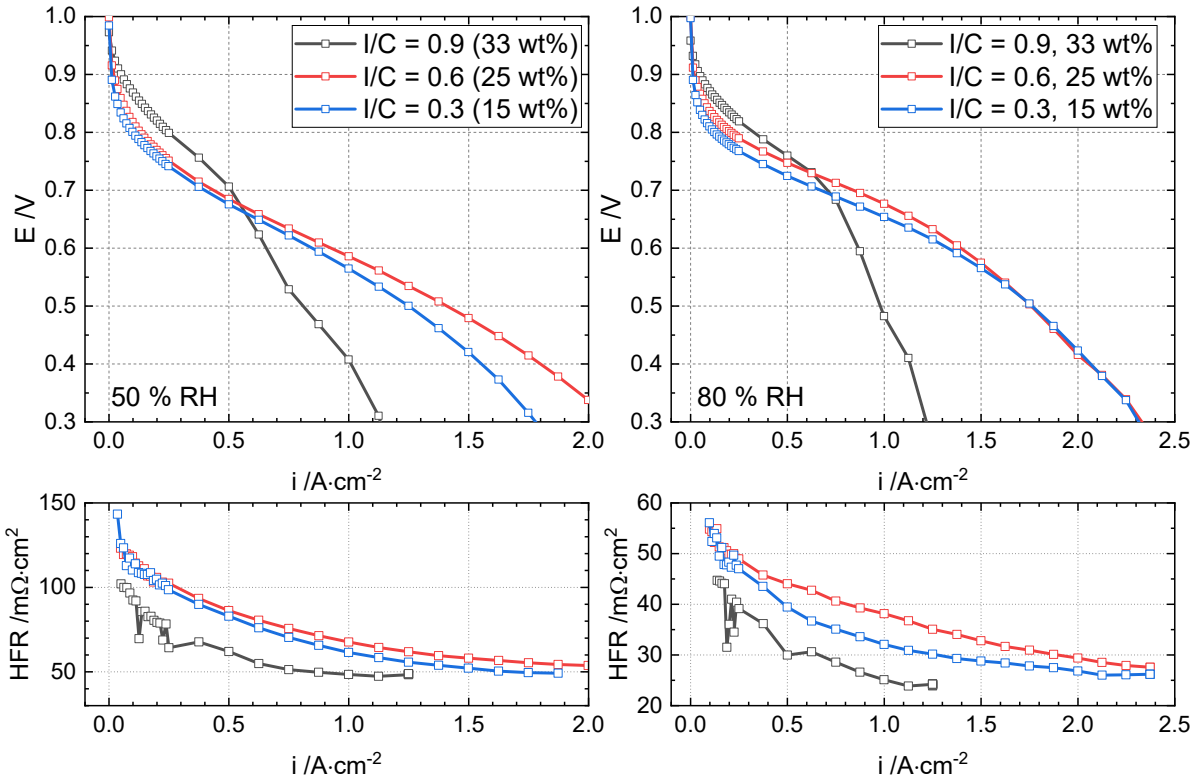

Figure S8: Performance of Nafion catalyst layers with different ionomer content/ionomer-to-carbon (I/C) ratio. Testing conditions: H_2/air, 95 °C, 250 kPa_{abs} and 50 % RH (left) or 80 % RH (right).