Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Linking Gas Diffusion Electrode Composition to CO_2 Reduction in a Flow Cell

Eric W. Lees,[1] Danielle A. Salvatore,[1] Benjamin A. W. Mowbray,[2] Grace L. Simpson,[2] David J. Dvorak,[3] Shaoxuan Ren,[2] Jacky Chau,[2] Katherine L. Milton,[2] and Curtis P. Berlinguette[1,2,3,4]

[1]Department of Chemical and Biological Engineering, The University of British Columbia, 2360 East Mall, Vancouver, British Columbia, V6T 1Z3, Canada.

[2]Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, V6T 1Z1, Canada.

[3]Stewart Blusson Quantum Matter Institute, The University of British Columbia, 2355 East Mall, Vancouver, British Columbia, V6T 1Z4, Canada.

[4]Canadian Institute for Advanced Research (CIFAR), 661 University Avenue, Toronto, Ontario, M5G 1M1, Canada.

Correspondence: cberling@chem.ubc.ca

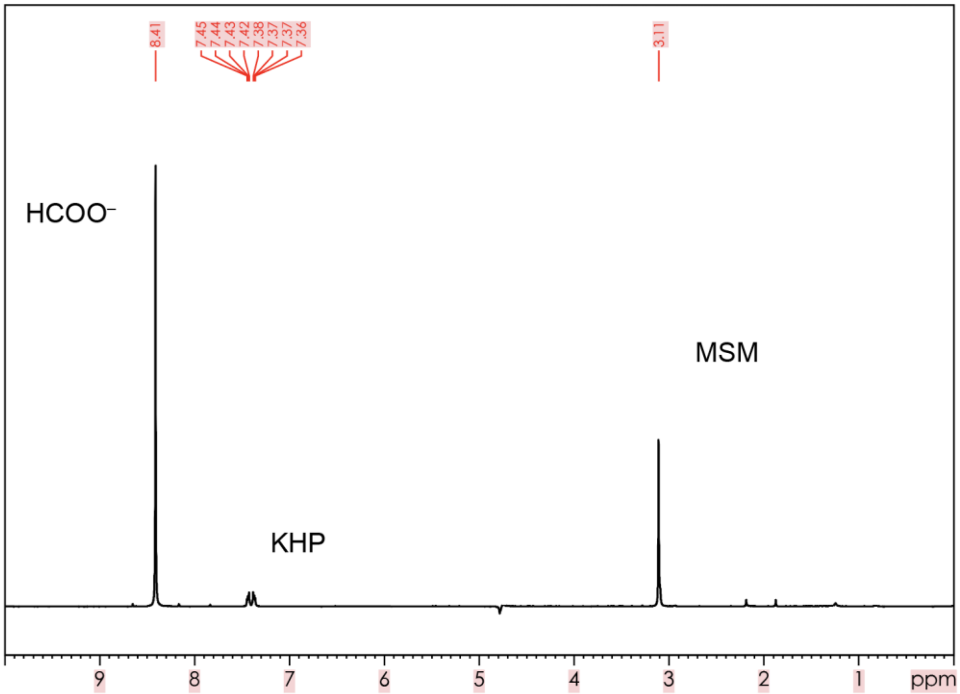

Figure S1: Sample ^{1}H NMR spectra for formate ($HCOO^-$) quantification. The singlet peaks at 8.40 ppm and 3.1 ppm are attributed to formate and methylsulfonylmethane (MSM; internal standard). The multiplet peaks at 7.4 ppm are attributed to the potassium hydrogen phthalate (KHP) internal standard. The MSM peak was used for formate quantification. The singlet peaks between 1 and 2.3 ppm are trace amounts of impurities in the reaction sample.

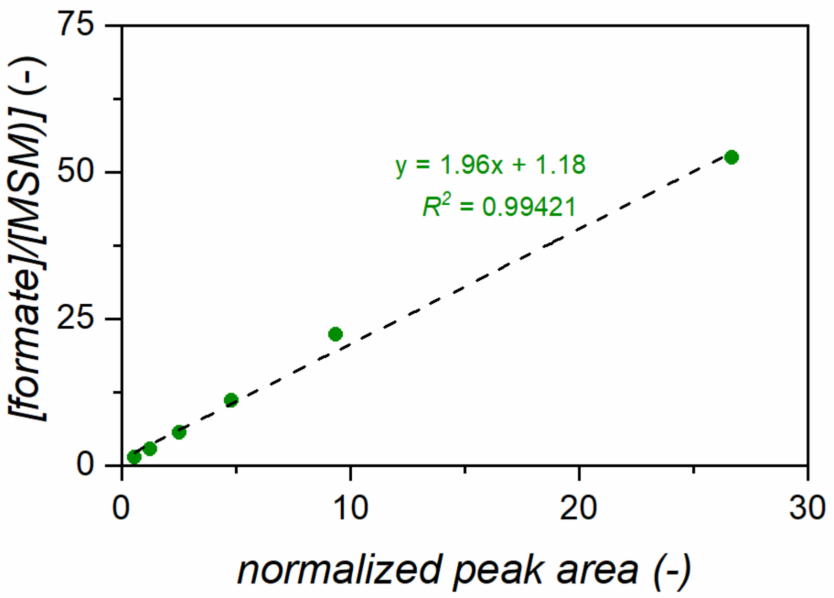

Figure S2. Calibration curve used for quantifying formate formation. Solutions with a range of known formate concentrations (129.9, 55.19, 27.60, 13.80, 6.90, and 3.45 mM) were analyzed by ^{1}H NMR and the resulting peak areas were normalized to the peak area of the KHP internal standard.

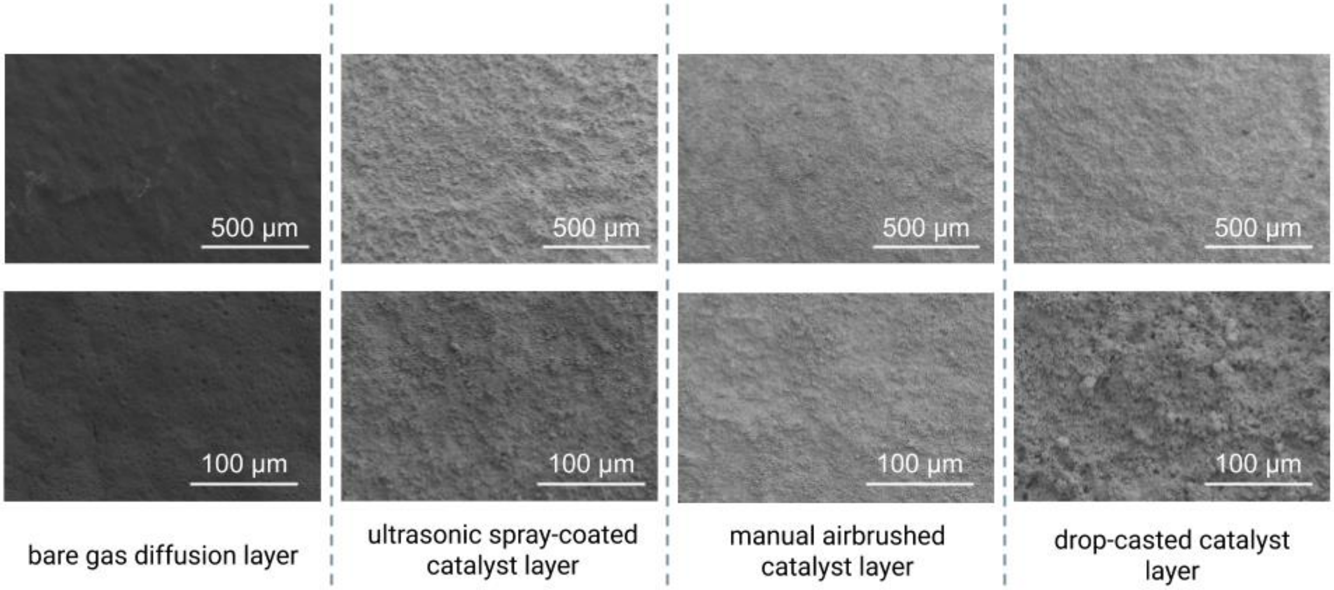

Figure S3: Top-view scanning electron microscopy (SEM) images of GDEs fabricated by depositing catalyst inks (5.5 wt% Nafion / 94.5 wt% Ag nanoparticles) onto carbon GDLs by ultrasonic spray-coating, manual airbrushing, and drop-casting deposition techniques. SEM images were obtained at 100x (top) and 200x (bottom) magnification.

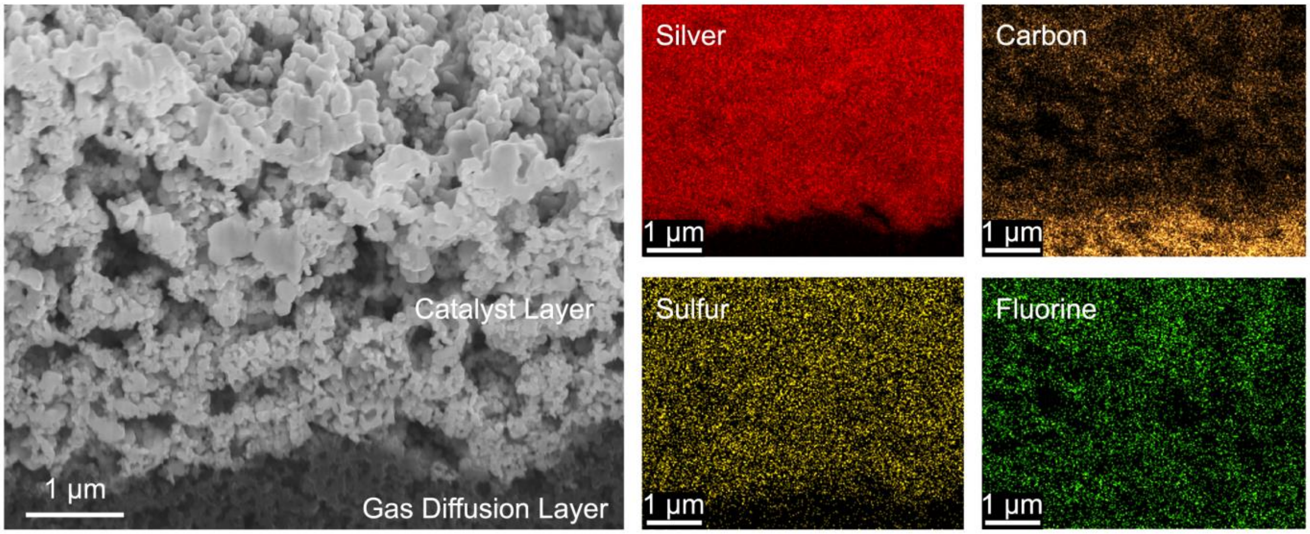

Figure S4: Cross-sectional SEM image of a GDE catalyst layer fabricated by ultrasonic spray-coating a catalyst ink onto a carbon GDL. Elemental analyses (measured using EDX) corresponding to the SEM micrograph are shown for silver, carbon, sulfur, and fluorine.

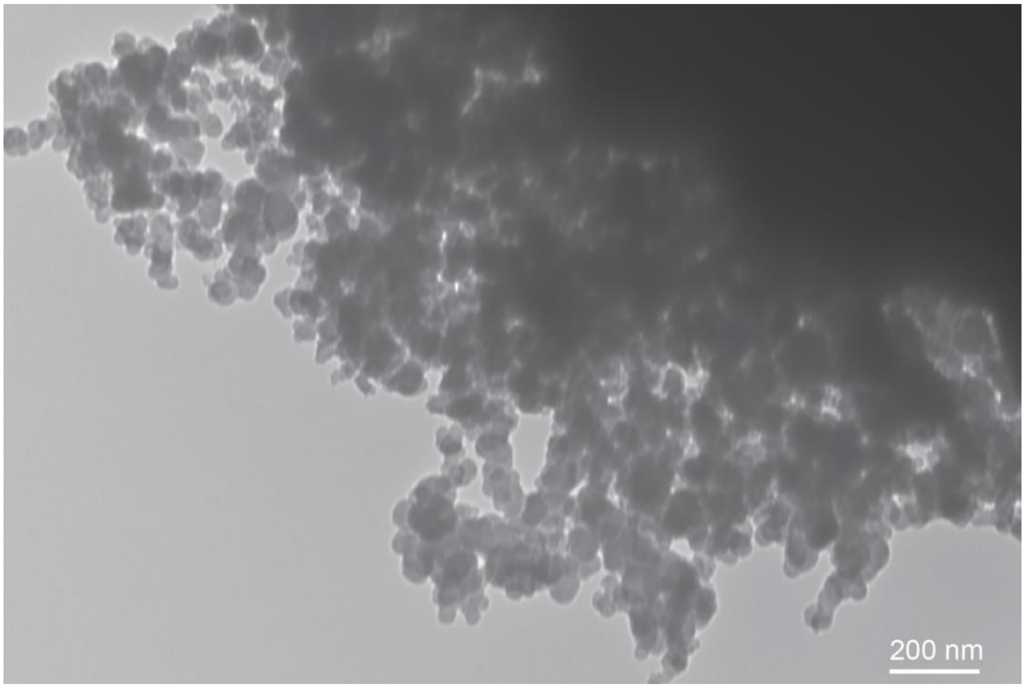

Figure S5: Transmission electron microscopy (TEM) image of a catalyst layer sample from an ultrasonic spray-coated GDE catalyst layer.

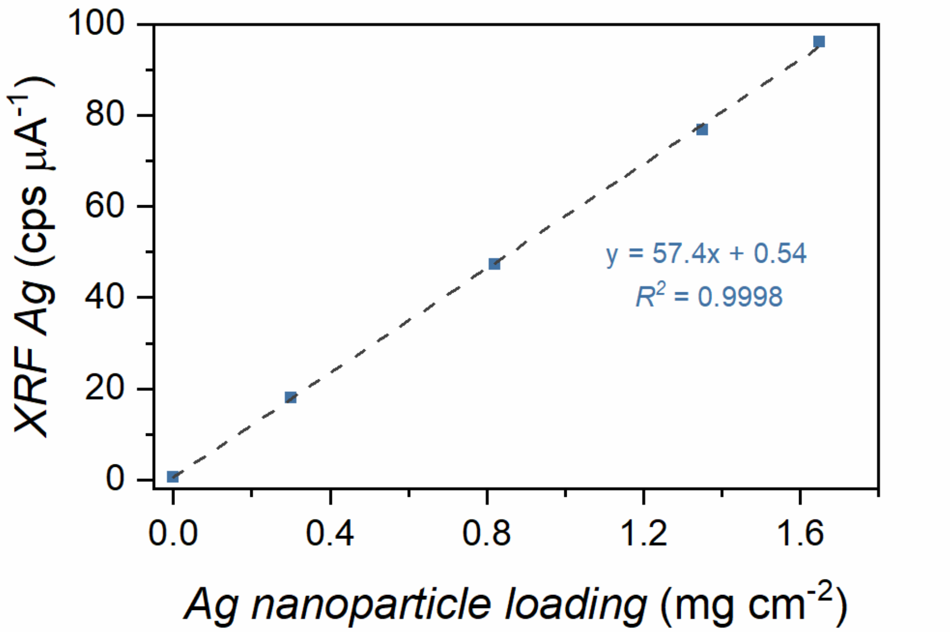

Figure S6. Ag XRF intensity as a function of Ag nanoparticle mass loading deposited on carbon GDLs. Linear regression fitting of the data yields a calibration curve corresponding to $y = 57.4x + 0.54$ with an R^2 of 0.9998.

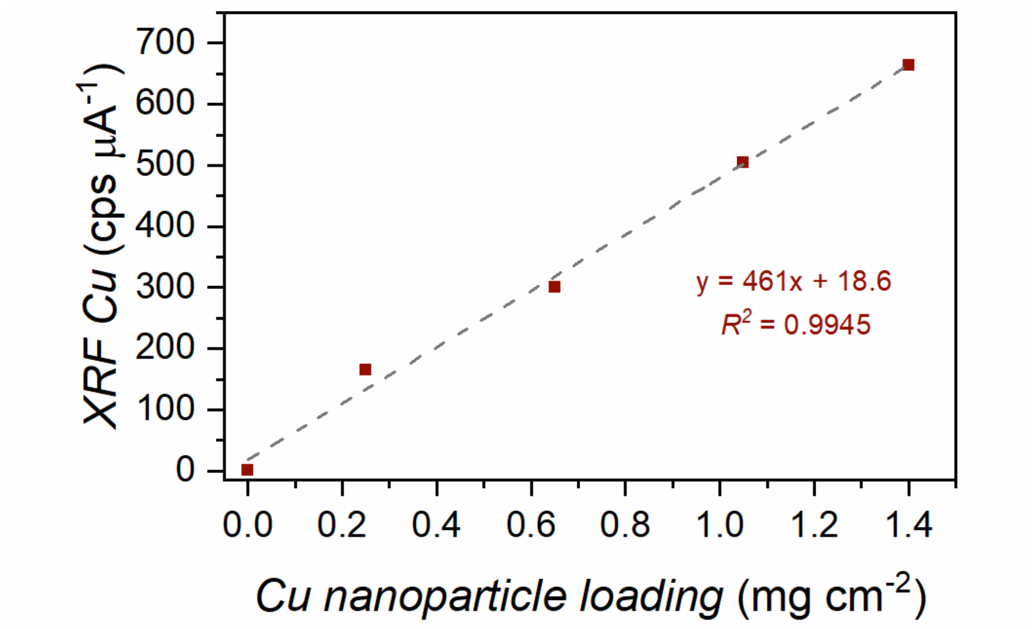

Figure S7. Cu XRF intensity as a function of Cu nanoparticle mass loading deposited on carbon GDLs. Linear regression fitting of the data yields a calibration curve corresponding to y = 461x + 18.6 with an R^2 of 0.9945.

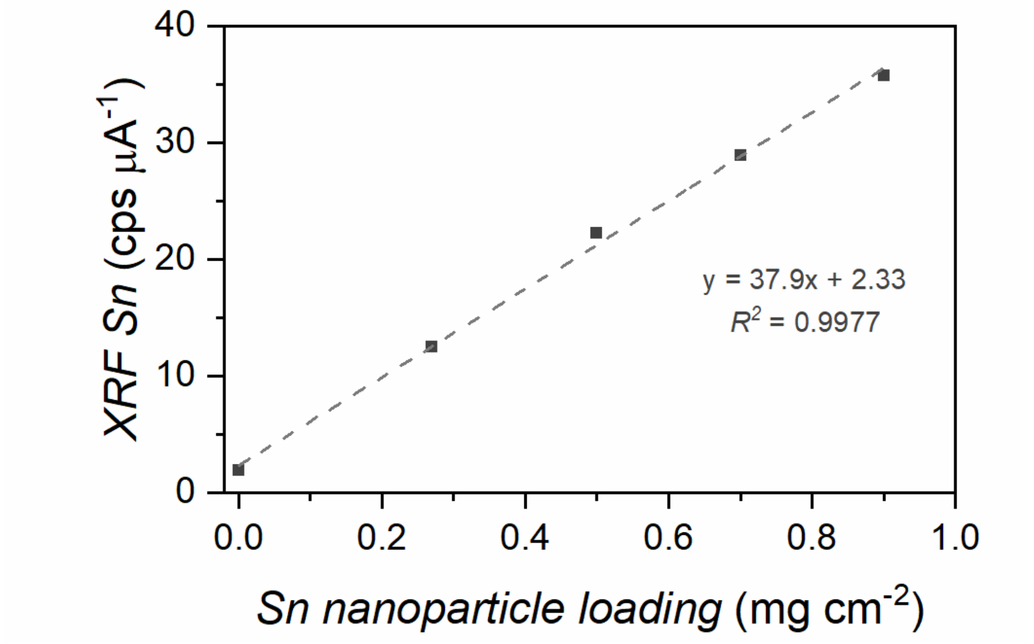

Figure S8. Sn XRF intensity as a function of Sn nanoparticle mass loading deposited on carbon GDLs. Linear regression fitting of the data yields a calibration curve corresponding to y = 37.9x + 2.33 with an R^2 of 0.9977.

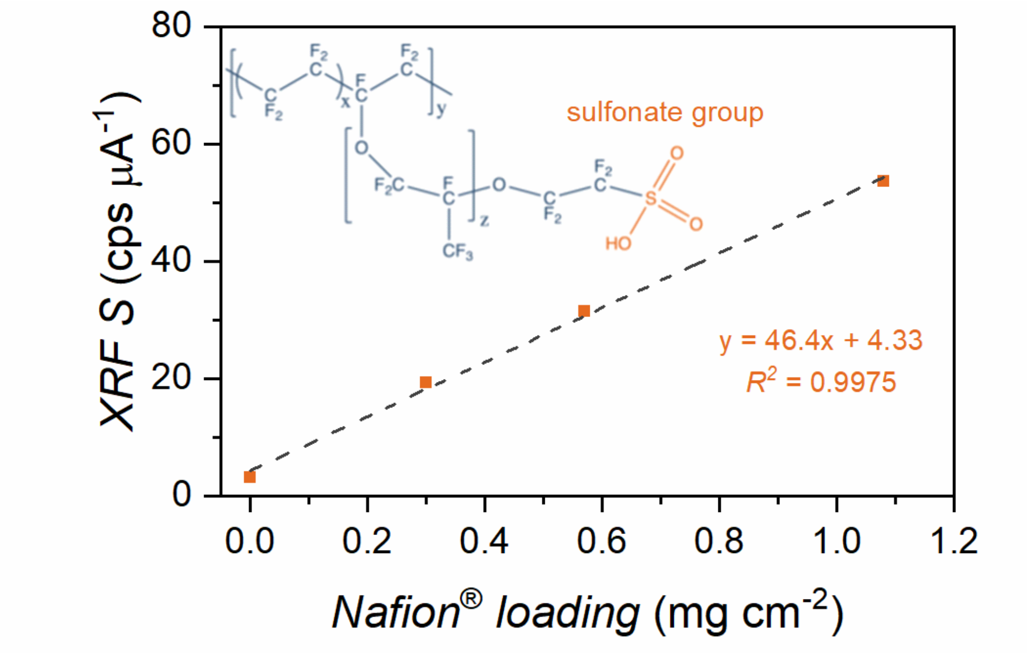

Figure S9. Relationship between sulfur XRF intensity and Nafion® mass deposited on carbon GDLs. The chemical structure of Nafion® is shown to highlight the sulfonate group appended to the PTFE backbone, which is used to report on the Nafion® mass. Linear regression fitting of the data yields a calibration curve corresponding to y = 46.4x + 4.33 with an R^2 of 0.9975.

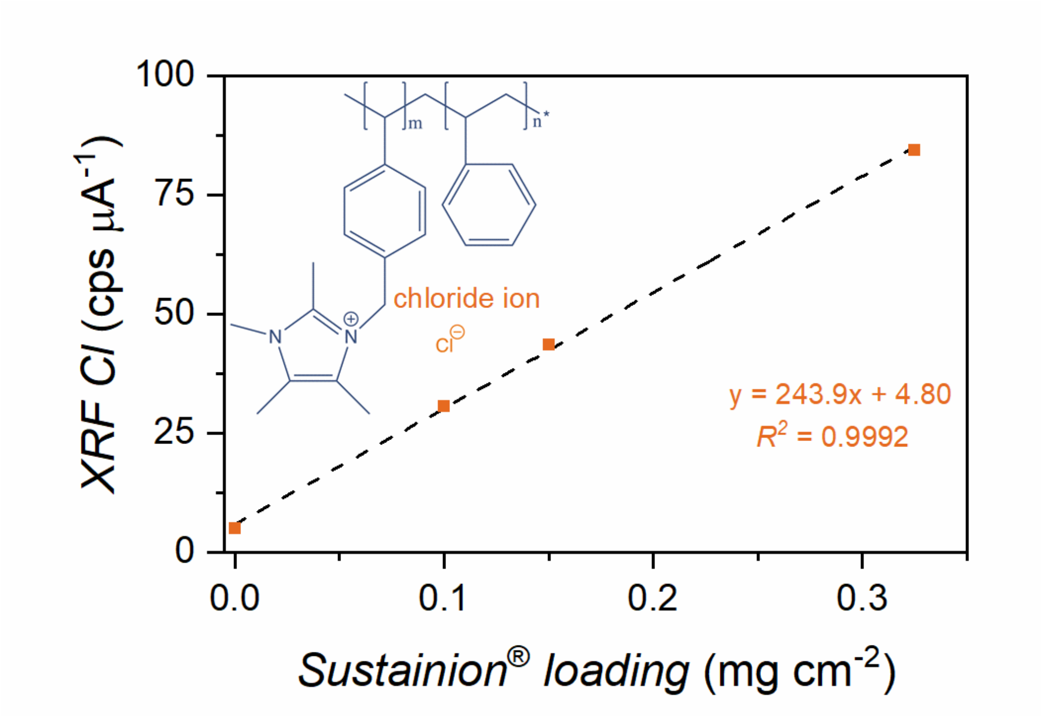

Figure S10. Relationship between chlorine XRF intensity and Sustainion® mass deposited on carbon GDLs. The chemical structure of Sustainion® is shown to highlight the chlorine that balances the charge of the quaternary ammonium cations in the chloride form of the ionomer. The chlorine atom is used to report on the Sustainion® mass. Linear regression fitting of the data yields a calibration curve corresponding to y = 243.9x + 4.80 with an R^2 of 0.9992.

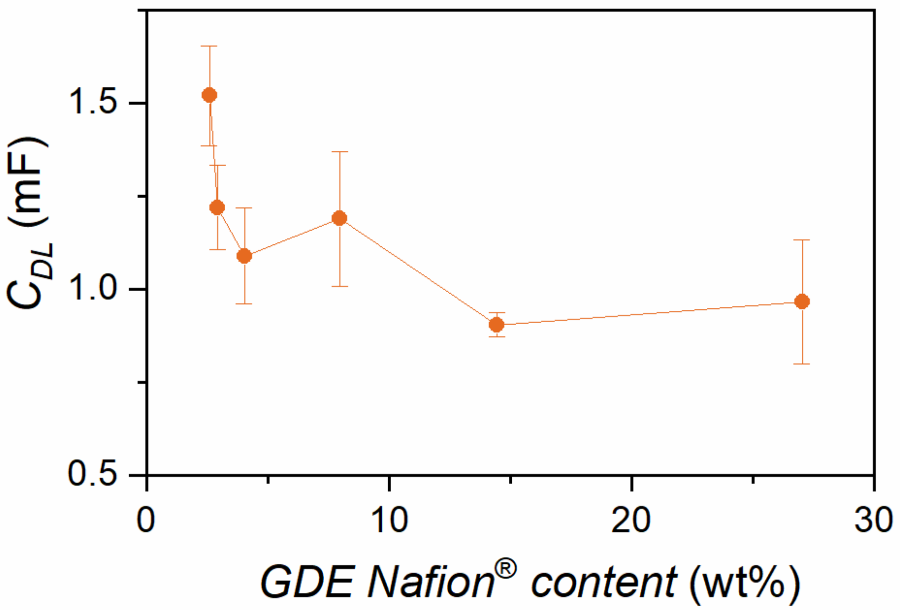

Figure S11: Double-layer capacitance (C_{DL}) as a function of GDE Nafion® content as determined by XRF. The C_{DL} was measured for each GDE by performing cyclic voltammetry measurements in 1 M KOH electrolyte in a non-faradaic potential window (from -0.8V–-1.0 V vs. Ag/AgCl) at scan rates ranging from 0.025–0.200 V s^{-1} using a platinum mesh counter electrode. Linear regression analyses of the currents (A) measured with each GDE at -0.90 V vs. Ag/AgCl as a function of scan rate (V/s) yielded slopes equal to the C_{DL}. Error bars represent the standard deviation of triplicate experiments with different GDEs from the same batch.

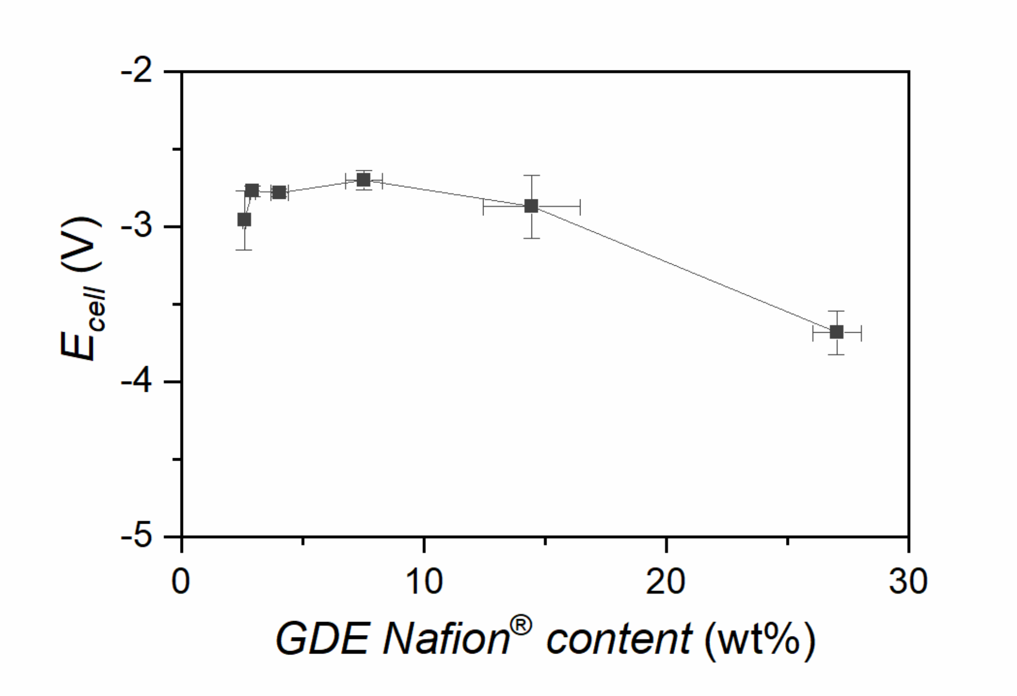

Figure S12: Cell potentials (E_{cell}) of a zero-gap membrane reactor operating at 200 mA cm^{-2} as a function of Nafion® content determined by XRF analysis for ultrasonic spray-coated GDEs. Error bars represent the standard deviation of triplicate experiments with different GDEs.

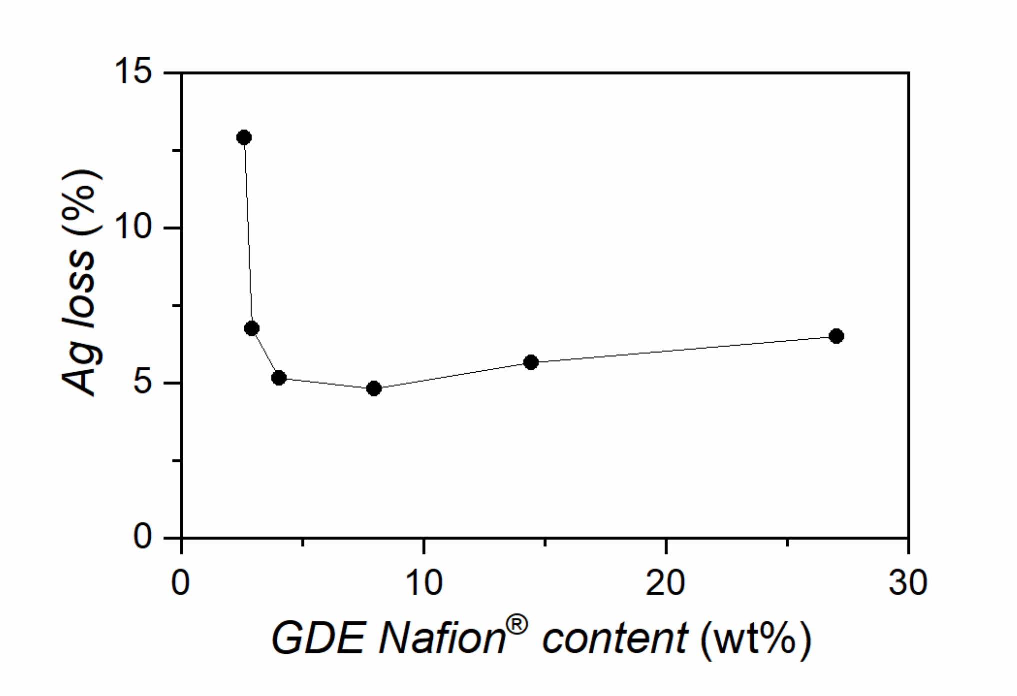

Figure S13: Silver losses measured after 20 minutes of electrolysis at 200 mA cm^{-2} (using XRF) as a function of Nafion® content for ultrasonic spray-coated GDEs.

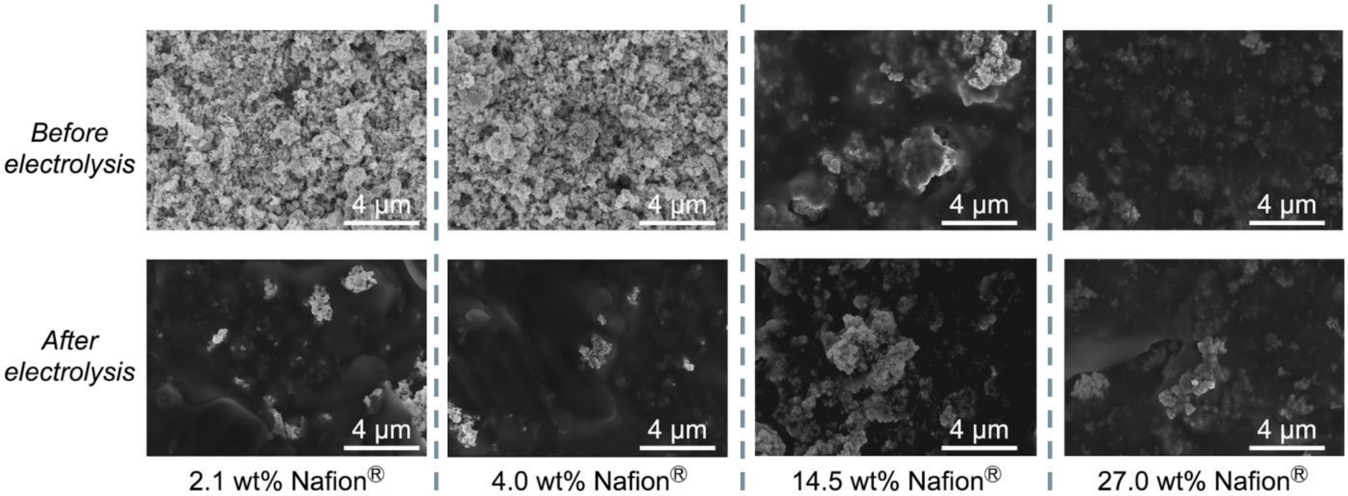

Figure S14: SEM images taken before and after electrolysis for GDEs with varying Nafion® contents (2.1, 4.0, 14.5, and 27.0 wt%) as determined by XRF analysis.