Supporting Information

Understanding Variability in the Hydrogen Evolution Activity of a Cobalt Anthracenetetrathiolate Coordination Polymer

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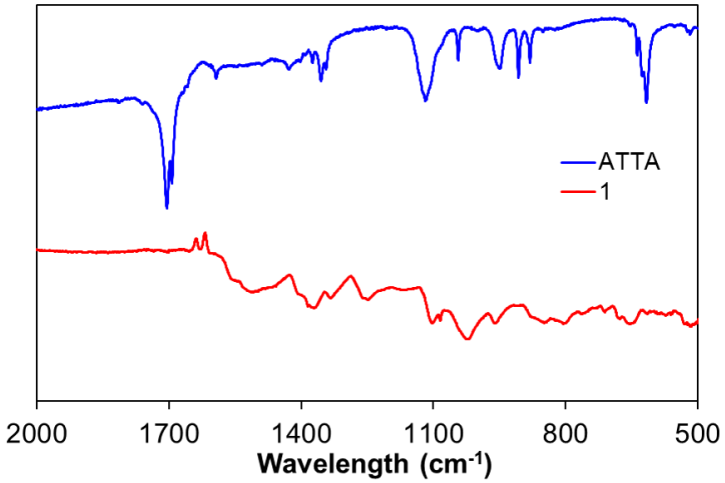

Figure S1. FT-IR spectra of 9,10-dimethyl-2,3,6,7-anthracenetetra(thioacetate) (blue) and **1** (red).

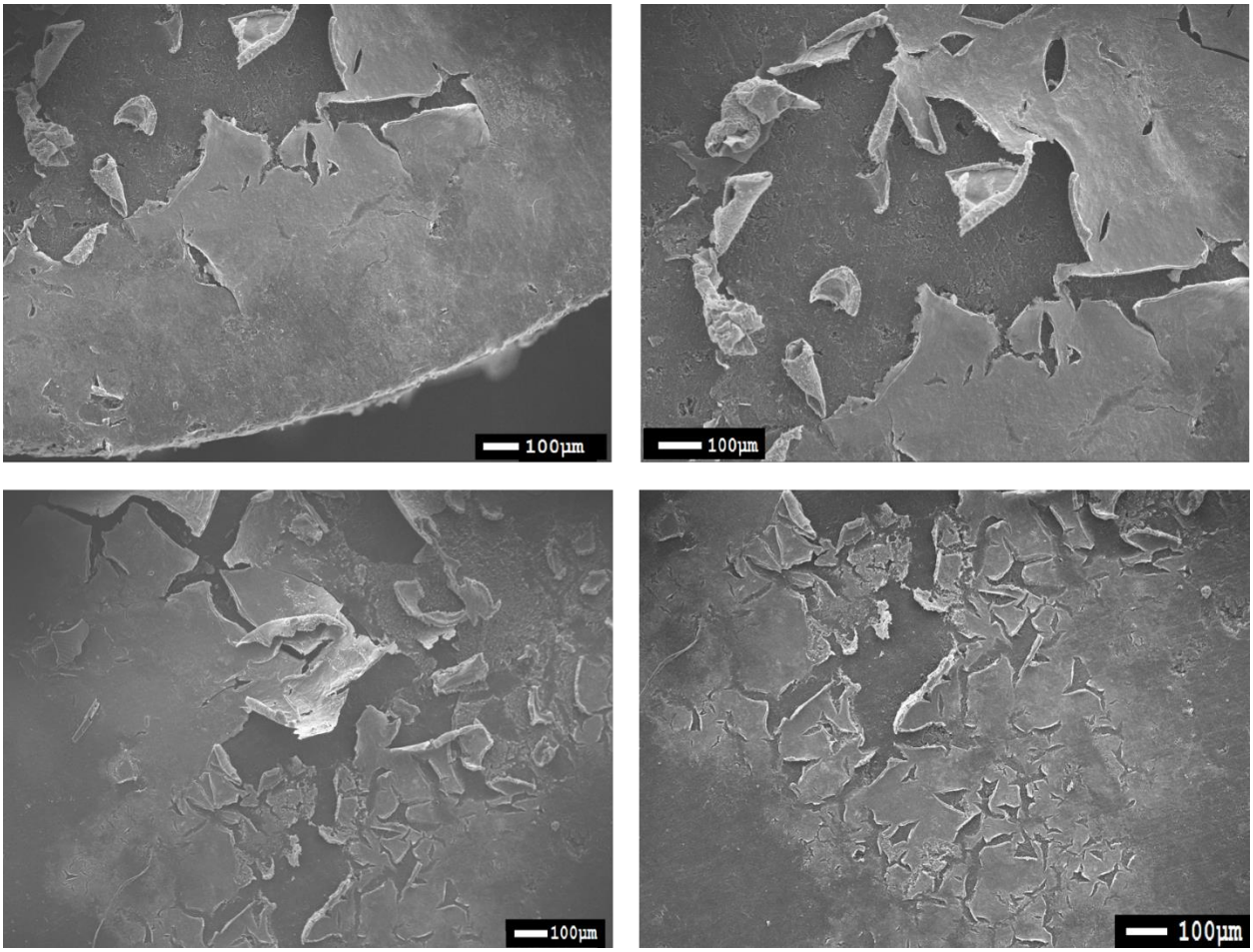

Figure S2. Top down scanning electron microscopy images of **1**.

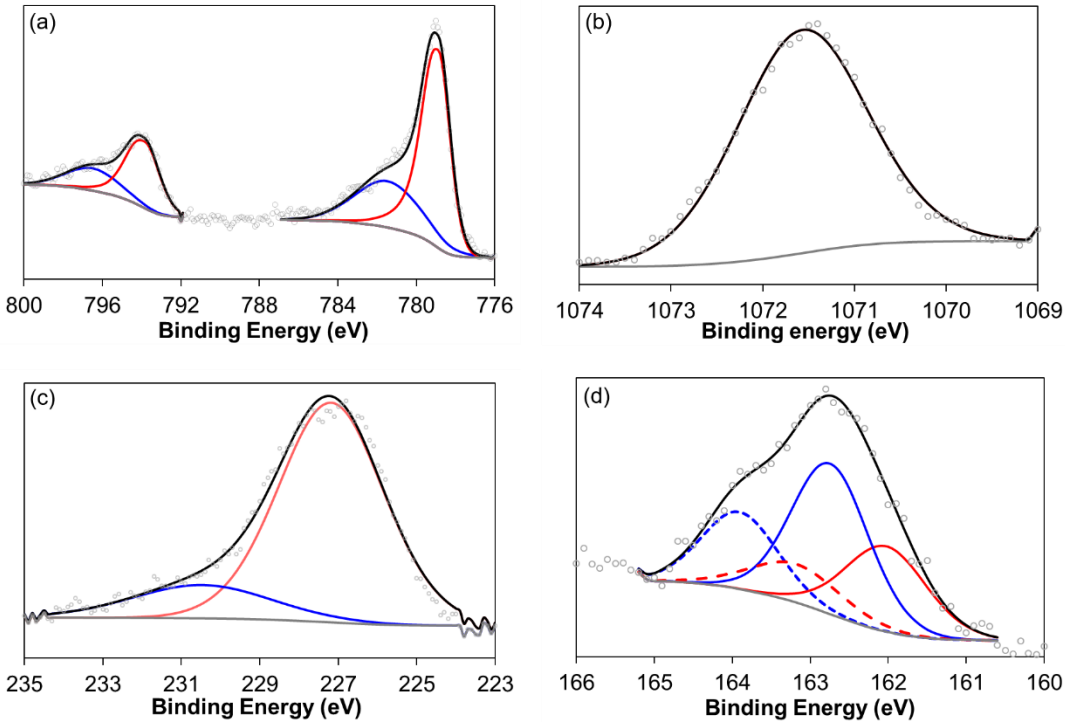

Figure S3. X-ray photoelectron spectroscopy analysis of **1** (a) Co 2p (b) Na 1s (c) S 2s (d) S 2p core level XPS spectra.

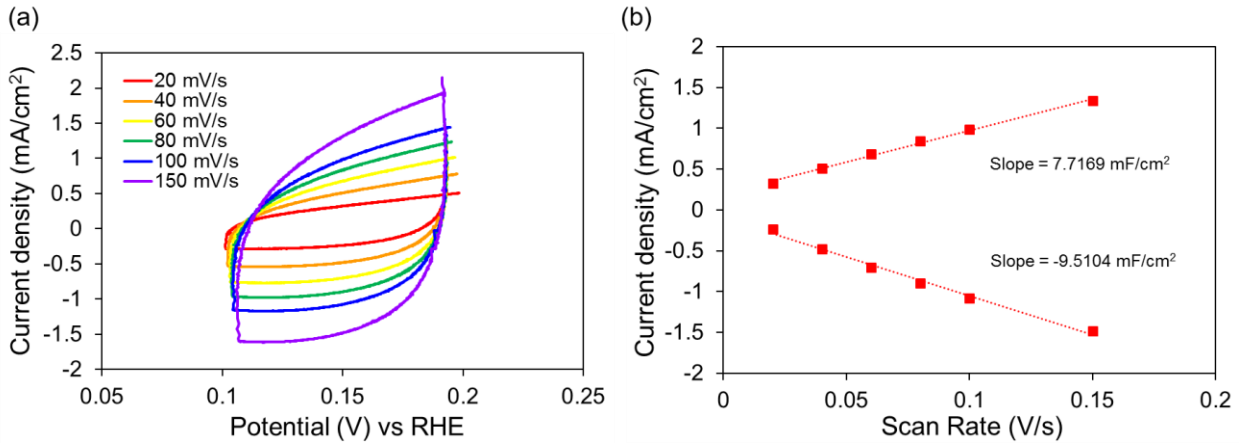

Figure S4. Electrochemically active surface area measurements of GCE-1 (a) CVs ranging from 20, 40, 60, 80, 100, and 150 mV/s in the region of 0.1-0.2 V vs RHE. (b) Reductive and oxidative current obtained at 0.15 V vs RHE versus scan rate.

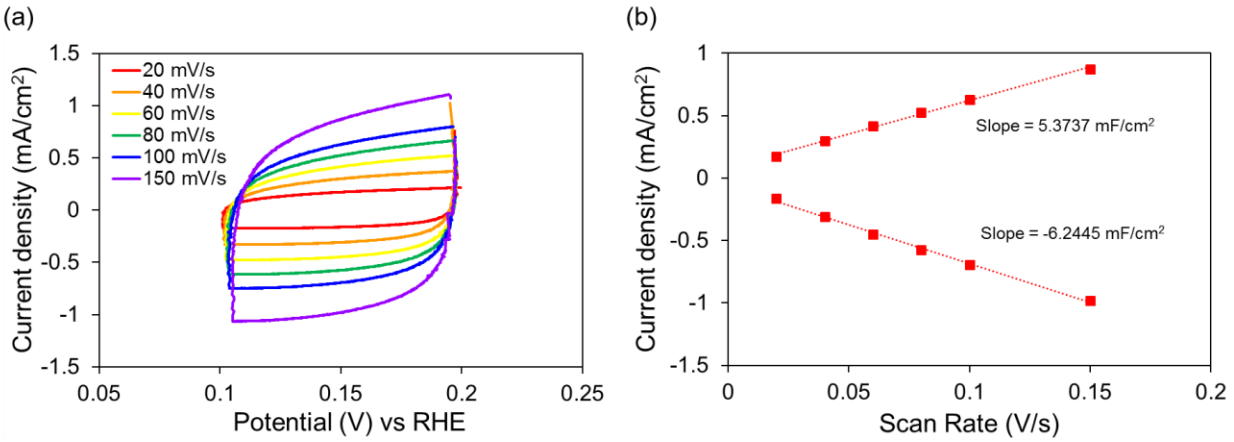

Figure S5. Electrochemically active surface area measurements of GCE-3 (a) CVs ranging from 20, 40, 60, 80, 100, and 150 mV/s in the region of 0.1-0.2 V vs RHE. (b) Reductive and oxidative current obtained at 0.15 V vs RHE versus scan rate.

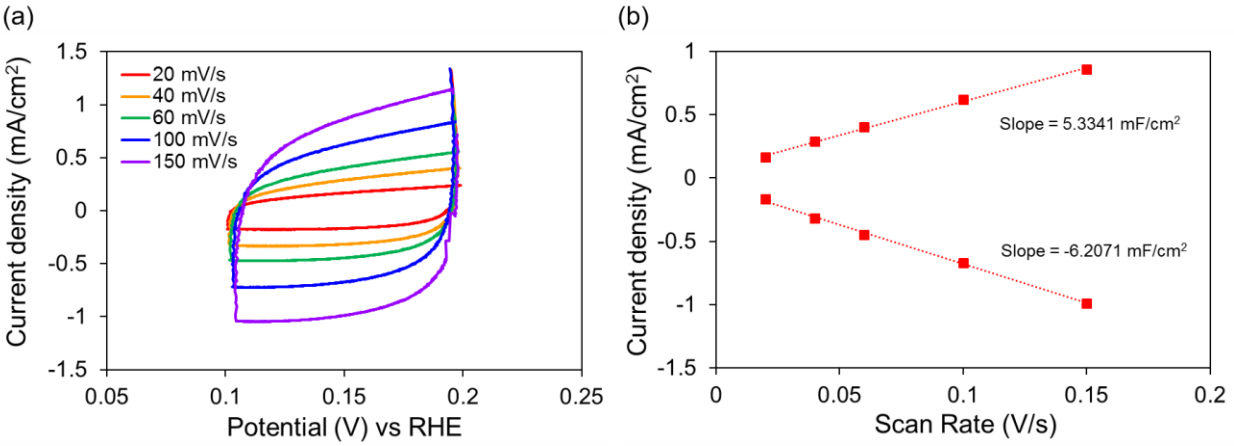

Figure S6. Electrochemically active surface area measurements of GCE-4 (a) CVs ranging from 20, 40, 60, 100, and 150 mV/s in the region of 0.1-0.2 V vs RHE. (b) Reductive and oxidative current obtained at 0.15 V vs RHE versus scan rate.

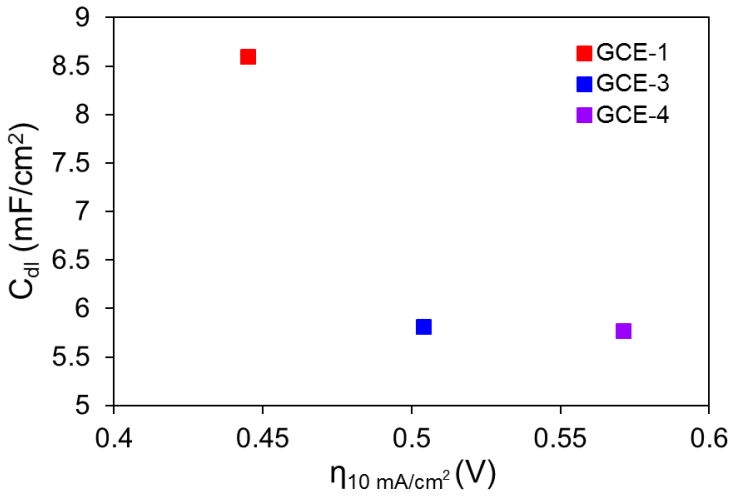

Figure S7. Double layer capacitance (C_{dl}) measured from cyclic voltammetry versus the overpotential to reach 10 mA/cm^2 of HER activity for GCE-1 (red), GCE-3 (blue), and GCE-4 (purple).

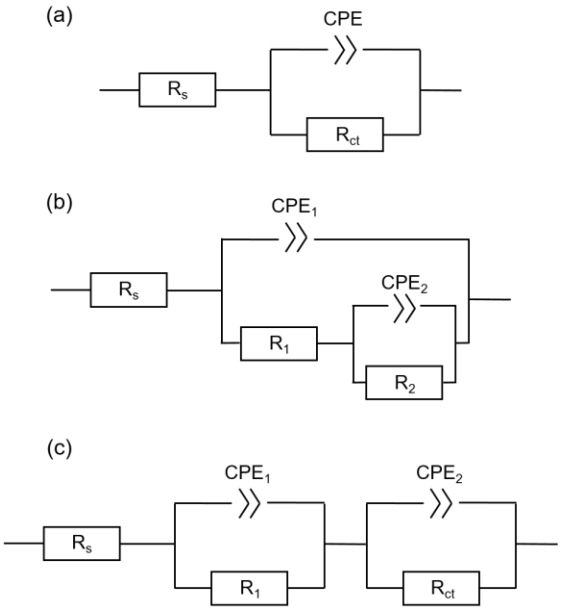

Figure S8. Equivalent circuit models used to explain the EIS response associated with HER: (a) one-time constant model (1T), (b) two-time constant parallel model (2TP), and (c) two-time constant serial model (2TS).

Table S1. Values from fitting EIS data to equivalent circuit at -0.57 V vs RHE for GCE-1.

η (V)	R_s (Ω)	R_{ct} (Ω)	n_1	CPE_1 (F)
0.57	57.33	714.6	0.8527	1.109×10^{-6}

Table S2. Values from fitting EIS data to equivalent circuit at -0.57 V vs RHE for GCE-2

η (V)	R_s (Ω)	R_{ct} (Ω)	n_1	CPE_1 (F)
0.57	57.65	853.3	0.9227	1.221×10^{-6}

.

Table S3. Values from fitting EIS data to equivalent circuit at -0.57 V vs RHE for GCE-3.

η (V)	R_s (Ω)	R_{ct} (Ω)	n_1	CPE_1 (F)
0.57	69.42	1061.0	0.881	7.917×10^{-7}

Table S4. Values from fitting EIS data to equivalent circuit at -0.57 V vs RHE for GCE-4.

η (V)	R_s (Ω)	R_{ct} (Ω)	n_1	CPE_1 (F)
0.57	57.26	1365.0	0.7983	1.752×10^{-6}

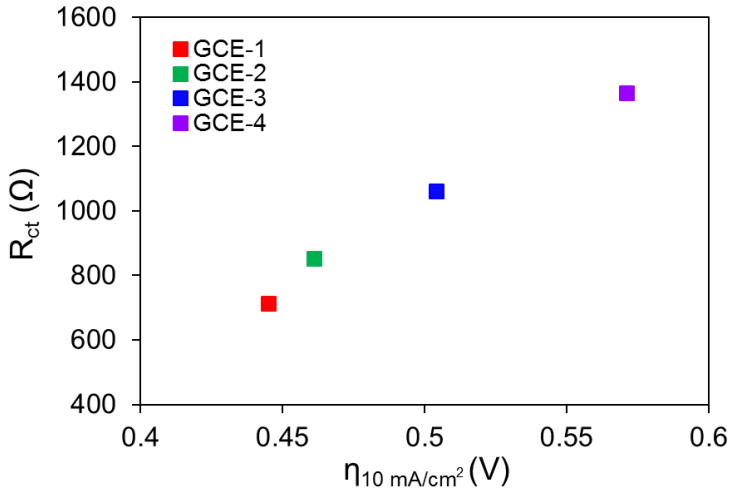

Figure S9. Calculated values of R_{ct} (Ω) from fitted EIS data recorded at -0.57 V vs RHE versus the overpotential to reach 10 mA/cm^2 of HER activity for GCE-1 (red), GCE-2 (green), GCE-3 (blue), and GCE-4 (purple).

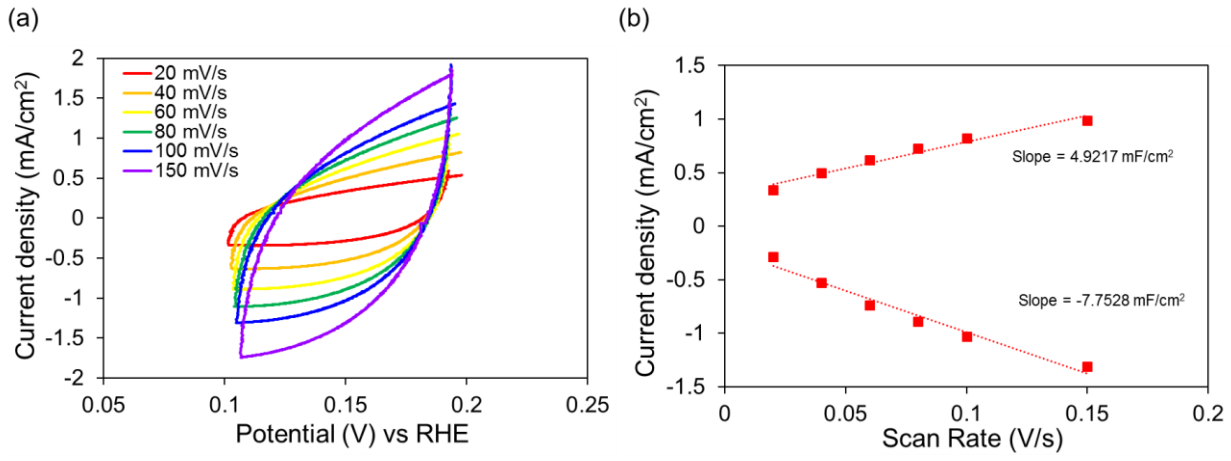

Figure S10. Electrochemically active surface area measurements of GR-2 (a) CVs ranging from 20, 40, 60, 80, 100, and 150 mV/s in the region of 0.1-0.2 V vs RHE. (b) Reductive and oxidative current obtained at 0.15 V vs RHE versus scan rate.

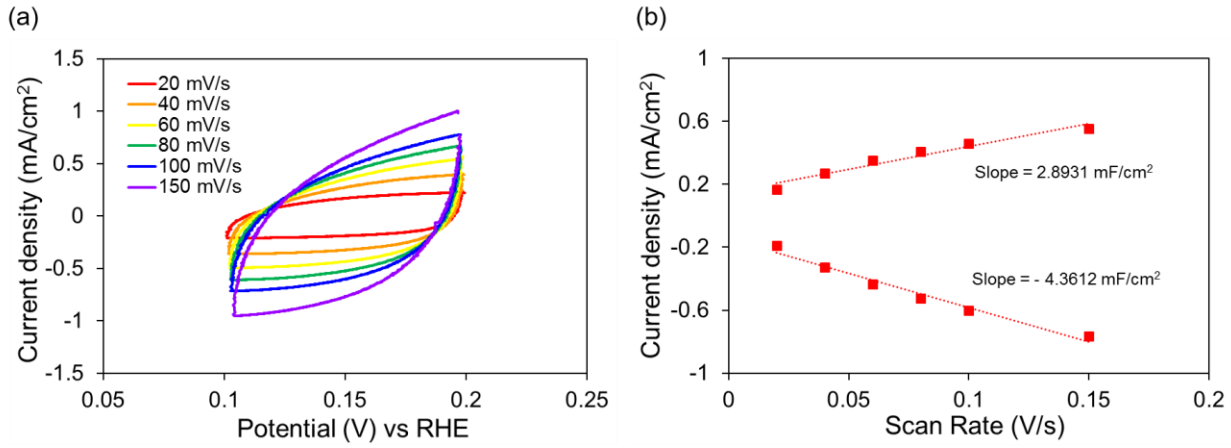

Figure S11. Electrochemically active surface area measurements of GR-3 (a) CVs ranging from 20, 40, 60, 80, 100, and 150 mV/s in the region of 0.1-0.2 V vs RHE. (b) Reductive and oxidative current obtained at 0.15 V vs RHE versus scan rate.

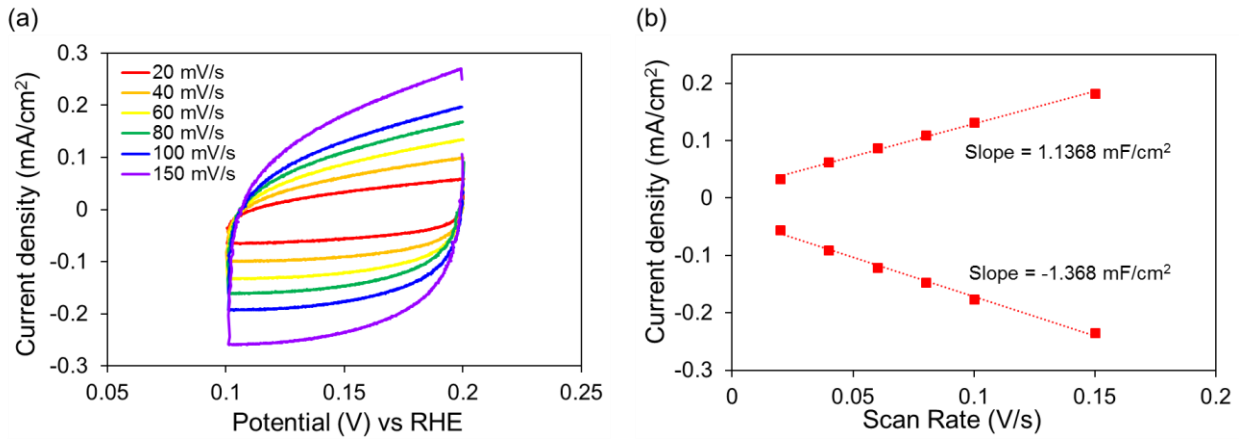

Figure S12. Electrochemically active surface area measurements of GR-4 (a) CVs ranging from 20, 40, 60, 80, 100, and 150 mV/s in the region of 0.1-0.2 V vs RHE. (b) Reductive and oxidative current obtained at 0.15 V vs RHE versus scan rate.

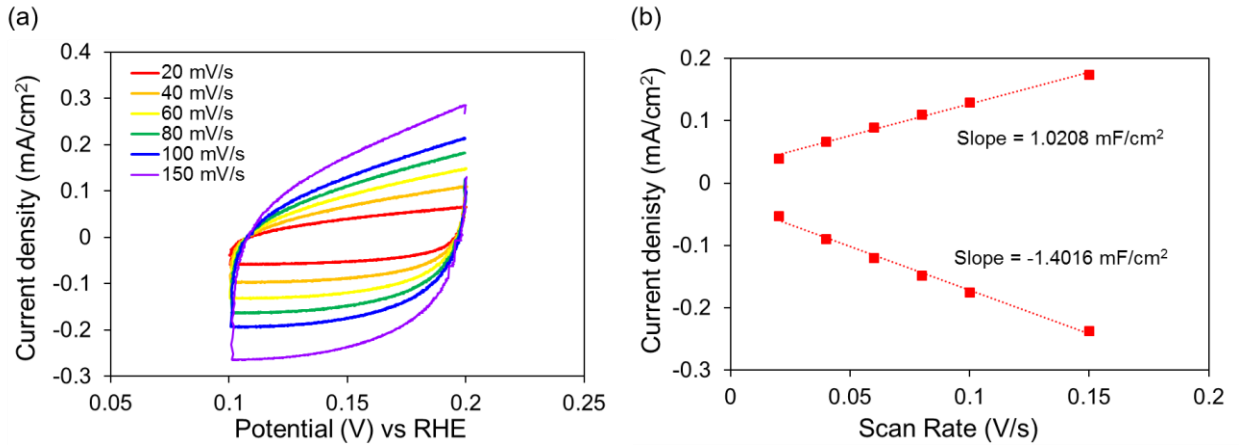

Figure S13. Electrochemically active surface area measurements of GR-5 (a) CVs ranging from 20, 40, 60, 80, 100, and 150 mV/s in the region of 0.1-0.2 V vs RHE. (b) Reductive and oxidative current obtained at 0.15 V vs RHE versus scan rate.

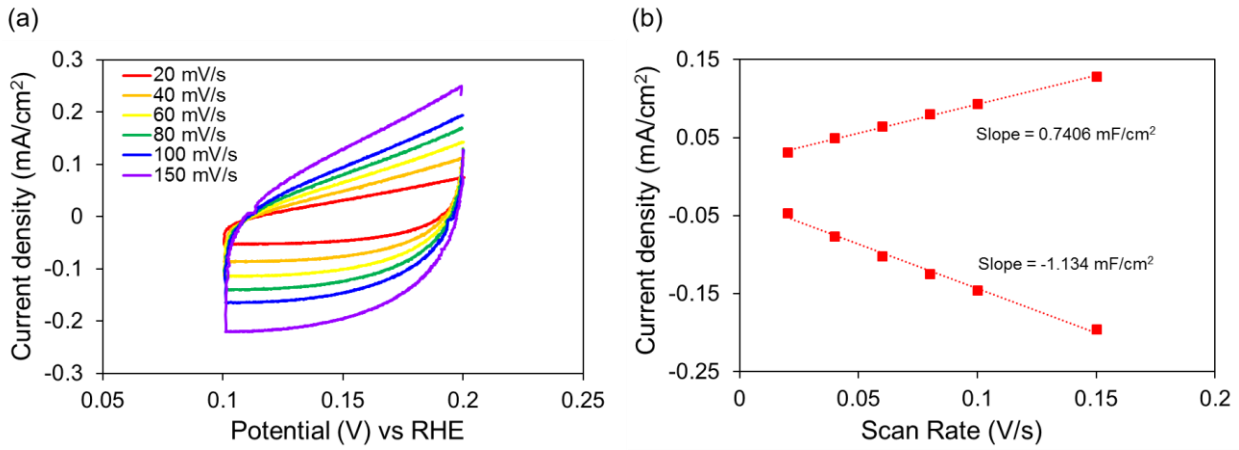

Figure S14. Electrochemically active surface area measurements of GR-6 (a) CVs ranging from 20, 40, 60, 80, 100, and 150 mV/s in the region of 0.1-0.2 V vs RHE. (b) Reductive and oxidative current obtained at 0.15 V vs RHE versus scan rate.

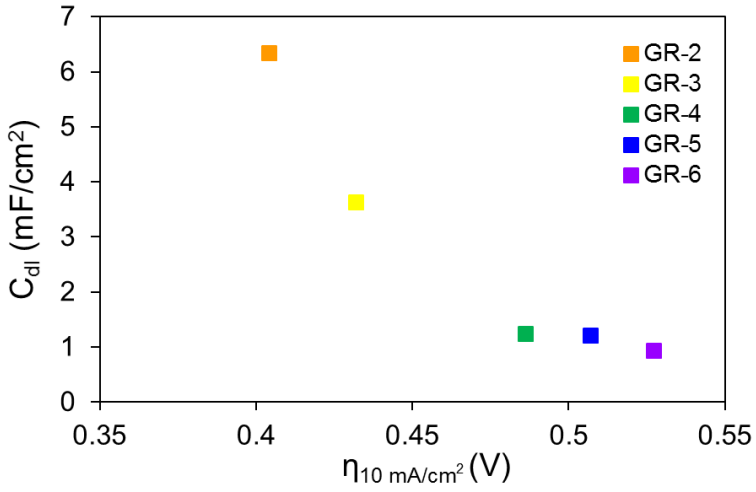

Figure S15. Double layer capacitance (C_{dl}) measured from cyclic voltammetry versus the overpotential to reach 10 mA/cm^2 of HER activity for GR-2 (orange), GR-3 (yellow), GR-4 (green), GR-5 (blue), and GR-6 (purple).

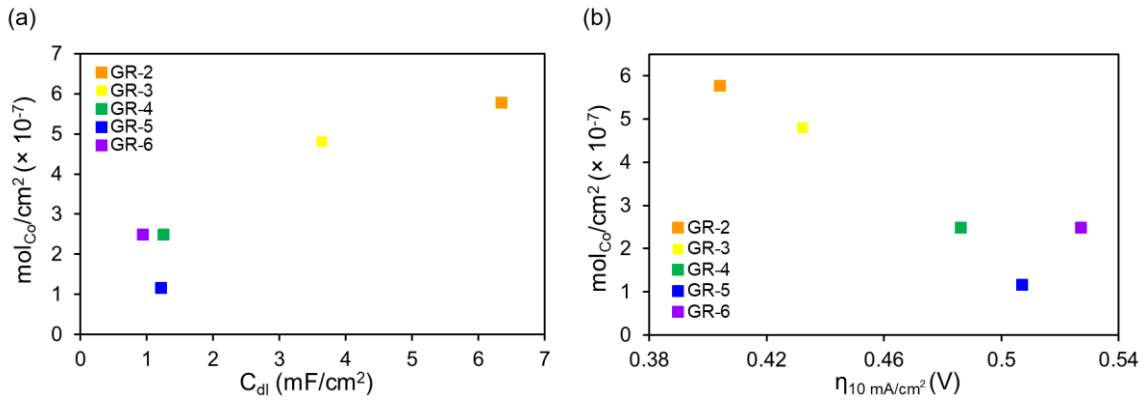

Figure S16. (a) Cobalt concentration (mol_{Co}/cm^2) measured via ICP versus the C_{dl} (mF/cm^2) measured via CV and (b) cobalt concentration (mol_{Co}/cm^2) measured via ICP versus the overpotential to reach 10 mA/cm^2 of HER activity for GR-2 (orange), GR-3 (yellow), GR-4 (green), GR-5 (blue), and GR-6 (purple).

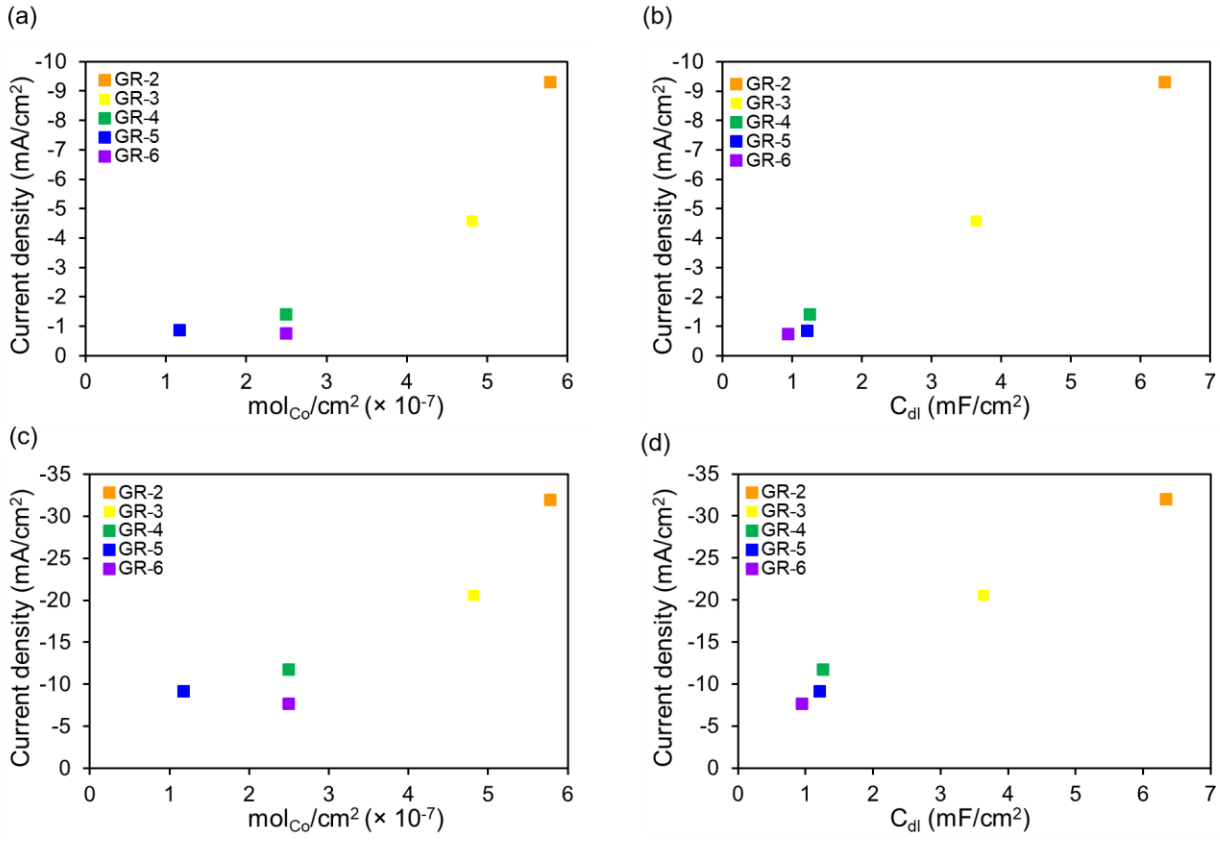

Figure S17. Current density at -0.40 V vs RHE versus (a) cobalt concentration (mol_{Co}/cm^2) and (b) the C_{dl} (mF/cm^2) and current density at -0.50 V vs RHE versus (c) cobalt concentration (mol_{Co}/cm^2) and (d) the C_{dl} (mF/cm^2) for GR-2 (orange), GR-3 (yellow), GR-4 (green), GR-5 (blue), and GR-6 (purple).

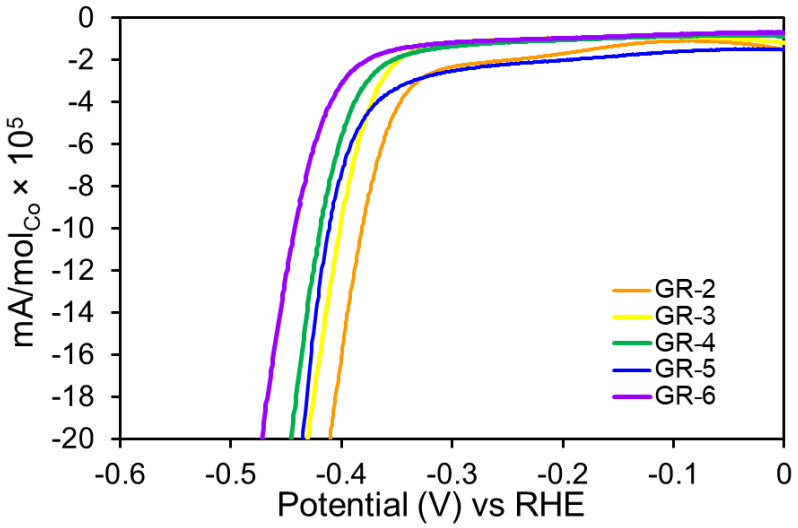

Figure S18. Polarization curves for GR-2 (orange), GR-3 (yellow), GR-4 (green), GR-5 (blue), and GR-6 (purple) where the y-axis represents current per concentration of cobalt measured via ICP (mA/mol$_{Co}$ × 10^5).

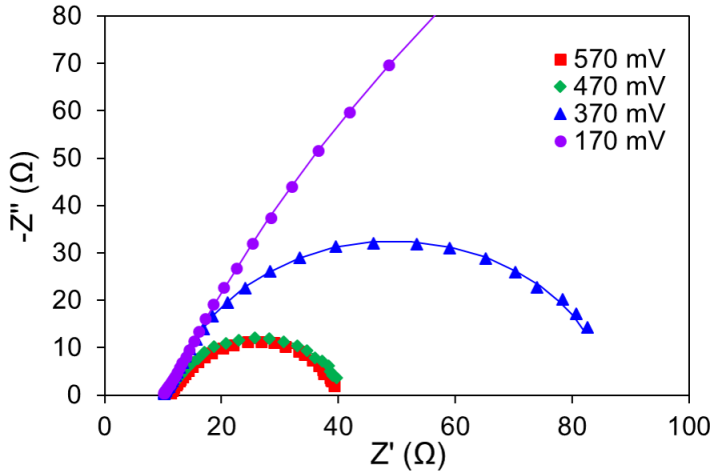

Figure S19. Nyquist plot of GR-2 showing experimental EIS response (markers) and fits (solid lines) at various overpotentials at pH 1.3.

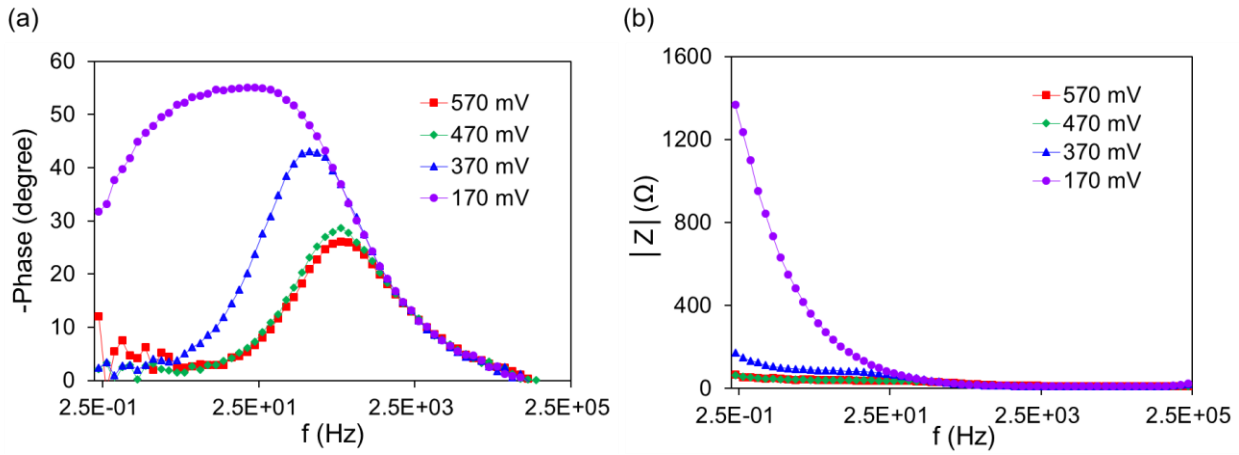

Figure S20. Bode plots showing EIS response of GR-2 at various overpotentials at pH 1.3.

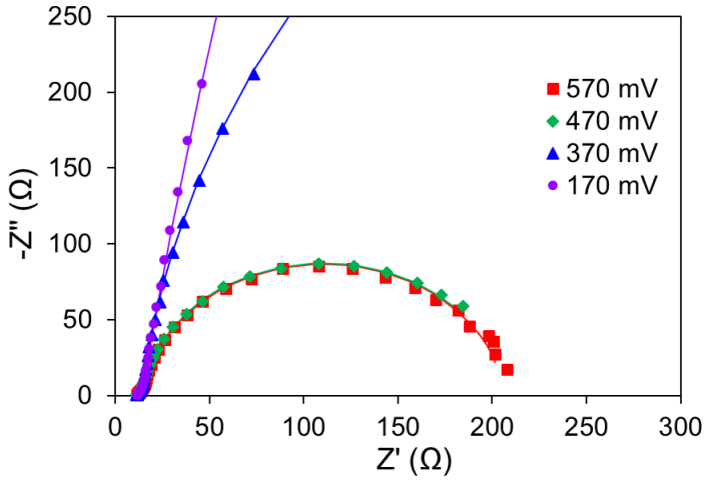

Figure S21. Nyquist plot of GR-4 showing experimental EIS response (markers) and fits (solid lines) at various overpotentials at pH 1.3.

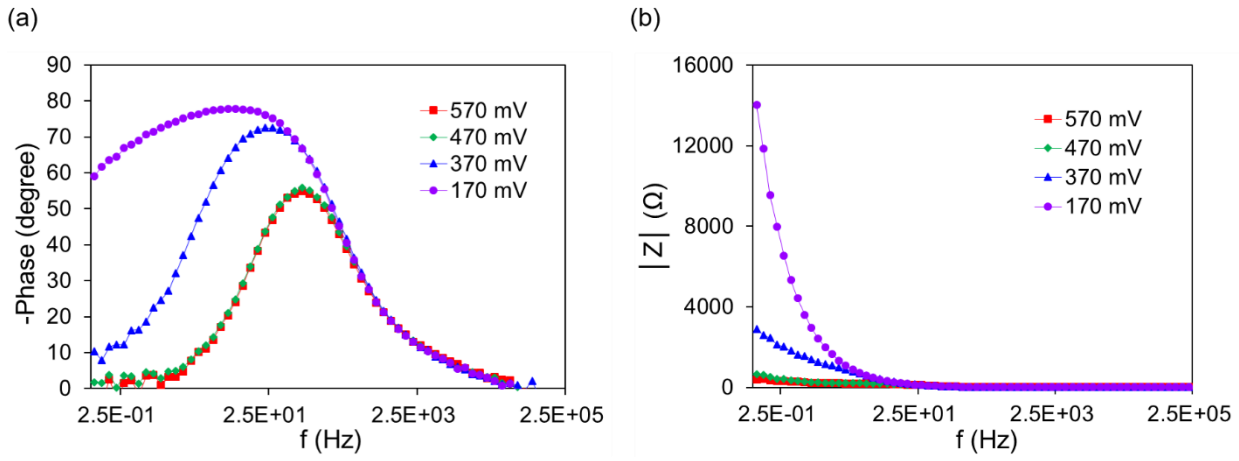

Figure S22. Bode plots showing EIS response of GR-4 at various overpotentials at pH 1.3.

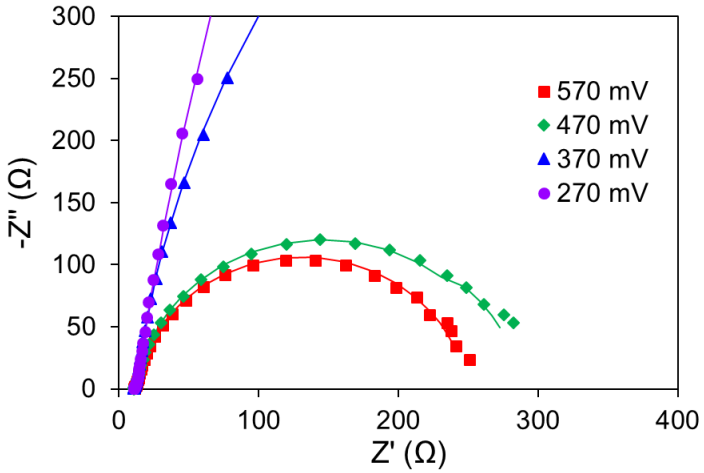

Figure S23. Nyquist plot of GR-5 showing experimental EIS response (markers) and fits (solid lines) at various overpotentials at pH 1.3.

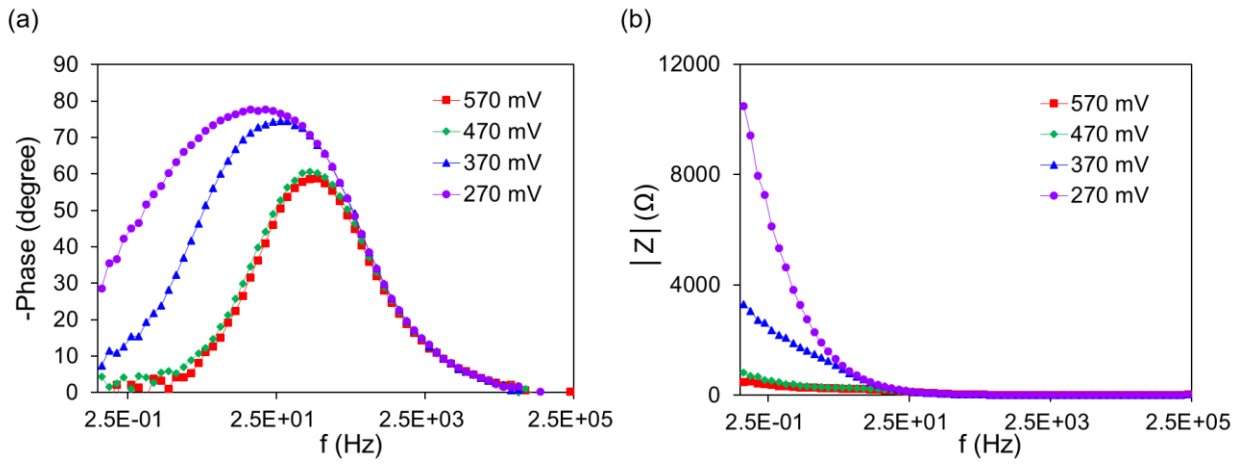

Figure S24. Bode plots showing EIS response of GR-5 at various overpotentials at pH 1.3.

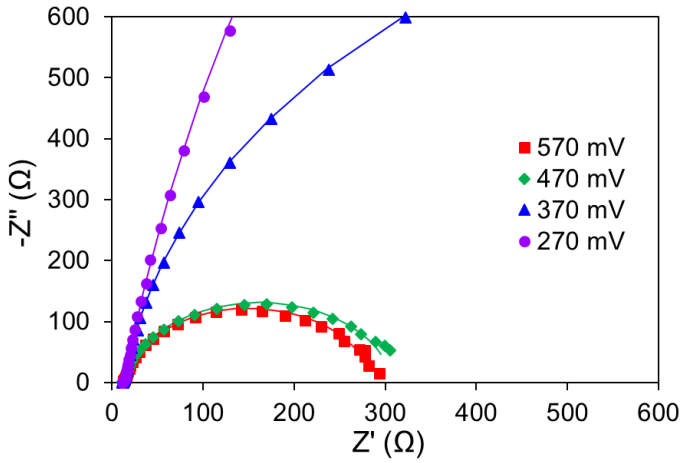

Figure S25. Nyquist plot of GR-6 showing experimental EIS response (markers) and fits (solid lines) at various overpotentials in pH 1.3.

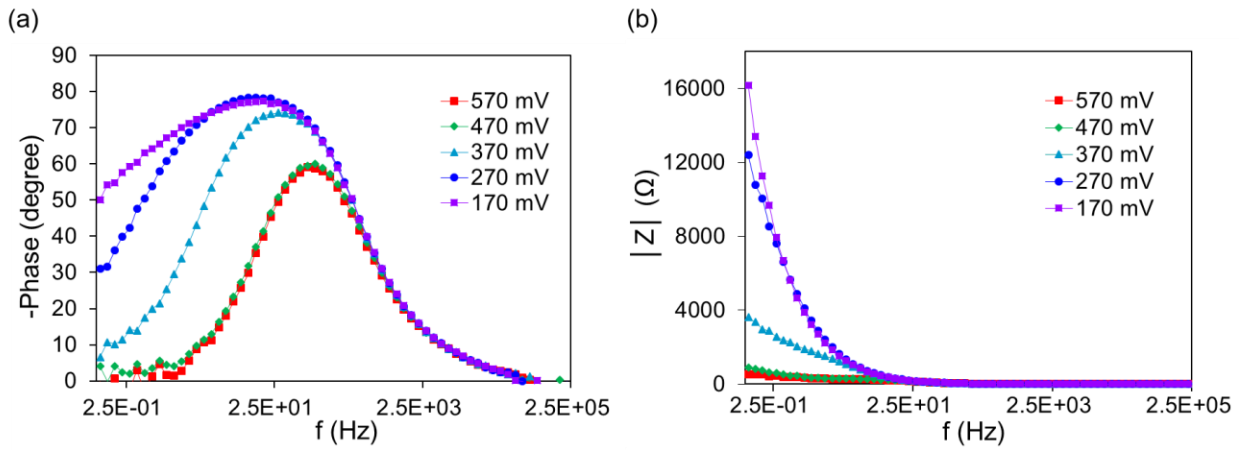

Figure S26. Bode plots showing EIS response of GR-6 at various overpotentials at pH 1.3.

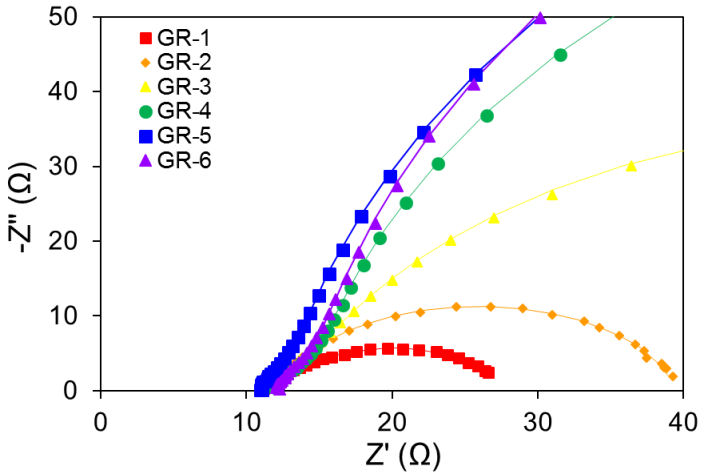

Figure S27. Expansion of the high frequency range of the Nyquist plots of GR-1 (red), GR-2 (orange), GR-3 (yellow), GR-4 (green), GR-5 (blue), and GR-6 (purple) showing experimental EIS response (markers) and fits (solid lines) at -0.57 V vs RHE at pH 1.3.

Table S5. Values from fitting EIS data to equivalent circuit shown in Figure S27 for GR-1.

η (V)	R_s (Ω)	R_1 (Ω)	n_1	CPE_1 (F)	R_{ct} (Ω)	n_2	CPE_2 (F)
0.57	11.04	3.479	0.7599	2.606×10^{-4}	13.05	0.8475	1.817×10^{-4}

Table S6. Values from fitting EIS data to equivalent circuit shown in Figure S19 for GR-2.

η (V)	R_s (Ω)	R_1 (Ω)	n_1	CPE_1 (F)	R_{ct} (Ω)	n_2	CPE_2 (F)
0.57	11.04	2.125	0.7667	2.77×10^{-4}	26.32	0.891	7.854×10^{-5}
0.47	10.42	2.638	0.726	3.894×10^{-4}	27.15	0.9172	7.079×10^{-5}
0.37	10.03	2.421	0.753	3.687×10^{-4}	74.26	0.9139	7.908×10^{-5}
0.17	9.947	0.5087	0.9408	1.149×10^{-4}	607.2	0.7583	2.536×10^{-4}

Table S7. Values from fitting EIS data to equivalent circuit shown in Figure S27 for GR-3.

η (V)	R_s (Ω)	R_1 (Ω)	n_1	CPE_1 (F)	R_{ct} (Ω)	n_2	CPE_2 (F)
0.57	11.81	3.611	0.767	2.14×10^{-4}	86.27	0.8822	5.23×10^{-5}

Table S8. Values from fitting EIS data to equivalent circuit shown in Figure S21 for GR-4.

η (V)	R_s (Ω)	R_1 (Ω)	n_1	CPE_1 (F)	R_{ct} (Ω)	n_2	CPE_2 (F)
0.57	11.53	3.725	0.7838	1.478×10^{-4}	191.2	0.9385	5.882×10^{-5}
0.47	11.46	3.242	0.8204	1.28×10^{-4}	192.1	0.9411	5.777×10^{-5}
0.37	11.37	3.348	0.7939	1.635×10^{-4}	1245	0.9437	5.718×10^{-5}
0.17	11.44	2.519	0.8945	6.339×10^{-5}	12050	0.9132	7.24×10^{-5}

Table S9. Values from fitting EIS data to equivalent circuit shown in Figure S23 for GR-5.

η (V)	R_s (Ω)	R_1 (Ω)	n_1	CPE_1 (F)	R_{ct} (Ω)	n_2	CPE_2 (F)
0.57	10.94	2.221	0.8628	1.301×10^{-4}	235.7	0.934	5.318×10^{-5}
0.47	10.75	1.943	0.9012	1.082×10^{-4}	266.5	0.9351	5.194×10^{-5}
0.37	10.69	1.873	0.9073	1.012×10^{-4}	1738	0.9342	5.147×10^{-5}
0.27	10.67	1.417	0.9697	5.462×10^{-5}	7019	0.915	5.872×10^{-5}

Table S10. Values from fitting EIS data to equivalent circuit shown in Figure S25 for GR-6.

η (V)	R_s (Ω)	R_1 (Ω)	n_1	CPE_1 (F)	R_{ct} (Ω)	n_2	CPE_2 (F)
0.57	12.01	2.71	0.8426	1.114×10^{-4}	270.6	0.9352	4.424×10^{-5}
0.47	11.91	2.271	0.8994	6.723×10^{-5}	294.7	0.9288	4.494×10^{-5}
0.37	11.85	2.573	0.8528	1.05×10^{-4}	1847	0.9362	4.254×10^{-5}
0.27	11.81	2.251	0.8849	7.359×10^{-5}	8227	0.9238	4.563×10^{-5}
0.17	11.93	1.441	1.0	2.568×10^{-5}	13740	0.8969	5.381×10^{-5}

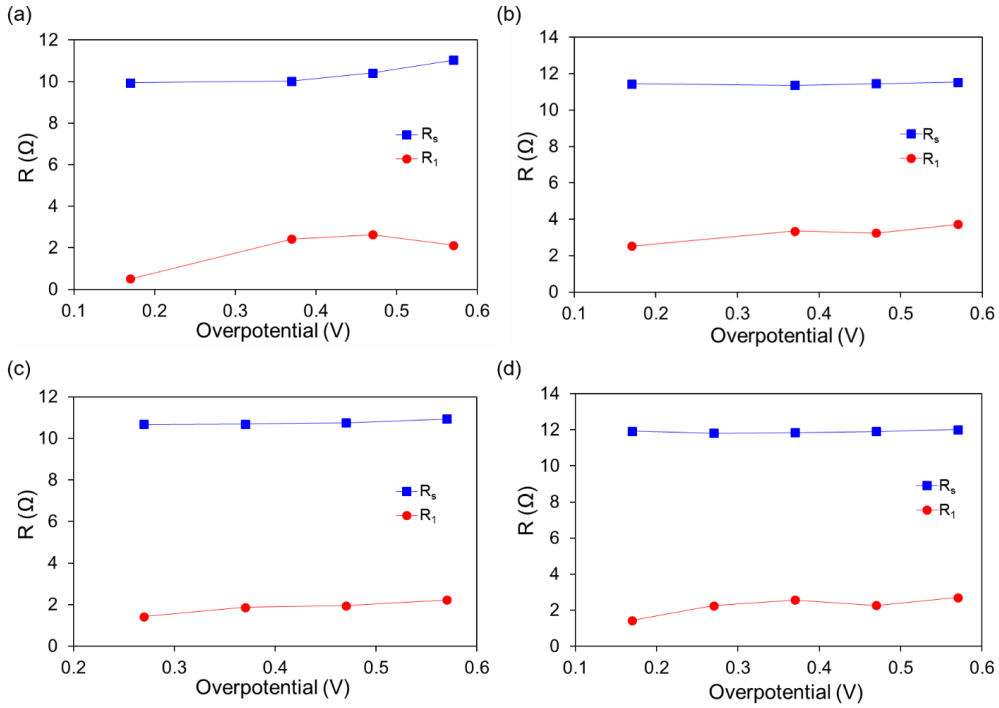

Figure S28. Values for R_s (blue) and R_1 (red) from EIS data in Tables S6, S8, S9, and S10 (a) GR-2 (b) GR-4 (c) GR-5 (d) GR-6.

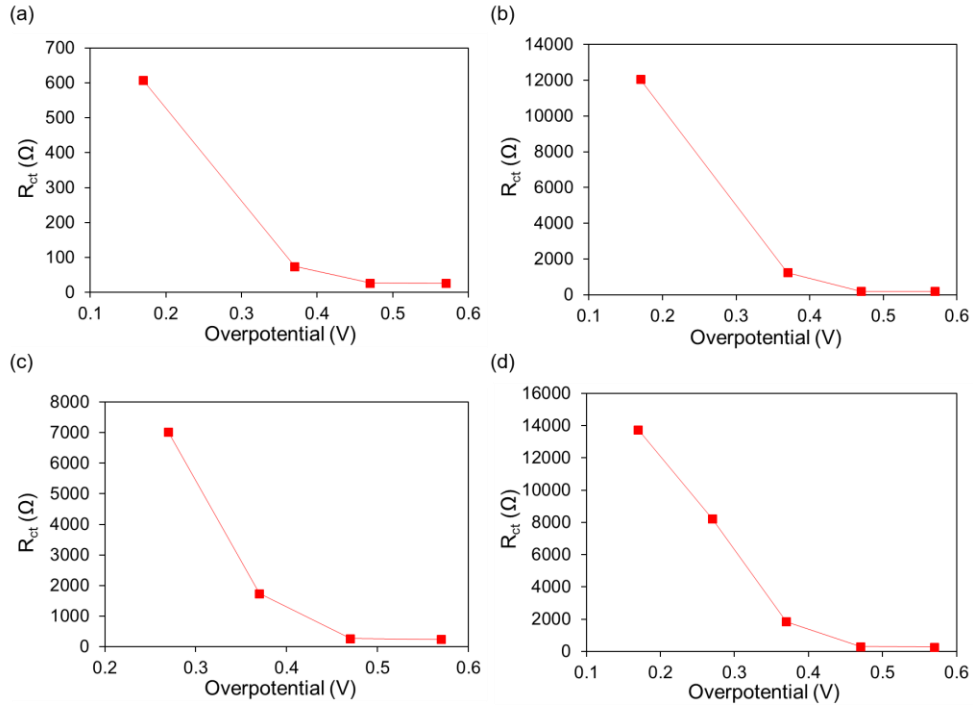

Figure S29. Values for R_{ct} from EIS data in Table S6, S8, S9, and S10 (a) GR-2 (b) GR-4 (c) GR-5 (d) GR-6.

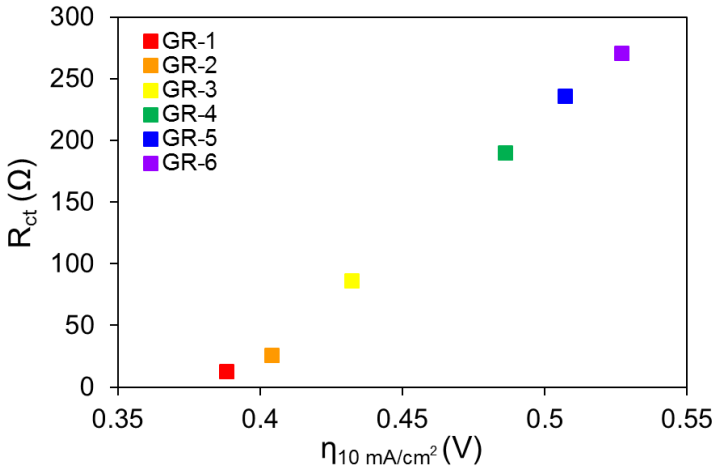

Figure S30. Calculated values of R_{ct} (Ω) from fitted EIS data recorded at -0.57 V vs RHE versus the overpotential to reach 10 mA/cm^2 of HER activity for GR-1 (red), GR-2 (orange), GR-3 (yellow), GR-4 (green), GR-5 (blue), and GR-6 (purple).

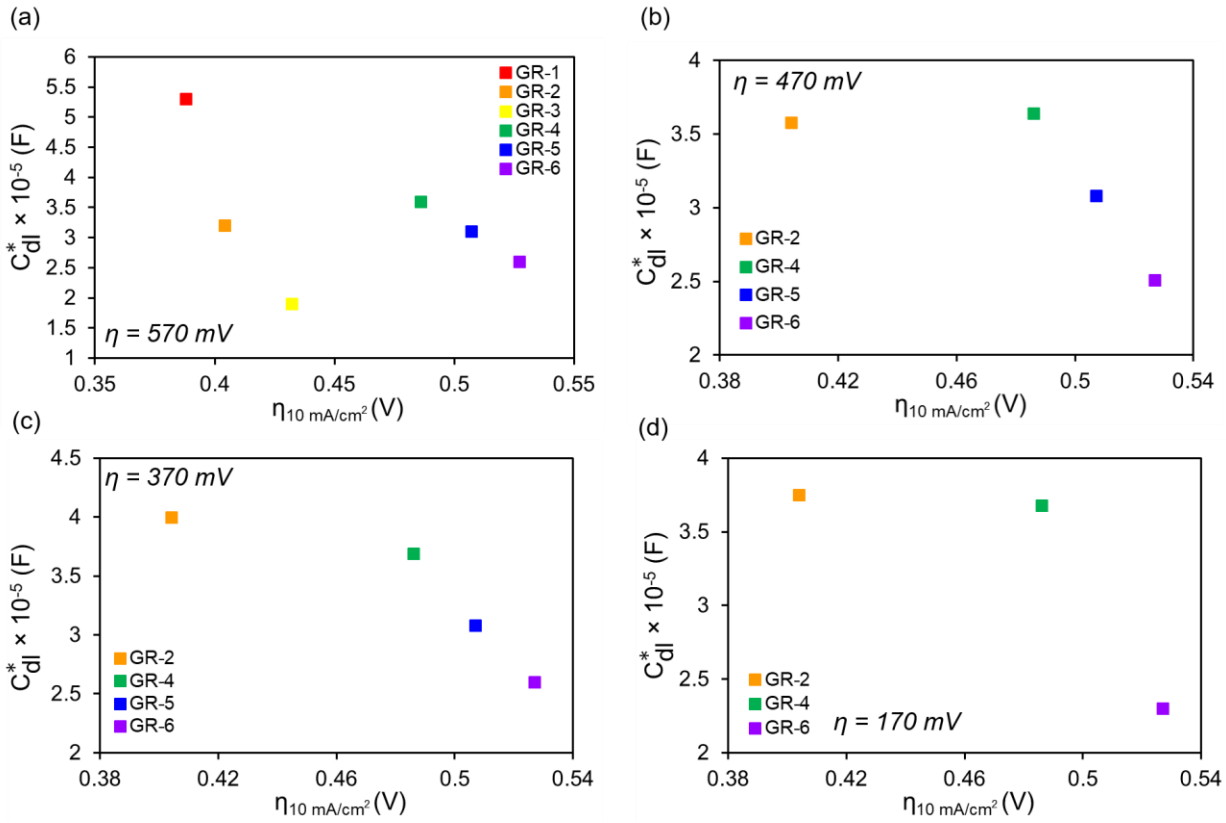

Figure S31. Double layer capacitance (C^*_{dl}) measured under HER conditions and calculated from the EIS data collected at the following overpotentials (a) 570 mV (b) 470 mV (c) 370 mV and (d) 170 mV versus the overpotential to reach 10 mA/cm^2 of HER activity for GR-1 (red), GR-2 (orange), GR-3 (yellow), GR-4 (green), GR-5 (blue), and GR-6 (purple).

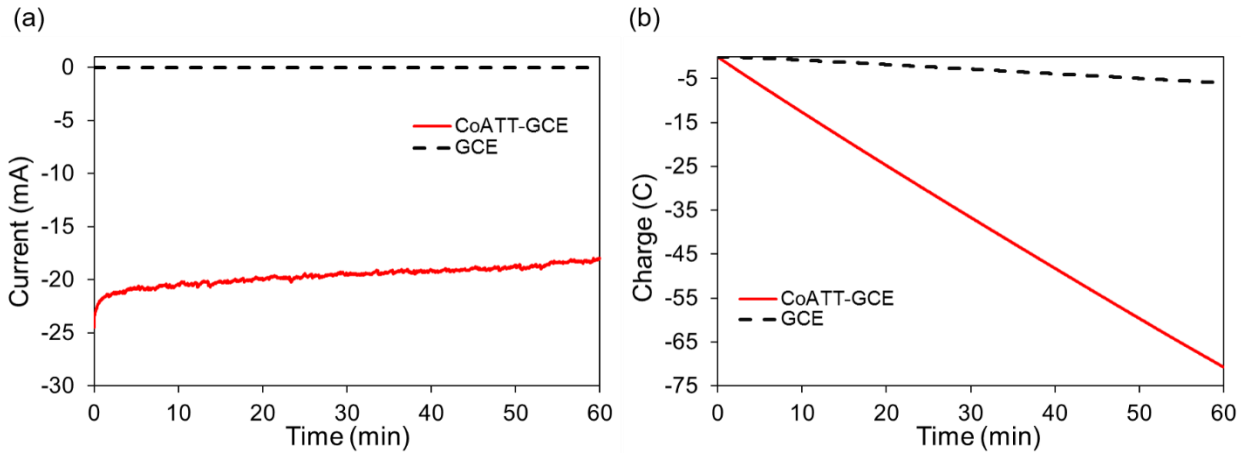

Figure S32. Controlled potential electrolysis of CoATT-GCE (red) and GCE (black dashed) in pH 1.3 solution at -0.72 V vs RHE.

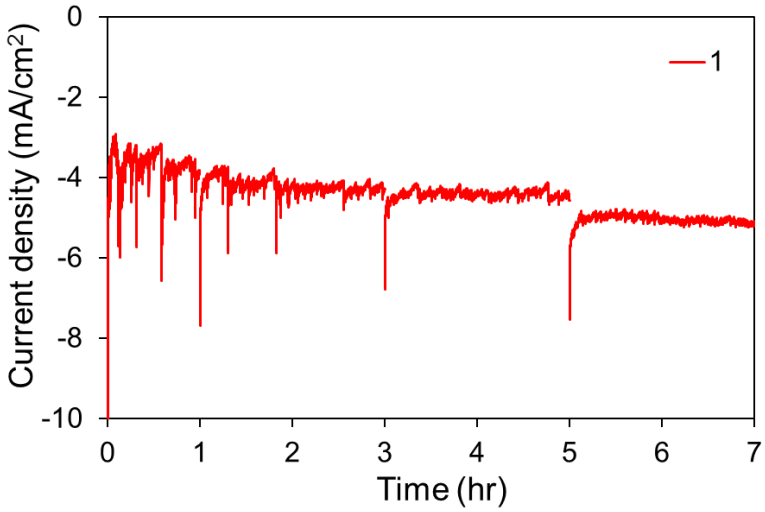

Figure S33. Chronoamperometry of **1** on graphite measured in pH 1.3 solutions at -0.72 V vs RHE.

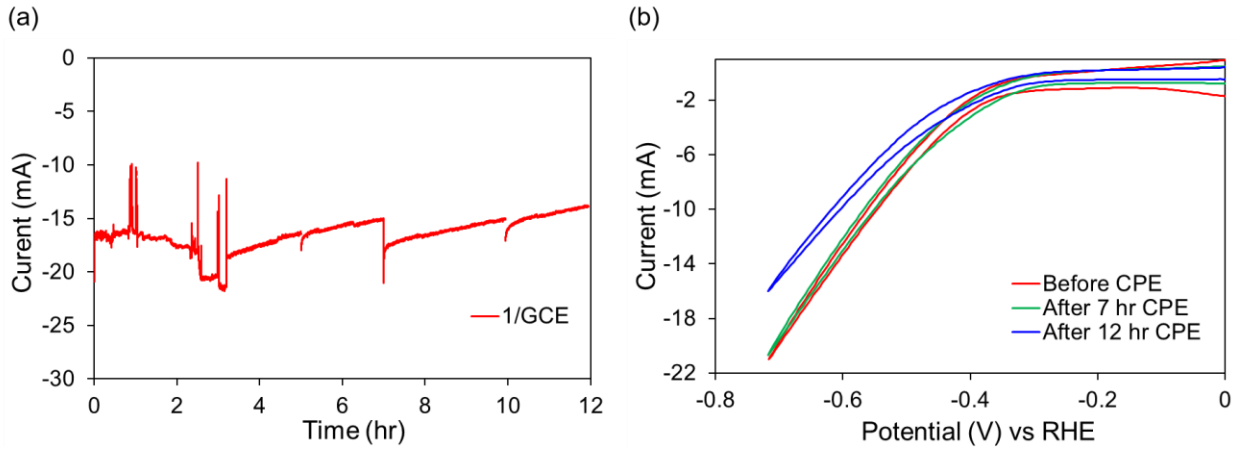

Figure S34. (a) Controlled potential electrolysis of 1/GCE (red) in pH 1.3 solution at -0.72 V vs RHE (b) Cyclic voltammetry experiments before CPE, after 7 hours of CPE (green), and after 12 hours of CPE (blue). Fluctuations in the CPE data are a result of removal of large H_2 bubbles from the electrode surface exposing more catalyst and jostling of the H-cell. Fresh pH 1.3 solution was added after 7 hours of CPE.

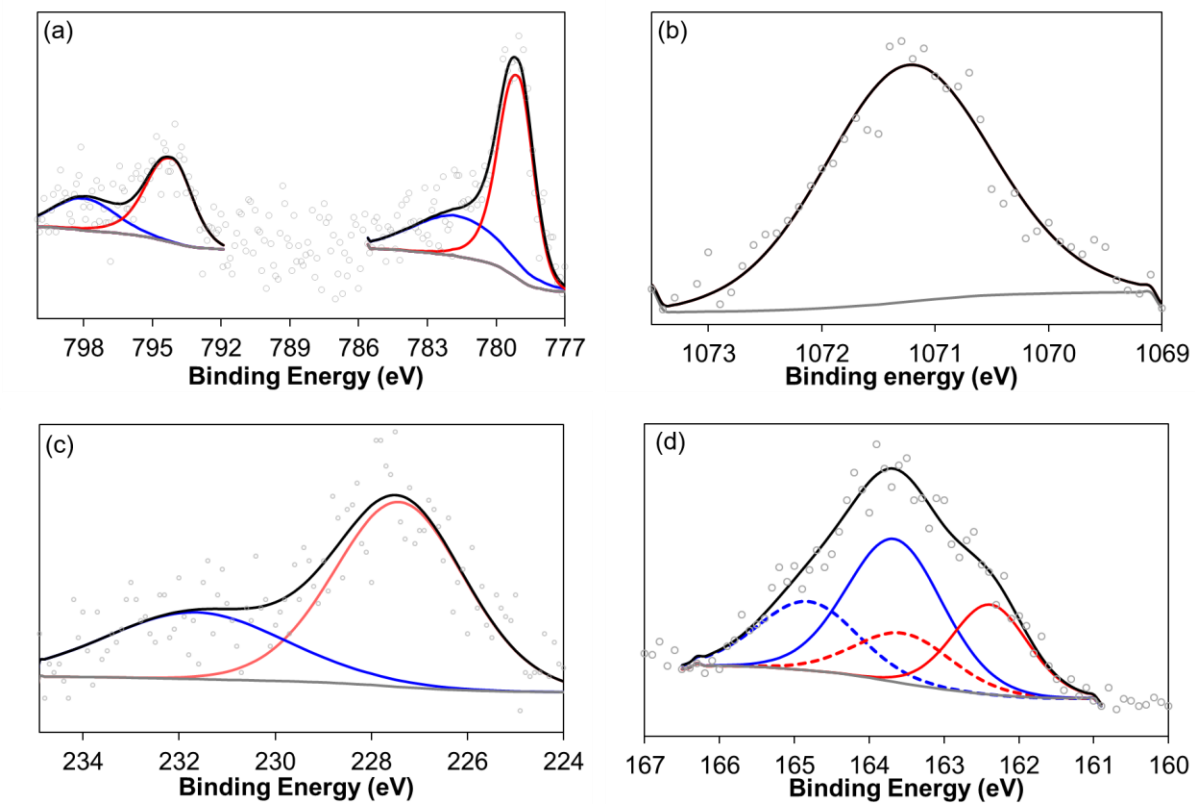

Figure S35. X-ray photoelectron spectroscopy analysis of **1** after 1 hour of controlled potential electrolysis in pH 1.3 solution at -0.72 V vs RHE (a) Co 2p (b) Na 1s (c) S 2s (d) S 2p core level XPS spectra.

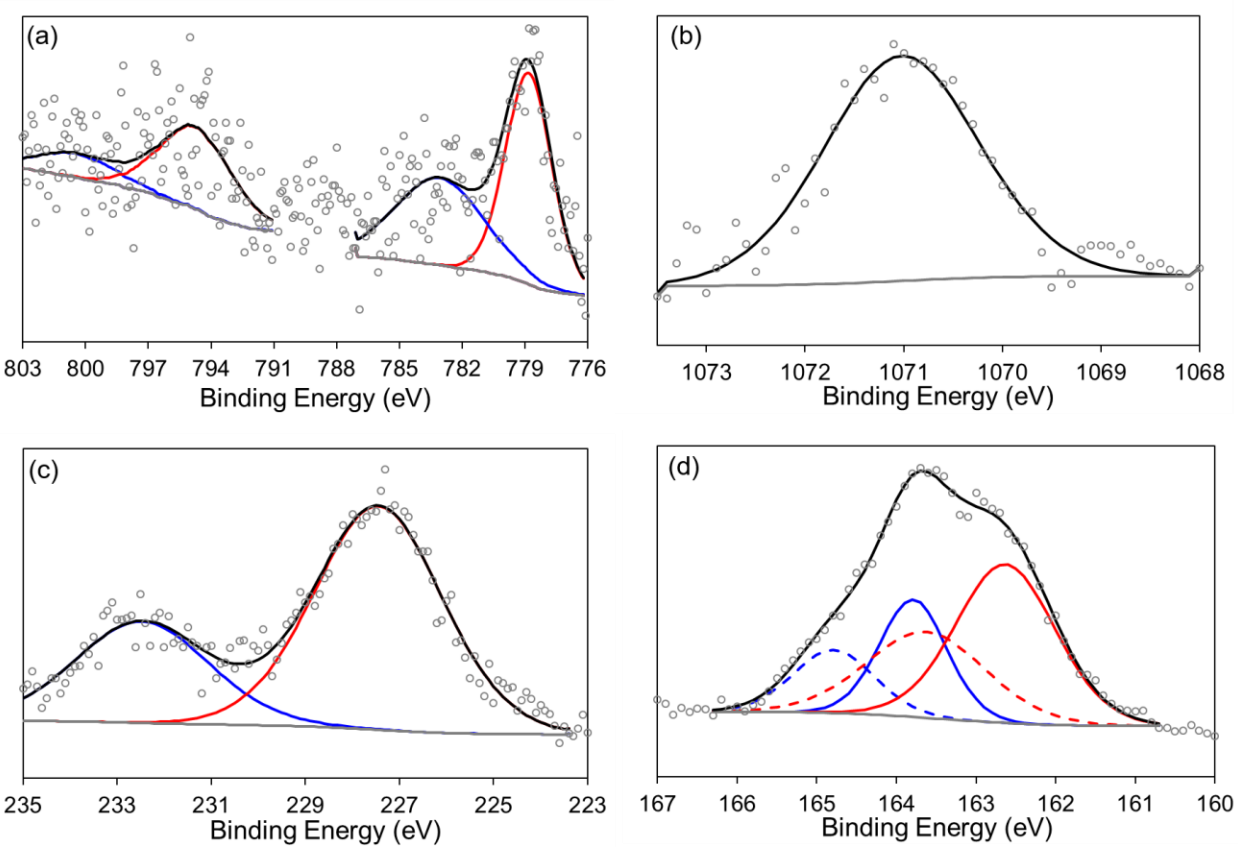

Figure S36. X-ray photoelectron spectroscopy analysis of **1** after 12 hours of controlled potential electrolysis in pH 1.3 solution at -0.72 V vs RHE (a) Co 2p (b) Na 1s (c) S 2s (d) S 2p core level XPS spectra.