

Supporting Information

Heterogenous HER Activity of Ni(II)N₂S₂ Molecular Catalysts

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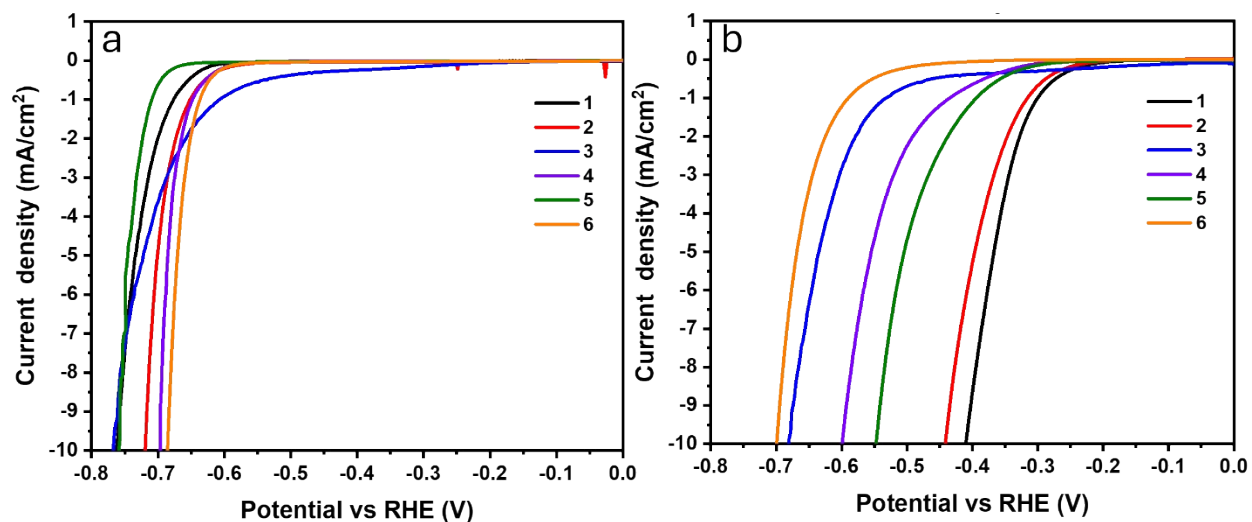


Figure S1. Linear sweep voltammetry plots of **1 – 6** a) before reductive cycling and b) after 1000 reductive cycles.

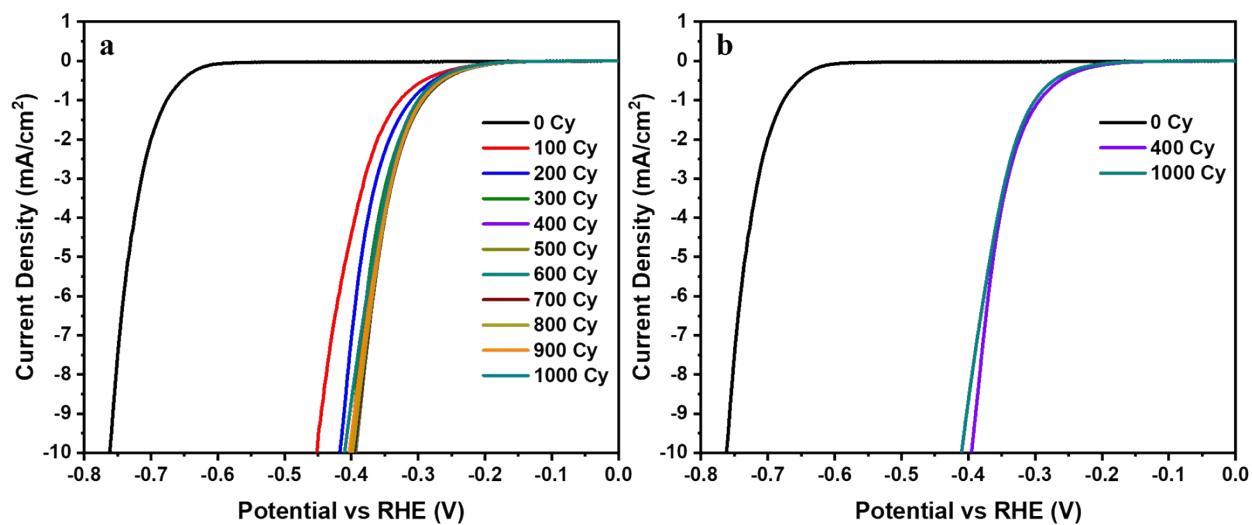


Figure S2. Linear sweep voltammetry plots of **1** a) from 0 to 1000 reductive cycles and b) before reductive cycling (0 Cy), at peak reductive cycling (400 Cy), and after 1000 reductive cycles.

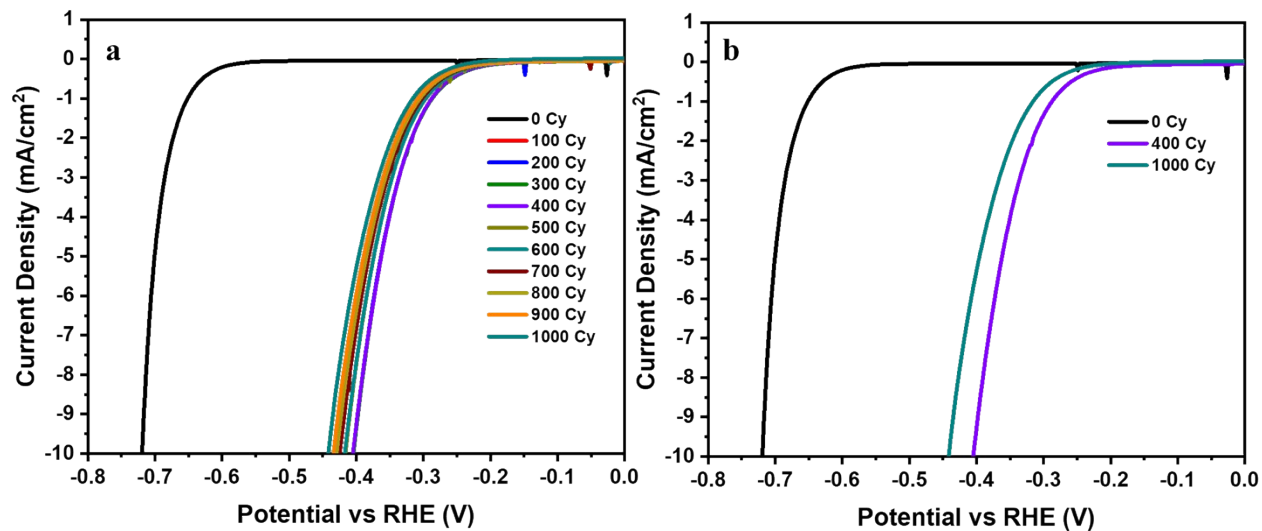


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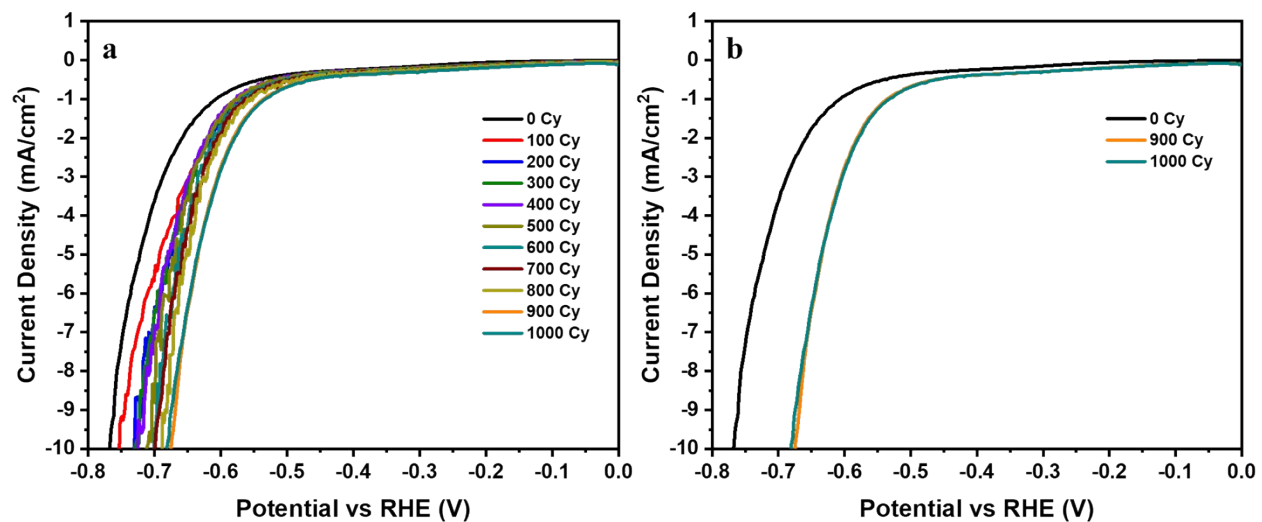


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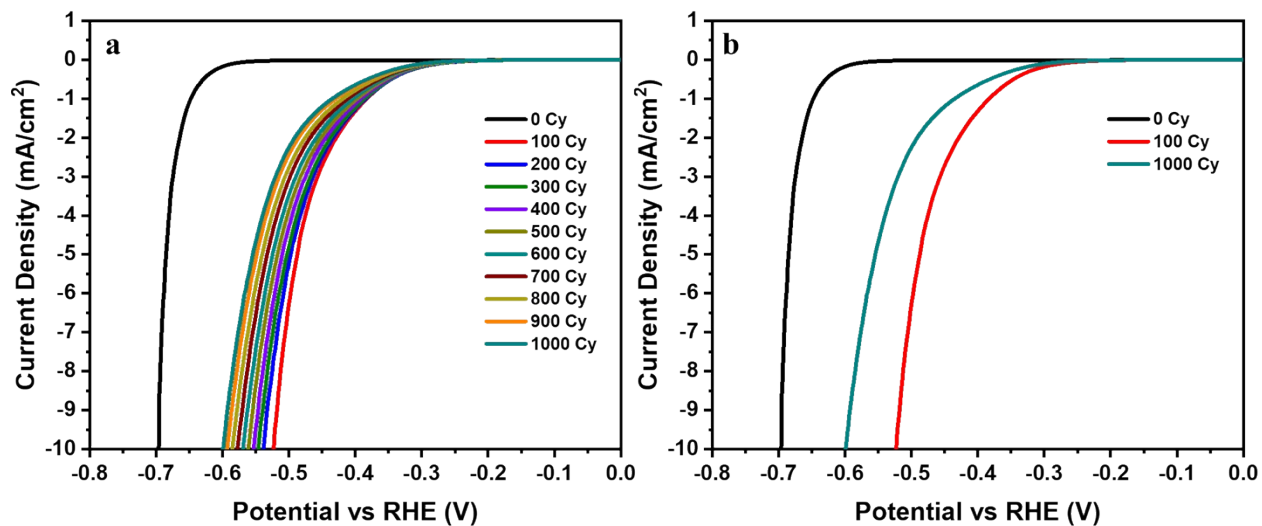


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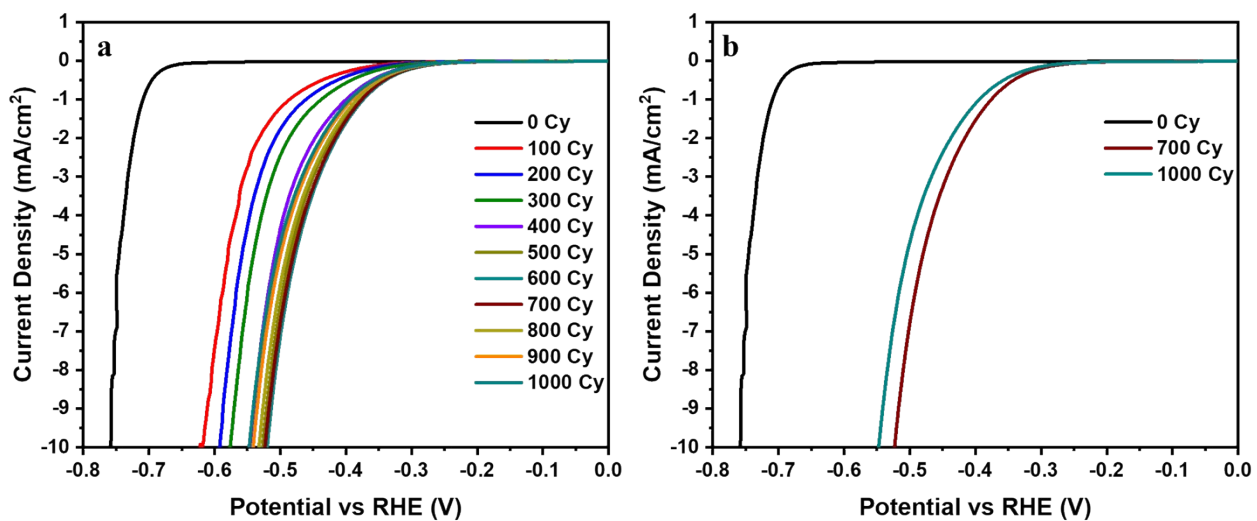


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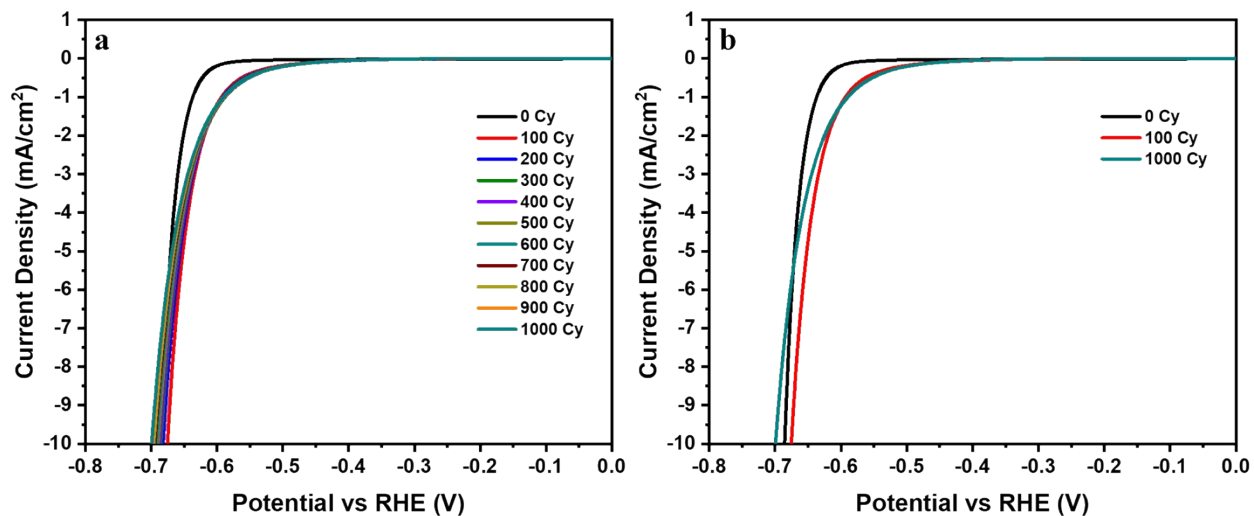


Figure S7. Linear sweep voltammetry plots of **6** a) from 0 to 1000 reductive cycles and b) before reductive cycling (0 Cy), at peak reductive cycling (100 Cy), and after 1000 reductive cycles.

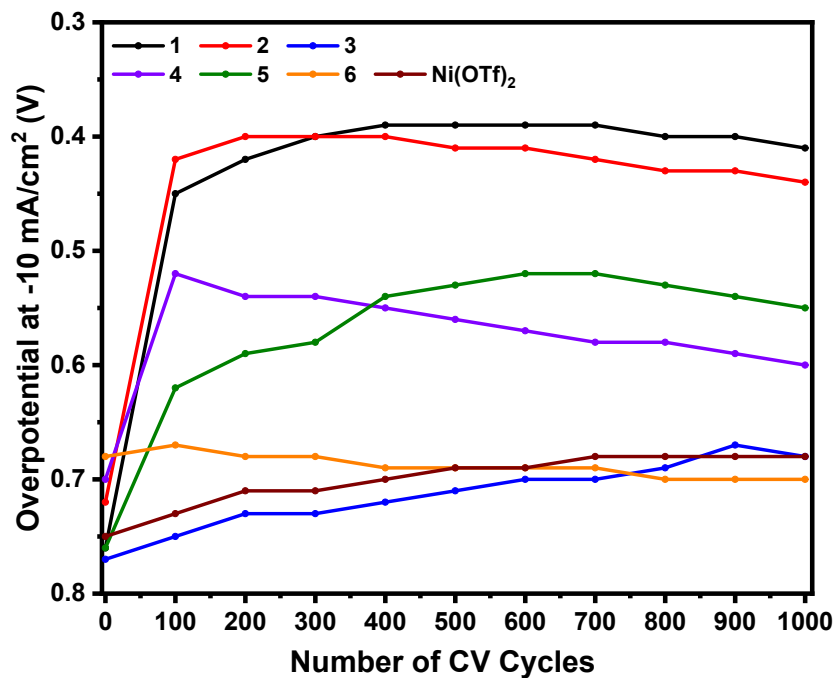


Figure S8. Plot of overpotential for **1** – **6** and Ni(OTf)₂ at -10 mA/cm² as a function of reductive cycles.

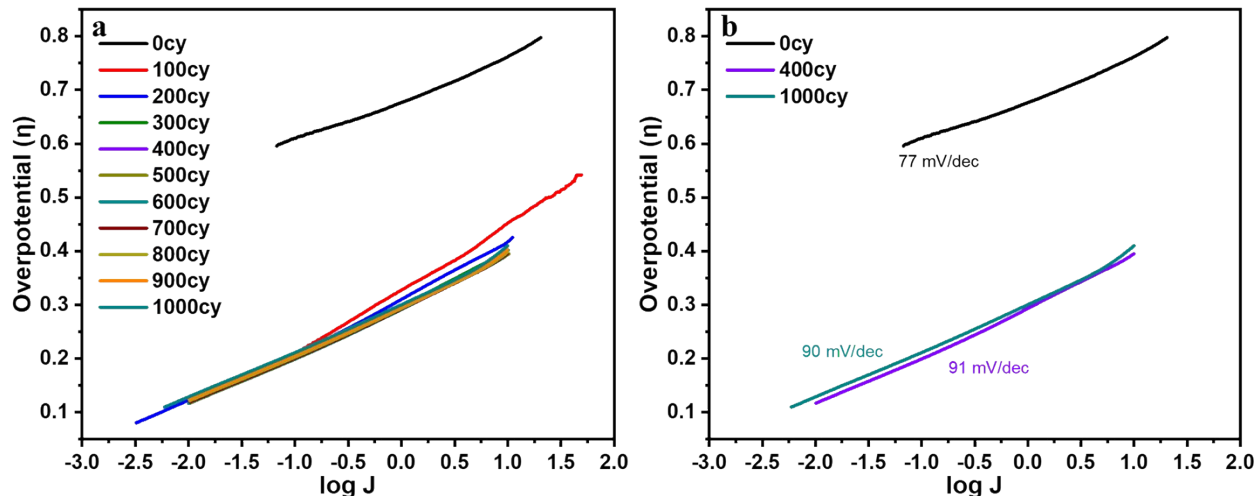


Figure S9. Tafel plot of 1 a) from 0 to 1000 reductive cycles and b) before reductive cycling (0cy), at peak reductive cycling (400cy), and at 1000 reductive cycles.

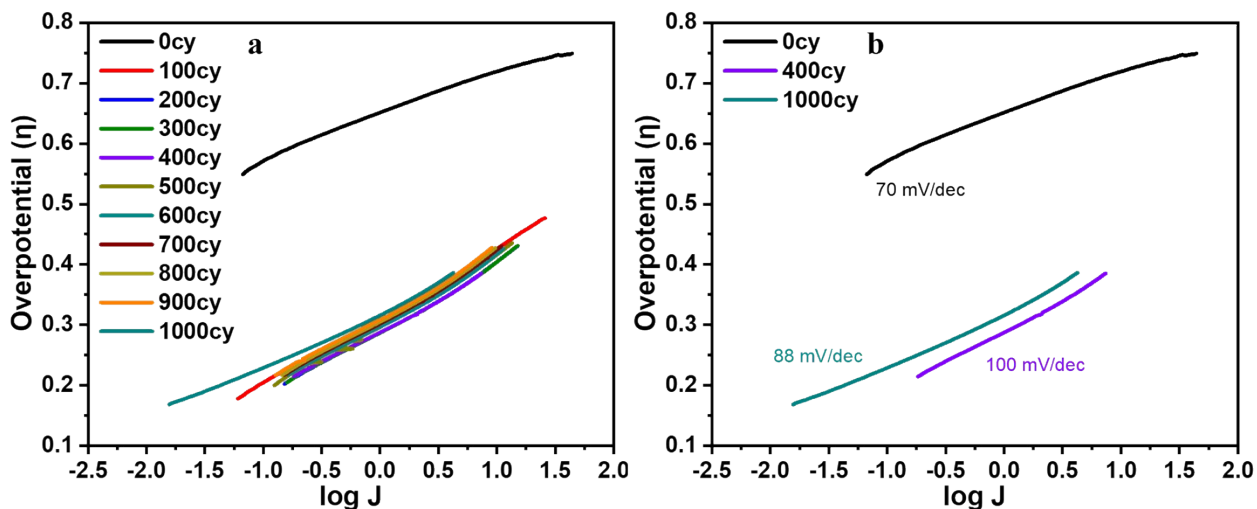


Figure S10. Tafel plot of 2 a) from 0 to 1000 reductive cycles and b) before reductive cycling (0cy), at peak reductive cycling (400cy), and at 1000 reductive cycles.

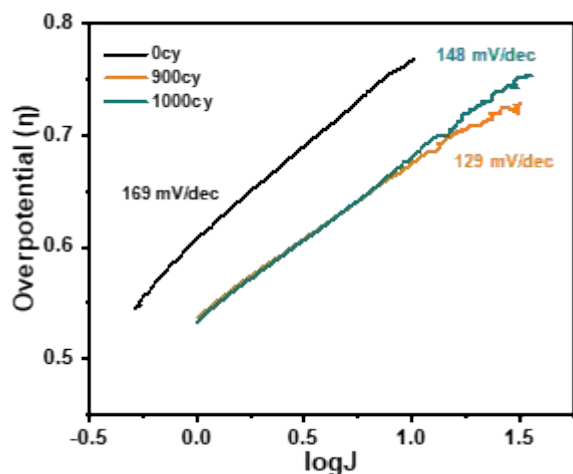


Figure S11. Tafel plot of **3** before reductive cycling (0cy), at peak reductive cycling (900cy), and at 1000 reductive cycles.

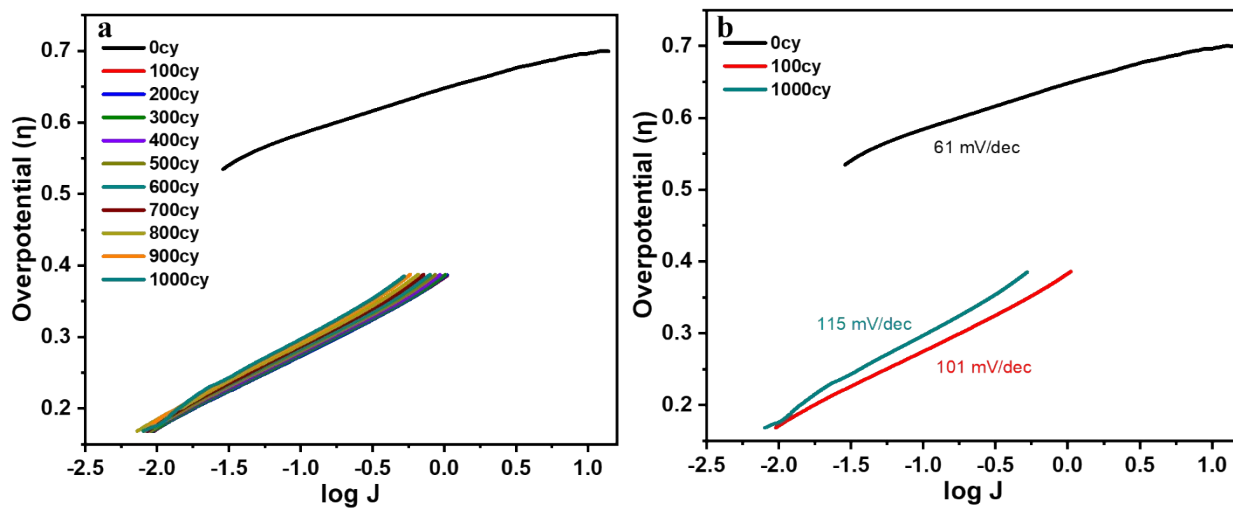


Figure S12. Tafel plot of **4** a) from 0 to 1000 reductive cycles and b) before reductive cycling (0cy), at peak reductive cycling (100cy), and at 1000 reductive cycles.

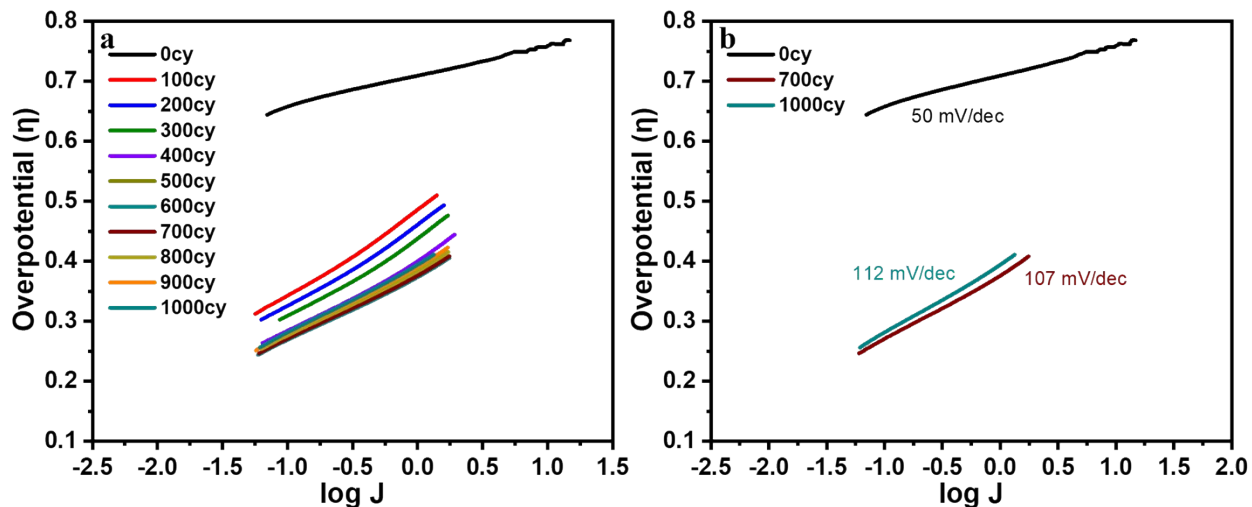


Figure S13. Tafel plot of **5** a) from 0 to 1000 reductive cycles and b) before reductive cycling (0cy), at peak reductive cycling (700cy), and at 1000 reductive cycles.

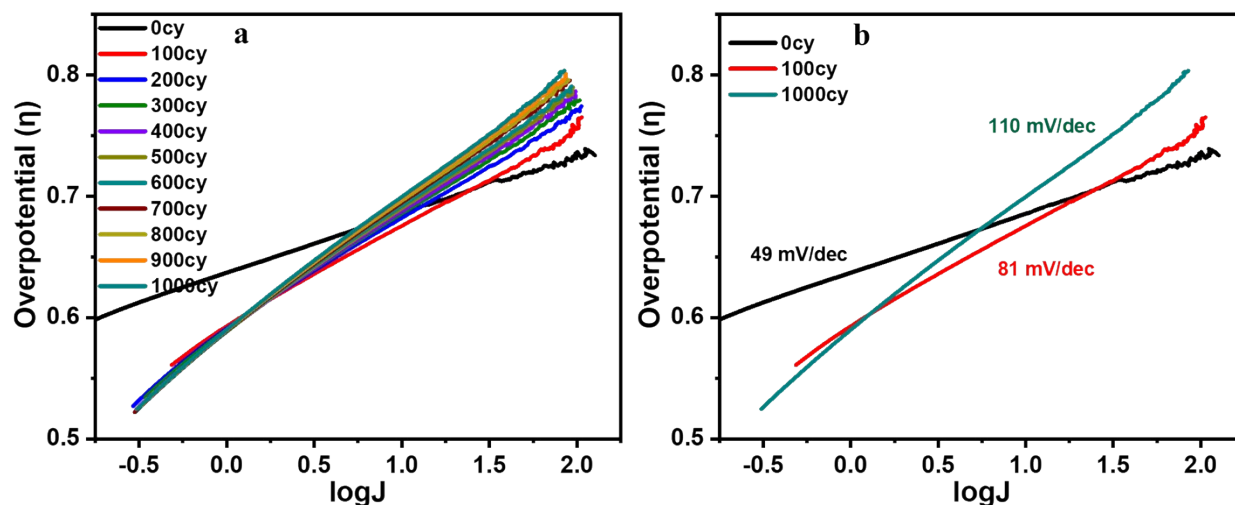


Figure S14. Tafel plot of **6** a) from 0 to 1000 reductive cycles and b) before reductive cycling (0cy), at peak reductive cycling (100cy), and at 1000 reductive cycles.

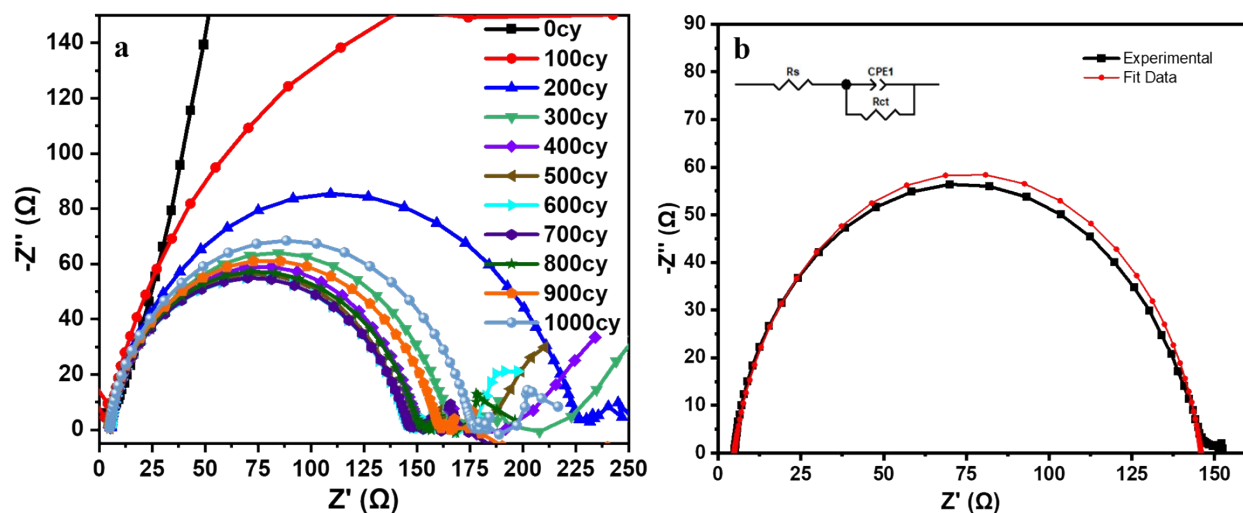


Figure S15. Nyquist Plot of **1** a) from 0 to 1000 reductive cycles and b) after peak reductive cycling with fitted impedance data. Inset: circuit used for fitting.

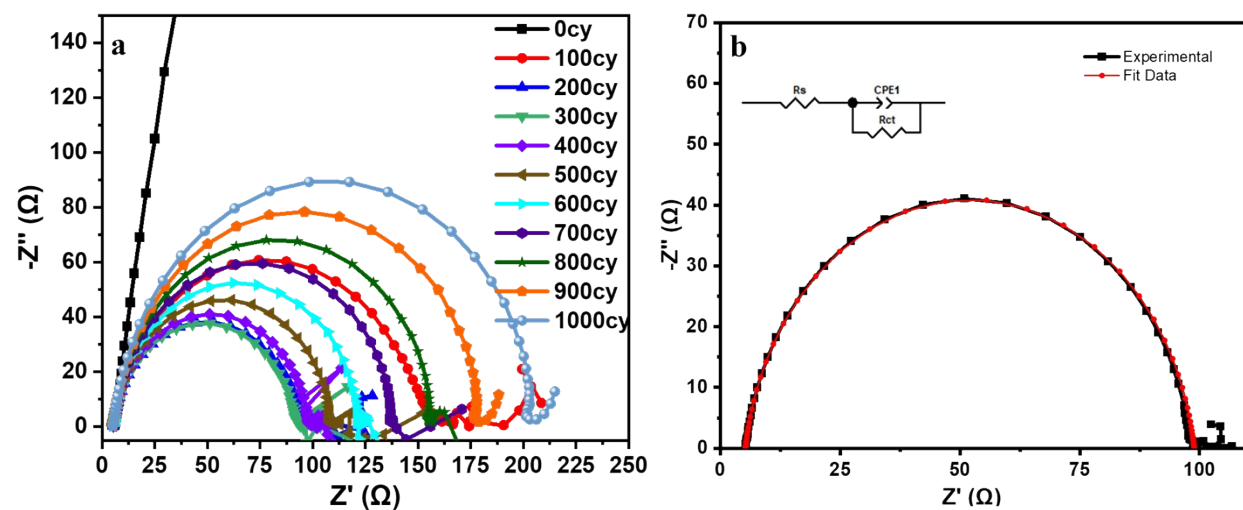


Figure S16. Nyquist Plot of **2** a) from 0 to 1000 reductive cycles and b) after peak reductive cycling with fitted impedance data. Inset: circuit used for fitting.

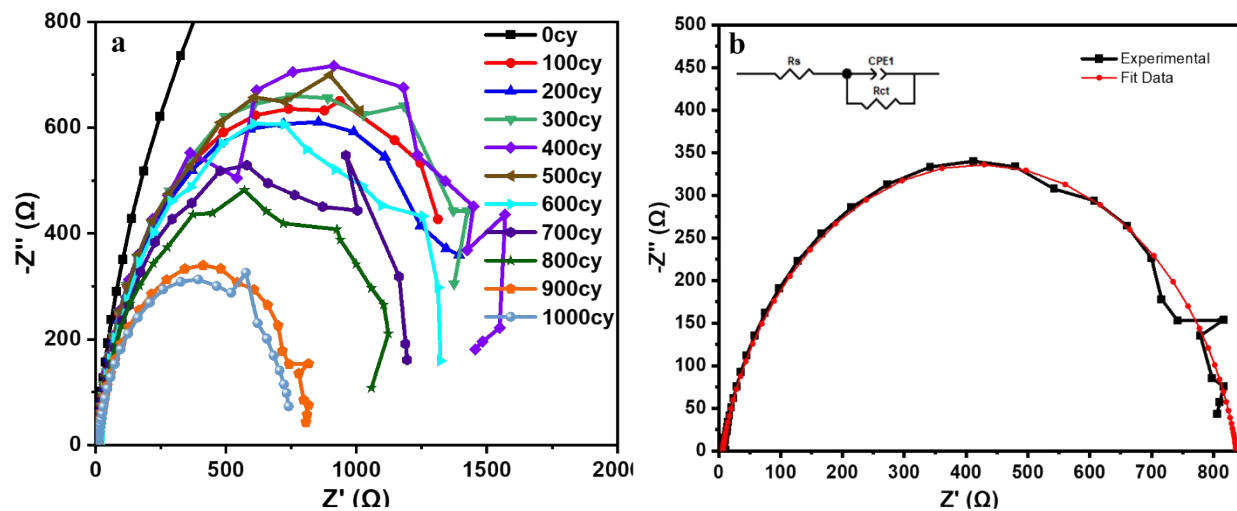


Figure S17. Nyquist Plot of 3 a) from 0 to 1000 reductive cycles and b) after peak reductive cycling with fitted impedance data. Inset: circuit used for fitting.

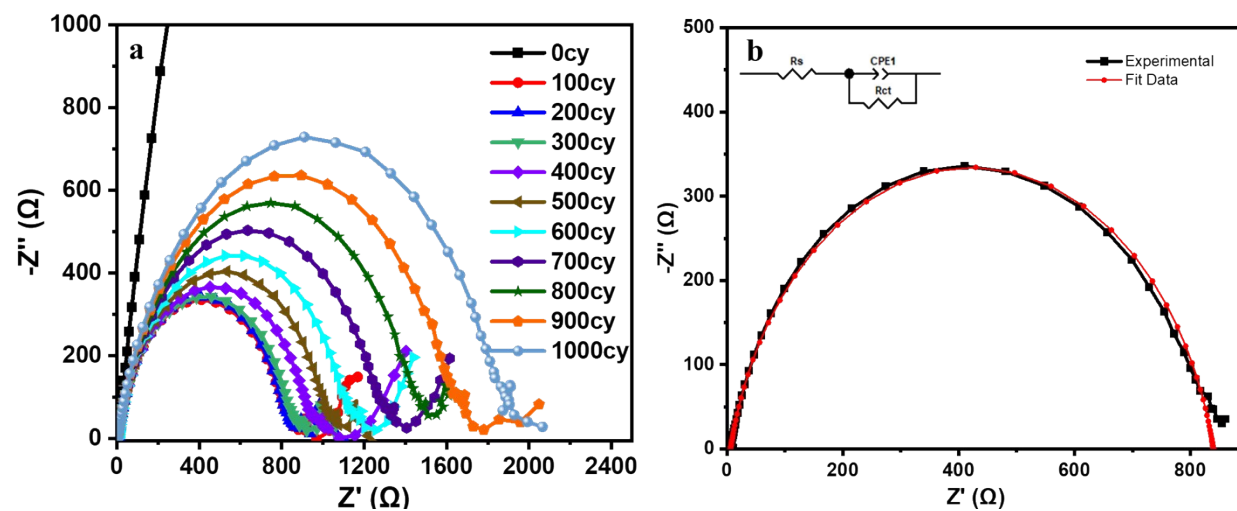


Figure S18. Nyquist Plot of 4 a) from 0 to 1000 reductive cycles and b) after peak reductive cycling with fitted impedance data. Inset: circuit used for fitting.

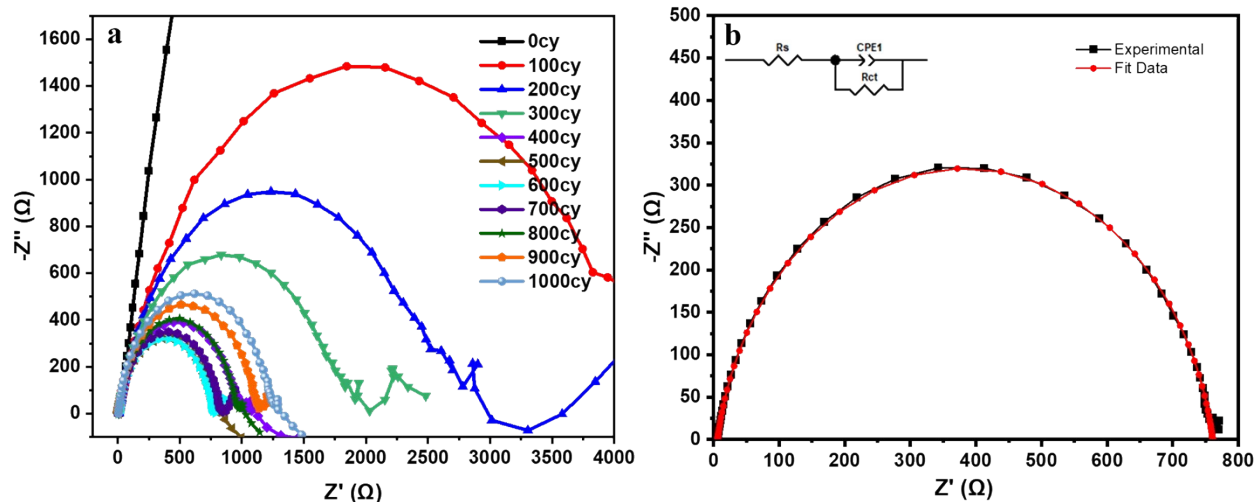


Figure S19. Nyquist Plot of **5** a) from 0 to 1000 reductive cycles and b) after peak reductive cycling with fitted impedance data. Inset: circuit used for fitting.

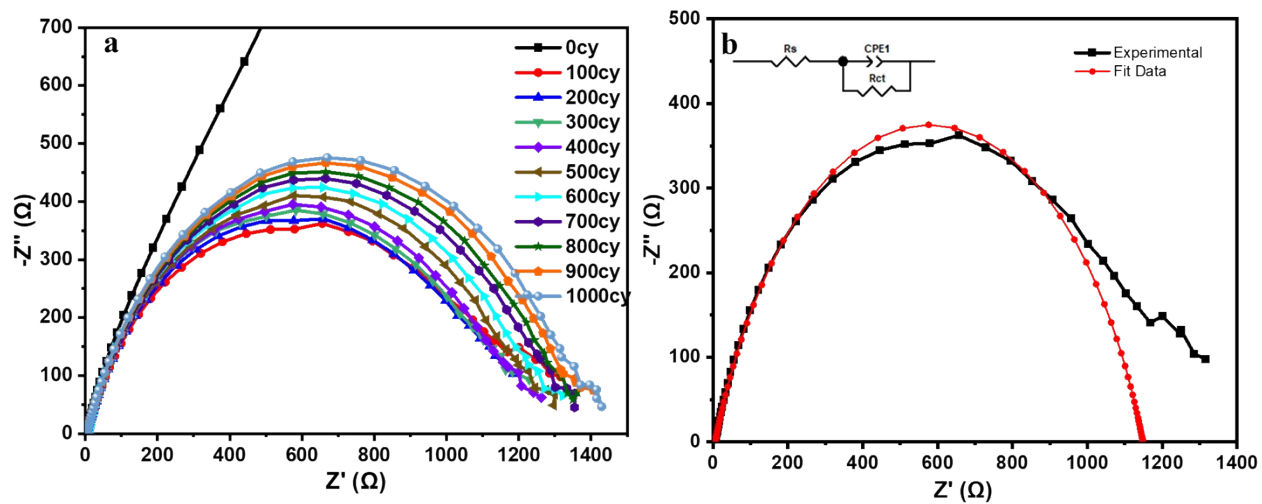


Figure S20. Nyquist Plot of **6** a) from 0 to 1000 reductive cycles and b) after peak reductive cycling with fitted impedance data. Inset: circuit used for fitting.

Table S1. Overpotentials (in mV) for **1 – 6** before reductive cycling, at peak reductive cycling (average of at least five trials with standard deviation), and after 1000 reductive cycles.

Complex	Before reductive cycling	Peak reductive cycling	1000 reductive cycles
1	759	397 ± 0.004	410
2	720	404 ± 0.007	439
3	766	674 ± 0.027	682
4	697	522 ± 0.003	599
5	757	518 ± 0.002	547
6	686	685 ± 0.010	698

Table S2. Tafel slope (in mV/dec.) for **1 – 6** before reductive cycling), at peak reductive cycling, and after 1000 reductive cycles.

Complex	Before reductive cycling	Peak reductive cycling	1000 reductive cycles
1	77	91	90
2	70	100	88
3	169	129	148
4	61	101	115
5	50	107	112
6	49	81	110

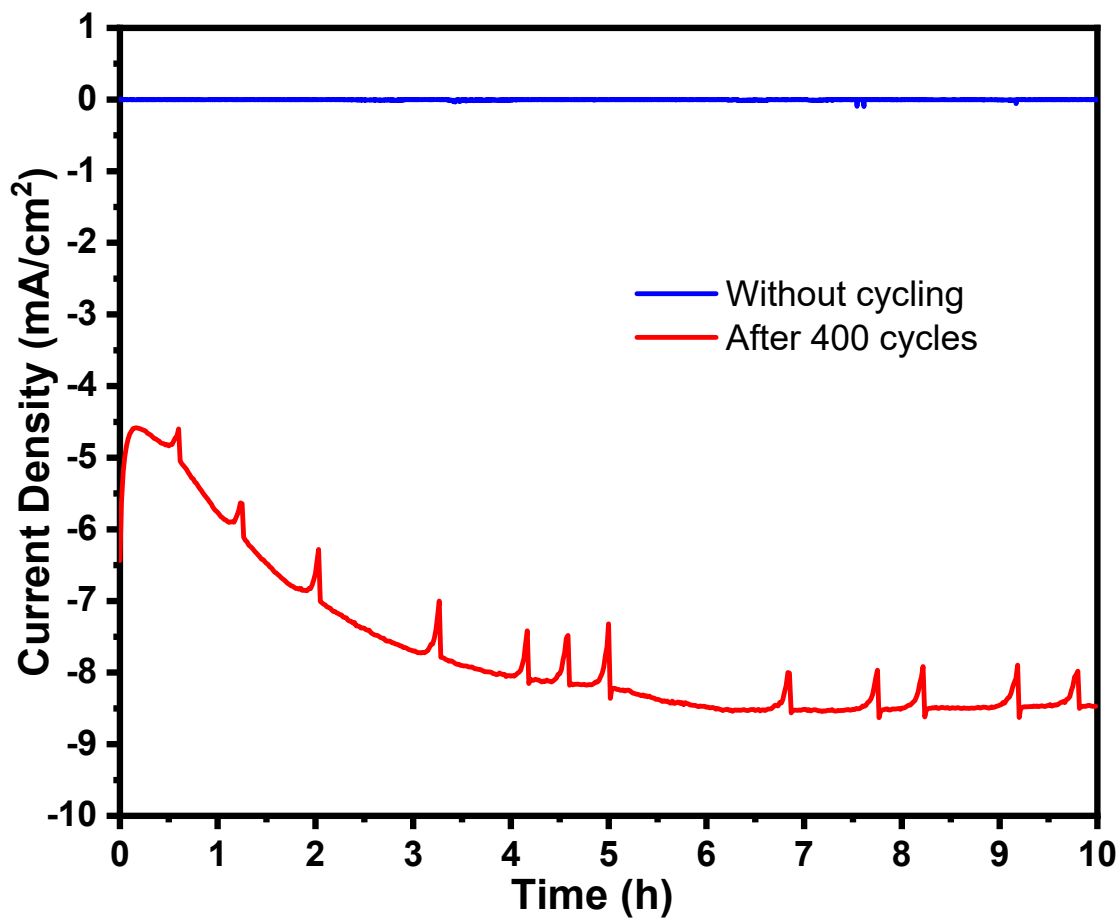


Figure S21. Chronoamperometry of **2** at a constant potential of -0.40 V without reductive cycling and after 400 reductive cycles.

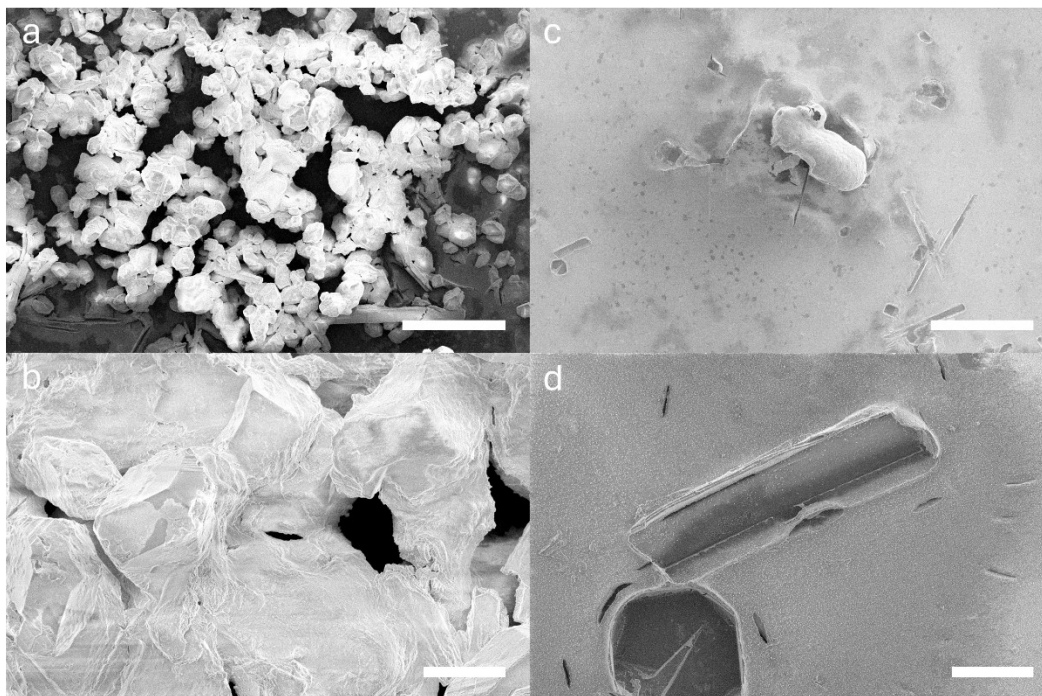


Figure S22. SEM image of **1** a,b) as drop cast on GCE c) and c,d) after 1000 reductive cycles. Scale bars correspond to 100 μm (a,c) or 5 μm (b,d).

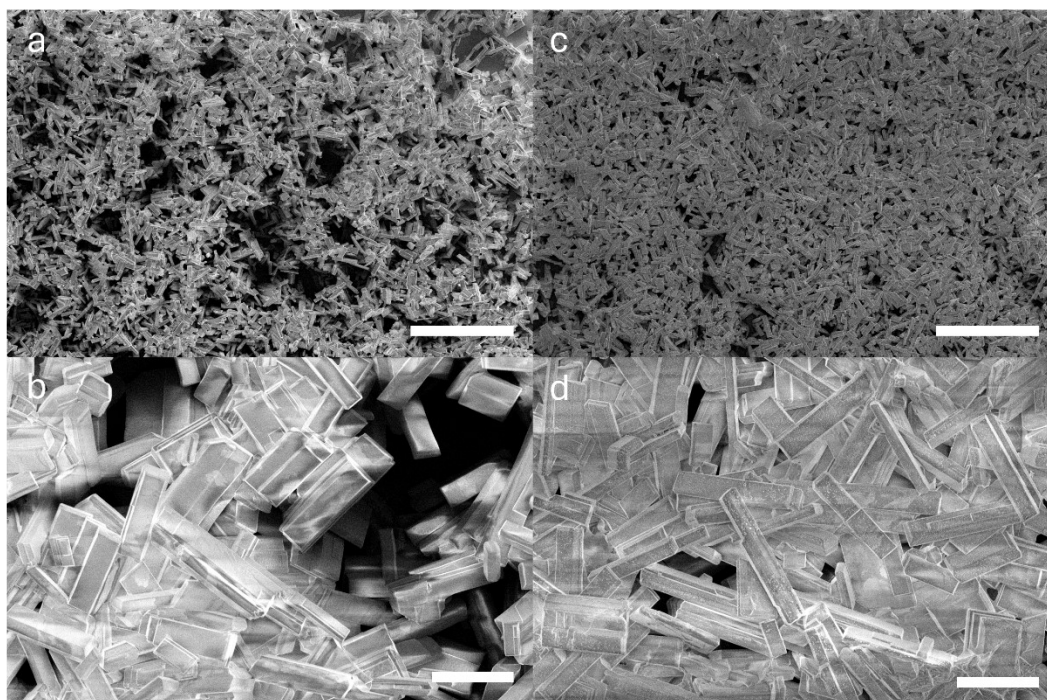


Figure S23. SEM image of **3** a,b) as drop cast on GCE c) and c,d) after 1000 reductive cycles. Scale bars correspond to 100 μm (a,c) or 5 μm (b,d).

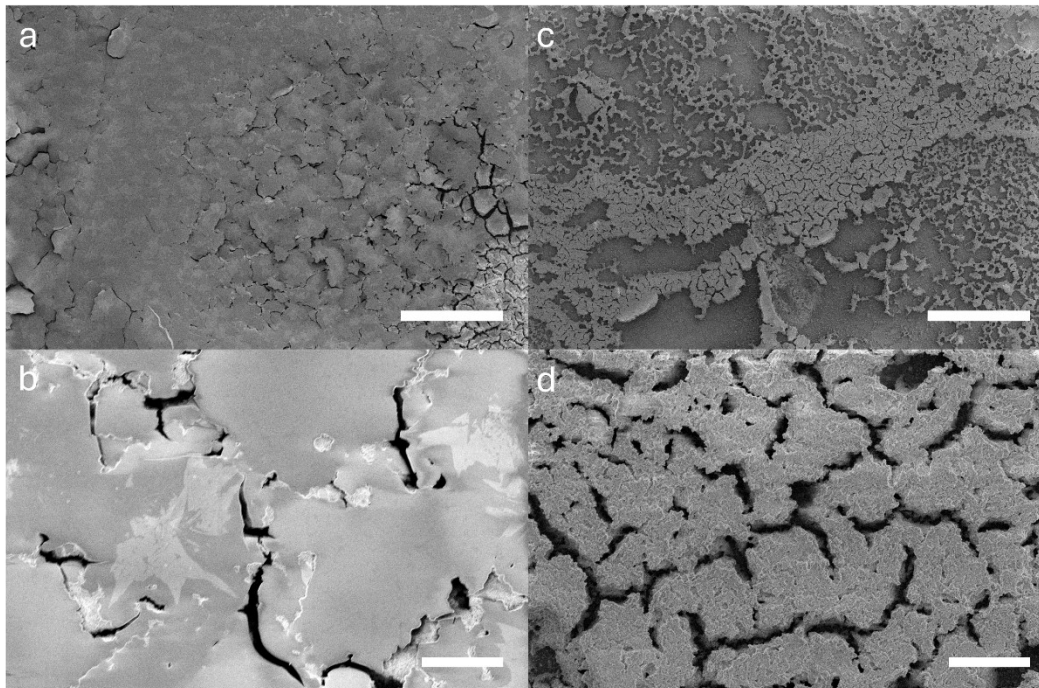


Figure S24. SEM image of **4** a,b) as drop cast on GCE c) and c,d) after 1000 reductive cycles. Scale bars correspond to 100 μm (a,c) or 5 μm (b,d).

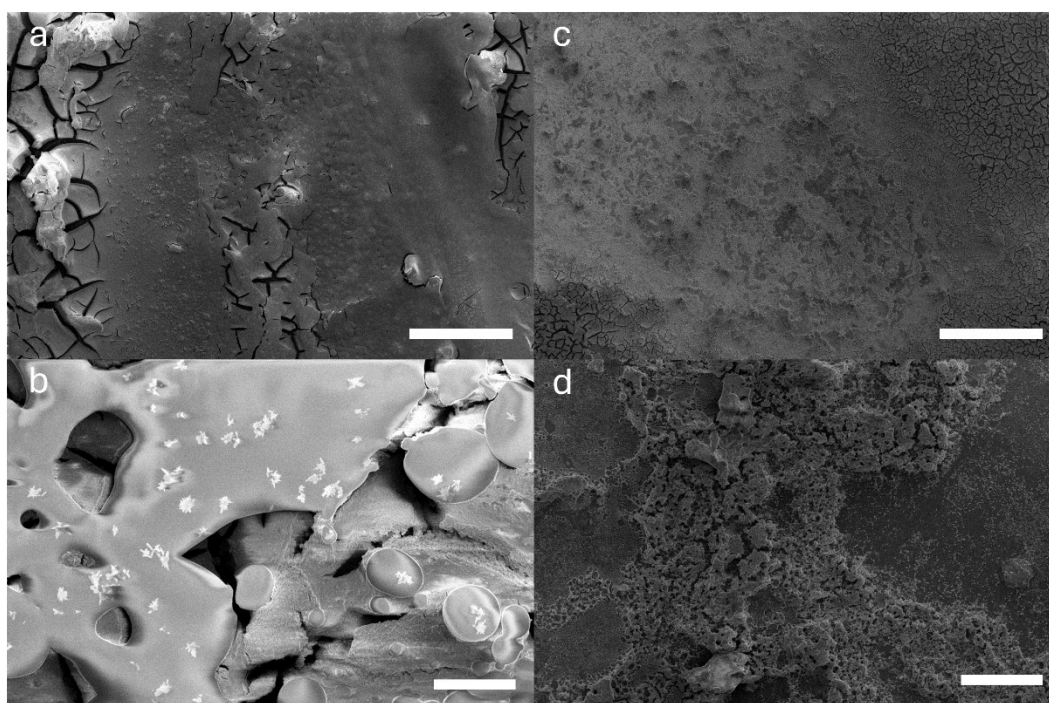


Figure S25. SEM image of **5** a,b) as drop cast on GCE c) and c,d) after 1000 reductive cycles. Scale bars correspond to 100 μm (a,c) or 5 μm (b,d).

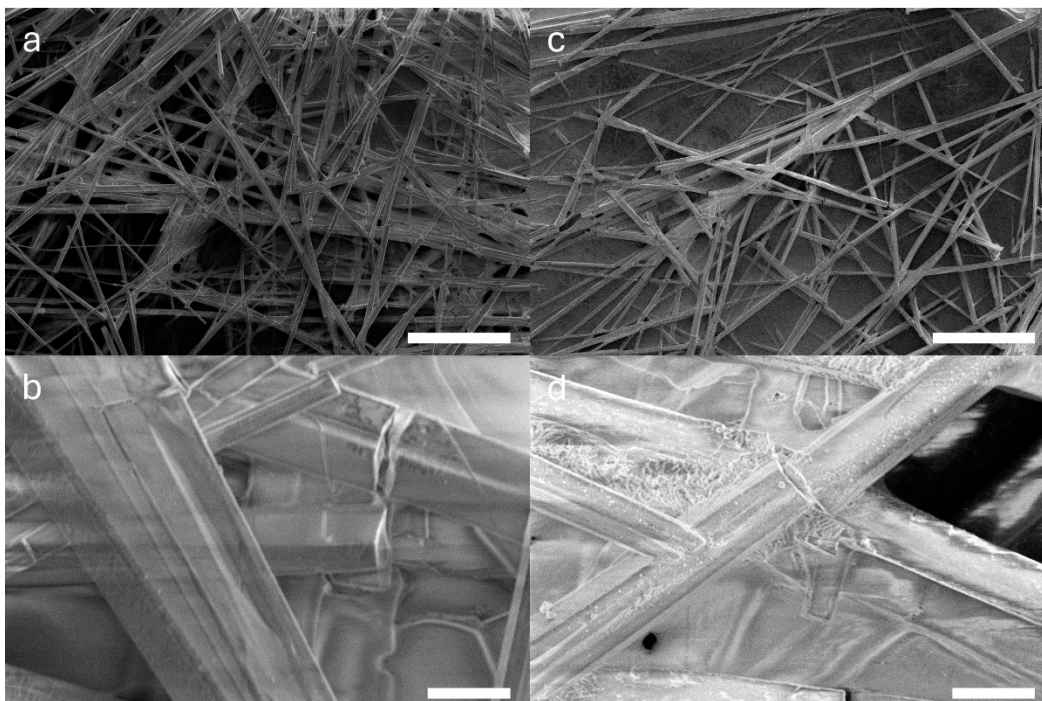


Figure S26. SEM image of **6** a,b) as drop cast on GCE c) and c,d) after 1000 reductive cycles. Scale bars correspond to 100 μm (a,c) or 5 μm (b,d).

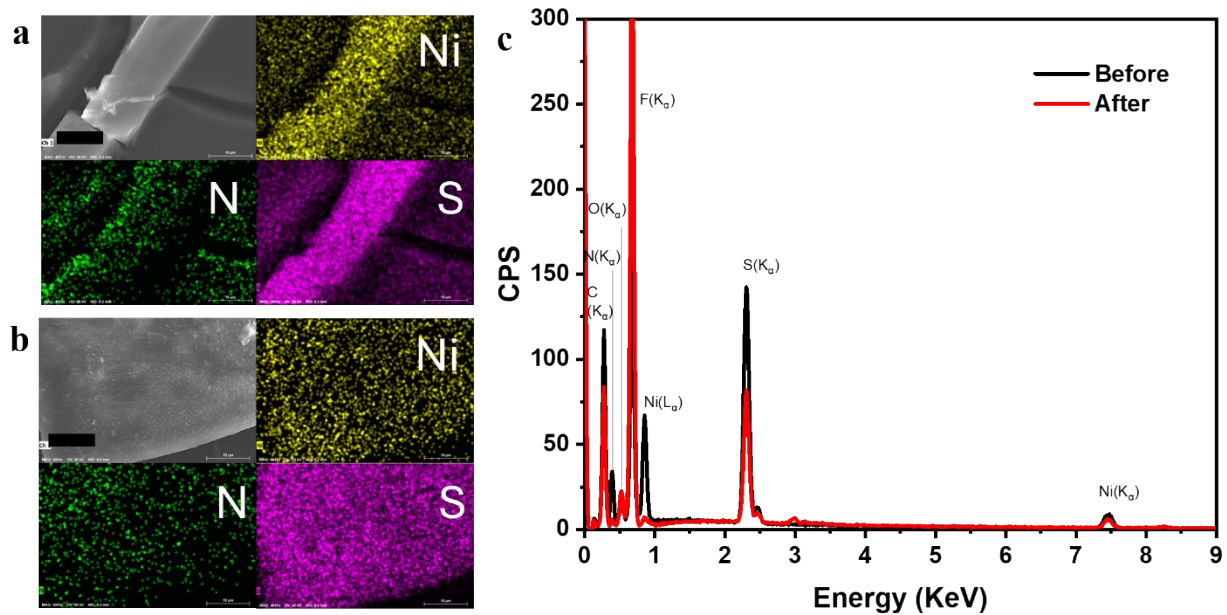


Figure S27. Elemental mapping of **1** a) as drop cast on GCE, showing SEM image (grayscale), nickel (yellow), nitrogen (green) and sulfur (pink) as labeled on top of each image and b) after 1000 reductive cycles. Scale bars at the bottom of SEM image correspond to 10 μm . c) Comparative elemental plot for before and after 1000 reductive cycles.

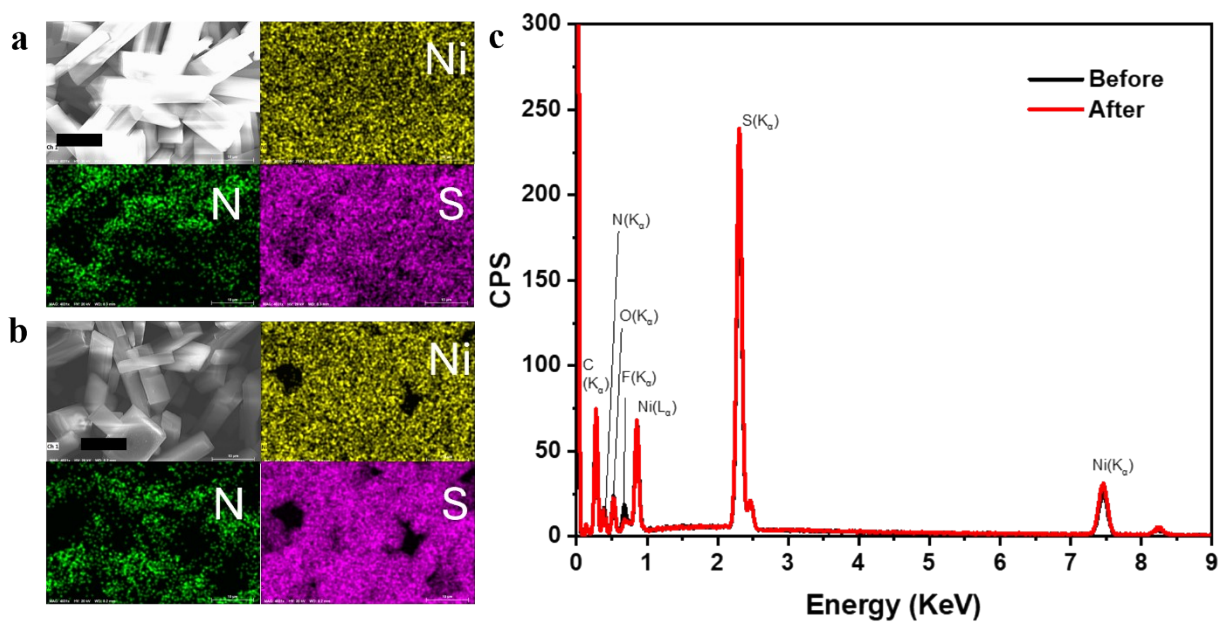


Figure S28. Elemental mapping of **3 a**) as drop cast on GCE, showing SEM image (grayscale), nickel (yellow), nitrogen (green) and sulfur (pink) as labeled on top of each image and **b**) after 1000 reductive cycles. Scale bars at the bottom of SEM image correspond to 10 μm. **c**) Comparative elemental plot for before and after 1000 reductive cycles.

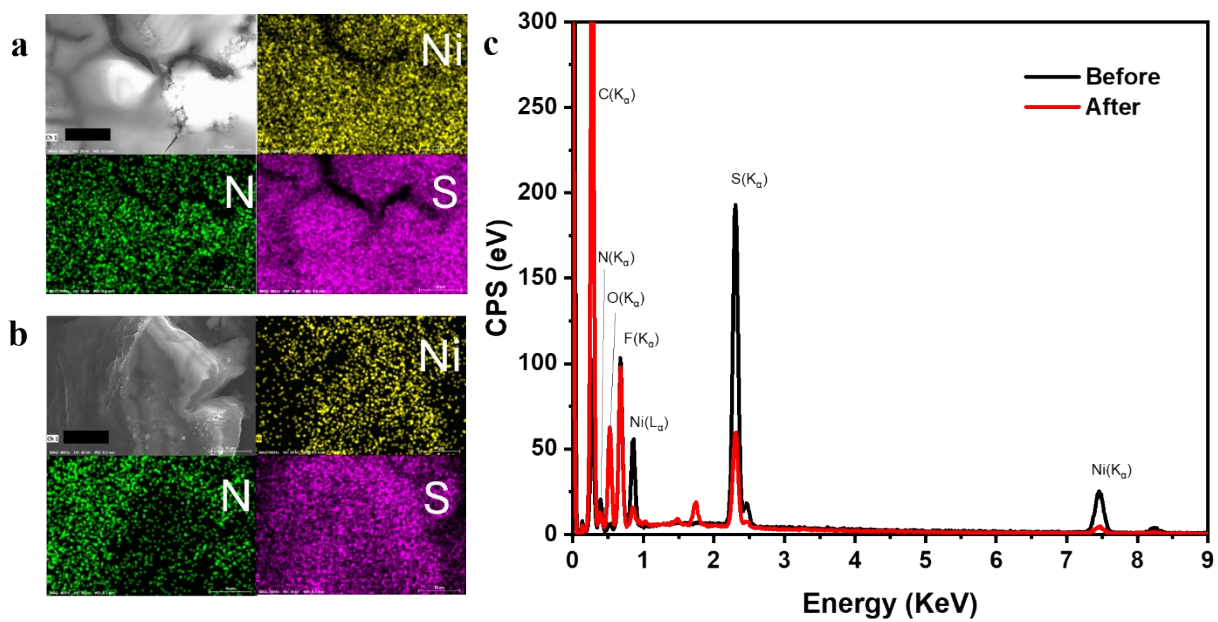


Figure S29. Elemental mapping of 4 a) as drop cast on GCE, showing SEM image (grayscale), nickel (yellow), nitrogen (green) and sulfur (pink) as labeled on top of each image and b) after 1000 reductive cycles. Scale bars at the bottom of SEM image correspond to 10 μm . c) Comparative elemental plot for before and after 1000 reductive cycles.

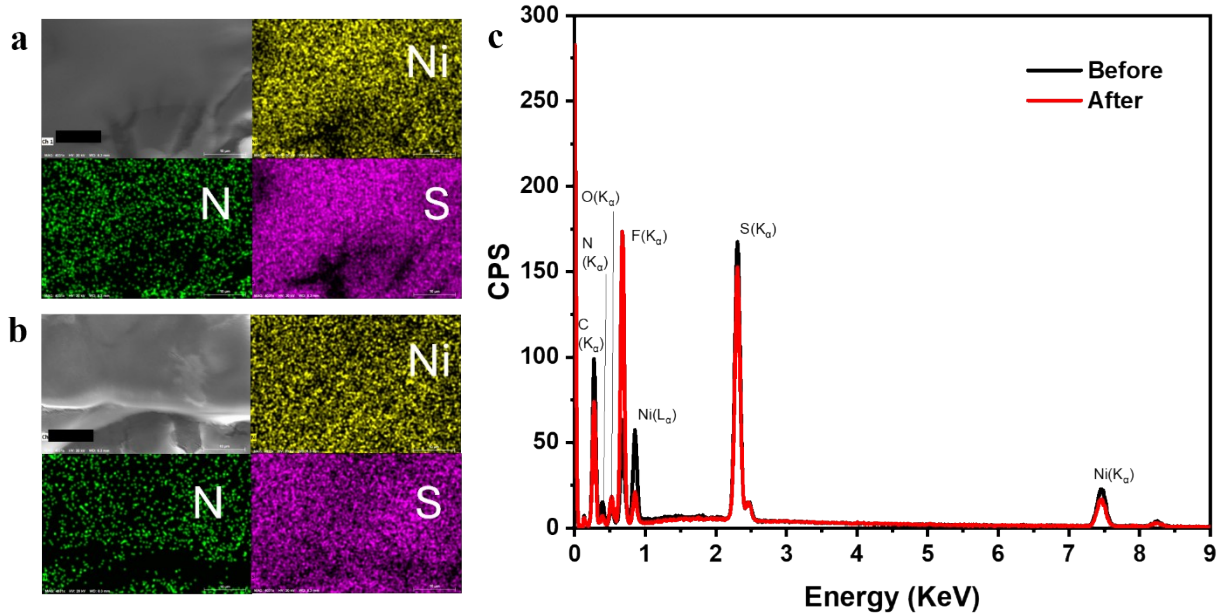


Figure S30. Elemental mapping of **5** a) as drop cast on GCE, showing SEM image (grayscale), nickel (yellow), nitrogen (green) and sulfur (pink) as labeled on top of each image and b) after 1000 reductive cycles. Scale bars at the bottom of SEM image correspond to 10 μm . c) Comparative elemental plot for before and after 1000 reductive cycles.

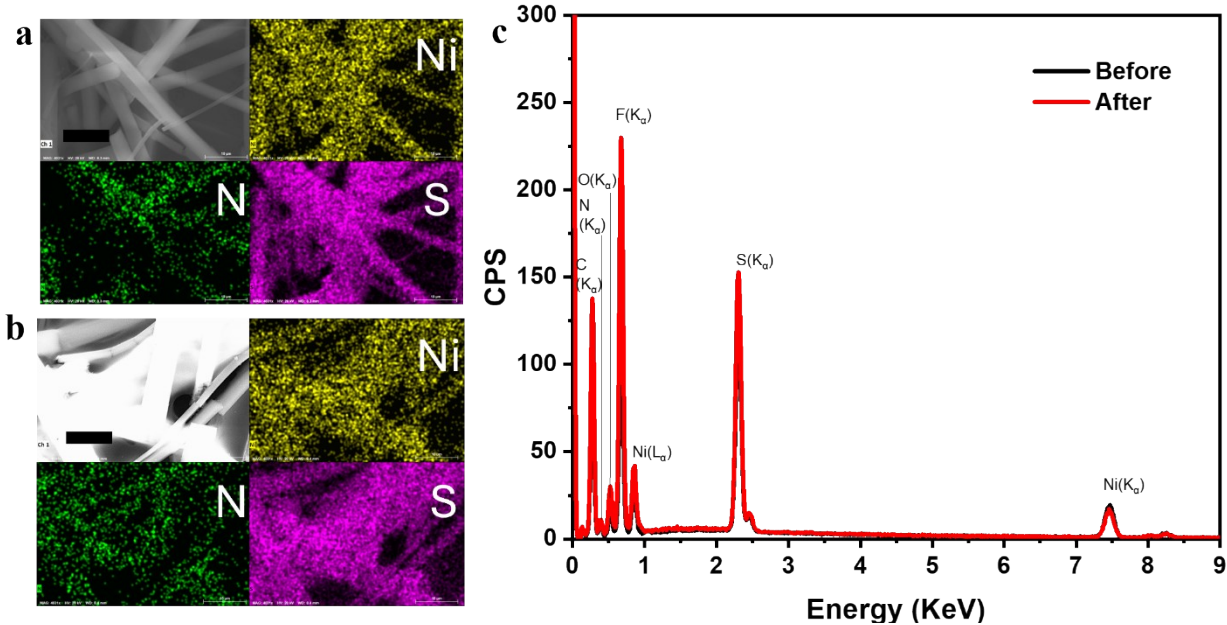


Figure S31. Elemental mapping of **6 a**) as drop cast on GCE, showing SEM image (grayscale), nickel (yellow), nitrogen (green) and sulfur (pink) as labeled on top of each image and **b**) after 1000 reductive cycles. Scale bars at the bottom of SEM image correspond to 10 μm. **c**) Comparative elemental plot for before and after 1000 reductive cycles.

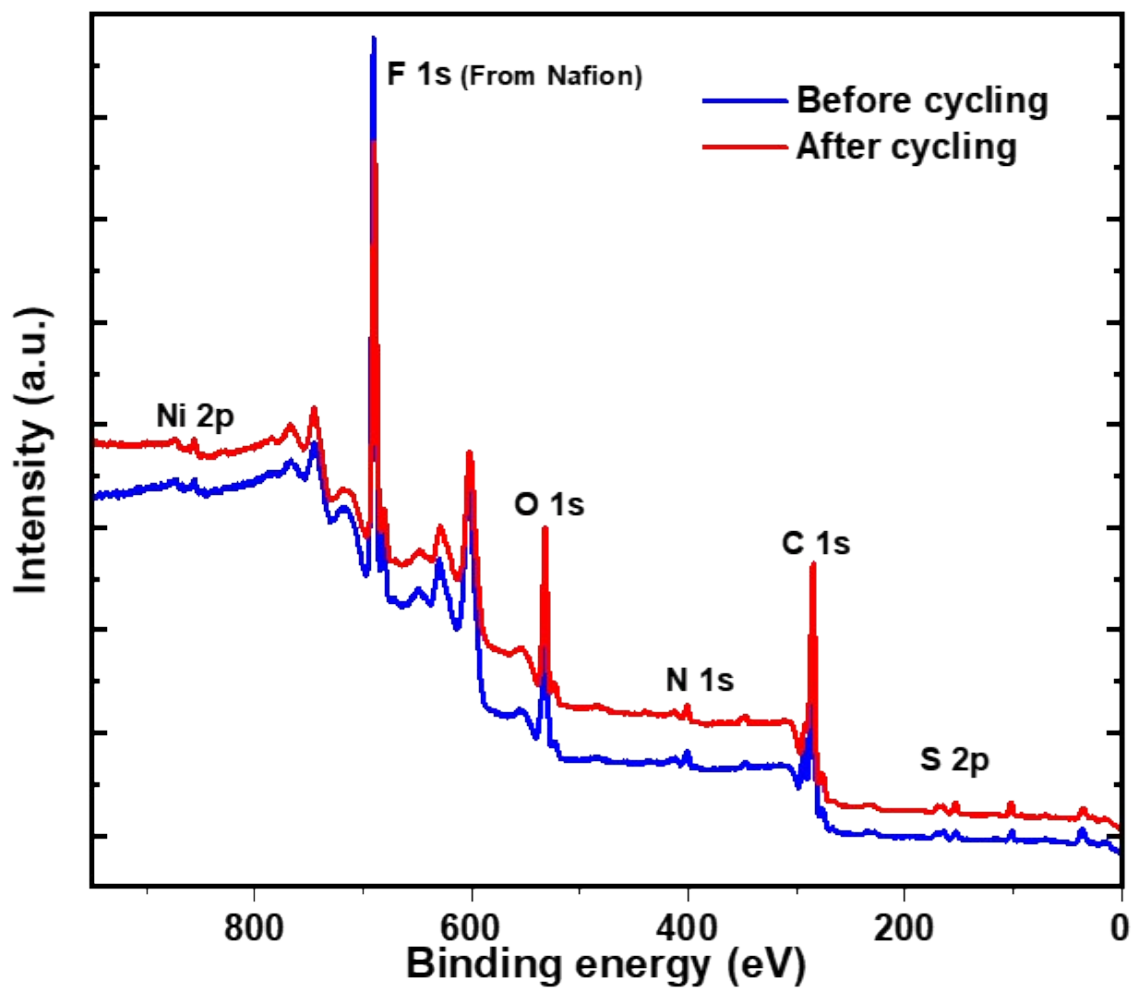


Figure S32. XPS survey scan of **2** before and after 1000 reductive cycles.

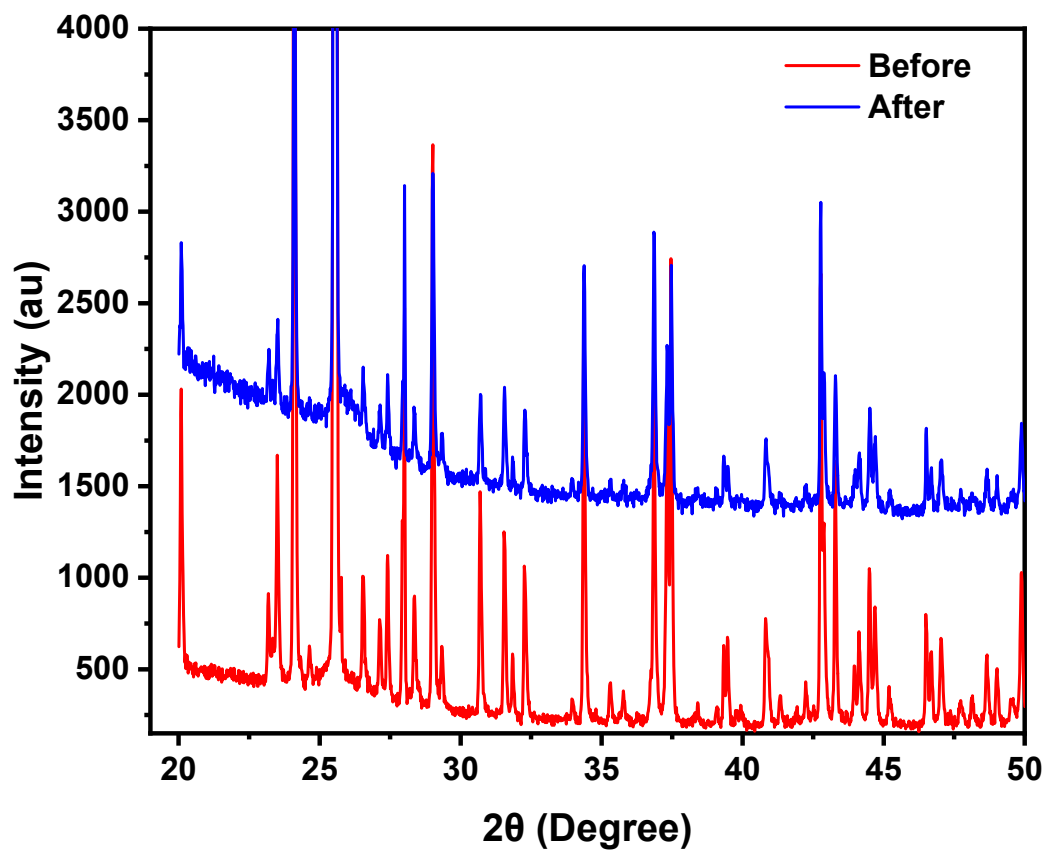


Figure S33. XRD pattern of **1** before and after 1000 reductive cycles.

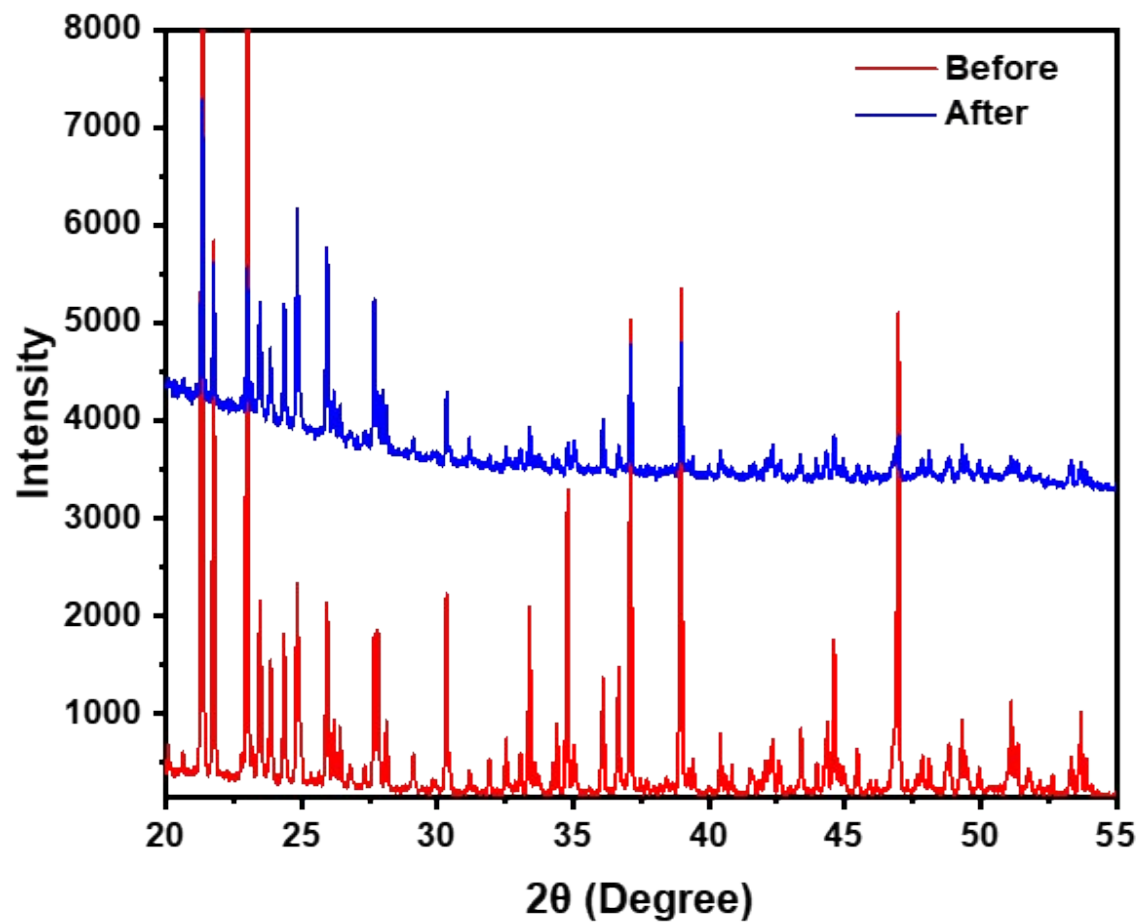


Figure S34. XRD pattern of **2** before and after 1000 reductive cycles.

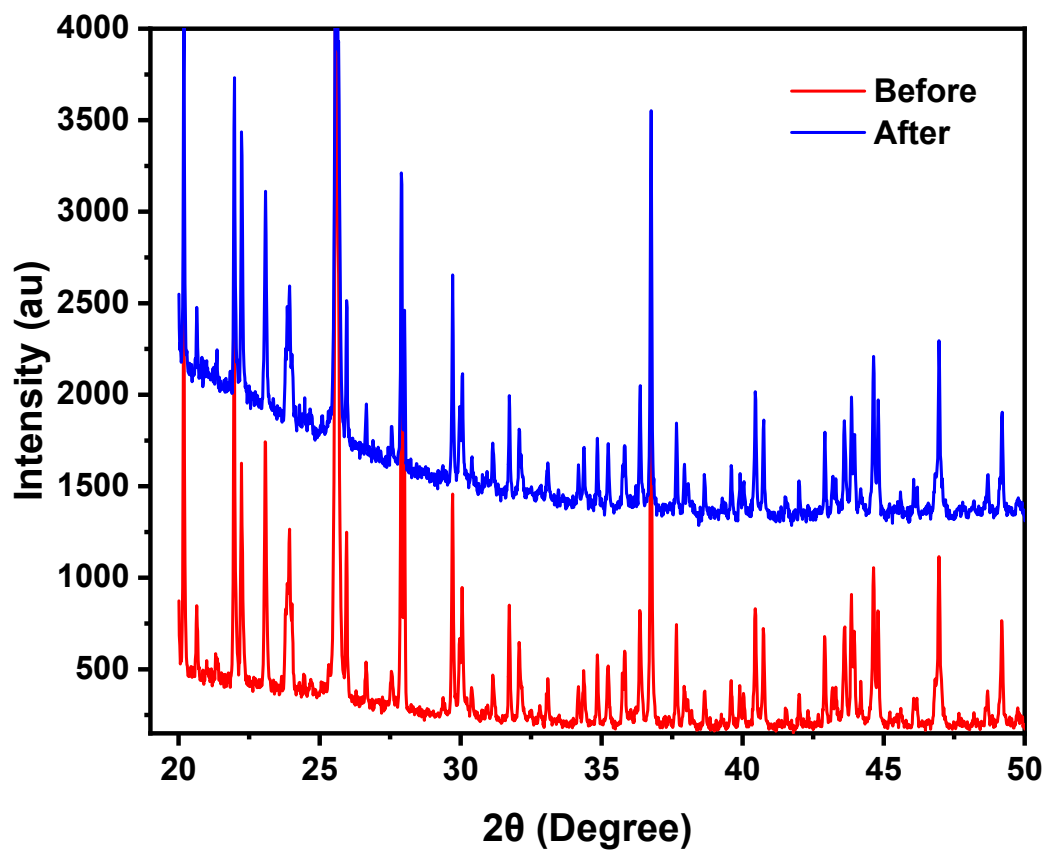


Figure S35. XRD pattern of 3 before and after 1000 reductive cycles.

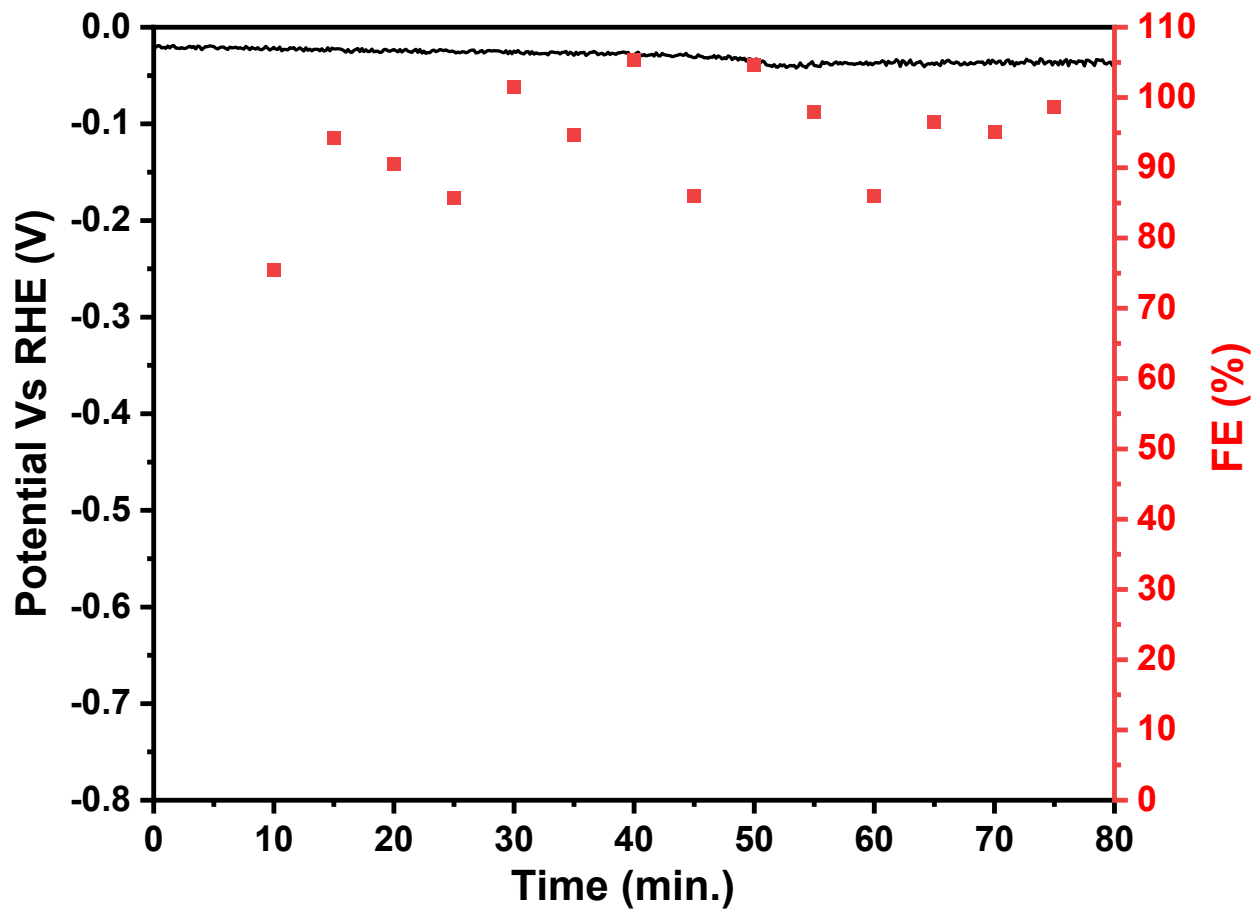


Figure S36. Chronopotentiometry at a constant current of -10 mA/cm^2 for 75 minutes and respective FE measurement for **40% Pt/C**.

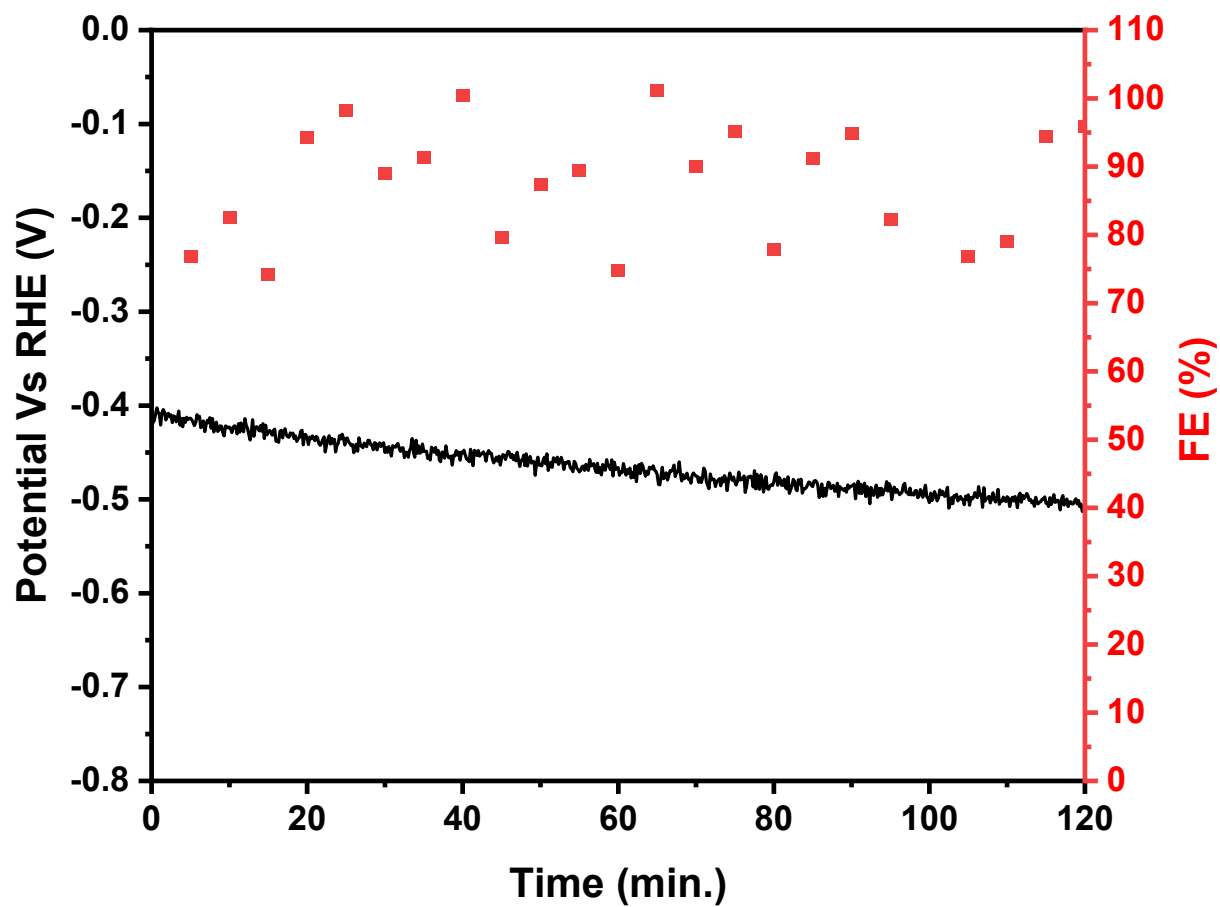


Figure S37. Chronopotentiometry at a constant current of -10 mA/cm^2 for 120 minutes and respective FE measurement for **1**.

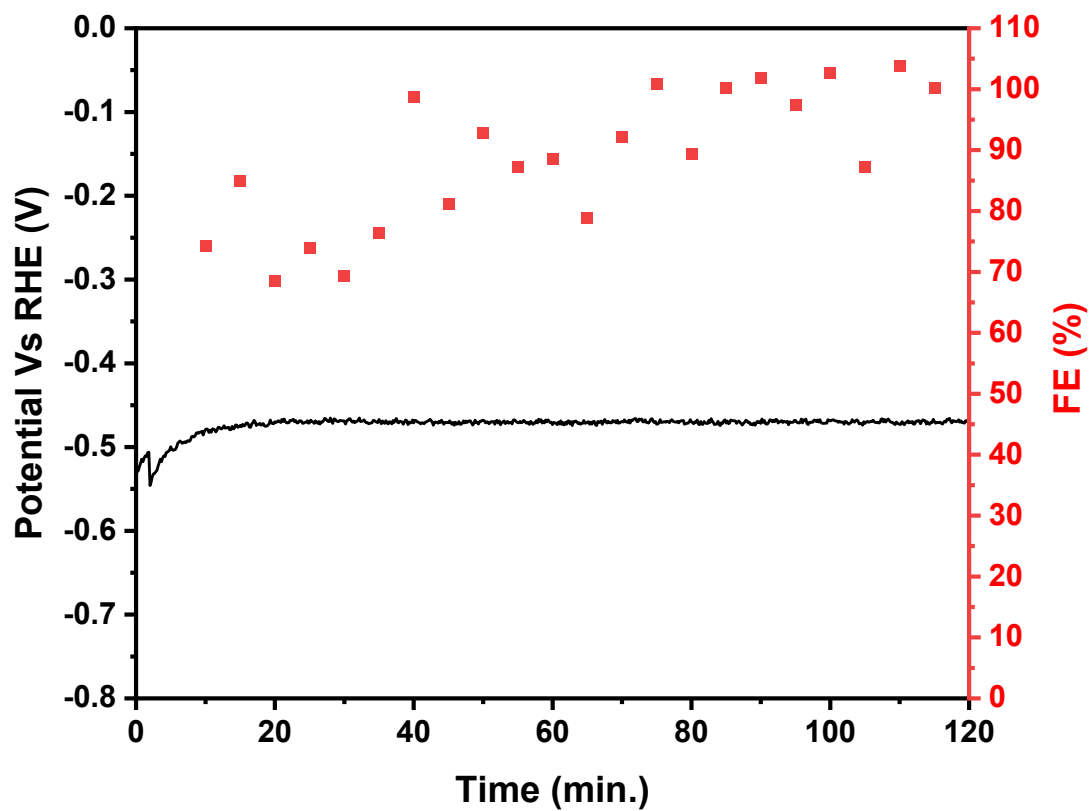


Figure S38. Chronopotentiometry at a constant current of -10 mA/cm^2 for 120 minutes and respective FE measurement for **2**.

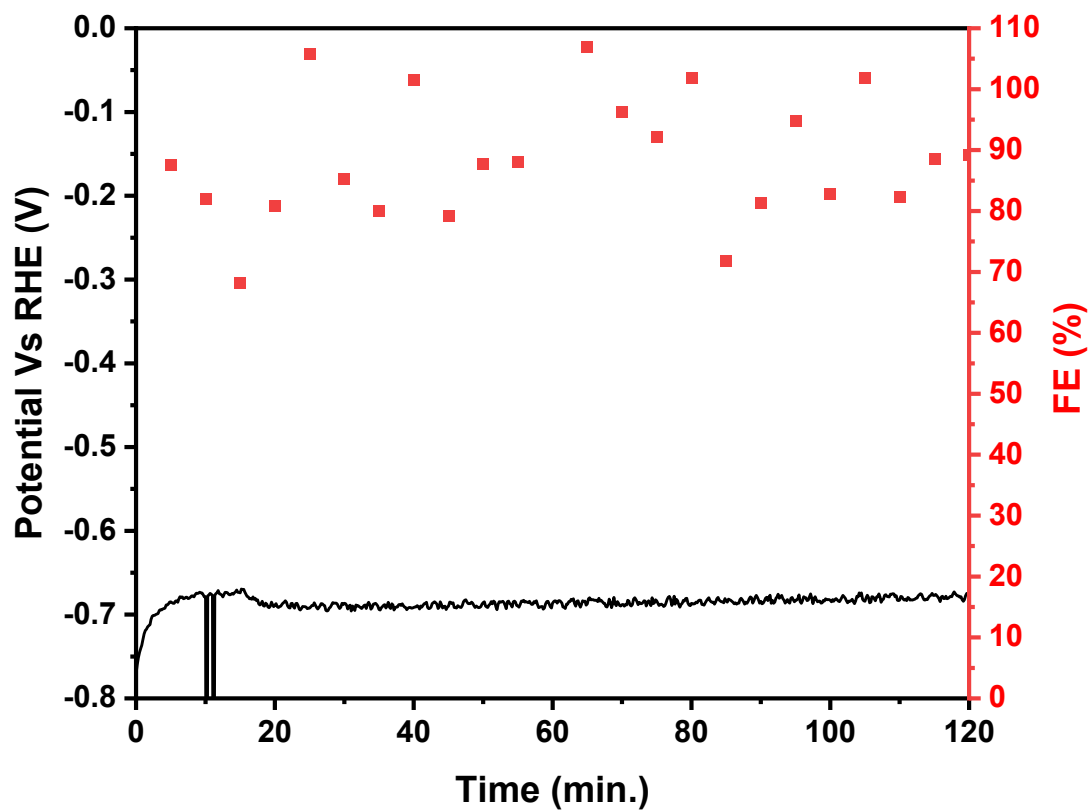


Figure S39 Chronopotentiometry at a constant current of -10 mA/cm^2 for 120 minutes and respective FE measurement for 3.

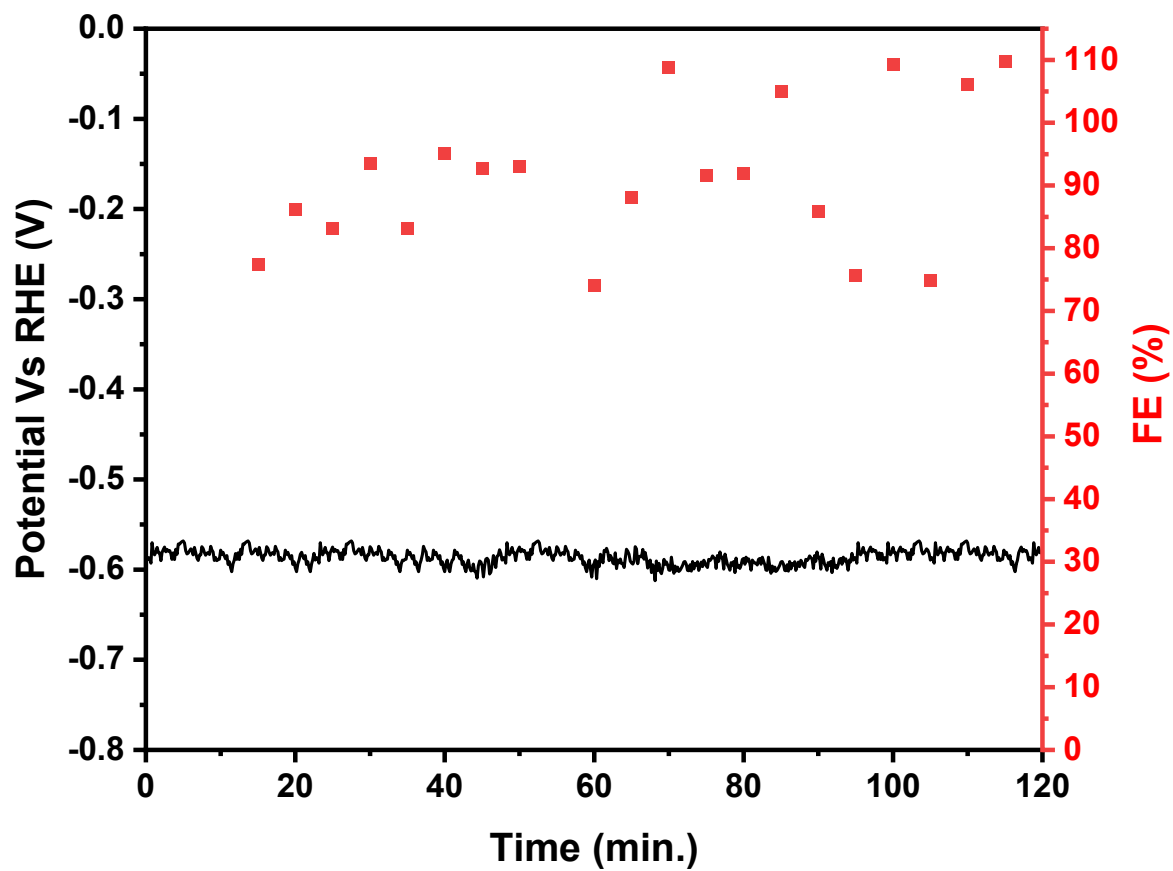


Figure S40. Chronopotentiometry at a constant current of -10 mA/cm^2 for 120 minutes and respective FE measurement for 4.

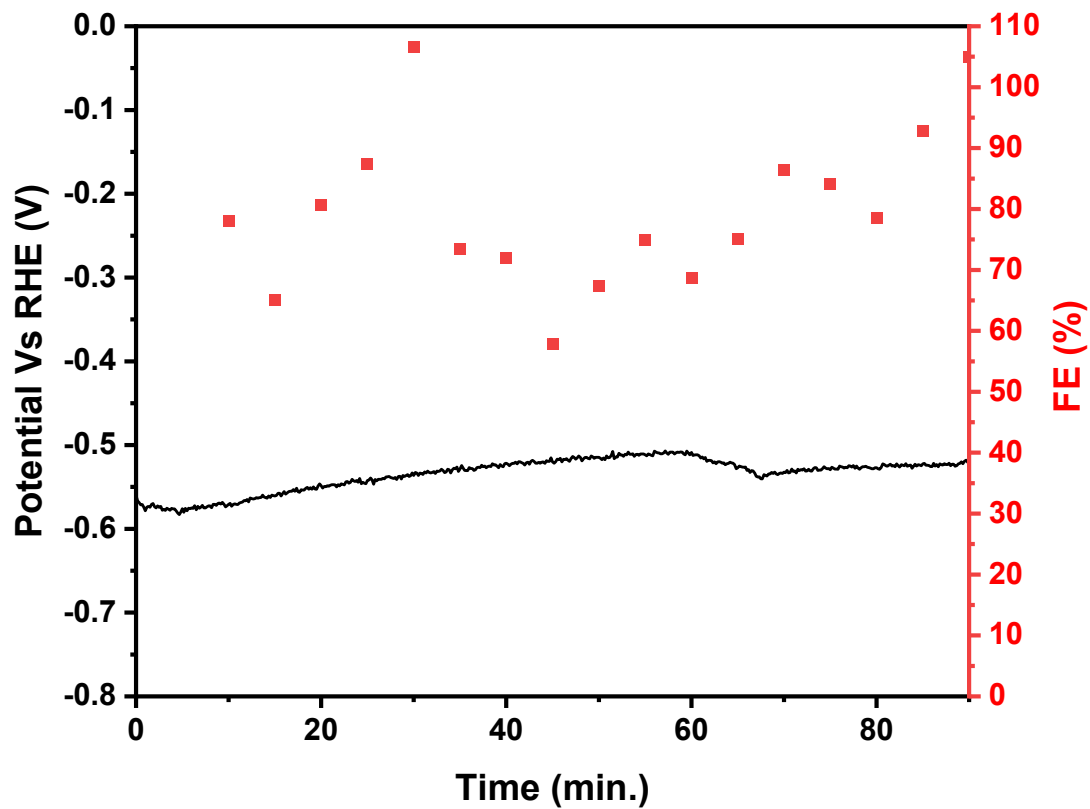


Figure S41. Chronopotentiometry at a constant current of -10 mA/cm^2 for 120 minutes and respective FE measurement for 5.

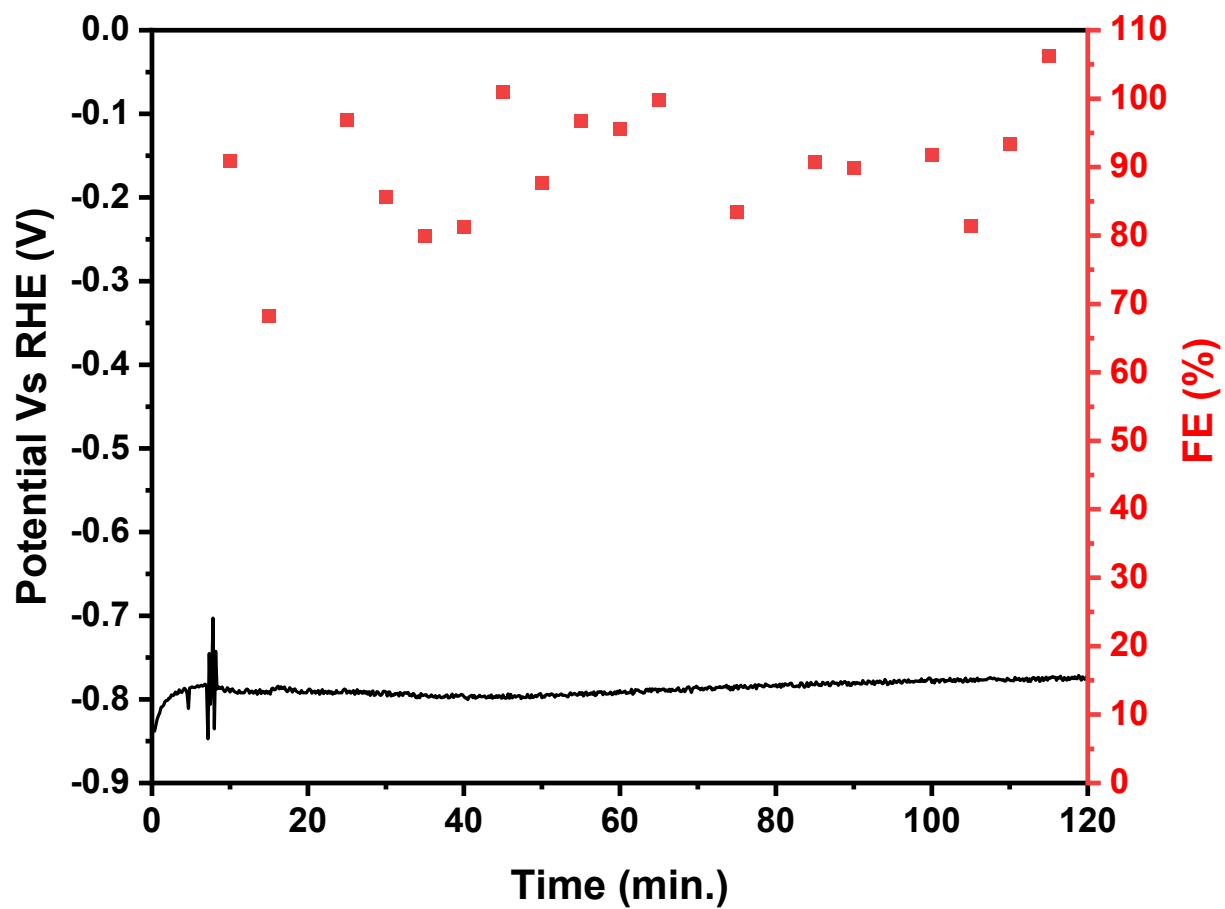


Figure S42. Chronopotentiometry at a constant current of -10 mA/cm^2 for 120 minutes and respective FE measurement for **6**.