Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Manganese-Cobalt Oxide as Effective Bifunctional Cathode for Rechargeable Zn-Air Battery with a Compact Quad-Cell Battery Design

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Figure S1 (a)

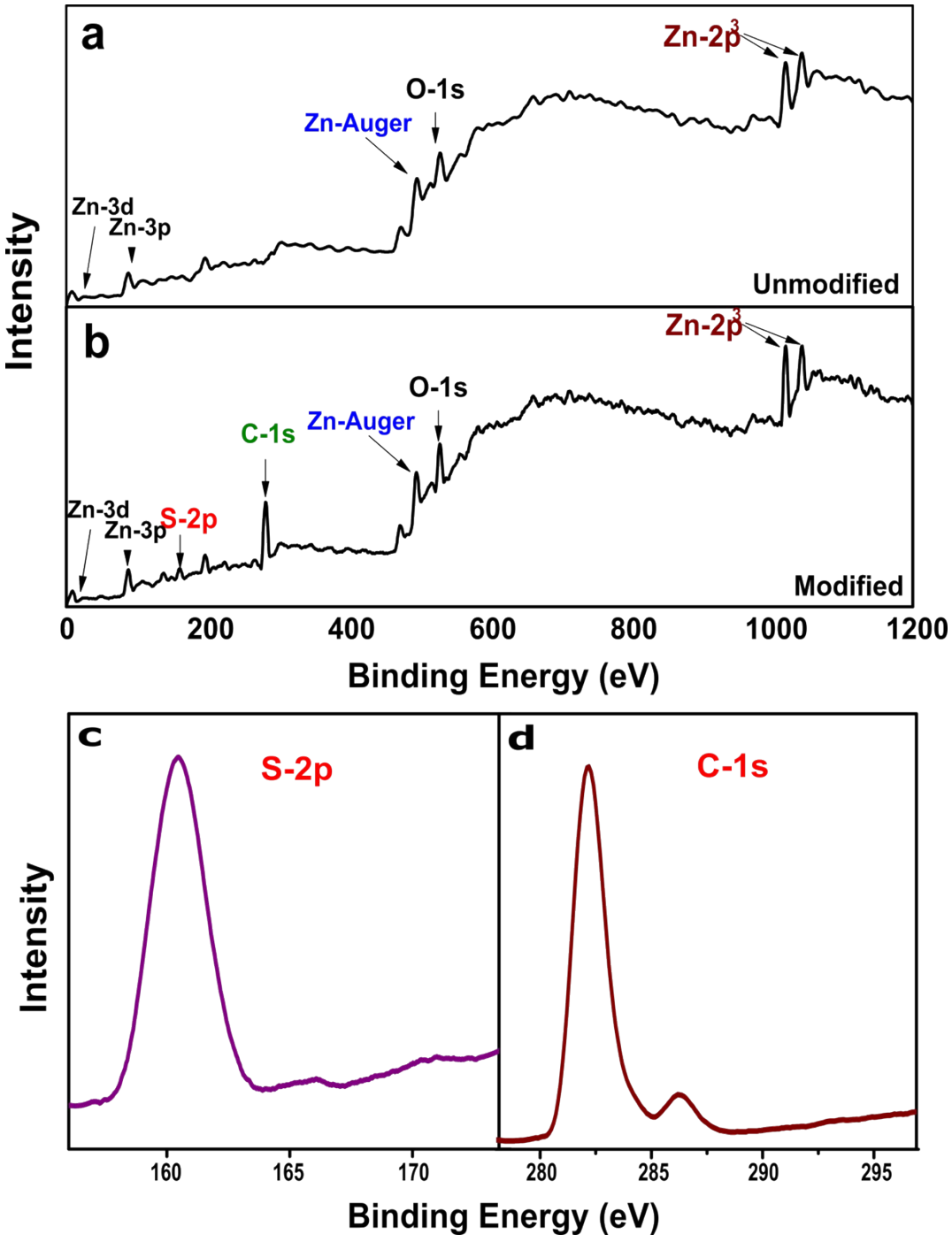


Figure S1a : Molecularly modified surface characterization results: **a)** full survey XPS spectrum of MPA treated Zn substrate prior to electrodeposition, **b)** unmodified zinc, **c)** and **d)** are high resolution XPS core spectra of S-2p and C-1s, respectively

Figure S1 (b)

FESEM images of unmodified and modified Zn are depicted in Figure S1. Clearly, the changes in surface structure of MPA-modified Zn can be observed compared to unmodified planar Zn.

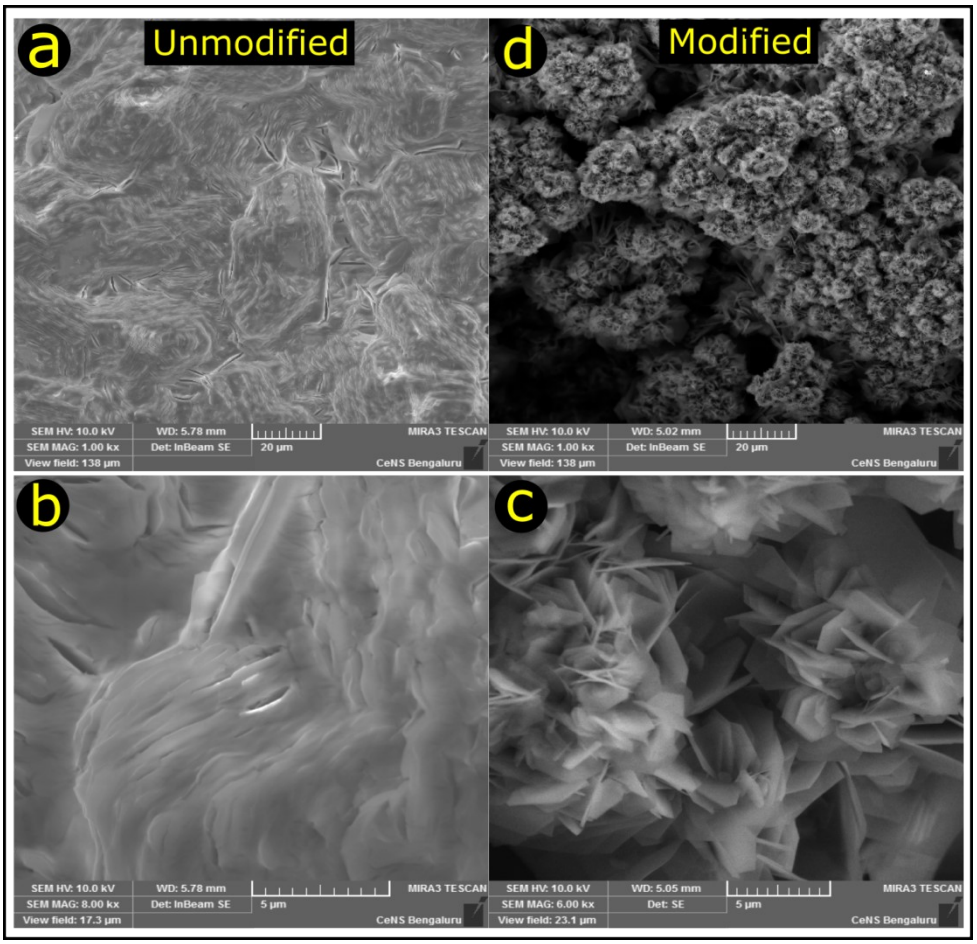


Figure S1b: FESEM images of electrodeposited zinc on unmodified Zn substrate [(a, b) low and high magnification, respectively], and modified Zn [(c, d) low and high magnification, respectively].

Figure S2

Electrochemical performance comparison data of Zn-Air battery assembled before and after zinc plate modification is shown below. The cycle stability of battery is examined by using a 'test-cathode'. Clearly, the modified Zn outperforms the unmodified planar Zn anode which is the basis for using modified anode opposite to bimetallic oxide air cathode catalyst in the present study.

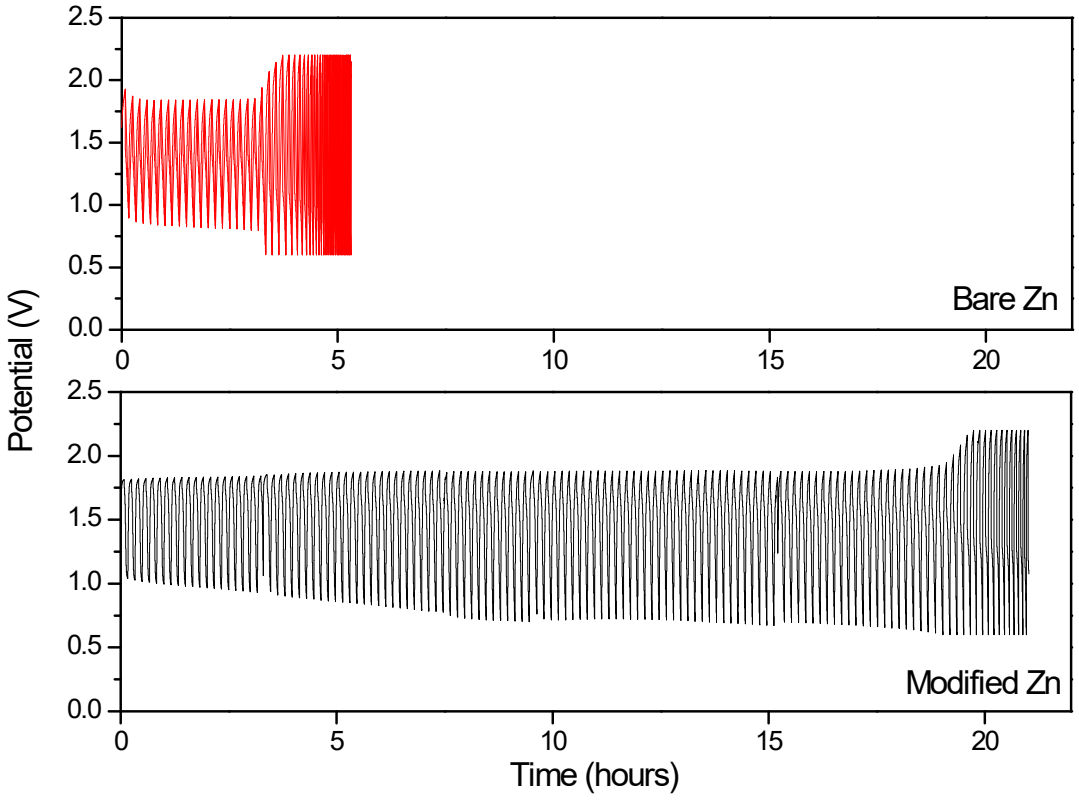
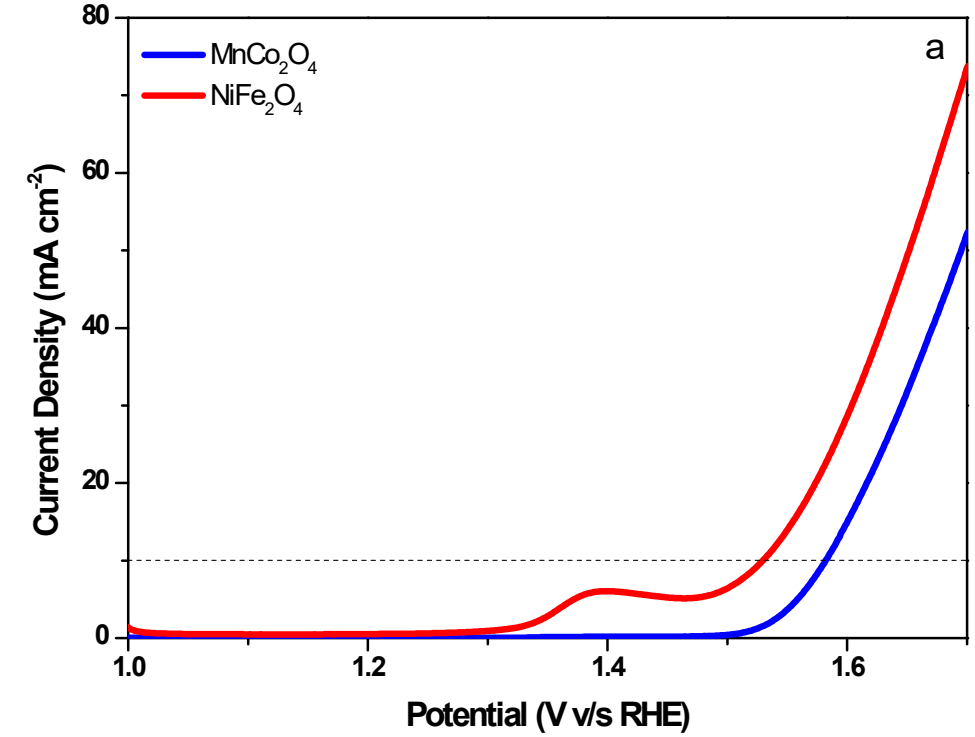
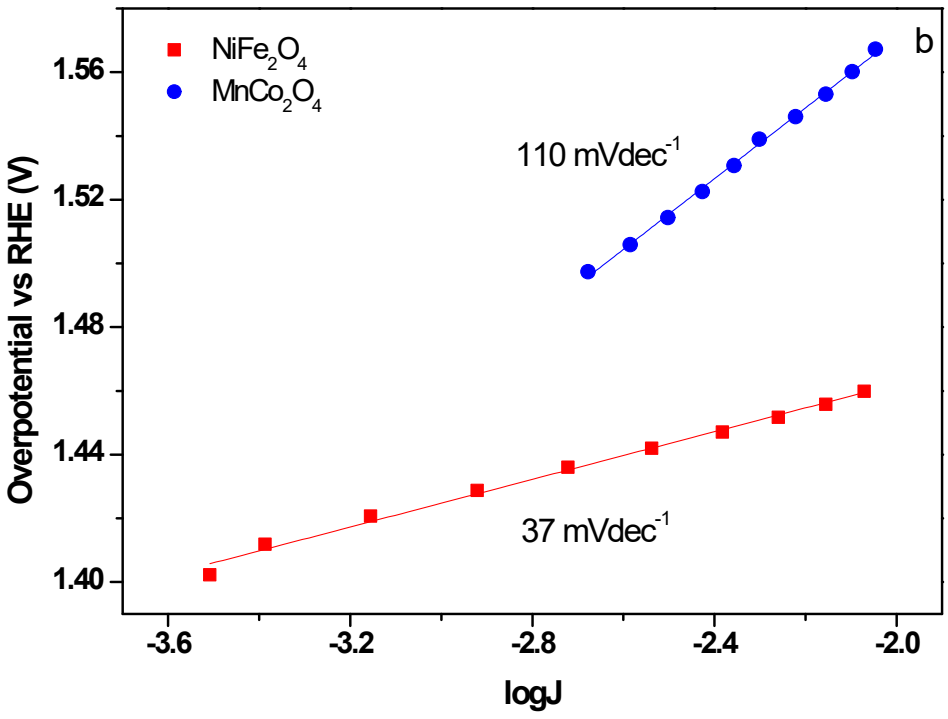


Figure S2: Comparative galvanostatic charge-discharge response of the battery assembled with modified and unmodified anodes with 10 min/ cycle at a current density of 5 mA cm^{-2}.

Figure S3


a
$MnCo_2O_4$
$NiFe_2O_4$
Current Density (mA cm^{-2})
Potential (V v/s RHE)
0
20
40
60
80
1.0
1.2
1.4
1.6


b
$NiFe_2O_4$
$MnCo_2O_4$
110 $mVdec^{-1}$
37 $mVdec^{-1}$
Overpotential vs RHE (V)
logJ
1.40
1.44
1.48
1.52
1.56
-3.6
-3.2
-2.8
-2.4
-2.0

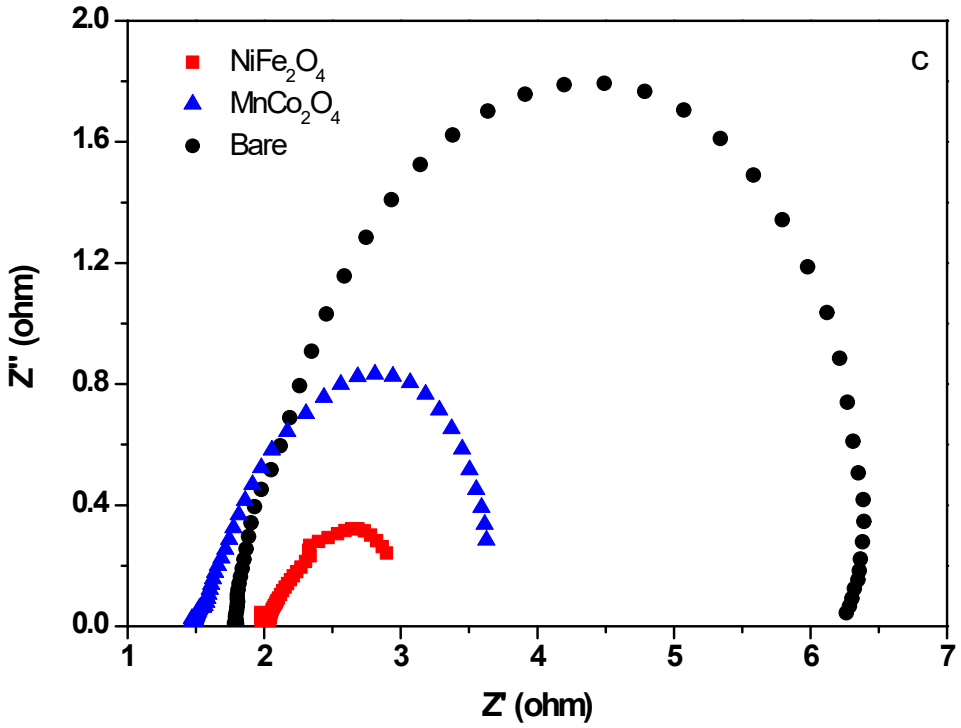


Figure S3: (a) OER polarization curves and (b) the corresponding Tafel plots of $NiFe_2O_4$ and $MnCo_2O_4$ catalysts. (c) EIS Nyquist plots and fitting curves at 1.49 V vs. RHE.

Figure S4

Material Stability

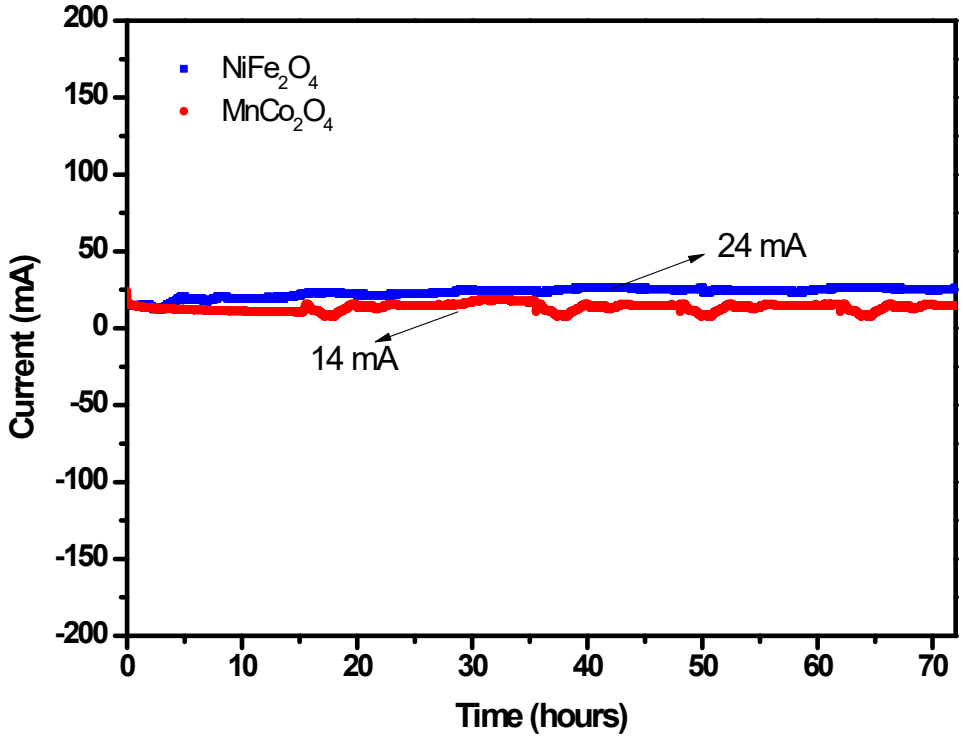
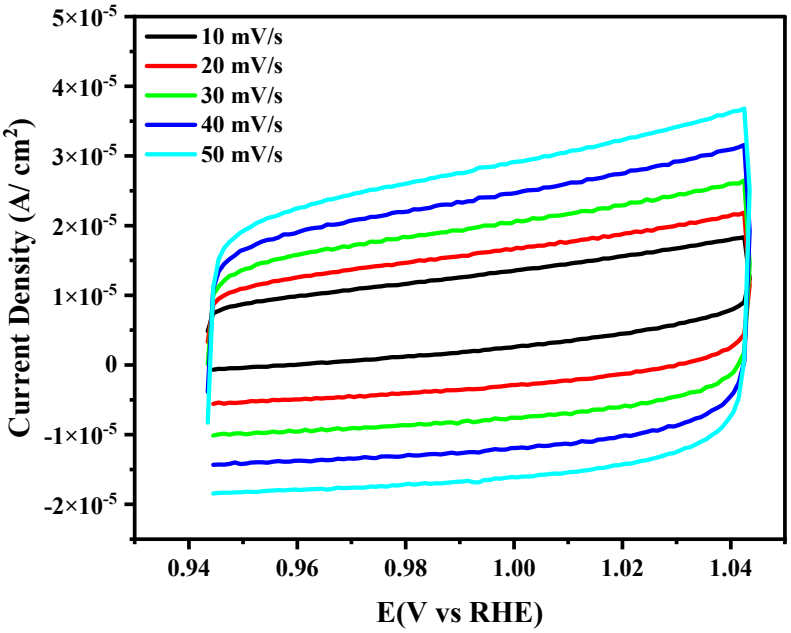


Figure S4: Material stability test of prepared catalysts tested for 72 hours.

Figure S5

The electrochemical surface area (ECSA) is estimated from double-layer electrochemical capacitance (C_{DL}). Figure S5 (a & b) represents the typical CV curves in non-faradaic region at a scan rate ranging from 50 to 150 mV s^{-1} for $NiFe_2O_4$ and $MnCo_2O_4$ respectively. At last, the calculated capacitance was further divided by average specific capacitance of 40 µF cm^{-2} for the transition metal oxide in 1 M KOH solution to obtain ECSA.



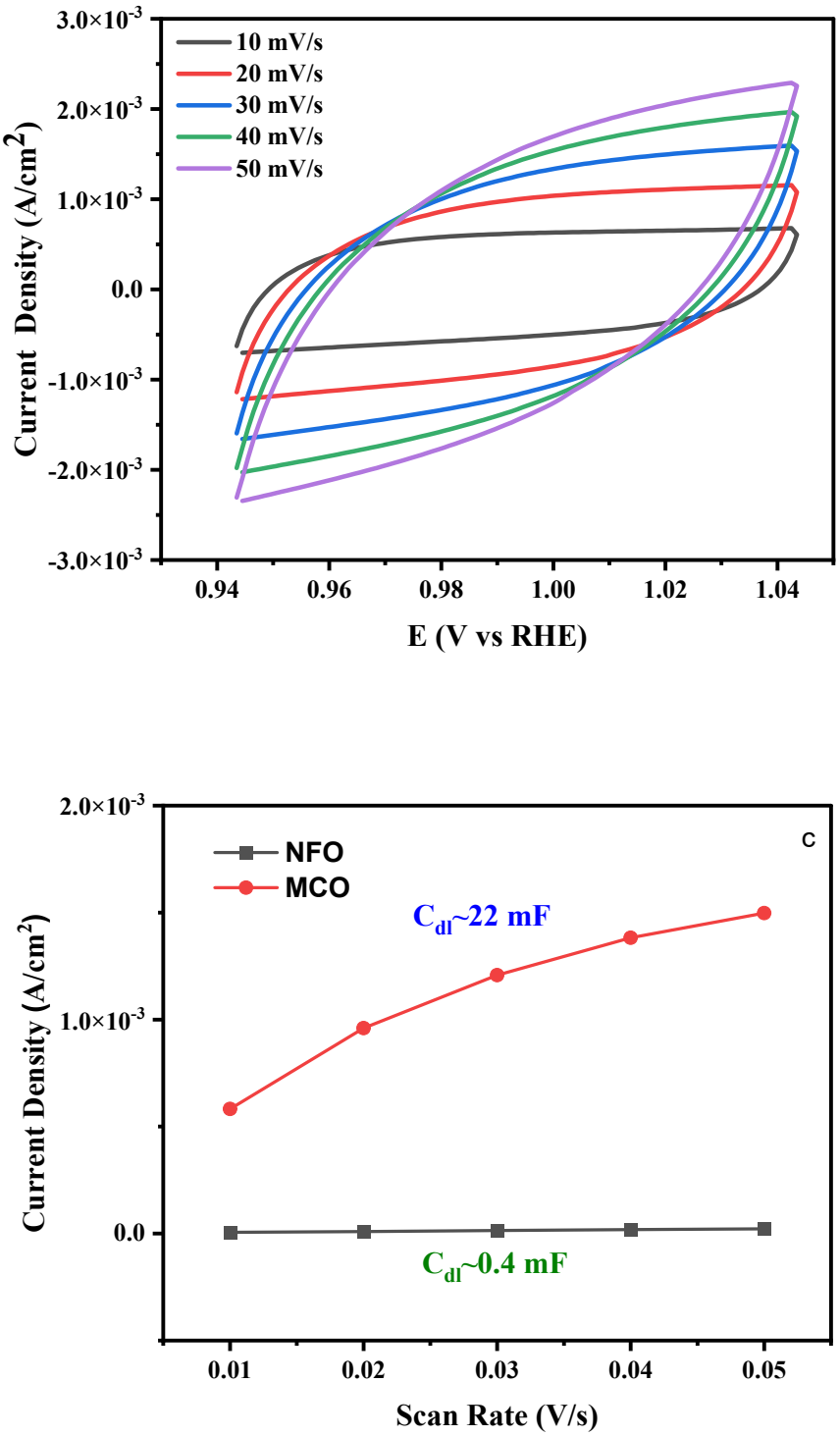
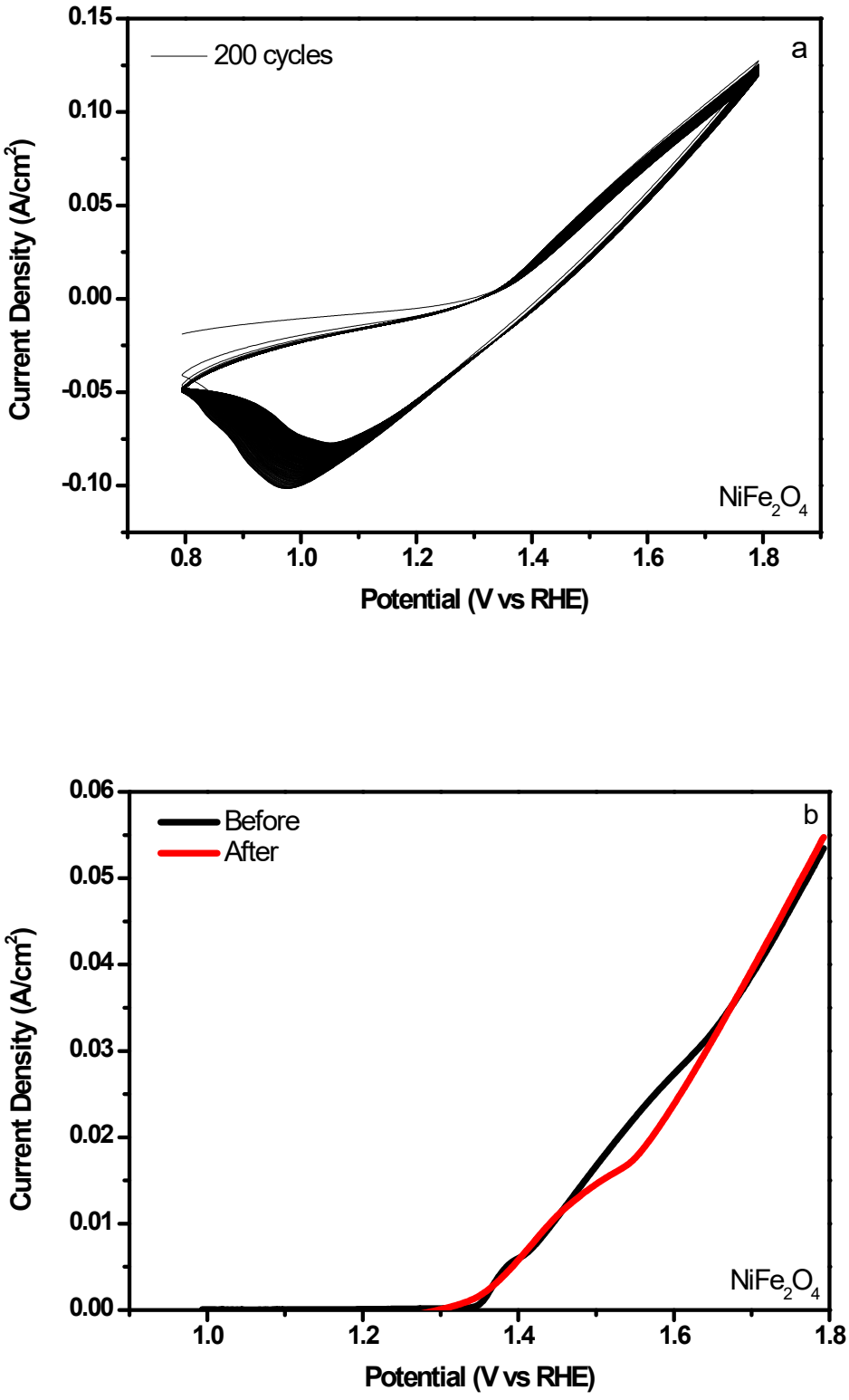


Figure S5: CV curves tested in a non-Faradaic potential range at a scan rate range of 50 to 150 mV s^{-1} for (a) $NiFe_2O_4$, (b) $MnCo_2O_4$, and (c) the calculated double-layer electrochemical capacitance.

Sample	C_{DL} (mF)	ECSA (cm^2)
$NiFe_2O_4$/NF	0.4	10
$MnCo_2O_4$/NF	22	550

Figure S6

Accelerated Data Test (ADT)



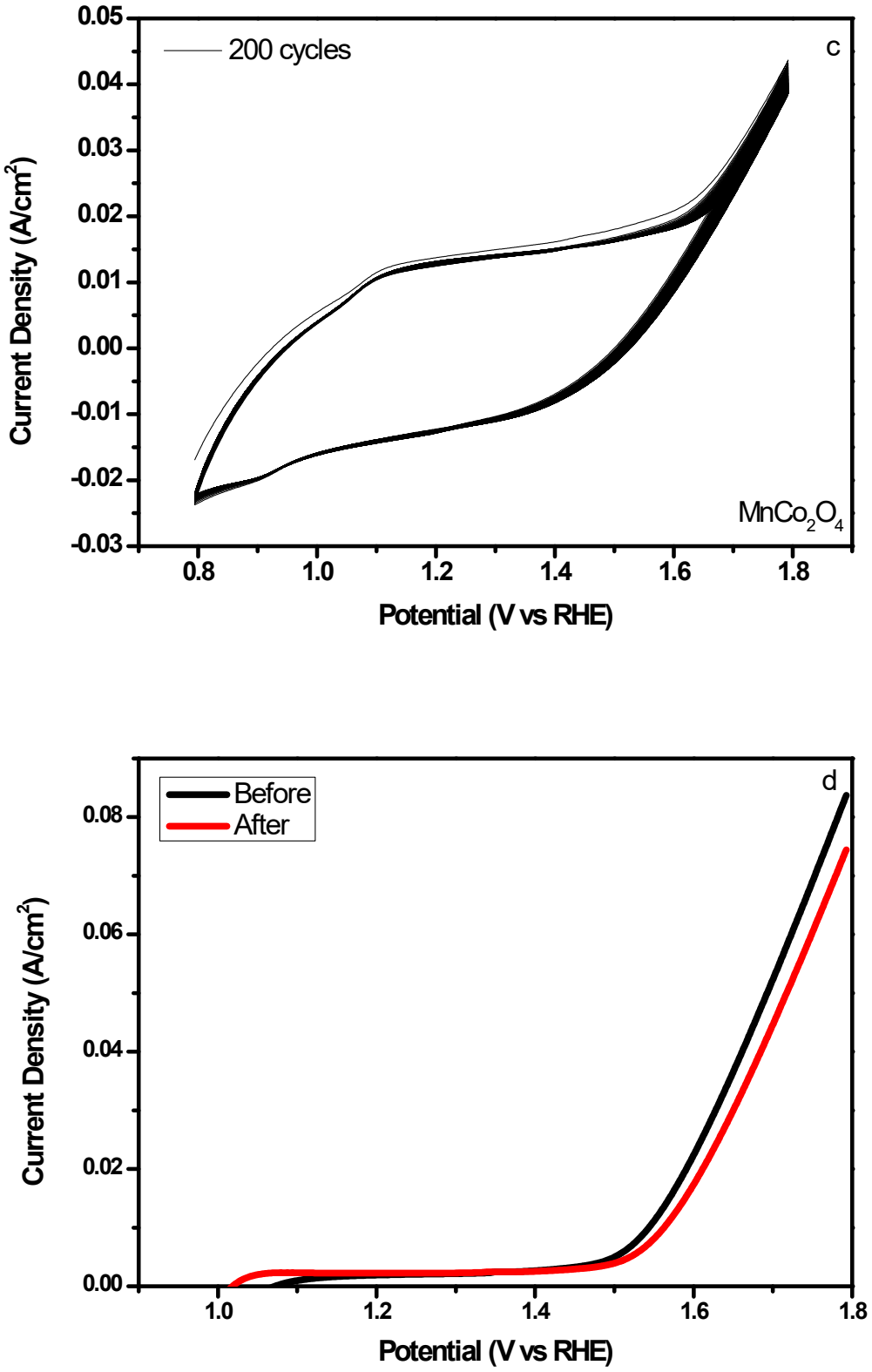


Figure S6: ADT for LSV before and after 200 cyclic voltammetry cycles.