

Supporting Information

‘Total Electrode’ and ‘Intrinsic’ Activity Parameters in Water Electrolysis: A Comprehensive Investigation

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This file contains 8 pages in which the details of Electrodes fabrications, material preparation for different characterizations, data for OER, comparative electrocatalysis datas are given in detail.

Number of Figure: 3

EXPERIMENTAL SECTION

Methods and Materials

NiO powder catalyst was obtained from Sigma-Aldrich. Hg/HgO reference electrode was purchased from CH Instruments Pvt. Ltd. DI water was used for the whole electrochemical characterization. The NiO-modified carbon cloth (CC) was used as the working electrode and a graphite rod was used as the counter electrode. The electrochemical analyzer AURT-M204 was used for all electrochemical characterizations. The used NiFe-LDH and NiFe-LDH@NF have been fabricated by hydrothermal method as reported earlier in our work.¹

Electrode Fabrications

Carbon cloth (CC) with total dimension of 1×4 cm² has been pre-treated with acid solution to make it hydrophilic followed by washing with water ethanol mixture, The dried CC were then used as substrate electrodes. A catalyst ink of composition 750 μL water, 200 μL of absolute ethanol and 50 μL 5% Nafion solution was prepared by dispersing exactly 3 mg of the NiO powder. The resulted solution was sonicated for 10 min to make the solution to be homogeneous. The volume of coated ink 67.0, 134 and 268 μL respectively to have the loadings of almost 0.2, 0.4 and 0.6 mg/cm² respectively.

Electrochemical Characterization:

All the resulting potential data that were collected by taking Hg/HgO as a reference electrode were later converted with respect to the reversal hydrogen electrode (E_{RHE}) by considering the Nernst equation,

$$E_{RHE} = E_{ref} + 0.059 \times 14 + 0.098 \dots \dots \dots \text{Equation S1}$$

Overpotential (η) values of all the catalysts at benchmarking current density of 10 mA/cm² calculation has been done by following this equation

$$\eta = E_{RHE} - 1.23 \text{ V} \dots \dots \dots \text{Equation S2}$$

Tafel slope was calculated by linear fitting η vs $\log(j)$ using the Tafel equation

$$\eta = b \cdot \log(j/j_0) \dots\dots\dots \text{Equation S3}$$

where b represents the Tafel slope, j signifies the current density and j₀ is the exchange current density. Electrochemical impedance spectroscopy (EIS) measurements were done on the frequency ranges from 10⁵ to 1 Hz at 300 mV vs RHE. The value of electrochemical active surface areas (ECSA) can be measured by determining the electrochemical double layer capacitance (C_{dl}) as follows:

$$i_c = \nu \times C_{dl} \dots\dots\dots \text{Equation S4}$$

$$\text{ECSA} = \frac{C_{dl}}{C_s} \dots\dots\dots \text{Equation S5}$$

Where i_c indicates the double-layer charging current resulting from scan-rates (ν) dependent CVs at non-faradic potential, C_s denotes a specific capacitance value of 0.040 mF/cm² depending on the typical reported values.^{2,3} The specific activity of the catalysts was determined by normalizing the geometrically normalized current density with respect to ECSA values i.e.,

$$J_{\text{ECSA}} = \frac{J_{\text{geo}}}{\text{ECSA}} \dots\dots\dots \text{Equation S6}$$

All the electrodes have been fabricated by the conventional drop-casting method. Typically, the catalyst ink was prepared by taking 3 mg of catalyst powder in a solution mixture containing 750 μL of H₂O, 200 μL of ethanol, and 50 μL of 5% Nafion solution.

The accumulate charge over the electrode surface was calculated by following equation:

$$\text{Surface accumulated charge} = \frac{\text{area under reduction curve}}{\text{scan rate} \times 1.602 \times 10^{-19}} \text{ C} \dots\dots\dots \text{Equation S7}$$

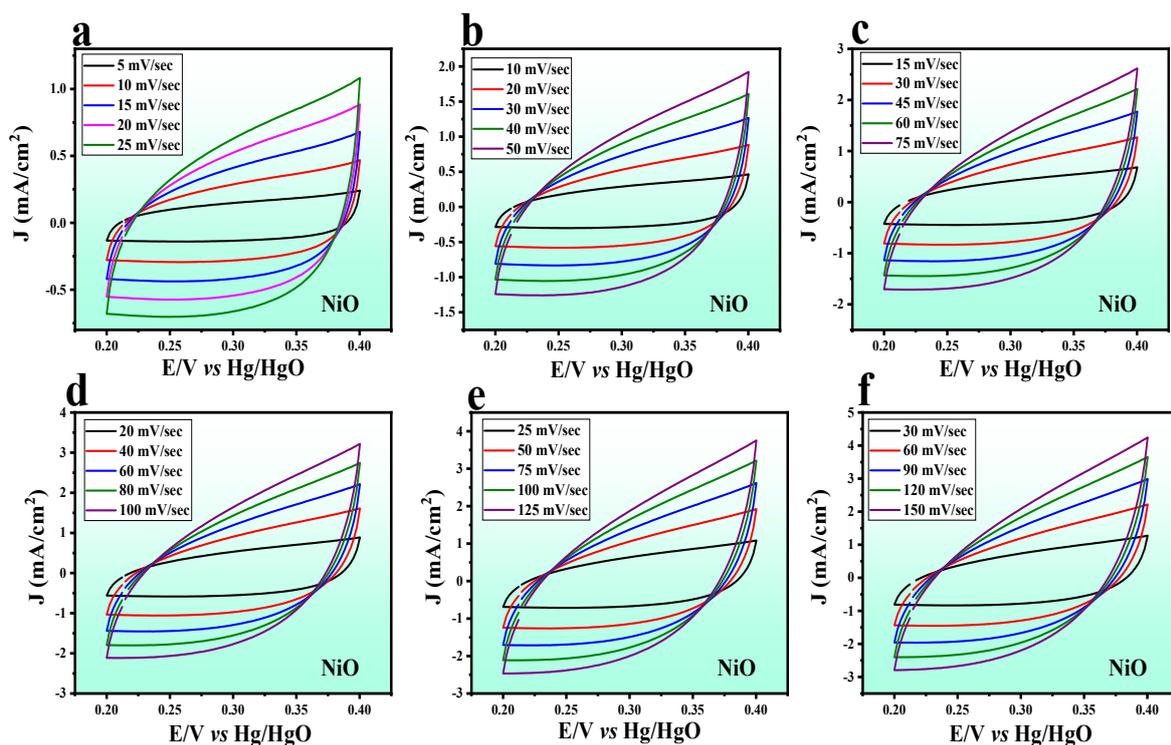


Figure S1a-f: Scan rate dependent CVs of NiO (loading 1.5 mg/cm^2) modified working electrode with different sets of scan rate difference values ($\Delta v = 20, 40, 60, 80, 100$ and 120 mV/sec).

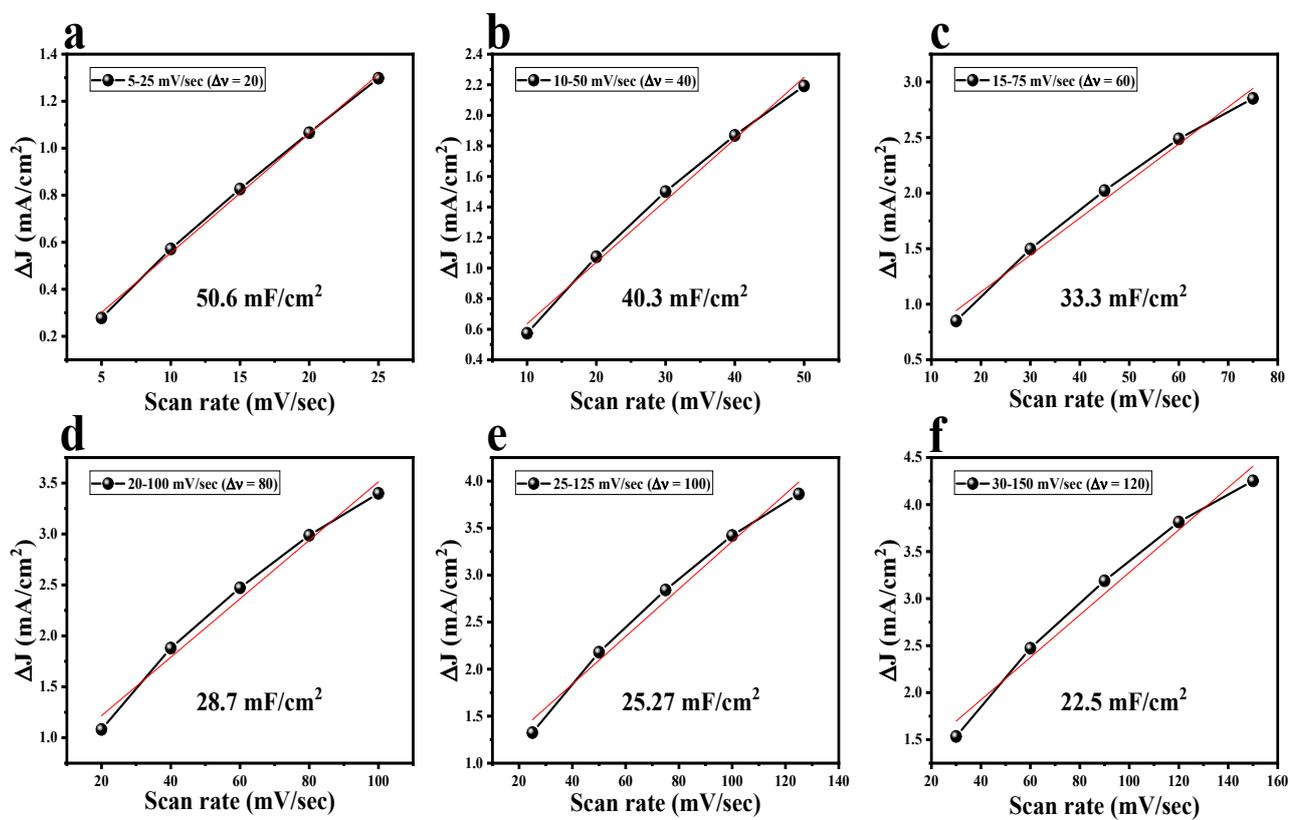


Figure S2a-f: ΔJ vs scan rate plots for estimating C_{dl} value from the linear fitting information for different sets of scan rate difference values ($\Delta v = 20, 40, 60, 80, 100$ and $120 \text{ mV}/\text{sec}$).

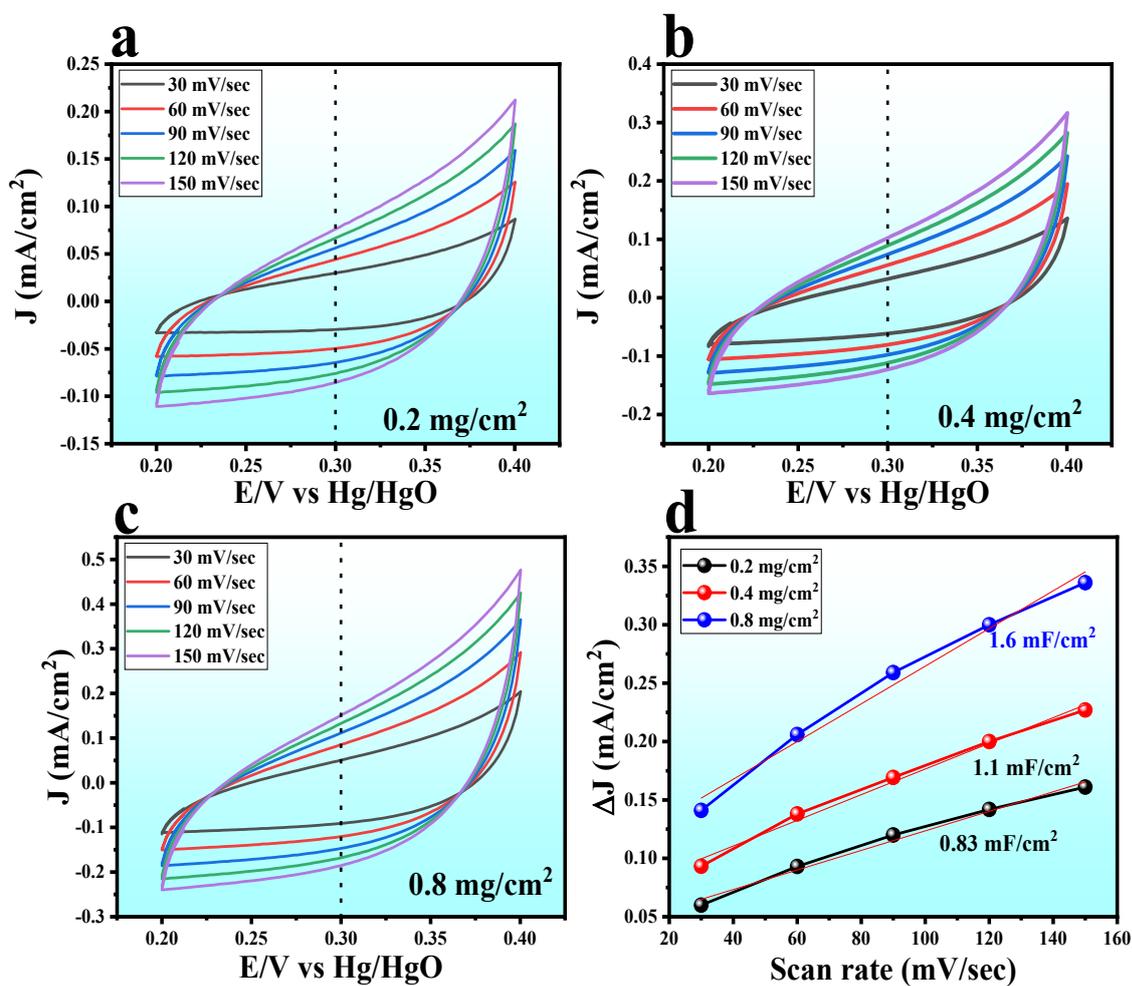


Figure S3: (a-c) scan rate dependent CVs of NiO modified electrode with various catalyst loading and (d) ΔJ vs scan rate plots for estimating C_{dl} value from the linear fitting information.

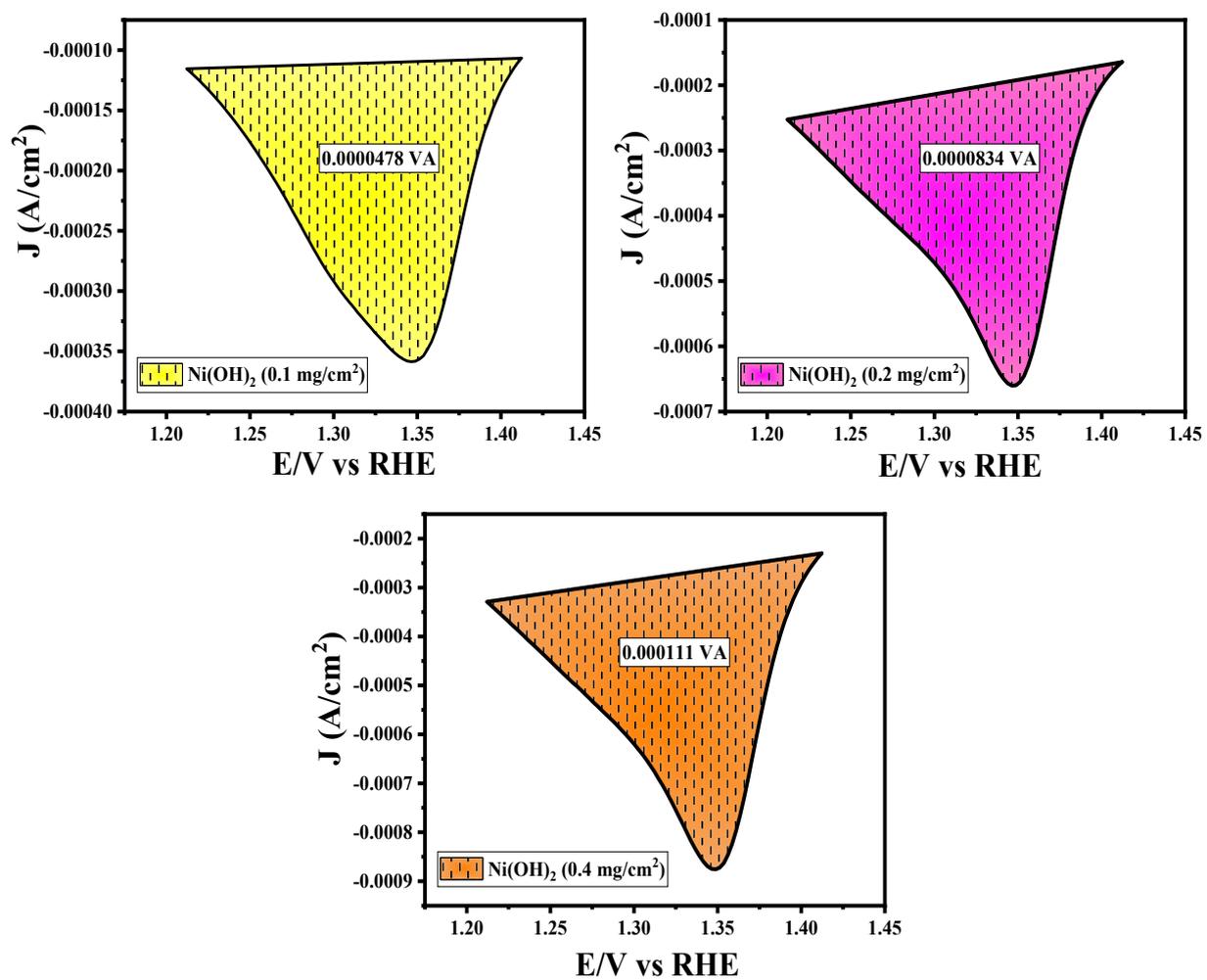


Figure S4: Respective reduction surface area of Ni(OH)_2 with different mass loading.

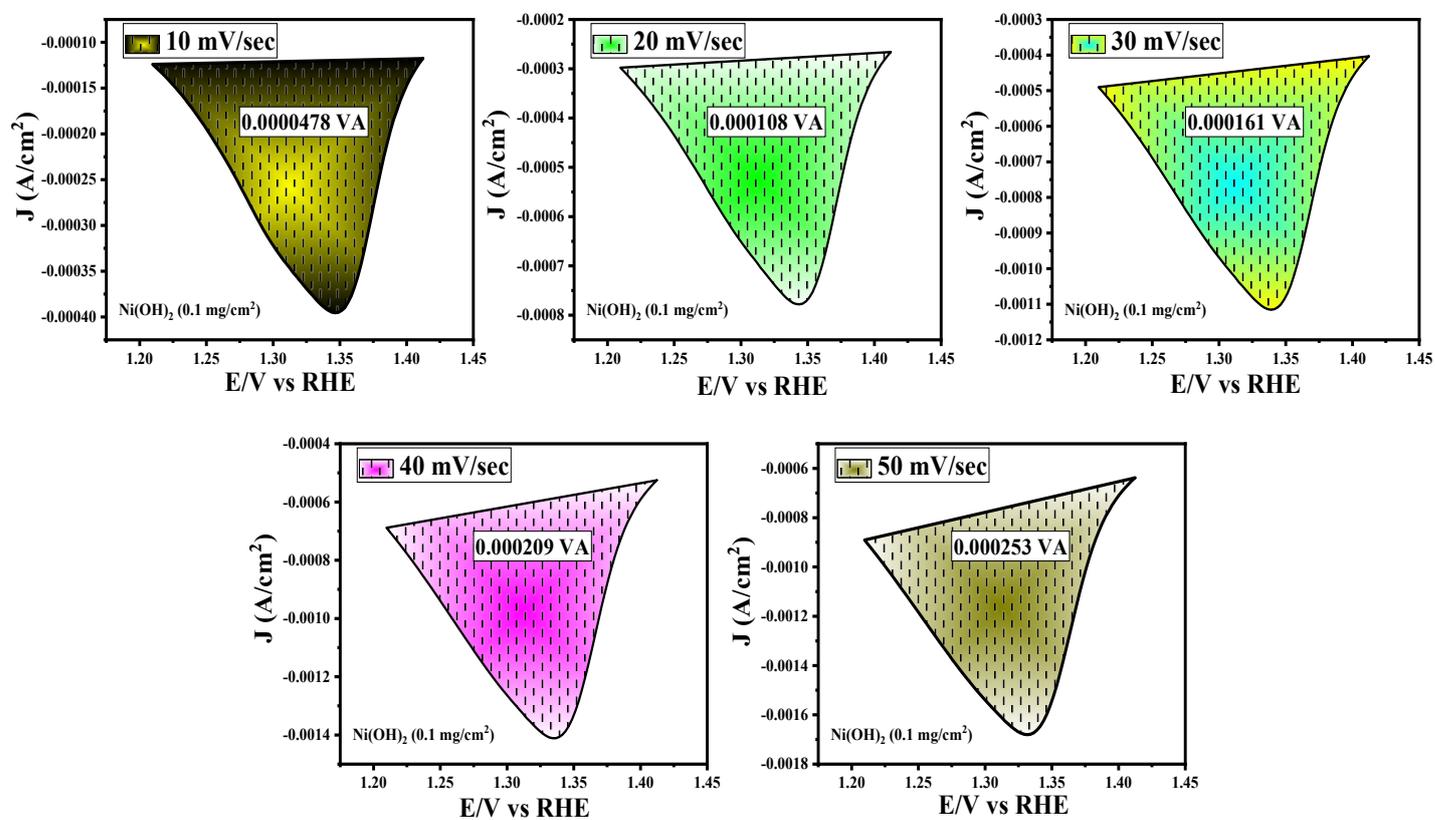


Figure S5: Respective reduction surface area of Ni(OH)_2 with different scan rate value.

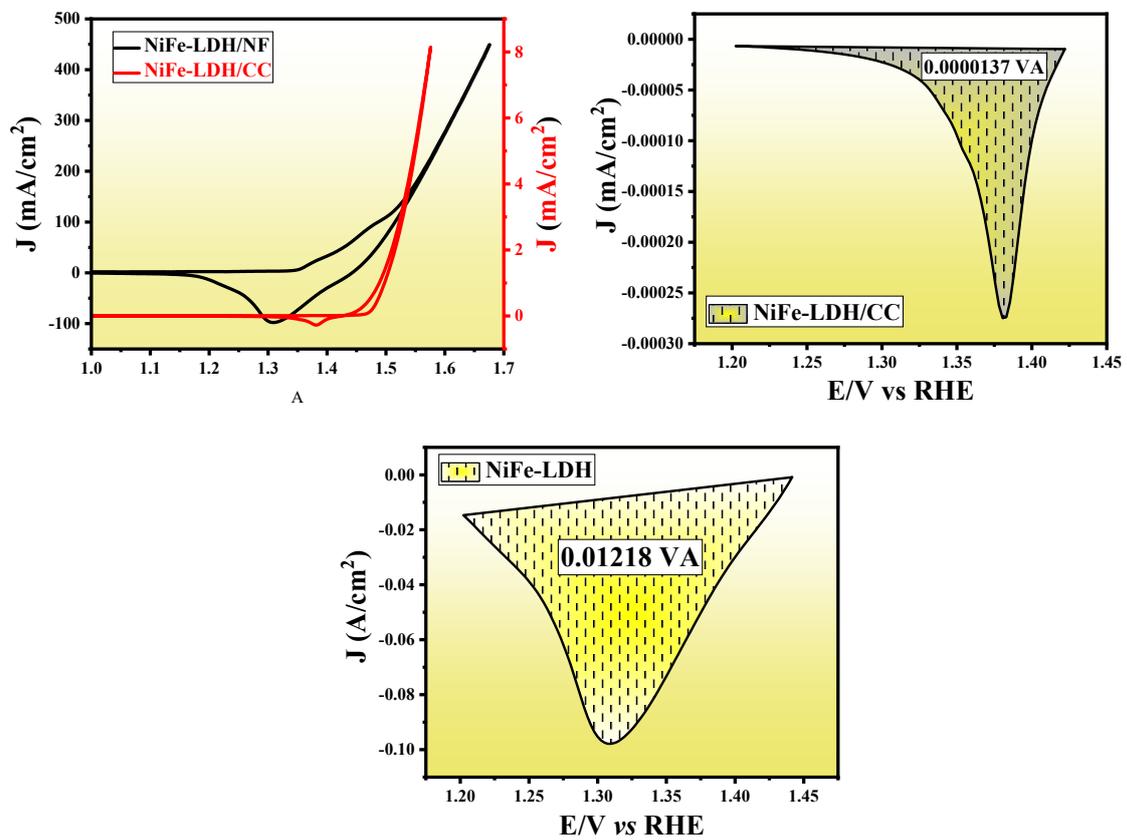


Figure S6: CV and reduction surface area information NiFe-LDH/NF and NiFe-LDH/CC.

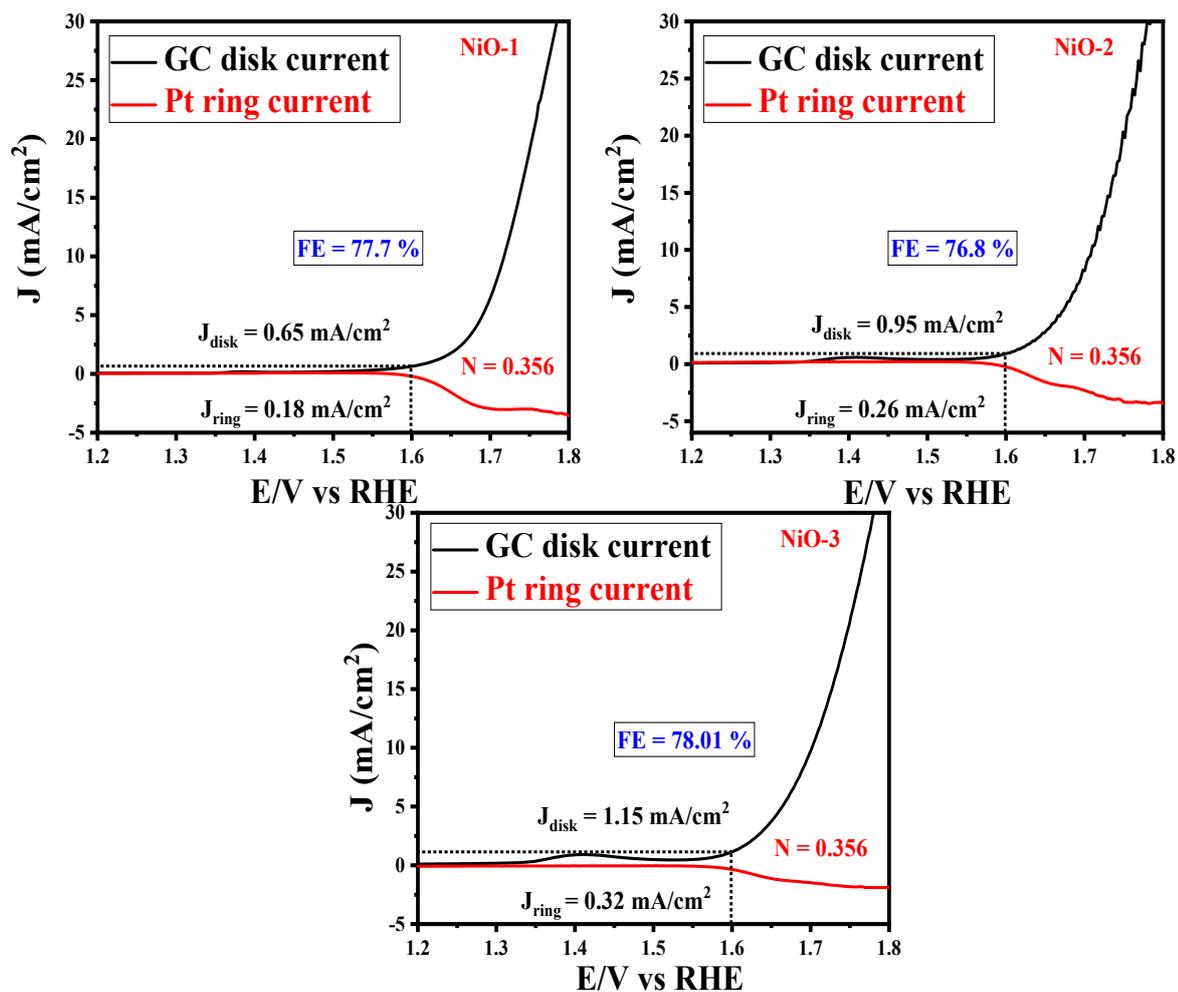


Figure S7: Linear sweep voltammetric response of NiO in disk electrode and corresponding ring current information for ORR. Collection efficiency (N) is equal to 0.356.

Reference

- (1) Karmakar, A.; Krishnan, A. V.; Jayan, R.; Madhu, R.; Islam, M. M.; Kundu, S. Structural Modulation of Low-Valent Iron in LDH-Derived Ni₃Se₄ Nanosheets: A Breakthrough Electrocatalyst for the Overall Water Splitting Reaction. *J. Mater. Chem. A* **2023**, 10684–10698. <https://doi.org/10.1039/d3ta00868a>.
- (2) McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F. Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *J. Am. Chem. Soc.* **2015**, *137* (13), 4347–4357. <https://doi.org/10.1021/ja510442p>.
- (3) McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.* **2013**, *135* (45), 16977–16987. <https://doi.org/10.1021/ja407115p>.