

Optimizing Oxygen Electrode Bifunctionality with Platinum and Nickel Nanoparticle-Decorated Nitrogen-Doped Binary Metal Oxides

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Supplementary data

S2.1 Physical characterization

The nitrogen content of Mn₂O₃-NiO-N support materials was determined using the Leco CHNS-932 model elemental analyzer. A Zeiss Sigma 300 model scanning electron microscope (SEM) was used to determine the surface morphology of the support materials, and energy dispersive X-ray spectroscopy (EDS) analysis was used to determine the elemental composition of the materials. The surface areas and pore size distributions of the synthesized Mn₂O₃-NiO structures were analyzed with the Micromeritics 3Flex Brunauer-Emmett-Teller (BET) Analyzer. X-ray photoelectron spectroscopy (XPS) analysis of the support materials was performed with the Specs-Flex XPS model device, and the general and partial spectra of the materials were obtained. In addition, N1 partial spectra were decomposed into sub-peaks using OriginPro 9.0. The percentage of Pt and Ni elements in the catalyst structures was determined using an inductively coupled plasma-mass spectrometer (Agilent 7800 ICP-MS). Rigaku Miniflex X-ray diffractometer Cu-K α radiation ($\lambda=1.5406$ Å) was used for the XRD patterns of the support materials and catalysts and characterized by measurements taken in the range of $10^\circ \leq 2\theta \leq 90^\circ$.

S2.2 Electrochemical measurements

Catalytic inks for electrochemical measurements were prepared by measuring 3 mg of each electrocatalyst in a plastic tube. Next, 0.4 mg of Vulcan (Cabot Vulcan XC72R) is added, followed by 450 μ L of distilled H₂O and 300 μ L of absolute ethanol. The ink was then treated for 10 min in an ultrasonic bath, after which 75 μ L of 0.5 wt.% Nafion was added,

followed by 20 min of ultrasonic bath treatment. Before each application to the glassy carbon electrode, the ink dispersion was homogenized in an ultrasonic bath for 10 min, after which 10 μL was applied onto the electrode. The electrode was then dried by blowing high-purity N_2 over it (N_2 , Messer, 99.9995 vol.%).

All electrochemical measurements were performed in a standard three-electrode electrochemical cell with Pt-mesh and saturated calomel electrode (SCE) as counter and reference electrodes, respectively. Gamry Interface 1010 galvanostat/potentiostat equipped with Gamry rotator (Gamry RDE710 rotating electrode) was used to perform electrochemical experiments and control the electrode's rotation rate. Linear scan voltammograms (LSVs) and cyclic voltammograms (CVs) were run at 20 mV s^{-1} , except CVs for double-layer capacitance measurements that were run at scan rates in the 10 – 50 mV s^{-1} range. The atmosphere in the electrochemical cell was controlled by bubbling in high-purity N_2 and O_2 (Messer, 99.9995 vol.%).

Stability tests were performed using the Arbin Instruments equipment in chronoamperometry mode with a pulse-shaped change of potential between ORR (0.6 V for 120 s) and OER (1.7 V for 30 s) potentials, simulating real operating conditions of a unitized regenerative fuel cell.

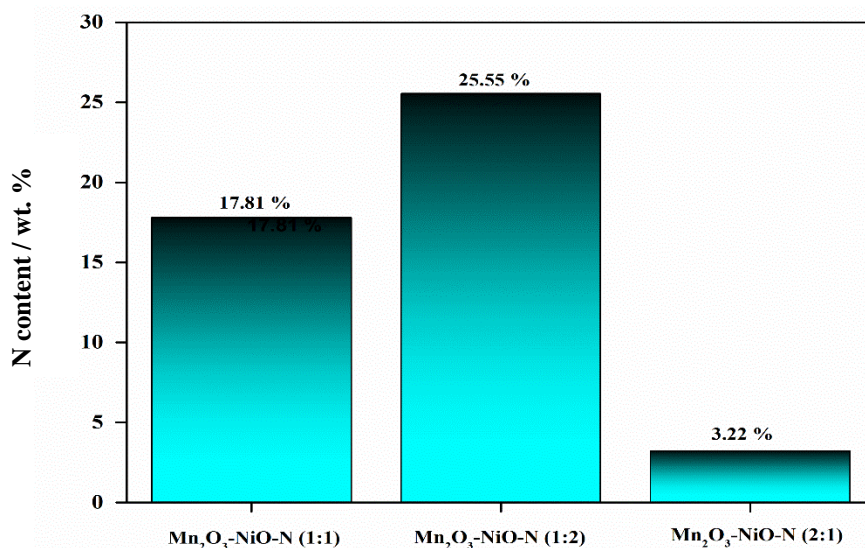


Figure S1. Elemental analysis results of the $\text{Mn}_2\text{O}_3\text{-NiO-N}$ samples.

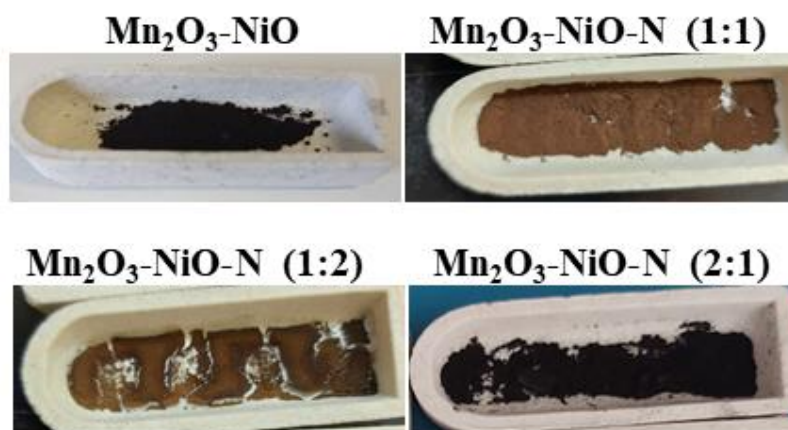


Figure S2. Images of the $\text{Mn}_2\text{O}_3\text{-NiO}$ sample, raw and after doping with different amounts of nitrogen.

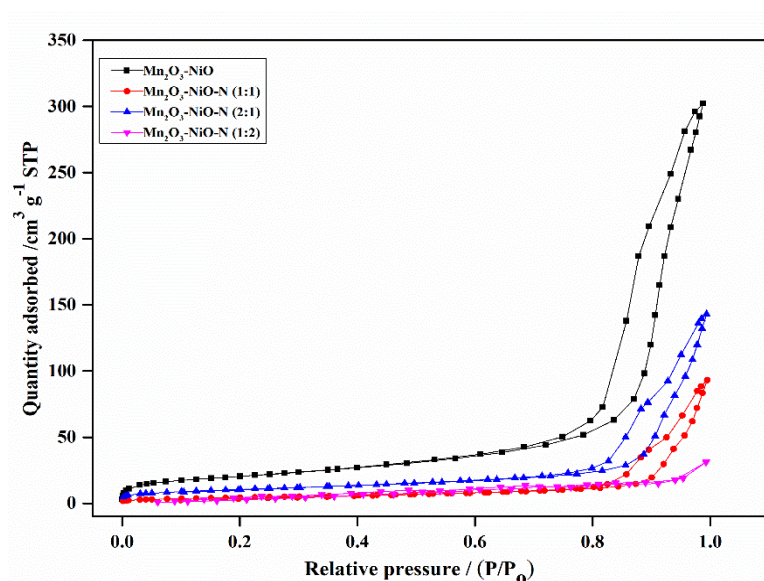


Figure S3. BET analysis results of BMOs.

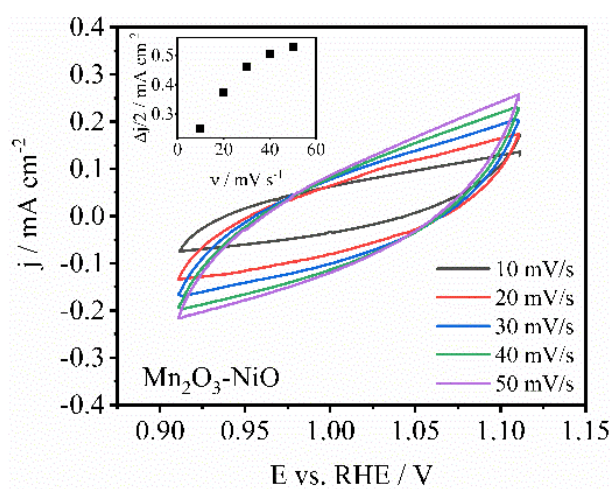


Figure S4. Double-layer capacitance investigation of pure $\text{Mn}_2\text{O}_3\text{-NiO}$ BMO.

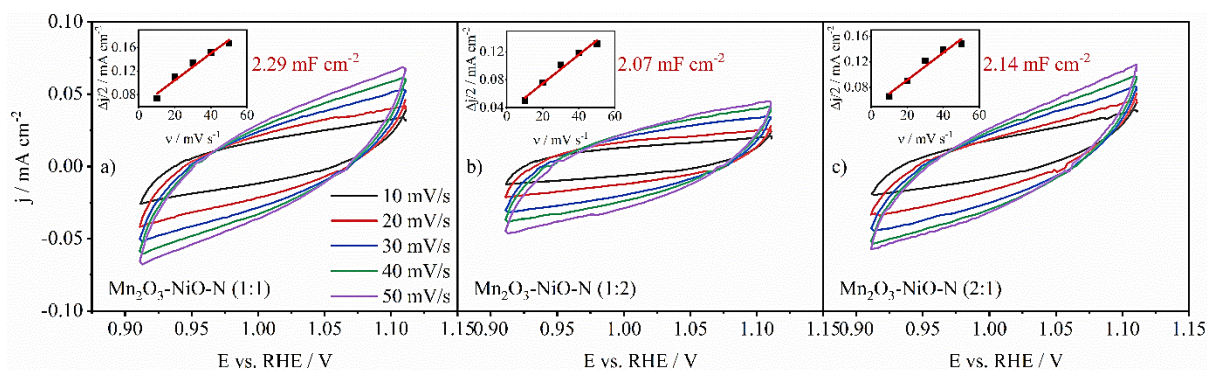


Figure S5. Double-layer capacitance investigation of N-doped $\text{Mn}_2\text{O}_3\text{-NiO}$ BMOs with BMO to N ratios of a) 1:1, b) 1:2, and c) 2:1.

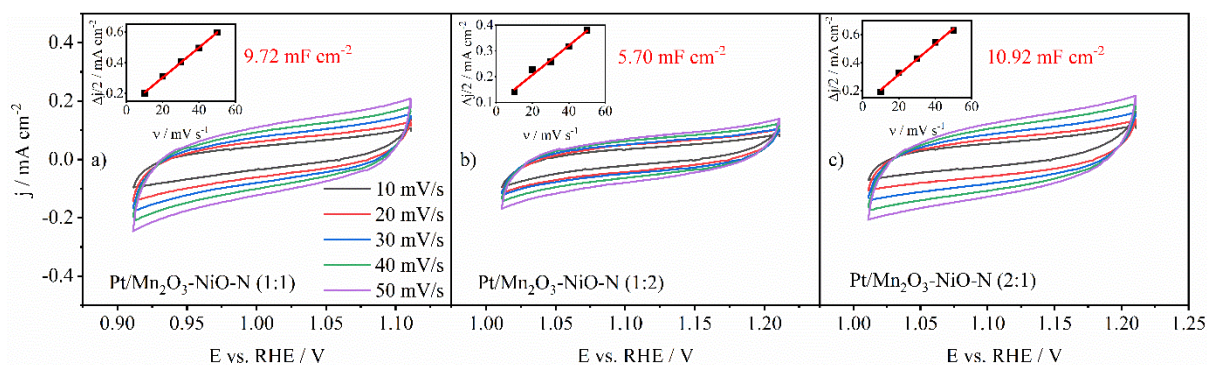


Figure S6. Double-layer capacitance investigation of Pt-decorated N-doped $\text{Mn}_2\text{O}_3\text{-NiO}$ BMOs with BMO to N ratios of a) 1:1, b) 1:2, and c) 2:1.

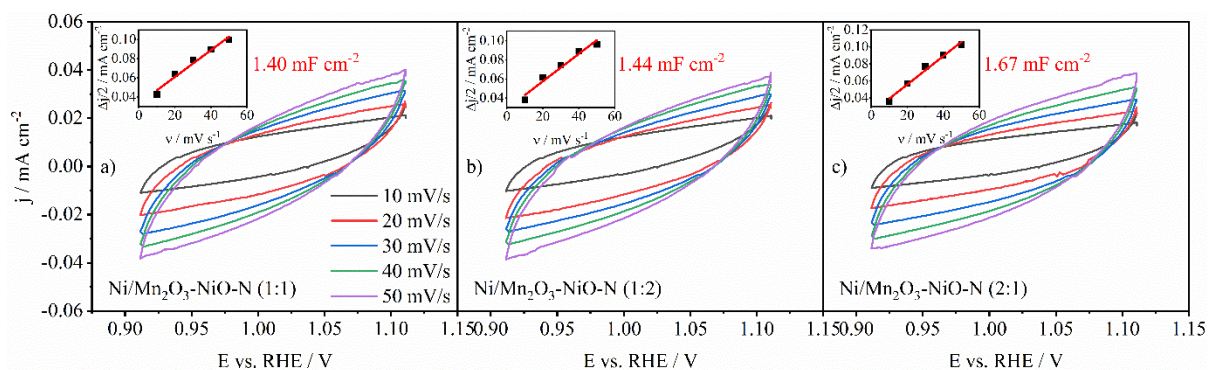


Figure S7. Double-layer capacitance investigation of Ni-decorated N-doped $\text{Mn}_2\text{O}_3\text{-NiO}$ BMOs with BMO to N ratios of a) 1:1, b) 1:2, and c) 2:1.

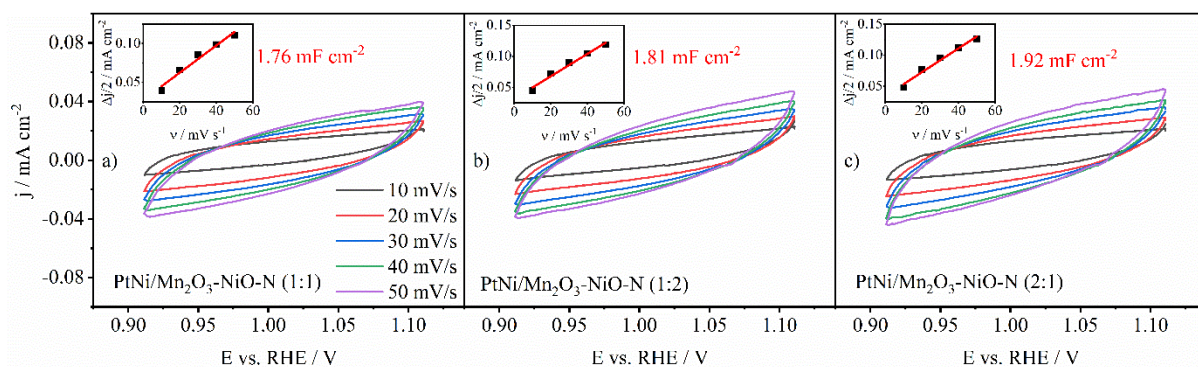


Figure S8. Double-layer capacitance investigation of PtNi decorated, N-doped $\text{Mn}_2\text{O}_3\text{-NiO}$ BMOs with BMO to N ratios of a) 1:1, b) 1:2, and c) 2:1.

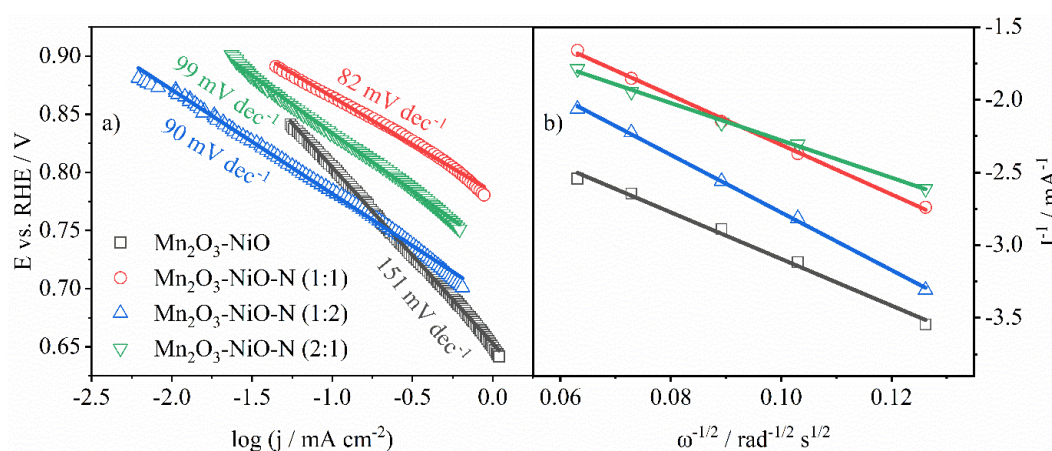


Figure S9. a) Tafel analysis of LSV (at 1800 rpm) of pure and N-doped $\text{Mn}_2\text{O}_3\text{-NiO}$ and b) Koutecký-Levich analysis of the same materials.

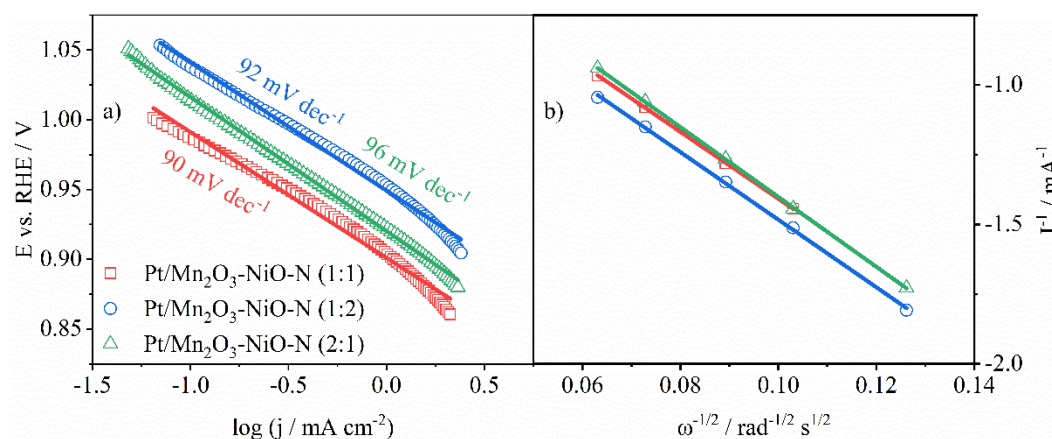


Figure S10. a) Tafel analysis of LSV (at 1800 rpm) of Pt-decorated N-doped $\text{Mn}_2\text{O}_3\text{-NiO}$ with different N to BMO ratios and b) Koutecký-Levich analysis of the same materials.

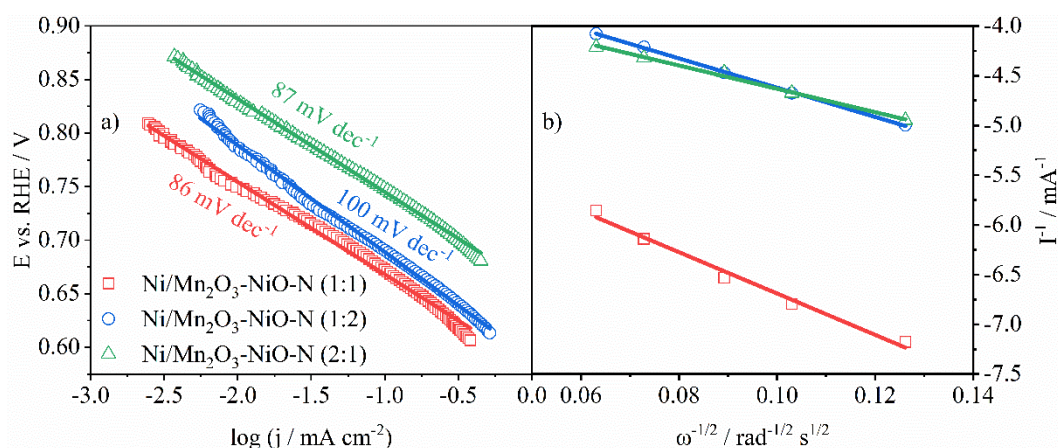


Figure S11. a) Tafel analysis of LSV (at 1800 rpm) of Ni-decorated N-doped $\text{Mn}_2\text{O}_3\text{-NiO}$ with different N to BMO ratios and b) Koutecký-Levich analysis of the same materials.

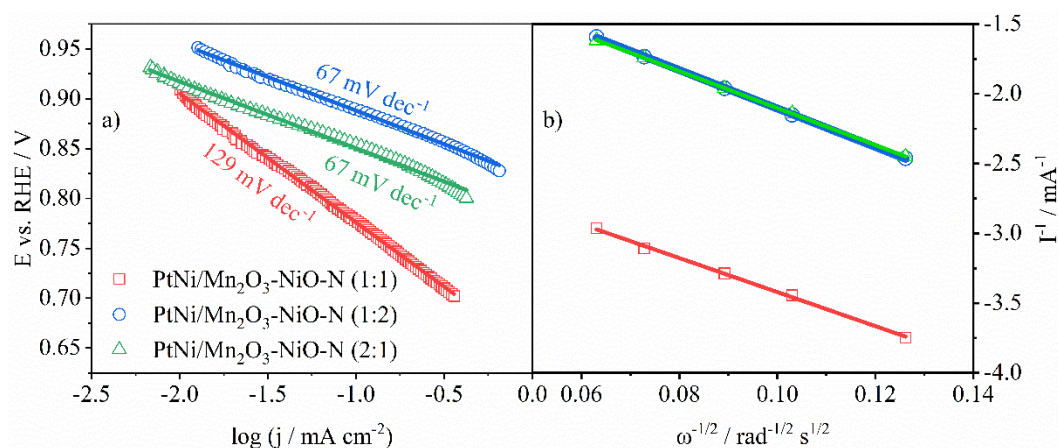


Figure S12. a) Tafel analysis performed at 1800 rpm LSV of PtNi-decorated N-doped $\text{Mn}_2\text{O}_3\text{-NiO}$ with different N to BMO ratios and b) Koutecký-Levich analysis of the same materials. KL plots of PtNi/ $\text{Mn}_2\text{O}_3\text{-NiO-N}$ (2:1) and PtNi/ $\text{Mn}_2\text{O}_3\text{-NiO-N}$ (1:2) are overlapped.

Table S1. ICP-MS results of synthesized catalysts.

| Sample | Pt (wt.%) | Ni (wt.%) |
|--|--------------|--------------|
| Pt/Mn ₂ O ₃ -NiO-N (1:1) | 19.87 | — |
| Pt/Mn ₂ O ₃ -NiO-N (1:2) | 18.75 | — |
| Pt/Mn ₂ O ₃ -NiO-N (2:1) | 18.26 | — |
| Ni/Mn ₂ O ₃ -NiO-N (1:1) | — | 14.89 |
| Ni/Mn ₂ O ₃ -NiO-N (1:2) | — | 14.12 |
| Ni/Mn ₂ O ₃ -NiO-N (2:1) | — | 13.48 |
| PtNi/Mn ₂ O ₃ -NiO-N (1:1) | 8.71 | 6.52 |
| PtNi/Mn ₂ O ₃ -NiO-N (1:2) | 8.33 | 6.47 |
| PtNi/Mn ₂ O ₃ -NiO-N (2:1) | 7.95 | 6.12 |

Table S2. Comparison of C_{dl}, ECSA, and BET surface area for all synthesized BMO-based electrocatalysts.

| Material | C _{dl} / mF cm ⁻² | ECSA / cm ² | BET surface area / m ² g ⁻¹ | Source |
|--|--|---------------------------|--|-----------|
| Mn ₂ O ₃ -NiO | - | - | 73.11 | This work |
| Mn ₂ O ₃ -NiO-N (1:1) | 2.29 | 57.3 | 16.19 | This work |
| Mn ₂ O ₃ -NiO-N (1:2) | 2.07 | 51.8 | 3.16 | This work |
| Mn ₂ O ₃ -NiO-N (2:1) | 2.14 | 53.5 | 37.52 | This work |
| Pt/Mn ₂ O ₃ -NiO-N (1:1) | 9.72 | 243.0 | - | This work |
| Pt/Mn ₂ O ₃ -NiO-N (1:2) | 5.70 | 142.5 | - | This work |
| Pt/Mn ₂ O ₃ -NiO-N (2:1) | 10.92 | 273.0 | - | This work |
| Ni/Mn ₂ O ₃ -NiO-N (1:1) | 1.40 | 35.0 | - | This work |
| Ni/Mn ₂ O ₃ -NiO-N (1:2) | 1.44 | 36.0 | - | This work |
| Ni/Mn ₂ O ₃ -NiO-N (2:1) | 1.67 | 41.8 | - | This work |
| PtNi/Mn ₂ O ₃ -NiO-N (1:1) | 1.76 | 44.0 | - | This work |
| PtNi/Mn ₂ O ₃ -NiO-N (1:2) | 1.81 | 45.3 | - | This work |
| PtNi/Mn ₂ O ₃ -NiO-N (2:1) | 1.92 | 48.0 | - | This work |
| FeCo@N-HC | 48.2 | - | 1151.7 | [15] |
| LaMnNiCoO ₃ (1:2:3) | 11.92 | - | - | [17] |
| Ni _{0.33} Co _{0.67} O _x | 5.09 | - | 109 | [18] |

| | | | |
|--|-------|---|------|
| NiO-Mn ₂ O ₃ -CDs | 22.06 | - | [45] |
| Pt/Mn ₂ O ₃ -NiO | 2.25 | - | [19] |
| PtNi/Mn ₂ O ₃ -NiO | 2.67 | - | [19] |
| Pt/C (40 wt.%) | 3.10 | - | [19] |

HC – honeycomb carbon; CDs – carbon dots.