Amorphous Ni-Fe Catalyst for Electrocatalytic Dehydrogenation of Alcohols to Value-added Chemicals

Mingzhu Zhao, ^{a, c} Chengying Guo, ^a Chengqing Liu, ^a Lingfeng Gao, ^{a *} Xiang Ren, ^a Hua Yang, ^b Xuan Kuang, ^a Xu Sun ^{a *} and Qin Wei ^a

^a Key Laboratory of Interfacial Reaction & Sensing Analysis in Universities of Shandong; School of Chemistry and Chemical Engineering Institution; University of Jinan, Jinan, Shandong 250022, (P. R. China). E-mail addresses: <u>chm_sunx@ujn.edu.cn</u> (Xu Sun); <u>chm_gaolf@ujn.edu.cn</u> (Lingfeng Gao)

^b School of Chemistry and Chemical Engineering, Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology; Liaocheng University; Liaocheng, 252059 (P. R. China)

° School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, China

Table of contents

1. Electrochemical measurement
2. XRD spectrum curve of NiFeO(OH)
3. XPS spectrum of NiFeO(OH)
4. EDS of NiFeO(OH)
5. Gas chromatograms before and after electrolytic oxidation reaction
6. NMR of BPM and BPC
7. Gas chromatograms of different potentials
8. Gas chromatograms of electrolyte after different reaction times7
9. Gas chromatograms of electrolyte after passing different charge
10. Gas chromatograms of electrolyte for the comparison experiments
11. Gas chromatograms of electrolyte after reaction without or with NiFeO(OH) $\dots 11$
12. FTIR spectrums
13. BPM oxidation stability
14. Characteristic of NiFeO(OH) after the BPM oxidation process
15. LSV curves of NiFeO(OH) in electrolyte with or without NaBr14
16. Gas chromatograms of electrolytes without or with NaBr
17. Equivalent circuit diagram15
18. Stability characterization and NaBrO yield15
19. Catalytic activity characterization of NiFeO(OH) in two electrode system16

1. Electrochemical measurement

The electrochemical characterization was carried out on electrochemical station (CHI660B, China) using a classical three-electrode system in 50 mL saturated NaHCO₃ and saturated NaBr solution in H-shaped electrolyzer. As-produced sample was used for the working electrode, carbon rod as the auxiliary electrode, and Ag/AgCl electrode as the contrast electrode. The potential was calibrated against and converted to reversible hydrogen electrode (RHE). For working electrode, the carbon paper (CP) electrode (1 cm × 1 cm) was adopted as the electrode, after which the catalyst gel was droped into it. For the preparation of catalyst gel, 5 mg of as-synthesized materials was dispersed in the 1 mL tailor-made solution of water/ethanol (5 : 5). Then, 50 μ L of superpolymer (Nafion solution, 5 wt%) was added to obtain a homogeneous emulsion with the help of sonication. 20 μ L of the obtained solution was dropped on the clearly CP electrode. Specifically, the surface area of the glassy carbon was about 1 cm².

Next, 20 times of Cyclic Voltammetry was carried out with the scan rate of 100 mV s⁻¹ to stabilize the catalyst in the voltage range of 1.0 V ~ 2.0 V (vs. RHE). Next, polarization curve was proceeded by linear sweep voltammetry at a sweep rate of 5 mV s⁻¹ in saturated NaHCO₃ and saturated NaBr. At the same time, the polarization curves of all catalysts were calculated with iR compensation using the software of CHI660B. Furthermore, the measurement of Ac impedance was recorded at the frequency range of 0.1 mHz to 100 kHz, take-off potential of 1.75 V (vs. RHE) and the amplitude of 5 mV.

2. XRD spectrum curve of NiFeO(OH)



Figure S1. XRD spectrum of NiFeO(OH).

3. XPS spectrum of NiFeO(OH)



Figure S2. XPS spectrum of NiFeO(OH).

4. EDS of NiFeO(OH)



Figure S3. EDS of NiFeO(OH).

Element	Percentage by Weight	Percentage by atom
0	41.59	71.62
Fe	40.04	19.76
Ni	18.37	8.62
Total	100.00	100.00

Table S1. The chart of EDS.

5. Gas chromatograms before and after electrolytic oxidation reaction



Figure S4. Gas chromatogram before (a) and after (b) electrolytic oxidation reaction.

6. NMR of BPC



Figure S5. (a) 1H NMR (600 MHz, CDCl3) δ [ppm] 7.65 – 7.61 (m, 2H), 7.40, 7.21 – 7.17 (m, 2H), 6.99 –6.95 (m, 2H); (b) 13C NMR (101 MHz, CDCl3) δ [ppm] 134.27, 132.85, 132.46, 132.39, 132.32, 129.95, 129.14, 125.88, 125.04;

7. Gas chromatograms of different potentials





FigureS6. Gas chromatograms of electrolytes that are obtained after electrolyzing under various potentials.

Potential	Product	Raw	P/RM
(V)		material	
1.65	50.82	1727.49	0.029
1.70	20.75	381.05	0.054
1.75	2564.21	178.57	14.404
1.80	575.13	402.84	1.428
1.85	408.95	125.37	3.262

Table S2. Gas chromatographic peak area data at different potentials and the peak area ratio of product and raw material (P/RM).



8. Gas chromatograms of electrolyte after different reaction times



Figure S7. Gas chromatograms of electrolytes obtained after electrolyzing for various reaction times.

Time (h)	Product	Raw material	P/RM
2	36.73	1311.32	0.028
4	759.42	5963.91	0.127
6	687.88	2057.72	0.334
8	1125.66	899.69	1.251
10	2564.21	178.57	14.359
15	776.33	/	/

Table S3. Gas chromatographic peak area data at different times and the peak area ratio of product and raw material.



9. Gas chromatograms of electrolyte after passing different charge



Figure S8. Gas chromatograms of electrolytes obtained after passing various charge.

10. Gas chromatograms of electrolyte for the comparison experiments



Figure S9. Gas chromatogram comparison experiment as open circuit (a) and working electrode (b).

11. Gas chromatograms of electrolyte after reaction without or with



NiFeO(OH)





12. FTIR spectrums



Figure S11. ATR-SEIRAS spectras of (a) BPM; (b) BPC; (c) NiFeO(OH); (d) NiFeO(OH) after 10 h electrolysis.



Figure S12. (a) Long-time chronoamperometric of organic test at 1.75 V, (b) Peak area ratio and corresponding NaBrO concentration during six recycling tests.



14. Characteristic of NiFeO(OH) after the BPM oxidation process

Figure S13. SEM image (a), (b) XRD and XPS (Fe (c), Ni (d), O (e)) of NiFeO(OH) after the BPM oxidation process. The NiFeO(OH)-BMO was collected from the GC electrode after the BPM oxidation reaction.

	peak position	half-peak width	peak area	Lorentz-Gaussian percentage
Ni2p _{3/2} (Ni ²⁺)	855.2	1.55	3104.75	80
Ni2p _{1/2} (Ni ²⁺)	873.7	2.27	4248.44	80
Ni2p _{3/2} (Ni ³⁺)	856.2	5.23	20837.85	80
Fe2p _{3/2}	711.6	0.3	330647.56	80
Fe2p _{1/2}	724.5	6.13	12700.17	80

Table S4. XPS fitting data for NiFeO(OH).

15. LSV curves of NiFeO(OH) in electrolyte with or without NaBr



Figure S14. LSV curves of NiFeO(OH) in saturated NaHCO₃ and 0.5 mM BPM electrolyte without or with NaBr at 5 mV s⁻¹.

16. Gas chromatograms of electrolytes without or with NaBr.



Figure S15. Gas chromatograms of saturated NaHCO₃ (with 0.5 mM BPM) electrolyte without (a) or with (b) NaBr after electrolyzing for 10 h under 1.75 V.

17. Equivalent circuit diagram



Figure S16. Equivalent circuit diagram of NiFeO(OH).

18. Stability characterization and NaBrO yield



Figure S17. Stability characterization. (a) Time-dependent current density curves of NiFeO(OH) for NaBr oxidation at 1.75 V for 20 h. (b) NaBrO yields and corresponding FE during five recycling.



system



Figure S18. (a) LSV curves of NiFeO(OH) and Ni₂P couple in saturated NaHCO₃ and NaBr with and without BPM. (b) Comparison of the current densities at different overpotentials for NiFeO(OH).