Supporting information

CoMo@NiC_2O_4/NF anode and Pb/CP cathode for a novel direct sodium borohydride-maleic acid fuel cell

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Experimental

Reagents and consumables

Sodium hydroxide (NaOH, Tianjin Kaitong Chemical Reagent Co., Ltd), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd), trisodium citrate dihydrate ($C_6H_5Na_3O_7$ $2H_2O$, Tianjin Wind Ship Chemical Reagent Technology Co., Ltd), sodium dodecyl sulphate ($CH_3(CH_2)_{11}OSO_2Na$, Tianjin Guangfu Fine Chemical Research Institute), ammonium sulfate ($(NH_4)_2SO_4$, Tianjin Guangfu Technology Development Co., Ltd), sodium molybdate dihydrate (Na_2MoO_4 $2H_2O$, Shanghai Maclean Biochemical Co., Ltd), nickel sulfate hexahydrate ($NiSO_4$ $6H_2O$, Tianjin Tianli Chemical Reagent Co., Ltd), cobalt sulfate heptahydrate ($CoSO_4$ $7H_2O$, Tianjin Beichen Founder Reagent Factory), maleic acid ($C_4H_4O_4$, Shanghai Aladdin Biochemical Technology Co., Ltd), ethanol anhydrous (C_2H_5OH, Tianjin Guangfu Technology Development Co., Ltd), oxalic acid ($H_2C_2O_4$, Tianjin Dongli District Tianda Chemical Reagent Factory), lead fluoborate (PbB_2F_8, Shanghai Aladdin

Biochemical Technology Co., Ltd), boric acid (H_3BO_3, Tianjin Kaitong Chemical Reagent Co., Ltd), sulfuric acid (H_2SO_4, Chengdu Kolon Chemical Co., Ltd), hydrochloric acid (HCl, Chengdu Cologne Chemicals Co., Ltd), acetone (CH_3COCH_3, Chengdu Cologne Chemicals Co., Ltd), nickel foam (PPI110, 380 g m^{-2}, Taiyuan Lizhiyuan Technology Co., Ltd), carbon paper (HCP030N, Shanghai Hesen Electric Co., Ltd), the saturated Ag/AgCl (saturated KCl) reference electrode (Model 218, INESA Scientific Instrument Co., Ltd), Pt electrode (10 mm×10 mm, Gaoss Union).

Instruments

The electrodeposition and electrochemical testing process were conducted by the Electrochemical Workstation (Autolab PGSTAT302 N). Quick assembly single cell test fixture is used for fuel cell assembly (FX301-2D). The crystal morphology structure of the electrodes were analyzed using an X-ray diffractometer (XRD, Bruker D8 ADVANCE), an X-ray photoelectron spectroscopy analyzer (XPS, Kratas AXIS SUPRA) is used for elemental composition and valence analysis of the electrode surfaces, a scanning electron microscope (SEM, JSM-7900F) and an energy dispersive spectrometer (EDS, X-MaxN50) are used for observing the surface morphology and element distribution of the electrode, transmission electron microscopy (TEM, Talos F200x) is used for studying the micromorphology of the catalyst, and X-ray energy spectrometry (EDX, Super-X) for studying the elemental distribution on the catalyst surface.

Electrochemical measurements

The preparation and electrochemical properties of various materials in this paper

were studied by linear scanning voltammetry (LSV), chronopotentiometry (CP), chrono amperometry fast and chronoamperometry (CA) in a standard three-electrode system.

EDS images of CoMo@NiC_2O_4/NF

Fig. S1a shows the SEM image of the CoMo@NiC_2O_4/NF electrode, and the obvious spherical nanoflower-like structure can be observed. Fig. S1(b-g) shows the corresponding EDS images of this electrode, from which it can be seen that Co, Mo, C, O and Ni are uniformly distributed on its surface. According to Fig. S1h, the C, O, Co, Ni and Mo contents on the surface of this electrode were 11.68%, 13.22%, 42.53%, 18.45% and 14.11%, respectively.

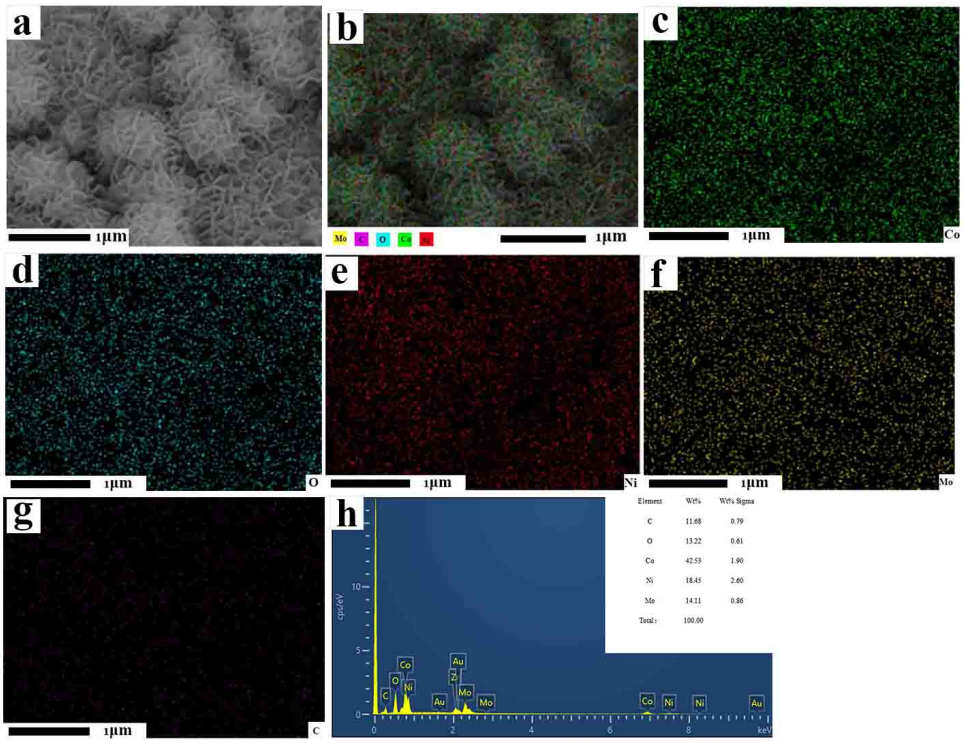

Fig. S1 The SEM image of CoMo@NiC_2O_4/NF electrode (a), EDS images of the corresponding element (b-g) and EDS data (h).

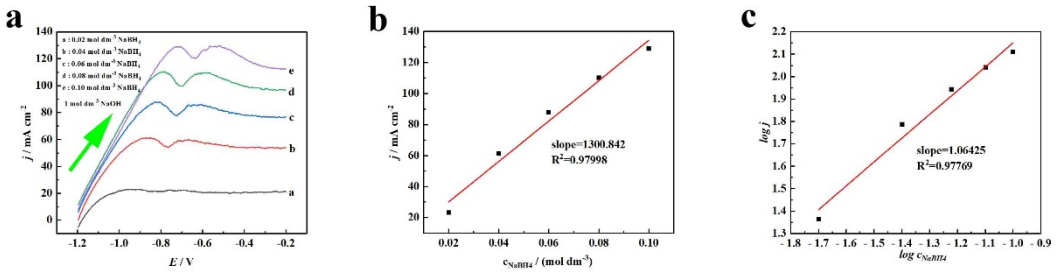

Fig. S2 LSV curves of $Co@NiC_2O_4$/NF electrode in 1.0 mol dm^{-3} NaOH with various concentrations of $NaBH_4$ (0.02~0.10 mol dm^{-3}), scan rate: 10 mV s^{-1} (a), fitting curve of $NaBH_4$ concentration (0.02~0.10 mol dm^{-3}) to peak of oxidation current density (b) and fitting curve for the logarithm of the concentration to the logarithm of the density of the peak oxidation current (c).

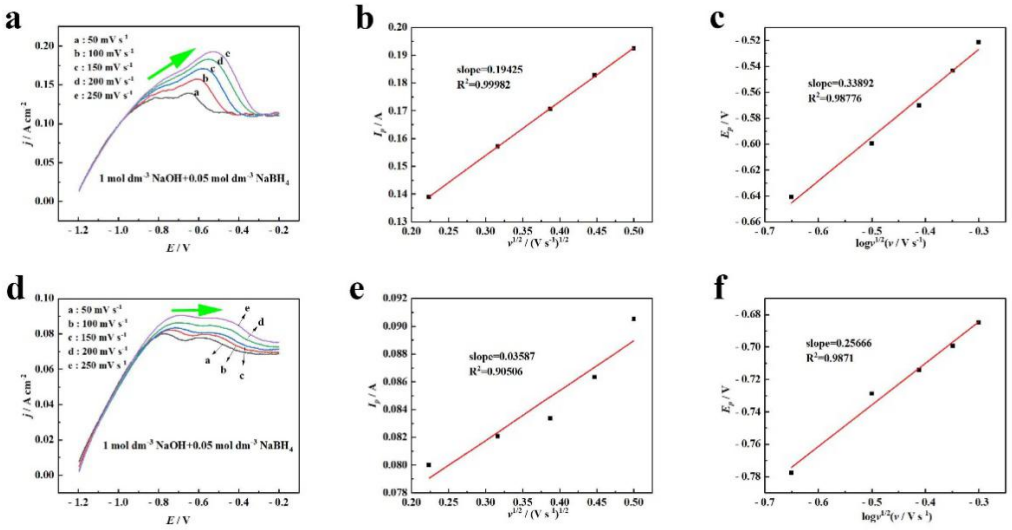

Fig. S3 LSV curves of $CoMo@NiC_2O_4$/NF electrode in the mixed solution of 1.0 mol dm^{-3} NaOH+0.05 mol dm^{-3} $NaBH_4$ at different scan rates (50~250 mV s^{-1}) (a), fitting curve of $v^{1/2}$ to I_p (b), fitting curve of $v^{1/2}$ and I_p (c); LSV curves of $Co@NiC_2O_4$/NF electrode in the mixed solution of 1.0 mol dm^{-3} NaOH+0.05 mol dm^{-3} $NaBH_4$ at different scan rates (50~250 mV s^{-1}) (d), fitting curve of $v^{1/2}$ to I_p (e) fitting curve of $v^{1/2}$ and I_p (f).

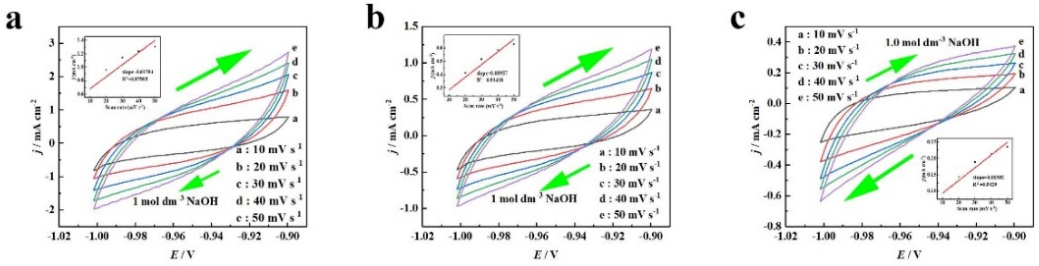

Fig. S4 CV curves of $CoMo@NiC_2O_4$/NF electrode (a), $Co@NiC_2O_4$/NF electrode (b) and NiC_2O_4/NF electrode (c) in 1.0 mol dm^{-3} NaOH at different scan rates (10~50 mV s^{-1}), and the illustration is the fitted curve of the scan rate to the oxidation current density.

Table S1 Comparison of electrooxidation performance of $NaBH_4$ on different electrodes.

Electrode	**Electrolyte**	***j* (mA cm^{-2})**	**Ref.**
$Au_{50}Fe_{50}$/C	3 mol dm^{-3} NaOH+0.1 mol dm^{-3} $NaBH_4$	About 30	[47]
Cu_2@Ag_1/C	2 mol dm^{-3} NaOH+0.1 mol dm^{-3} $NaBH_4$	About 40	[48]
Co_4-Au_1/C	2 mol dm^{-3} NaOH+0.1 mol dm^{-3} $NaBH_4$	About 58	[49]
Pt_2Cu/NPC	3 mol dm^{-3} NaOH+0.1 mol dm^{-3} $NaBH_4$	About 60	[50]
$NiBCu_{0.09}$/C	2 mol dm^{-3} NaOH+0.1 mol dm^{-3} $NaBH_4$	About 70	[51]
Pt/C_{HSA}	1 mol dm^{-3} KOH+0.1 mol dm^{-3} $NaBH_4$	About 73	[52]
Co@MWNTs-Plastic	3 mol dm^{-3} NaOH+0.1 mol dm^{-3} $NaBH_4$	About 110	[44]
CoMo@NiC_2O_4/NF	1 mol dm^{-3} NaOH+0.1 mol dm^{-3} $NaBH_4$	About 200	This work

Table S2 Comparison of electroreduction performance of $C_4H_4O_4$ on different electrodes.

Electrode	**Electrolyte**	***j* (mA cm^{-2})**	**Ref.**
Lead electrode	1 mol dm^{-3} H_2SO_4+0.04 mol dm^{-3} $C_4H_4O_4$	About 8	[17]
Ti/nano TiO_2-ZrO_2	1 mol dm^{-3} H_2SO_4+0.60 mol dm^{-3} $C_4H_4O_4$	About 20	[54]
Ti/nano-TiO_2	1 mol dm^{-3} H_2SO_4+0.25 mol dm^{-3} $C_4H_4O_4$	About 20	[55]
Ti/Ce nano-TiO_2	1 mol dm^{-3} H_2SO_4+0.10 mol dm^{-3} $C_4H_4O_4$	About 20	[56]
Ti/TiO_2	1 mol dm^{-3} H_2SO_4+1.00 mol dm^{-3} $C_4H_4O_4$	About 85	[10]
Pb-Zn porous	1 mol dm^{-3} H_2SO_4+1.00 mol dm^{-3} $C_4H_4O_4$	About 100	[57]
Pb/CP	1 mol dm^{-3} H_2SO_4+0.20 mol dm^{-3} $C_4H_4O_4$	About 230	This work

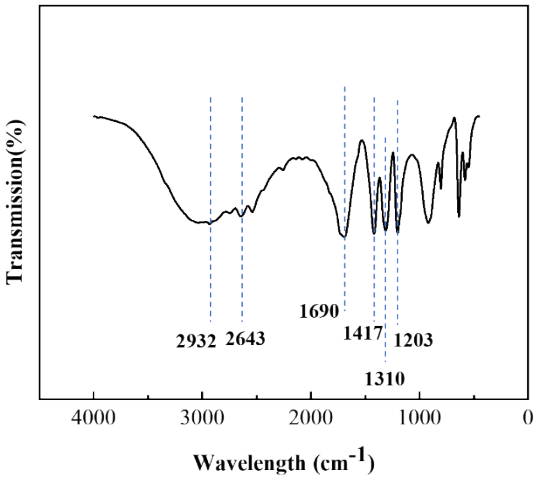

Fig. S5 FT-IR pattern of $C_4H_6O_4$.