Supplementary Information

Study of the Electro-Oxidation of Borohydride on Directly Formed CoB/Ni-foam Electrode and Its Application in Membraneless Direct Borohydride Fuel Cells

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SAED analysis

Fig. S1 The SAED patterns of CoB particles in (A) CoB/Ni-foam (7EP) and (B) CoB plate

The SEAD tests were performed to clarify the structure of CoB in CoB/Ni-foam (7EP) and CoB plate, the results were shown in Fig. S1. Both the patterns demonstrated dispersive ring which indicated non-crystalline nature of CoB and the results were in good accordance with the Lu’s work.1

Note: Because of the high stability of CoB/Ni-foam, the CoB in CoB/Ni-foam (7EP) could only be detached from the Ni-foam substrate by sonicating it in deoxygenated water for 1 hour.
The method for analyzing the active surface areas of CoB/Ni-foam

The active surface areas of CoB/Ni-foam (or CoB plate) were evaluated by scanning CVs in a solution with redox couple of K₃[Fe(CN)₆] and K₄[Fe(CN)₆] and calculated according to Randles–Sevcik equation:²

\[ i_p = 0.4463 \times 10^{-3} n^{3/2} F^{3/2} A (RT)^{-1/2} D_R^{1/2} C_R^{1/2} \]  

(1)

where \( i_p \) was the peak current (A), \( n \) was the number of electron transferred (for K₃[Fe(CN)₆] / K₄[Fe(CN)₆], \( n = 1 \)), \( F \) was the Faraday constant (96485 C mol⁻¹), \( C_R \) was the concentration of K₄[Fe(CN)₆] (mol L⁻¹), \( D_R \) was the diffusion coefficient of K₄[Fe(CN)₆] (3.7 × 10⁻⁶ cm² s⁻¹), \( v \) was the scan rate (V s⁻¹) and \( A \) was the active surface area (cm²). Because of the instability of CoB in K₄[Fe(CN)₆] solution, only the active surface area of Ni-foam substrate could be measured by this method and the result was 0.355 cm².

It was also known that the double layer capacitance was proportional to the active surface area.³⁻⁵ Hence, the active surface areas of the CoB/Ni-foam catalysts could be calculated according to the following equation:

\[ \frac{A_{\text{Ni-foam}}}{A_{\text{CoB/Ni-foam}}} = \frac{C_{\text{Ni-foam}}}{C_{\text{CoB/Ni-foam}}} \]  

(2)

Where \( C_{\text{Ni-foam}} \) and \( C_{\text{CoB/Ni-foam}} \) were the double layer capacitances of Ni-foam substrate and CoB/Ni-foam, respectively. \( A_{\text{Ni-foam}} \) and \( A_{\text{CoB/Ni-foam}} \) were the active surface areas of Ni-foam substrate and CoB/Ni-foam, respectively.

The double layer capacitances of the catalysts could be estimated in N₂ saturated 2 mol L⁻¹ KOH solution at a scan rate of 0.05 V s⁻¹ in the potential range of −0.4 V to −0.35 V vs. Hg/HgO according to the following equation:⁶

\[ C = \frac{\int \text{IdV}}{\nu \Delta V} \]  

(3)

where \( \nu \) was the scan rate (V s⁻¹), \( \Delta V \) was the potential range (V), and \( \int \text{IdV} \) was the charge of double layer.
XPS analysis

**Fig. S2** XPS spectra of the Ag-sensitized Ni-foam, CoB/Ni-foam, CoB catalysts: (A) the survey spectra and the high resolution spectra for (B) Co 2p, (C) B 1s and (D) Ni 2p

XPS was performed to further investigate the surface existing states and the compositions of CoB/Ni-foam and CoB plate catalysts. The survey spectra of CoB/Ni-foam and CoB plate were shown in Fig. S2 (A). The existence of O was attributed to the surface oxidation during the XPS analysis. The surface composition and binding energy of each element were summarized in Table S1. The surface concentrations of Co for CoB/Ni-foam catalysts were much higher than that of CoB plate indicated the severe coverage of CoB by PTFE in CoB plate which was confirmed by the high surface concentration of F. Co was regarded as the active species for BH$_4^-$ oxidation reaction, and the lower surface concentration of Co for CoB plate could account for its low catalytic activity. The Co 2p$_{3/2}$ bands of CoB/Ni-foam and CoB plate (Fig. S2 (B)) could be deconvoluted into three bands, corresponding to Co$^0$, Co$^{2+}$ and satellite peak respectively and all the catalysts showed similar binding energy of Co$^0$. The high resolution B 1s spectra were shown in Fig. S2 (C), the binding energy of B$^0$ for CoB/Ni-foam catalysts and CoB plate were higher than the literature (187.1 eV) which was attributed to the electron-donating effects from B$^0$ to Co$^0$. Interestingly, the binding energy of B$^0$ in CoB/Ni-foam catalysts were about 0.3 eV higher than that of CoB plate which might be due to the further electron transfer from B$^0$ to Ni$^0$. The high-resolution of spectra Ni 2p were shown in Fig. S2 (D). As expected, the binding energy of Ni$^0$ for CoB/Ni-foam catalysts decreased compared to the Ag-sensitized Ni-foam substrate which confirmed the electron transfer between B$^0$ and Ni$^0$. Based on the XPS results, it could be clearly seen that there was a strong interaction between CoB and Ni-foam substrate in the directly formed CoB/Ni-foam catalysts prepared by electroless plating method which gave them a nice all-around performance boost.
Study the cyclic voltammetry (CV) in NaOH solution

Fig. S3 Cyclic voltammograms of CoB/Ni-foam catalysts and CoB plate in N₂-saturated 3 mol L⁻¹ NaOH solution (at scan rate of 50 mV s⁻¹ at 298 K)

Fig. S3 showed the cyclic voltammograms of CoB/Ni-foam and CoB plate in a potential range of −1.2 V to 0.6 V vs. Hg/HgO at a scan rate of 50 mV s⁻¹ in 3 mol L⁻¹ N₂ saturated NaOH solution. All the CoB/Ni-foam catalysts with different plating times showed similar electrochemical behaviors which were typical irreversible electrochemical process and in good accordance with the work reported by Y. Liu. During the positive potential sweep, it could be clearly seen that a wide oxidation peak denoted as A₀₁ appeared between −0.9 V and 0.1 V vs. Hg/HgO which was attributed to the electrooxidation of CoB alloy to Co(OH)₂. Corresponding to peak A₀₁, the reduction peak denoted as C₀₁ in negative scanning process was attributed to the reduction of Co(OH)₂. In addition, there were several anodic peaks emerged in the high potential range of positive scanning process (denoted as A₀₂). These peaks were attributed to the oxidation of Co to higher oxidation states step by step according to the following reactions:

\[
3 \text{Co(OH)}_2 + 2 \text{OH}^- \rightarrow \text{Co}_3\text{O}_4 + 4 \text{H}_2\text{O} + 2 \text{e}^- \quad E^\circ = -0.192\text{V vs. Hg/HgO} \quad (4)
\]

\[
\text{Co(OH)}_2 + \text{OH}^- \rightarrow \text{CoOOH} + \text{H}_2\text{O} + \text{e}^- \quad E^\circ = -0.054\text{V vs. Hg/HgO} \quad (5)
\]

\[
\text{Co}_3\text{O}_4 + 4 \text{OH}^- \rightarrow 3\text{CoO}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \quad E^\circ = +0.477\text{V vs. Hg/HgO} \quad (6)
\]

\[
\text{CoOOH} + \text{OH}^- \rightarrow \text{CoO}_2^+ + \text{H}_2\text{O} + \text{e}^- \quad E^\circ = +0.562\text{V vs. Hg/HgO} \quad (7)
\]

The beginning of peak A₀₂ was about +0.1 V vs. Hg/HgO. Compared to the thermodynamically calculated value ($E^\circ$) of −0.192V mentioned above, the positive potential shift indicated that there was a big overpotential involved in the oxidation of Co(OH)₂ to Co₃O₄ or might be attributed to existence of B in CoB alloy. As shown in Fig. S3, the currents of peak A₀₁ and A₀₂ increased with the plating times which accorded well with the CoB loading amount, XRD and SEM analysis results.
Study BOR activity by linear sweep voltammetry (LSV)

Fig. S4 Linear sweep voltammograms of CoB/Ni-foam catalysts with different electroless plating times in N\textsubscript{2}-saturated 0.05 mol L\textsuperscript{-1} NaBH\textsubscript{4} + 3 mol L\textsuperscript{-1} NaOH solution with scan rate of 20 mV/s at 298 K

Fig. S5 Linear sweep voltammograms of CoB/Ni-foam catalysts with different electroless plating times in N\textsubscript{2}-saturated 0.05 mol L\textsuperscript{-1} NaBH\textsubscript{4} + 3 mol L\textsuperscript{-1} NaOH solution with different scan rates at 298 K
The relationship of $E_p$ with $\log v$ and $I_p$ with $v^{1/2}$ (for calculating electron transferred number of $n$)

Fig. S6 (A) the dependence of peak current $I_p$ on the square root of scan rate ($v^{1/2}$) and (B) the dependence of peak potential $E_p$ on the logarithm of scan rate ($\log v$)
Determination of heterogeneous rate constants ($k_s$)

Fig. S7 Plots of $\ln I_p A^2$ vs. $(E_{p A^2} - E^0)$ of CoB/Ni-foam catalysts with different electroless plating times in N$_2$-saturated 0.05 mol L$^{-1}$ NaBH$_4$ + 3 mol L$^{-1}$ NaOH solution at 298 K

The standard heterogeneous rate constants $k_s$ / cm s$^{-1}$ during borohydride electrooxidation process could be calculated by the following equation 2:

$$I_p = 0.227nFAc_{BH_4}k_s \exp\left\{\frac{(1-\alpha)n_F}{RT}\left(E_p - E^0\right)\right\},$$

where $I_p$ was the peak current (A), $n$ was the number of electron transferred (calculated in section 3.2), $F$ was the Faraday constant (96485 C mol$^{-1}$), $A$ was the active surface area (cm$^2$), $C_{BH_4}$ was the concentration of BH$_4^-$ (mol dm$^{-3}$), $E_p$ was the peak potential (V) and $E^0$ was the formal potential (V). The standard heterogeneous rate constants $k_s$ could be obtained by plotting $\ln I_p A^2$ vs. $(E_{p A^2} - E^0)$ curves, and the intercepts of the curves was proportional to $k_s$. The results were summarized in Table S2.
Cell performance using CoB plate as anode

\textbf{Fig. S8} Cell polarization and power density curves of the membraneless DBFC with CoB plate anode in 1 mol L$^{-1}$ NaBH$_4$ + 3 mol L$^{-1}$ NaOH solution at 303 K
Table S1 The surface compositions and the corresponding binding energies of CoB/Ni-foam, CoB plate, Ag-sensitized Ni-foam

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>5EP</th>
<th>7EP</th>
<th>11EP</th>
<th>CoB Plate</th>
<th>Ag-sensitized Ni-foam</th>
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<tr>
<td>Surface composition (At. %)</td>
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<tr>
<td>Co</td>
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<td>16.7</td>
<td>19.1</td>
<td>1.8</td>
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<tr>
<td>B</td>
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<td>8.1</td>
<td>10.9</td>
<td>0.7</td>
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<tr>
<td>Ni</td>
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<td>4.6</td>
<td>*</td>
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<tr>
<td>Ag</td>
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<td>0.05</td>
<td>0.06</td>
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<td>–</td>
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<tr>
<td>O</td>
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<td>36.6</td>
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<td>29.4</td>
<td>29.7</td>
<td>36.7</td>
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<tr>
<td>F</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<th>Binding energy / eV</th>
<th>Co$^0$</th>
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<tr>
<td>B$^0$</td>
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<td>187.9</td>
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<tr>
<td>Ni$^0$</td>
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<td>852.2</td>
<td>–</td>
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* The surface Ni content could not be obtained because the Ni 2$p$ band of CoB plate was overlapped with F auger band and the Ni 3$p$ band was too weak to be used for quantification.
Table. S2 Standard heterogeneous rate constants $k_s$ / cm s$^{-1}$ calculated from the plots of ln $I_{pA2}$ vs. ($E_{pA2} - E^0$)

<table>
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<tbody>
<tr>
<td>$k_s$ / cm s$^{-1}$</td>
<td>$6.3 \times 10^{-5}$</td>
<td>$6.9 \times 10^{-5}$</td>
<td>$6.7 \times 10^{-5}$</td>
<td>$6.3 \times 10^{-5}$</td>
<td>$6.2 \times 10^{-5}$</td>
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References