

Electronic supplementary information for
Succulent-plant-like Ni-Co alloy efficient catalysts for direct
borohydride fuel cells

Jinliang Cai^a, Peng Chen^a, Bihao Hu^a, Chuanlan Xu^a, Ying Yang^a, Jiazhi Meng^a,

Biao Zhang^a, Danmei Yu^{,a}, Xiaoyuan Zhou^{*,b}, and Changguo Chen^a*

^a School of Chemistry and Chemical Engineering, Chongqing University, Chongqing,
401331, P.R. China

^b College of Physics, Chongqing University, Chongqing, 401331, P.R. China

Corresponding Authors

***Danmei Yu's** e-mail: yudanmei-1@163.com.

***Xiaoyuan Zhou's** e-mail: xiaoyuan2013@cqu.edu.cn.

Notes

The authors declare no competing financial interest.

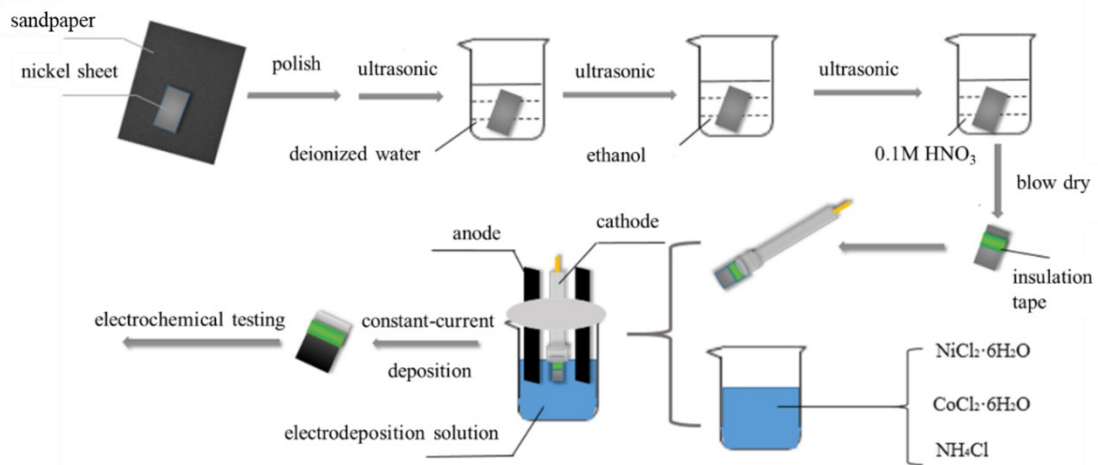


Figure S1. Schematic diagram of catalyst preparation process

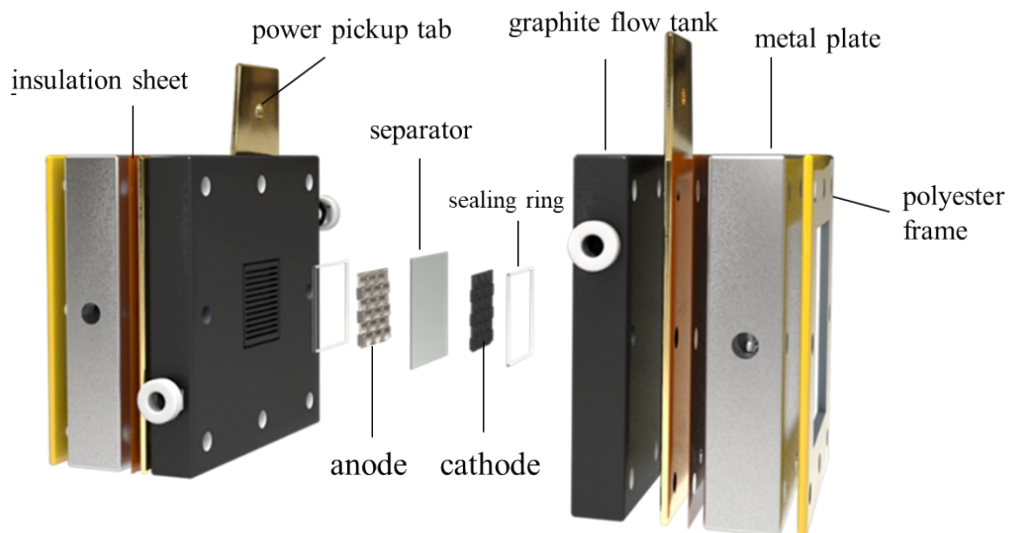


Figure S2. The structure diagram of the DBFC device.

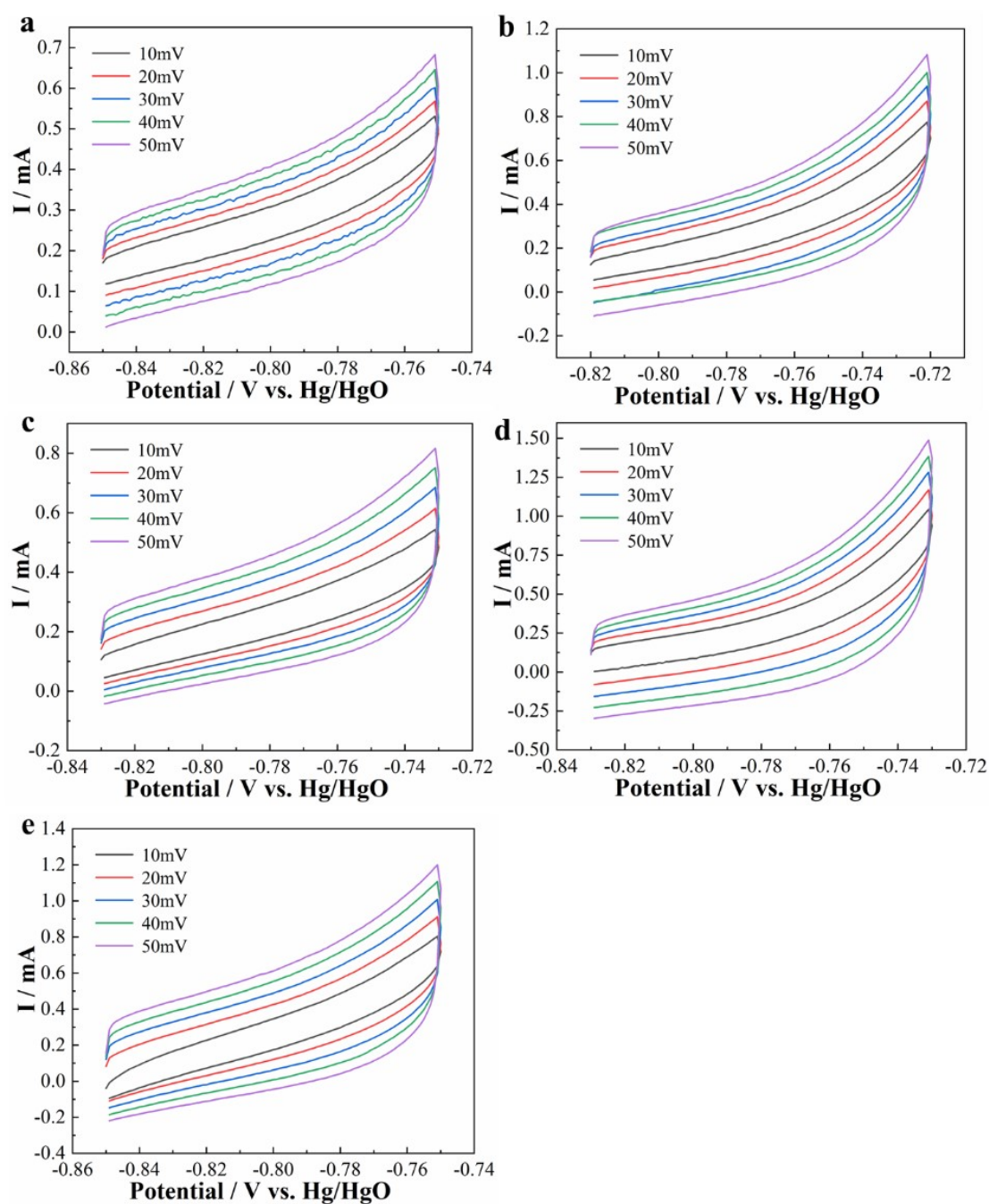


Figure S3. The CV curves on (a) Ni, (b) Ni_{0.935}-Co_{0.065}, (c) Ni_{0.909}-Co_{0.091}, (d) Ni_{0.889}-Co_{0.111}, and (e) Ni_{0.87}-Co_{0.13} catalysts in 1 M KOH solution.

Calculation of Electrochemical Active Surface Area (ECSA) by CV test using the double-layer capacitance method. The CV test was performed in 1 M KOH solution in the range of ± 0.5 V open circuit potential and the results are shown in Figure S3. According to the CV curves in Figure S3, the ECSA of the prepared catalyst can be calculated by equations 1 and 2

$$i_c = vC_{DL} \quad (1)$$

$$ECSA = C_{DL}/C_S \quad (2)$$

Where C_s represents the theoretical specific capacitance of Ni catalyst in alkaline electrolyte, which is $40 \mu\text{F cm}^{-2}$. Moreover, all calculation results can be found in Table S1.

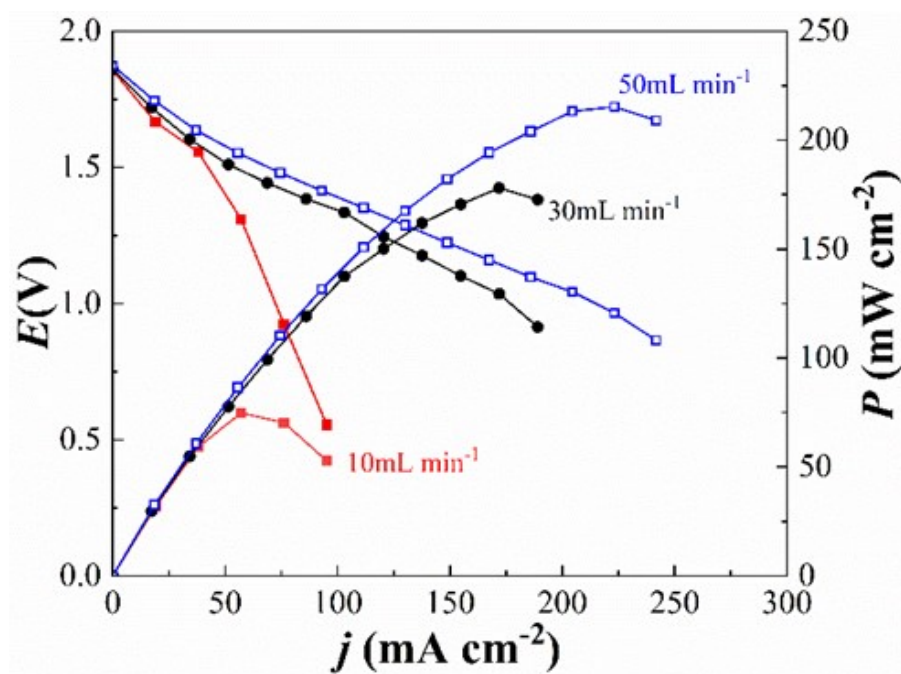


Figure S4. Performance of a DBFC using $\text{Ni}_{0.889}\text{-Co}_{0.111}$ anode under different flowrate

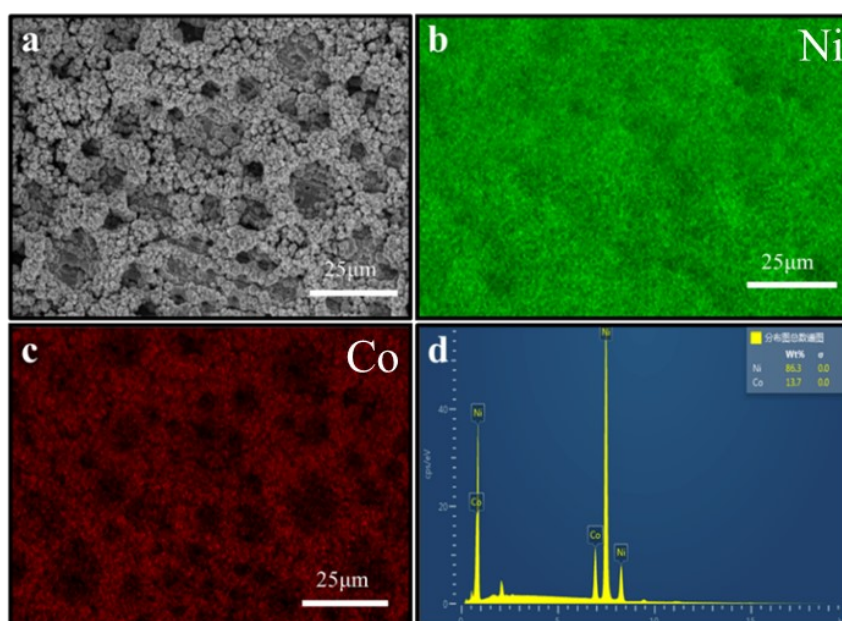


Figure S5. (a) SEM images of $\text{Ni}_{0.889}\text{-Co}_{0.111}$, (b-c) Ni and Co elemental distribution of $\text{Ni}_{0.889}\text{-Co}_{0.111}$, (d) EDS spectra of $\text{Ni}_{0.889}\text{-Co}_{0.111}$

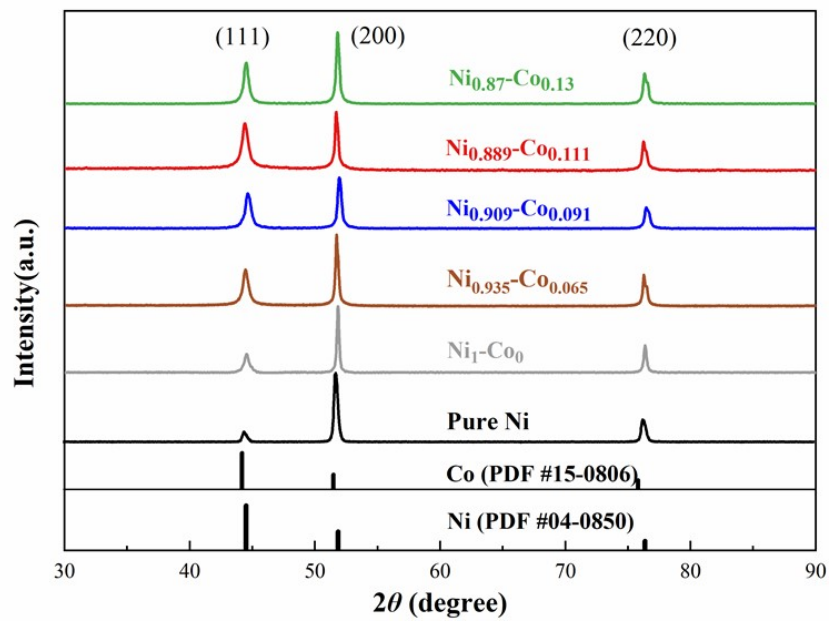


Figure S6. XRD patterns of prepared catalysts.

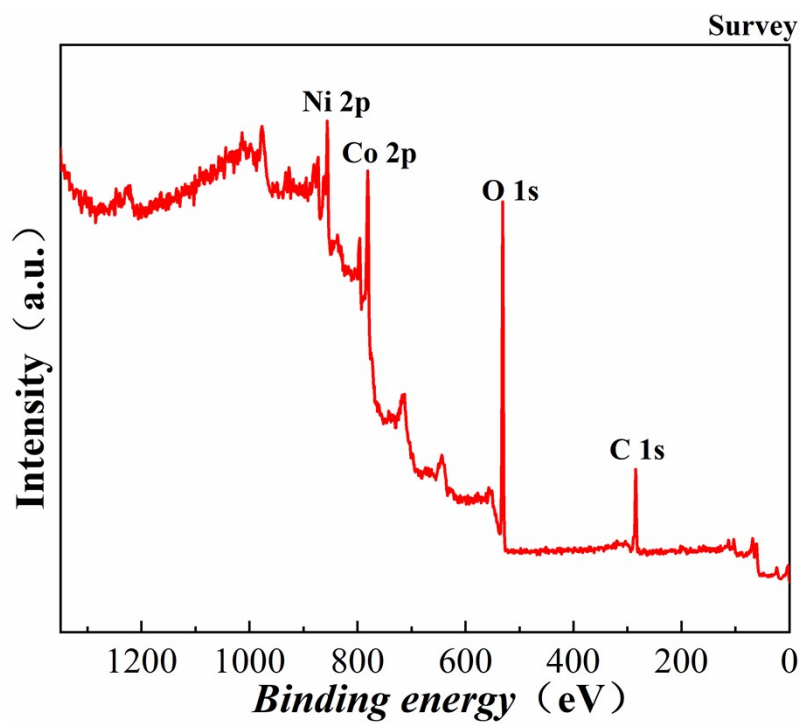


Figure S7. XPS spectra of survey for $\text{Ni}_{0.889}\text{-Co}_{0.111}$ catalyst

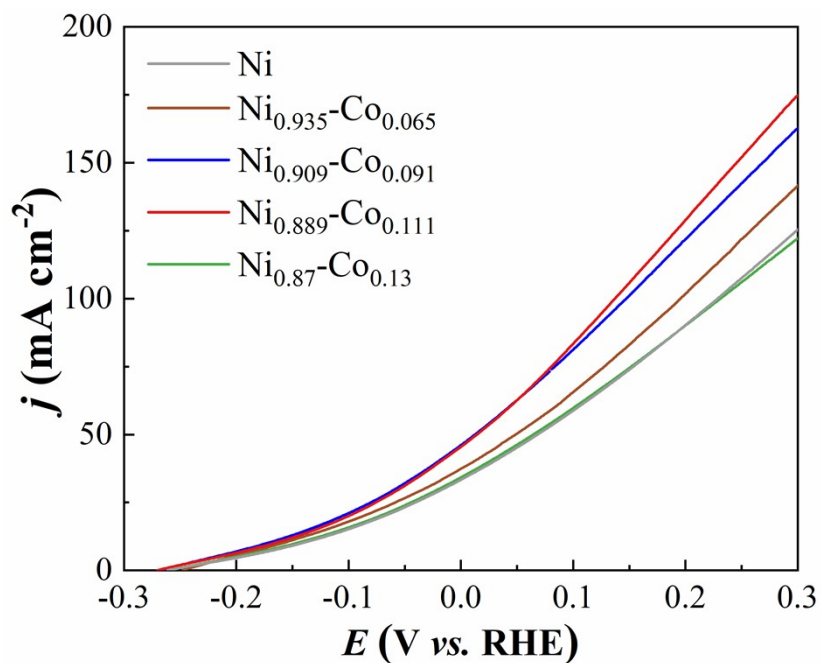


Figure S8. LSV curves of BOR on Ni_x-Co_y catalysts in the mixed solution of 0.135 mol L⁻¹ NaBH₄ and 2 mol L⁻¹ NaOH at scan rate of 10 mV s⁻¹ and 298 K

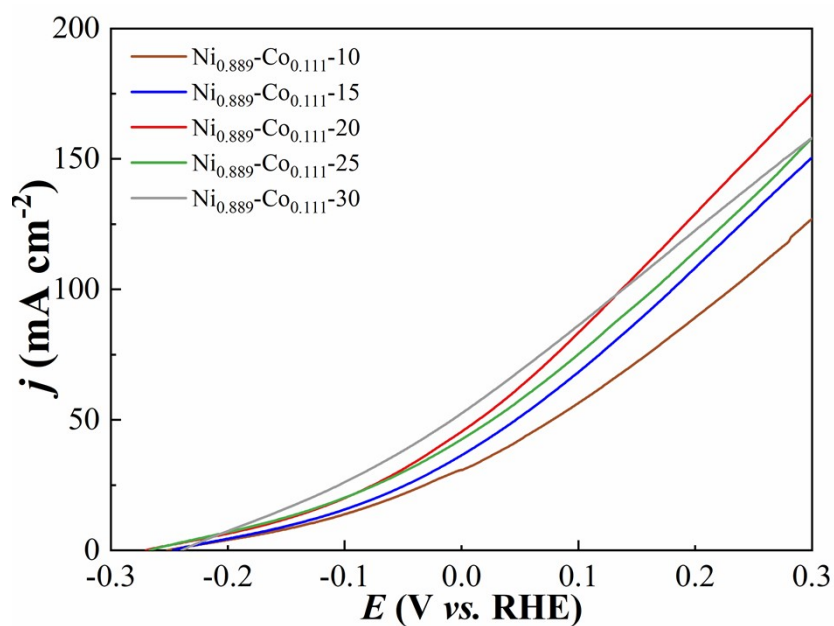


Figure S9. LSV curves of BOR on Ni_x-Co_y catalysts in the mixed solution of 0.135 mol L⁻¹ NaBH₄ and 2 mol L⁻¹ NaOH at scan rate of 10 mV s⁻¹ and 298 K

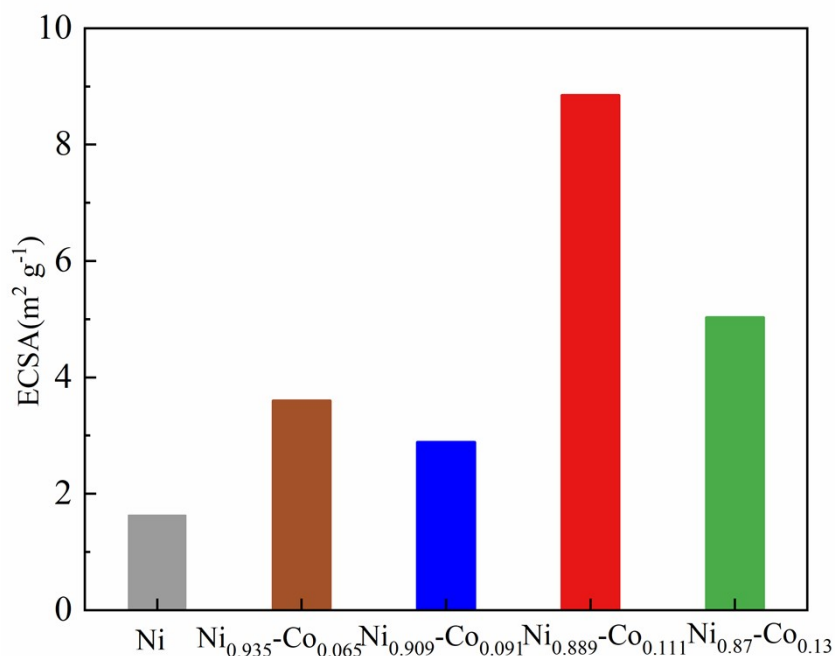


Figure S10. ECSA of different catalysts

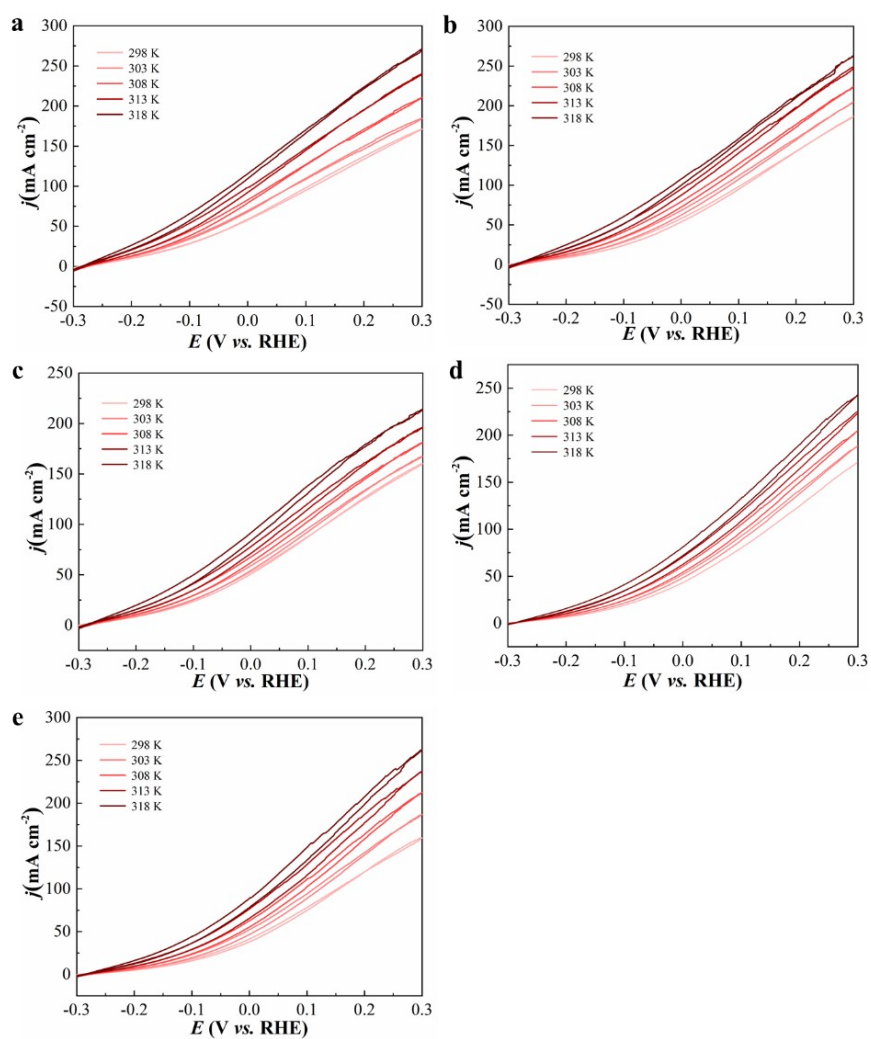


Figure S11. CV curves of BOR on (a) Ni_{0.935}-Co_{0.065}, (b) Ni_{0.909}-Co_{0.091}, (c) Ni_{0.889}-Co_{0.111}, (d) Ni_{0.87}-Co_{0.13} and (e) Ni catalyst at different temperatures in the mixed solution of 0.135 mol L⁻¹ NaBH₄ and 2 mol L⁻¹ NaOH

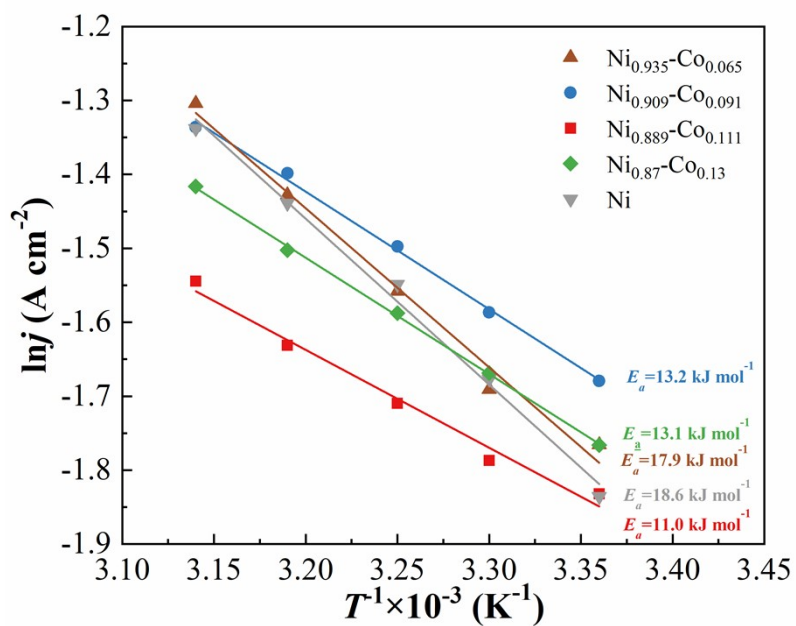


Figure S12. Arrhenius plots of BOR on different catalysts at 0.3 V vs. RHE under scan rate of 10 mV s^{-1}

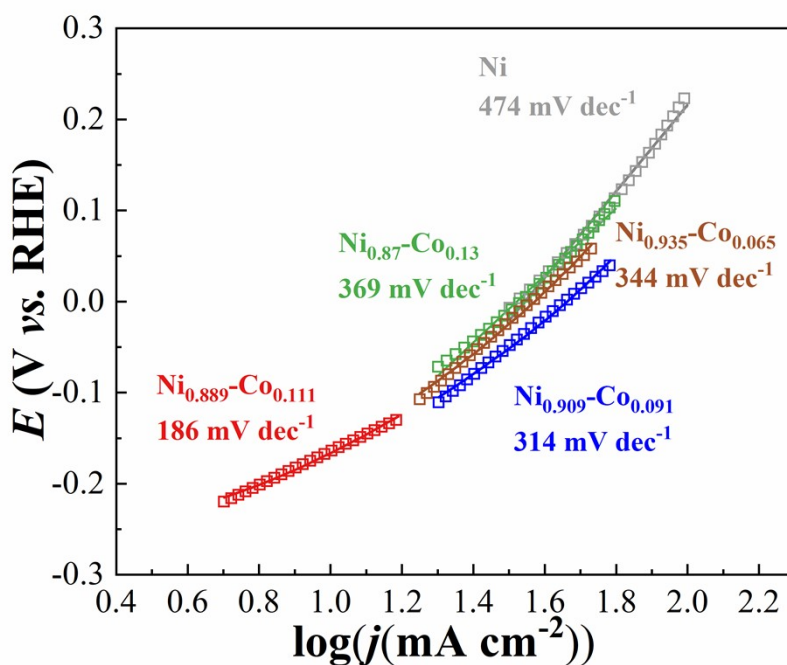


Figure S13. The corresponding Tafel slopes fitted based on the results in Figure S8

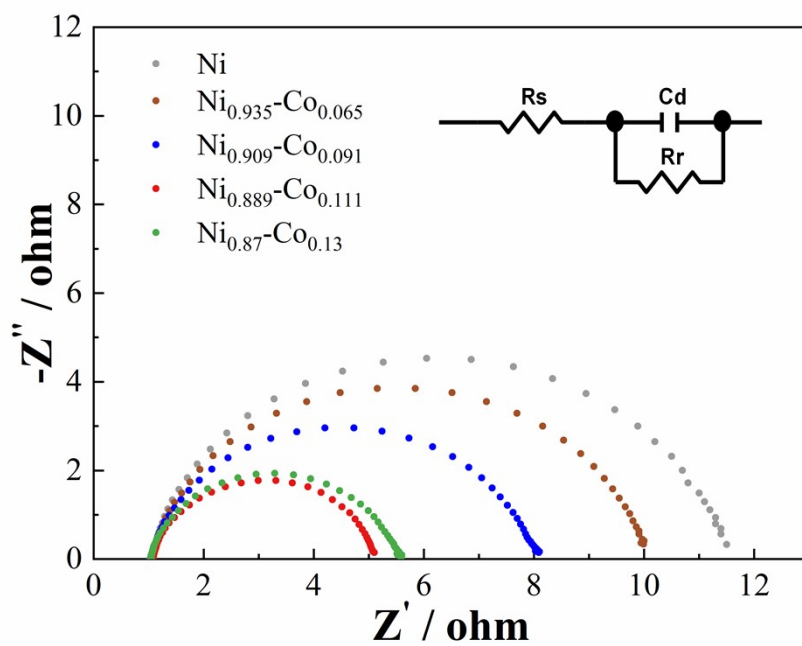


Figure S14. Nyquist plots of the Ni_x-Co_y catalysts

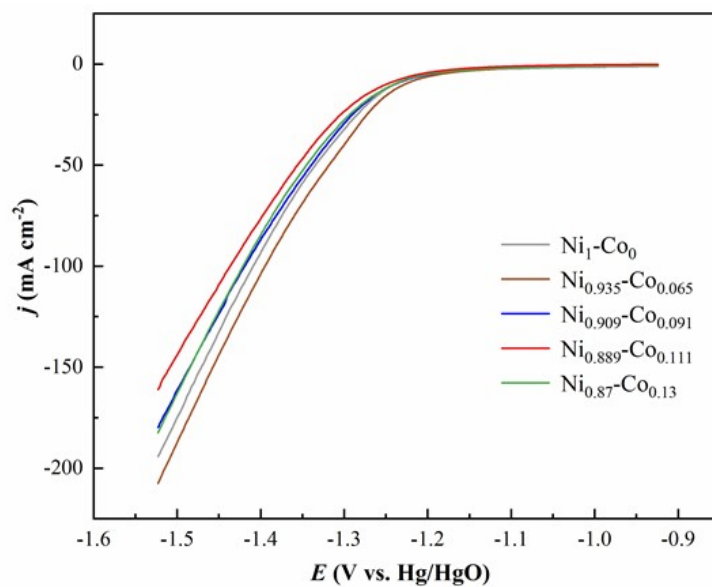


Figure S15. LSV curves of HER on Ni-Co catalyst

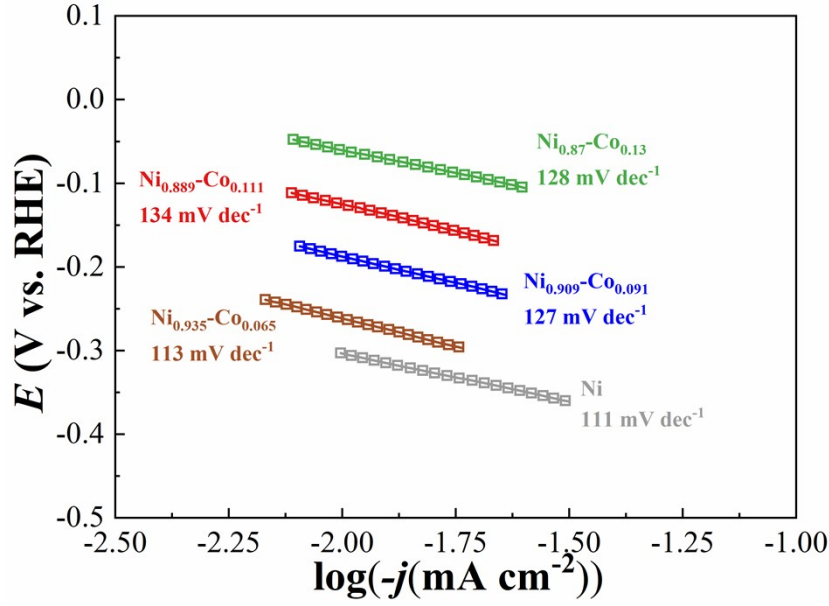


Figure S16. The corresponding Tafel slopes fitted based on the results in Figure S14

Measurement of the transfer electron number

The prepared catalyst was cut into a size of about 3 mm × 3 mm and fixed on the surface of a rotating disc electrode (RDE). CV was done in a conventional three-electrode system using RDE as WE, carbon rod as CE, Hg/HgO electrode as RE, and a mixed solution of 5 mM NaBH₄ and 1 M NaOH as electrolyte at different disc speeds (200, 400, 600, 800, and 1000 rpm) and a potential scan rate of 20 mV s⁻¹. The transfer electron number was calculated according to the Koutecky-Levich equation follow as:

$$j^{-1} = j_k^{-1} + j_d^{-1} = j_k^{-1} + B^{-1}\omega^{-0.5}$$

(3)

In the formula, j_k^{-1} is the dynamic current density, and j_d^{-1} is the diffusion-limited current density, ω is the rotational speed of RDE. B can be calculated according to Levich equation (4).

$$B = 0.62nD^{2/3}F\nu^{-1/6}c_0 \quad (4)$$

Here, n is the transfer electron number, D is the diffusion coefficient of BH₄⁻ (2.6×10^{-5} cm² s⁻¹), F is the Faraday constant (96485 C mol⁻¹), ν is the kinematic viscosity of the electrolyte (0.0118 cm² s⁻¹), and c_0 is the concentration of NaBH₄ (5 mM).

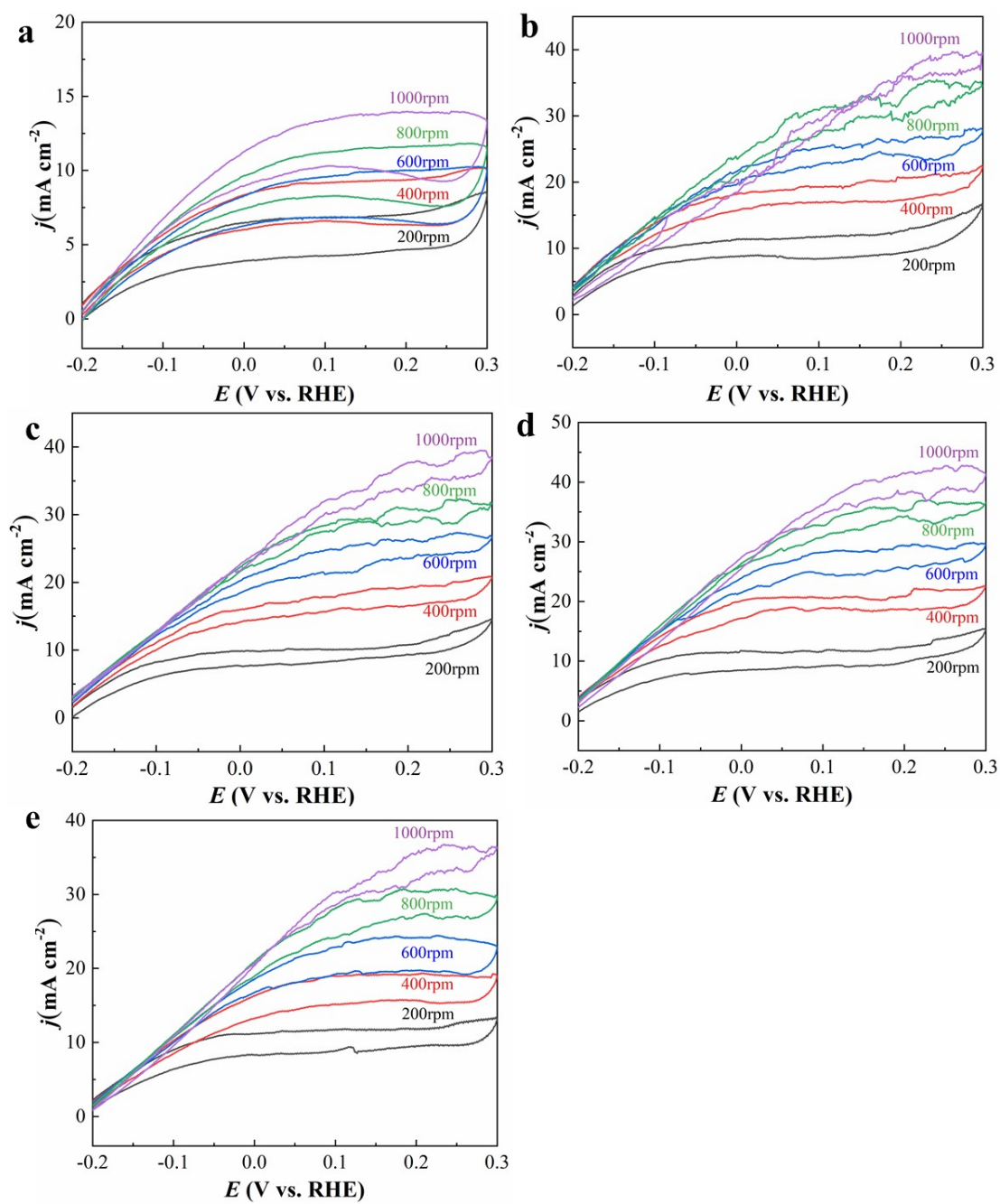


Figure S17. CV curves of BOR on (a) Ni, (b) Ni_{0.935}-Co_{0.065}, (c) Ni_{0.909}-Co_{0.091}, (d) Ni_{0.889}-Co_{0.111}, and (e) Ni_{0.87}-Co_{0.13} catalysts at different speeds (the five curves in each picture from top to bottom correspond to 1000, 800, 600, 400, 200rpm)

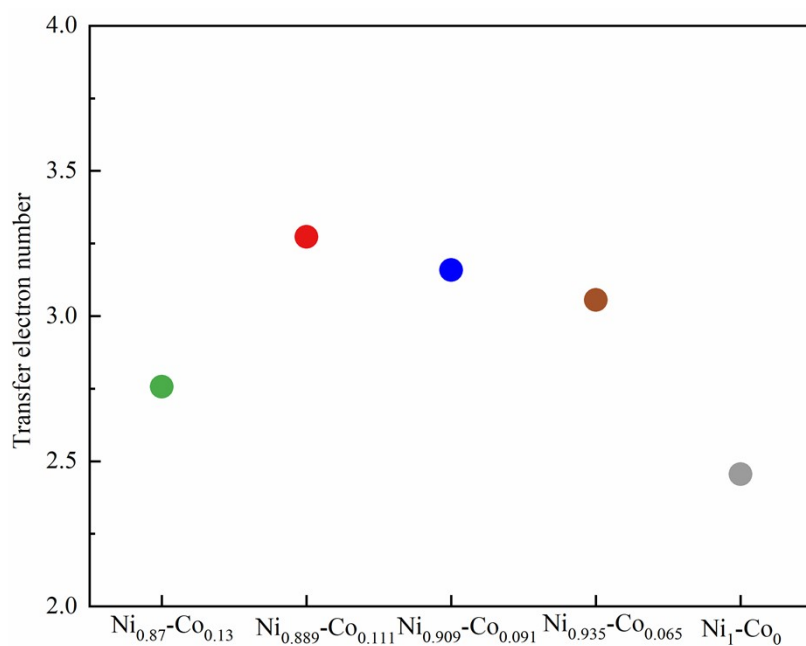


Figure S18. Transfer electron number of BOR on different catalysts

Table S1. Summary of electrochemical performances on prepared catalysts.

Catalyst	Loading quality /mg	ECSA /m ² g ⁻¹	Activation energy of BOR /kJ mol ⁻¹	BOR <i>j</i> /mA cm ⁻²	BOR Tafel slope /mV dac ⁻¹	HER Tafel slope /mV dac ⁻¹	Electron transfer number	η /%
Ni	6	1.6343	18.65	125.4	473.8	111.0	2.45	61.1
Ni _{0.935} -Co _{0.065}	6	3.6	17.89	141.6	344.1	113.3	3.06	83.8
Ni _{0.909} -Co _{0.091}	4	2.8875	13.22	162.7	314.0	126.6	3.16	81.3
Ni _{0.889} -Co _{0.111}	6	8.85	11.00	174.8	186.1	134.1	3.27	85.1
Ni _{0.87} -Co _{0.13}	8	5.0333	13.08	122.1	368.8	127.9	2.76	79.7

Table S2. Operating conditions of DBFC with different anode catalysts. Symbols: T is the operating temperature, OCV is the open circuit voltage, P is the power density.

Ref.	Anode	Cathode	Separator	Anolyte	Catholyte	$T(K)$	OCV(V)	$P(mW\ cm^{-2})$
[4]	<u>NiMoN@NC</u>	FeN-HPC	non	1.0 M NaBH ₄ + 3.0 M NaOH	O ₂	333	2.0	112
[36]	<u>Pd-Ni/N-rGO</u>	Pt/C	<u>Nafion 117</u>	1.0 M NaBH ₄ + 2.0 M NaOH	2 M H ₂ O ₂ +0.5 M H ₂ SO ₄	333	2.0	354
[36]	<u>Pd-Co/N-rGO</u>	Pt/C	<u>Nafion 117</u>	1.0 M NaBH ₄ + 2.0 M NaOH	2 M H ₂ O ₂ +0.5 M H ₂ SO ₄	333	1.9	275
[41]	<u>Au-NP@rGO</u>	Pd/C	<u>Nafion 117</u>	0.4 M NaBH ₄ + 2.0 M NaOH	0.8 M H ₂ O ₂ +2 M H ₂ SO ₄	343	1.63	60
[49]	<u>PdAuNi/C</u>	Pt	<u>Nafion 117</u>	1.0 M NaBH ₄ + 4.0 M NaOH	5 M H ₂ O ₂ +1.5 M HCl	348	1.9	175
[50]	<u>C_{Ni}-S_{Pt}/rGO</u>	Pt/C	<u>Nafion</u>	1.0 M NaBH ₄ + 2.0 M NaOH	2 M H ₂ O ₂ +0.5 M H ₂ SO ₄	333	1.9	234
[51]	<u>Ni_{ED}/eNFT</u>	Pt/C	Bipolar interface (175)	1.5 M NaBH ₄ + 3.0 M KOH	15 wt% H ₂ O ₂ +1.5 M H ₂ SO ₄	343	2.0	446
This work	<u>Ni_{0.889}-Co_{0.111}</u>	Pt/C	<u>Nafion 117</u>	1.5 M NaBH ₄ + 3 M NaOH	1.5 M H ₂ O ₂ +2 M H ₂ SO ₄	343	1.87	490
This work	Pt/C	Pt/C	<u>Nafion 117</u>	1.5 M NaBH ₄ + 3 M NaOH	1.5 M H ₂ O ₂ +2 M H ₂ SO ₄	343	1.79	178
This work	Ni	Pt/C	<u>Nafion 117</u>	1.5 M NaBH ₄ + 3 M NaOH	1.5 M H ₂ O ₂ +2 M H ₂ SO ₄	343	1.76	265