Electronic Supplementary Information

Enhancing Bifunctional Catalytic Activity of Cobalt Nickel Sulfide Spinel Nanocatalysts through Transition Metal Doping and its Application in Secondary Zinc-Air Batteries

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S1. Schematic of continuous hydrothermal flow synthesis

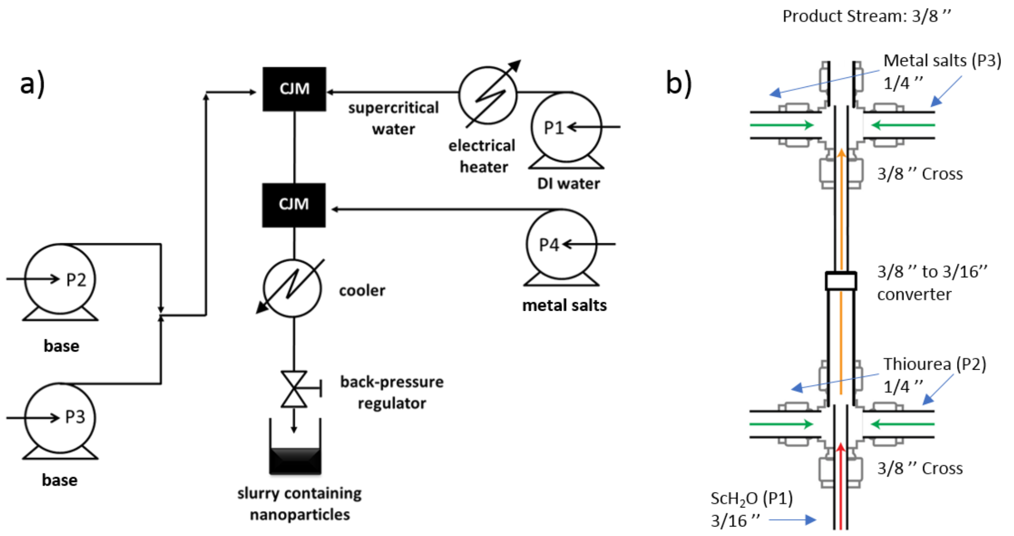

Fig. S1 Diagram of the (a) laboratory-scale CHFS apparatus and (b) dual CJM mixer setup.

S2. Digital image of the battery tester and the Zn-air battery

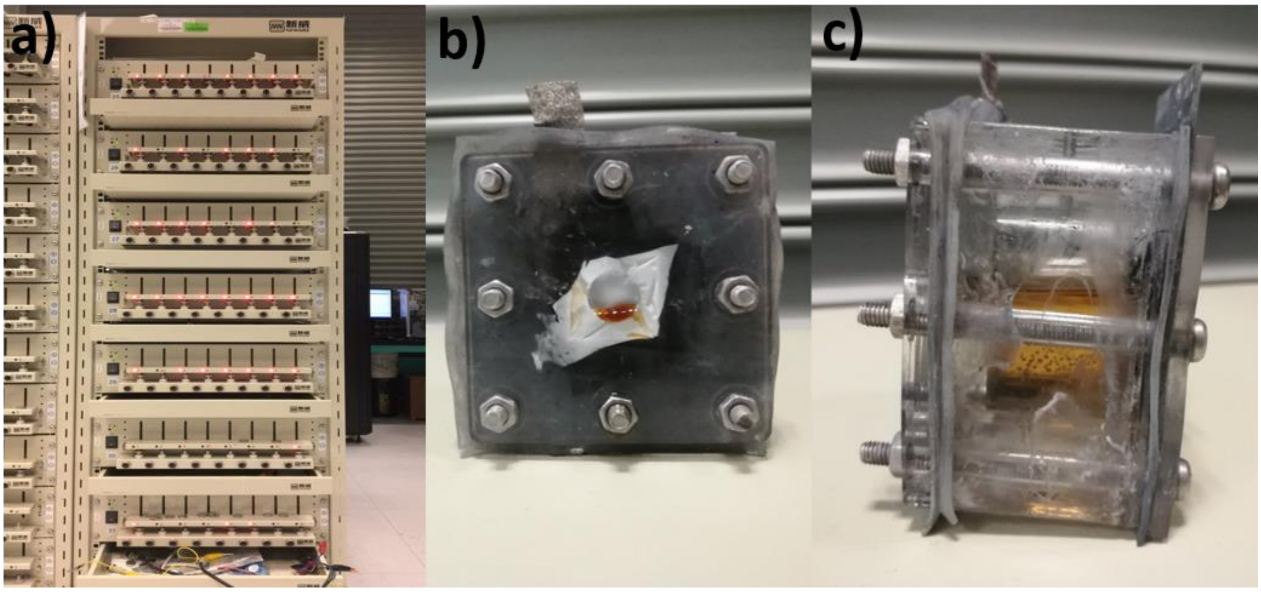

Fig. S2 a) Illustration of the Neware battery tester (Model V5, China). b) and c) the home-made Zinc-Air cell

S3. EDS mapping and STEM measurement of the samples

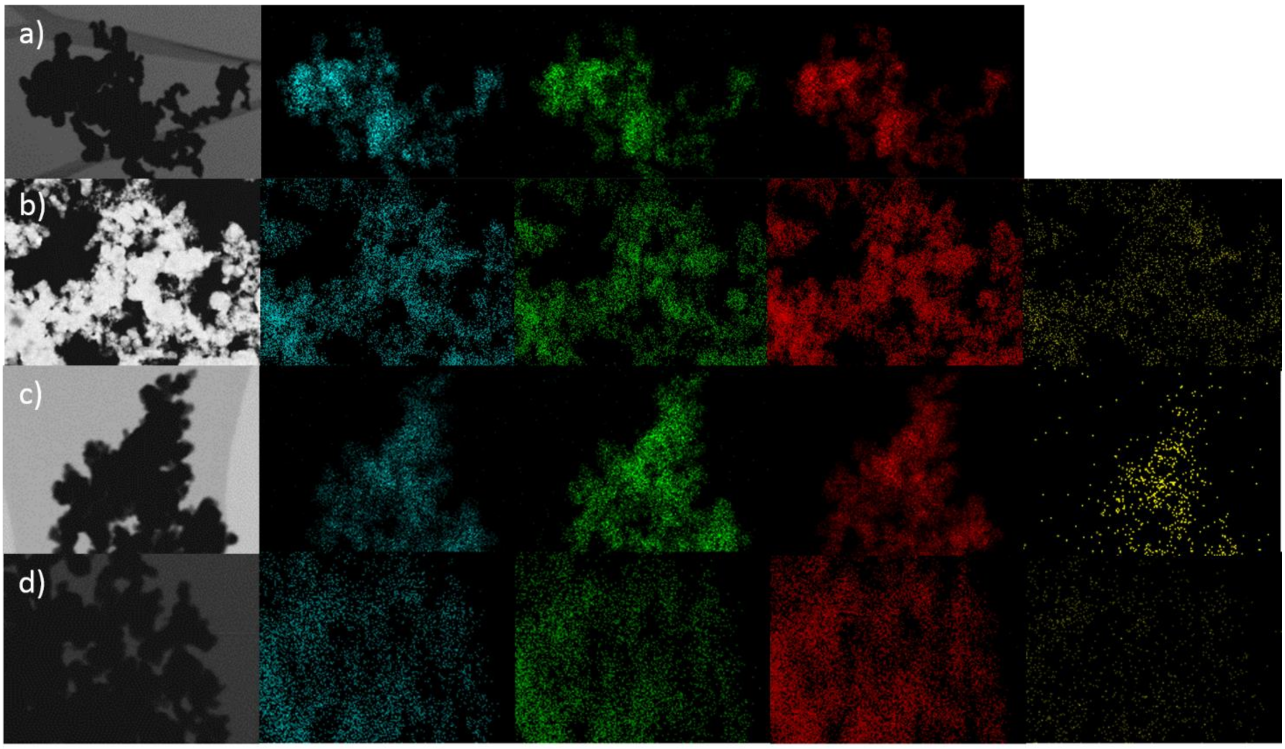

Fig. S3 EDS Mapping of the a) undoped, b) chromium-doped, c) manganese-doped, d) iron-doped nickel-cobalt sulfide samples, with nickel (blue), cobalt (green), sulfur (red), and their respective dopants (yellow) shown together with the reference STEM image.

S4. XPS measurement of the remaining samples

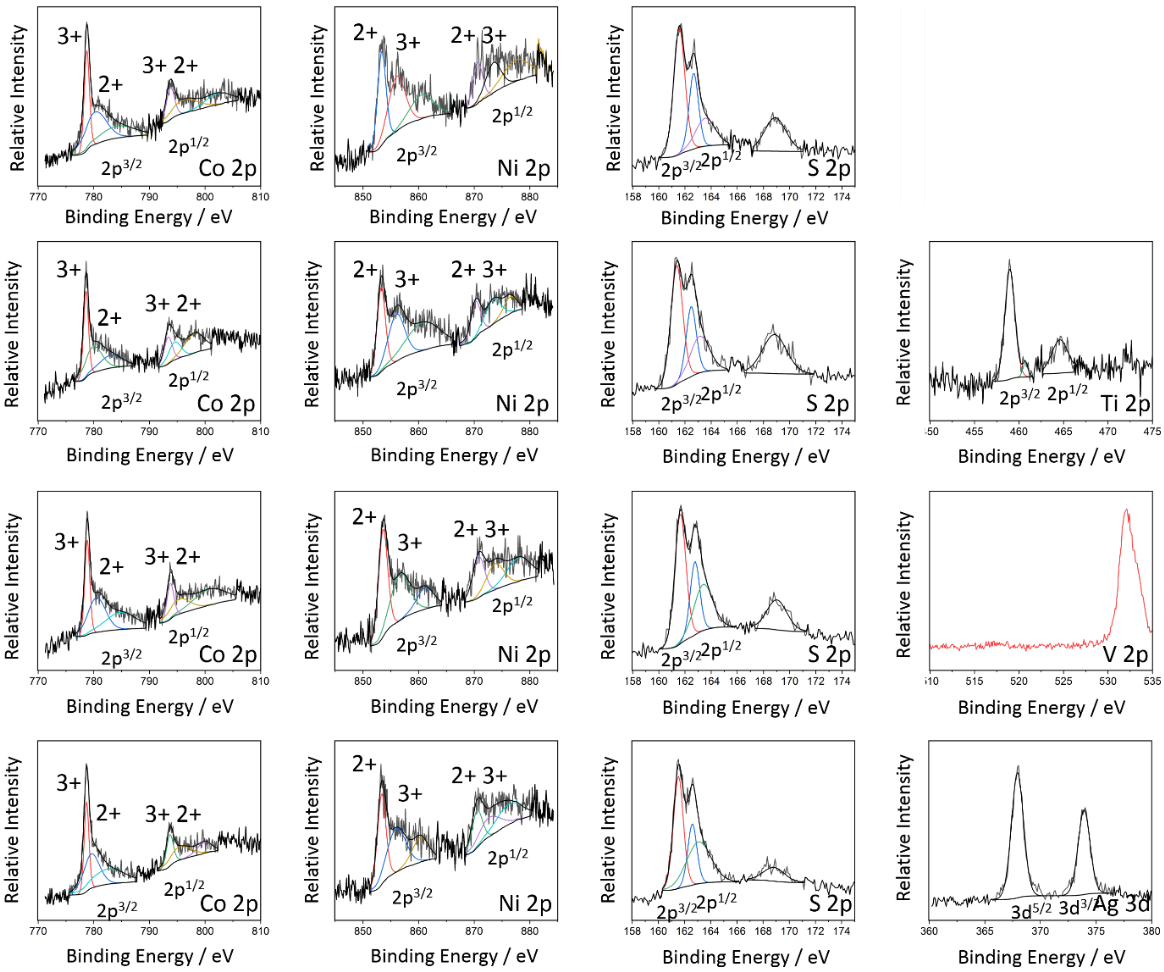

Fig. S4 XPS spectra of the undoped, titanium-, vanadium-, and silver-doped cobalt nickel sulfide samples belonging to the cobalt, nickel, sulfur, and their respective dopant species.

S5. Electrochemical characterizations

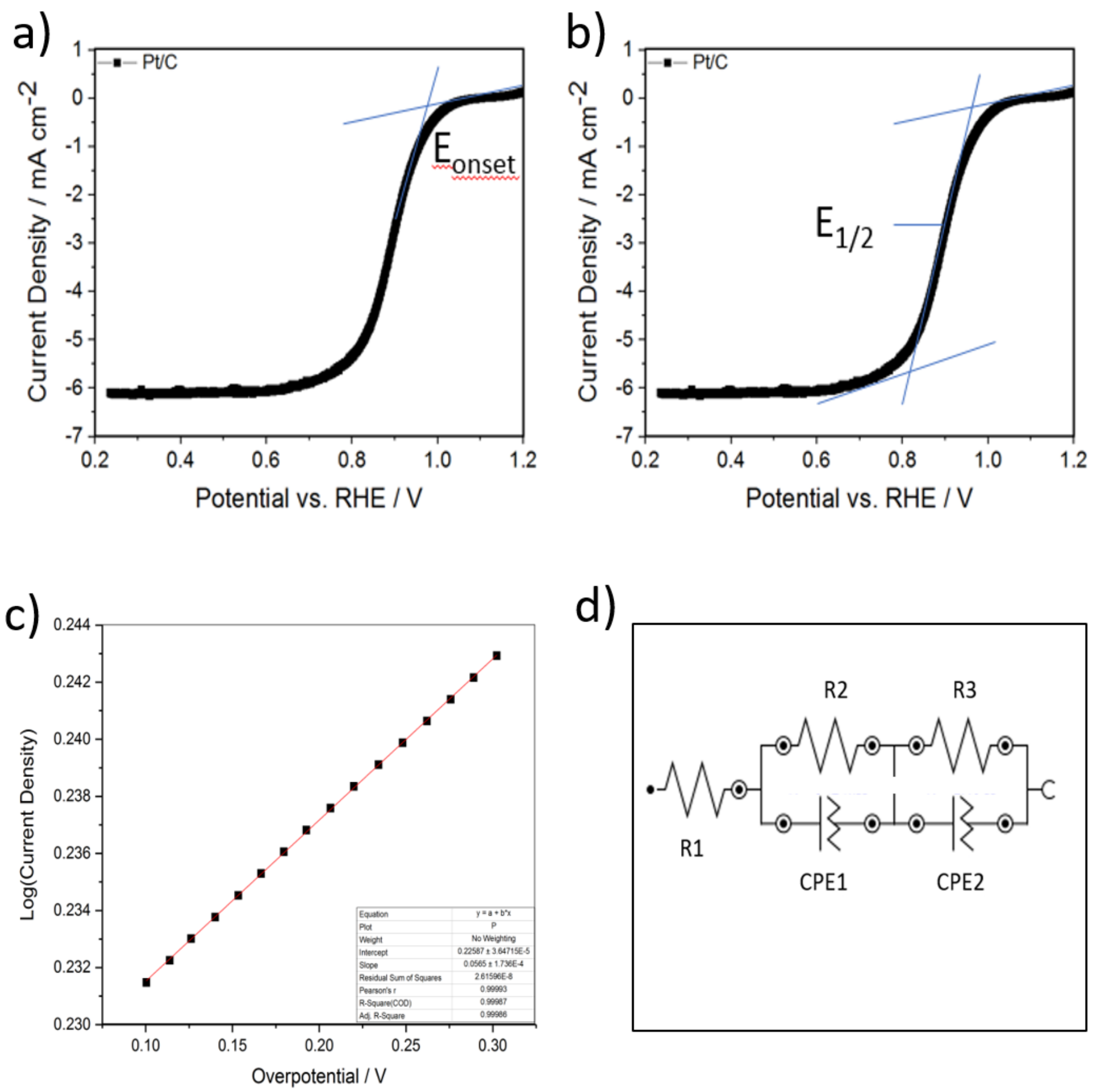

Fig. S5 a) Illustration of the tangential method (blue) of determining ORR onset and b) half-wave potentials for Pt/C. c) Tafel slope plot of the commercial RuO_2 catalyst derived from the LSV curves from Figure 4. d) Idealized circuit layout of the Zn-air cells made with cobalt-nickel sulfide catalysts as cathodes, derived from Nyqvist plots from Figure 6c.

S6. Determination of Electrochemical Surface Area (ECSA) from Electrochemical Impedance Spectroscopy

It has been argued in the literature that the double-layer capacitance of a material such as $NiCo_2S_4$ is linearly proportional to the ECSA.[1] Acharya et al. have previously shown that ECSA can be determined from the Nyqvist plots obtained from EIS results by calculating the double layer capacitance C_{dl} given that a parallel circuit consisting of a resistor and a constant phase element are present.[2, 3] This is given by the equation:

$$C_{dl} = \frac{(Y_0 * R_p)^{\frac{1}{n}}}{R_p},$$

Where C_{dl} is the capacitance of the double layer (F), Y_0 is a parameter that relates to the magnitude of capacity ($S*s^{\alpha}$), R_p is the polarization resistance connected in parallel with the constant phase element (CPE), and n is a dimensionless exponent that relates to inhomogeneity of the surface, used to calculate CPE. The calculated C_{dl} values for the undoped-, chromium-doped, manganese-doped, and iron-doped samples were 7.777 mF, 9.571 mF, 8.614 mF, respectively, in broad agreement with literature for $NiCo_2S_4$.[1]

Table S1. Bet surface areas of the as-synthesized pure and doped nickel cobalt sulfides**.**

Sample	Surface Area / m^2g^{-1}
NC11	10.69
NC11 (Ti)	19.67
NC11 (V)	16.42
NC11 (Cr)	32.58
NC11 (Mn)	22.19
NC11 (Fe)	18.82
NC11 (Ag)	18.76

Table S2. Elemental composition results based on XRF analysis, normalized to the amount of sulphur in $NiCo_2S_4$.

Dopant Species	Ni	Co	S	Dopant
Pure	2.42	2.84	4	None
Titanium	2.54	2.72	4	0.44
Vanadium	2.34	2.73	4	0.14
Chromium	2.06	2.36	4	0.39
Manganese	2.16	2.50	4	0.36
Iron	2.17	2.51	4	0.44
Silver	2.14	2.50	4	0.37

Table S3. The average crystallite size of the as-synthesized pure and doped nickel cobalt sulfides, estimated via the Scherrer Equation from the (001) and (220) peaks of the XRD patterns.

Sample	Average crystallite size/nm
NC11	15.1
NC11 (Ti)	10.3
NC11 (V)	7.6
NC11 (Cr)	7.4
NC11 (Mn)	17.0
NC11 (Fe)	8.9
NC11 (Ag)	10.2

References

1. X.-Z. Song, F.-F. Sun, Y.-L. Meng, Z.-W. Wang, Q.-F. Su and Z. Tan, *New Journal of Chemistry*, 2019, **43**, 3601-3608.
2. P. Acharya, J. Burrow, M. Abolhassani and L. F. Greenlee, *ECS Transactions*, 2018, **85**, 81.
3. V. Jovic, *Gamry Instruments Inc*, 2003, 9-11.