Supporting Information

Bifunctionally Active Nanosized Spinel Cobalt Nickel Sulfides for Sustainable Secondary Zinc-Air Batteries: Examining the effects of compositional tuning on OER and ORR activity

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

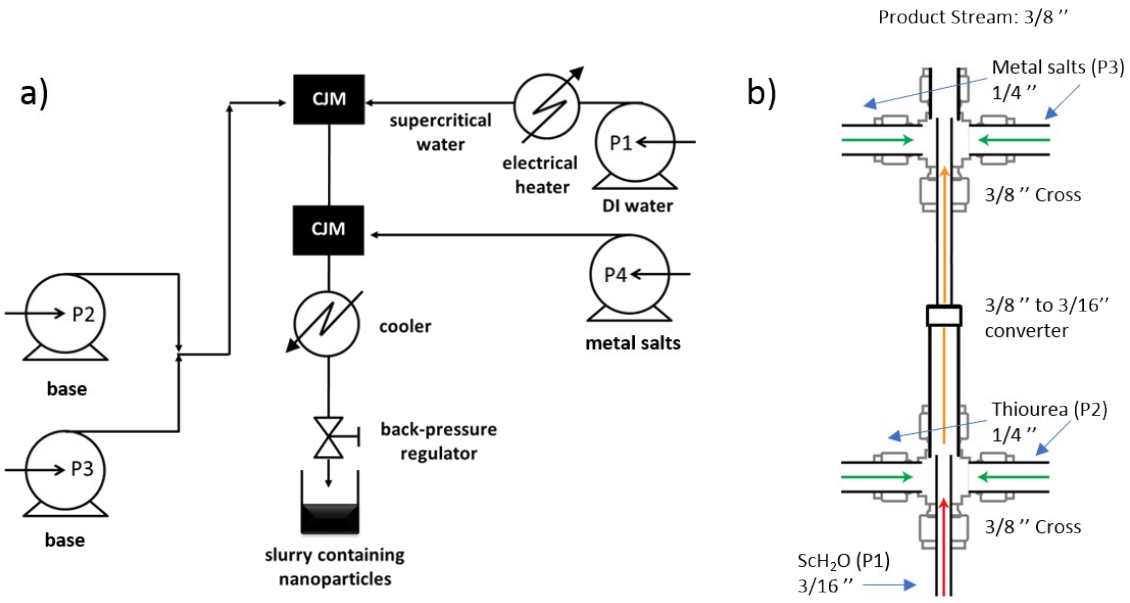


Figure S2. Illustration of the Neware battery tester (Model V5, China).

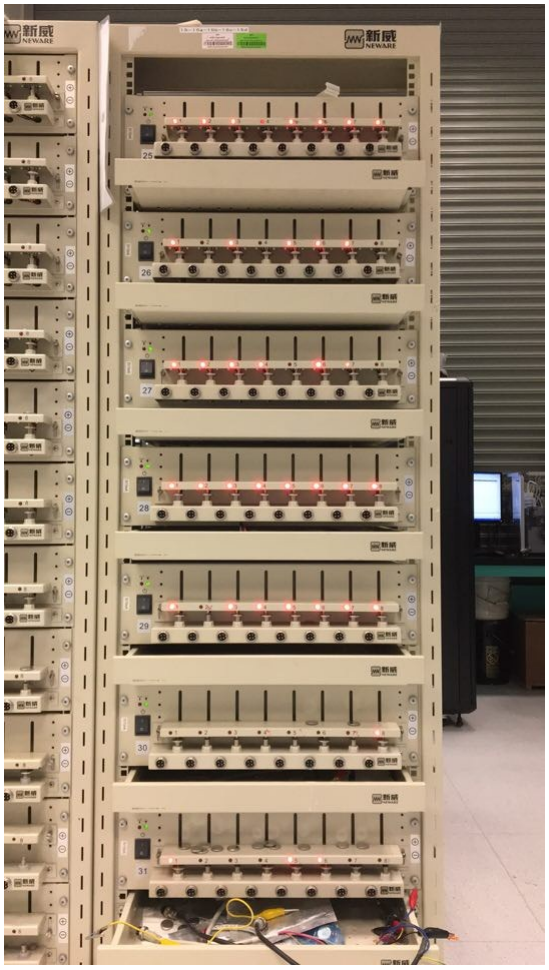


Figure S3. Illustration of the tangential method (green) of determining ORR onset potential for NC11 at 925 mV.

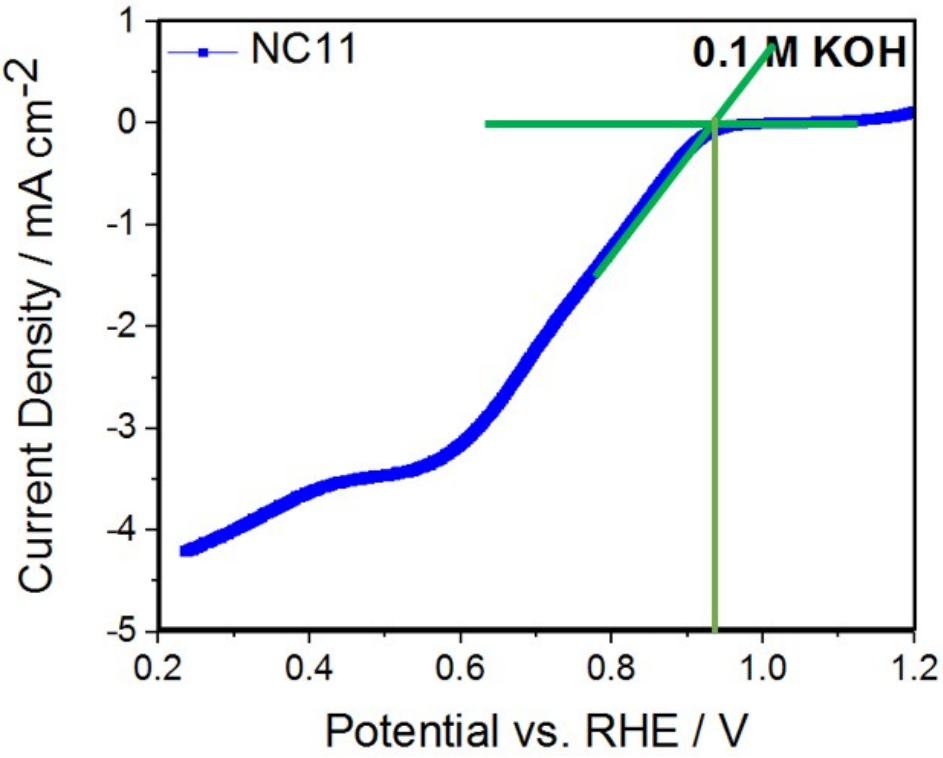
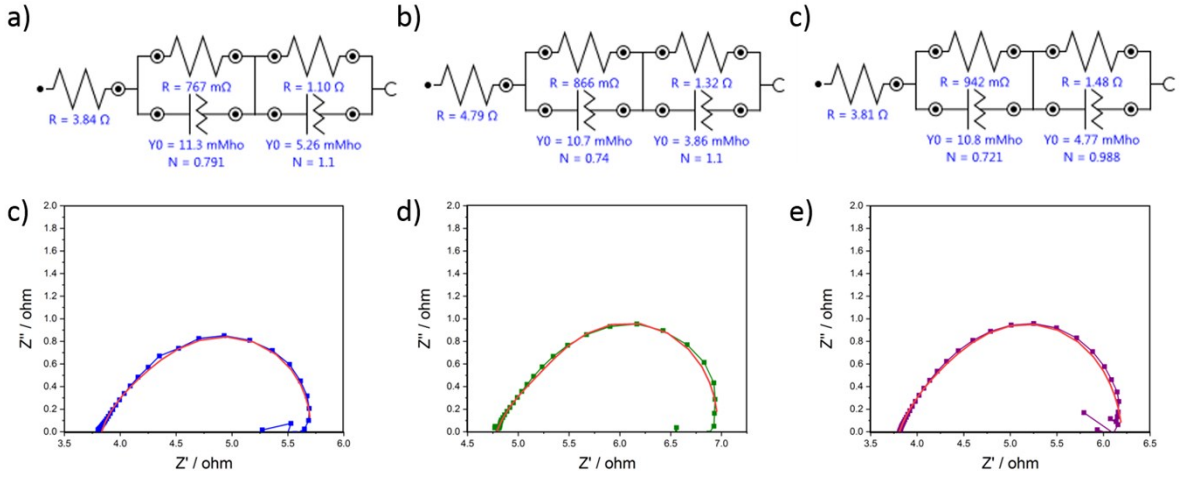


Figure S4a). (Top) Fitted equivalent circuits for a) NC11, b) NC13, and c) NC31. (Bottom) Fitted circuit Nyqvist plots (red) against Nyqvist plots of c) NC11, d) NC13, and e) NC31.



S4b). Determination of Electrochemical Surface Area (ECSA) from Electrochemical Impedance Spectroscopy

It has been argued in 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 calculation of 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 NC11, NC13, and NC31 were 8.402 mF, 6.238 mF, and 4.491 mF, respectively, in broad agreement with literature for $NiCo_2S_4$. [1]

Figure S5. a) XRD spectrum of the as-made NiS_2 sample. b) Ni 2p spectrum of the as-made NiS_2 sample. The oxidation state ratio of Ni(II):Ni(III) was 15:85. c) S 2p spectrum of the as-made NiS_2 sample.

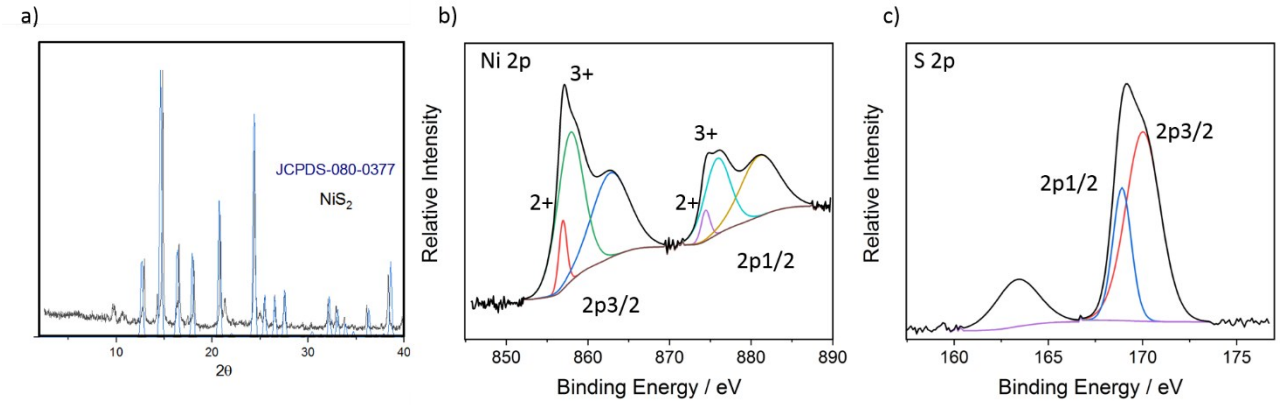


Table S1. Elemental composition of nickel cobalt sulfides based on XPS, EDS, XRF, and ICP analysis**.**

	Ni/Co/S		
	NC13	**NC11**	**NC31**
XPS	1.7/3.1/4	1.8/1.8/4	4/1.7/4
EDS	1.3/3.3/4	1.8/1.8/4	4.5/1.5/4
XRF	1/2.6/4	1.7/1.7/4	2.9/1/4
ICP	0.8/2.2/4	1.5/1.5/4	2.4/0.8/4

Table S2. Relative ratio of cation pairs of nickel cobalt sulfides, based on XPS analysis.

	Sample		
	NC31	**NC11**	**NC13**
Co(II):Co(III)	87% : 13%	85% : 15%	67% : 33%
Ni(II) :	5% : 95 %	23% : 77%	31% : 69%

[1] Song, Xue-Zhi, et al. "Hollow core–shell NiCo 2 S 4@ MoS 2 dodecahedrons with enhanced performance for supercapacitors and hydrogen evolution reaction." *New Journal of Chemistry* 43.8 (2019): 3601-3608

[2] Acharya, Prashant, et al. "Role of Surface Area on the Performance of Iron Nickel Nanoparticles for the Oxygen Evolution Reaction (OER)." *ECS Transactions* 85.11 (2018): 81-89.

[3] Jovic, V. D. "Determination of the correct value of Cdl from the impedance results fitted by the commercially available software." *Research solutions & Resources* (2003).