Electronic Supplementary Information for

Hydrangea-like $NiCo_2S_4$ hollow microsphere as an advanced bifunctional electrocatalyst for aqueous metal/air batteries

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Experimental Details

Synthesis of $NiCo_2S_4$

The hydrangea-like $NiCo_2S_4$ microsphere was prepared by a one-step hydrothermal method. All reagents were of analytical grade and used without further treatment. All homogeneous solutions were obtained with deionized water. In a typical experiment, 0.894 g $Ni(NO_3)_2$•$6H_2O$ and 1.74 g $Co(NO_3)_2$•$6H_2O$ were completely dissolved in 90 mL deionized water under stirring, and following by the addition of 0.912 g thiourea(Tu) and 6 mL ethanediamine(En). Then the mixed solution was stirred at room temperature for 1 h until a clear solution was acquired. The mixture was put into a 150 mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 200^{o}C for 12 h and then cooled to room temperature. The black sample was collected and rinsed with distilled water and ethanol with the assistance of ultrasonication for several times, and dried at 70^{o}C overnight. The Co_3S_4 and NiS was synthesized by the same method with the absence of Ni salt and Co salt. The $NiCo_2O_4$ was synthesized by the method which was reported in literature[1].

Physicochemical Characterization

The XRD patterns were recorded with an X-ray powder diffractometer (Rigaku–TTRIII) (Cu Ka, l=0.154056 nm). The morphology of samples was characterized with scanning electronmicroscopy (SEM, JSM-6360LV, JEOL), transmission electronmicroscopy (TEM, Tecnai G2 20ST), and selected-area electron diffraction (SAED, Tecnai G2 20ST). The surface area was evaluated by the Brunauer–Emmett–Teller (BET) method and the pore size distribution was obtained by the desorption branch using the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS, ESCA LAB 250Xi) was used to characterize the chemical state of

the metal element in the material. And Energy Dispersive Spectrometer (EDS) was used to obtain the composition of elements in material.

Electrochemical Characterization

The ORR and OER activities of the $NiCo_2S_4$ were evaluated on an electrochemical workstation (Solartron 1470E) at room temperature using rotating disk electrode (RDE) technique. The linear sweep voltammetry (LSV) measurement was carried out using a catalyst loaded glassy carbon, spiral platinum wire and Ag/AgCl electrode as the working, counter and reference electrode in the range of 0.1-1.0 V and 0-0.8 V, respectively. The working electrode was prepared as follows: 80 μL of 5wt % nafion solution was added to 2 mL of 3:1 v/v water/ethanol, and then, 8 mg of the catalyst was dispersed in it by sonicating to obtain a homogeneous ink. Then, 5 μL of the catalyst ink was loaded onto a glassy carbon electrode of 5 mm in diameter (the catalysts loading was ~0.1mg cm^{-2} for all samples). The electrochemical catalytic activity was tested in the O_2-saturated alkaline solution (0.1 M KOH).

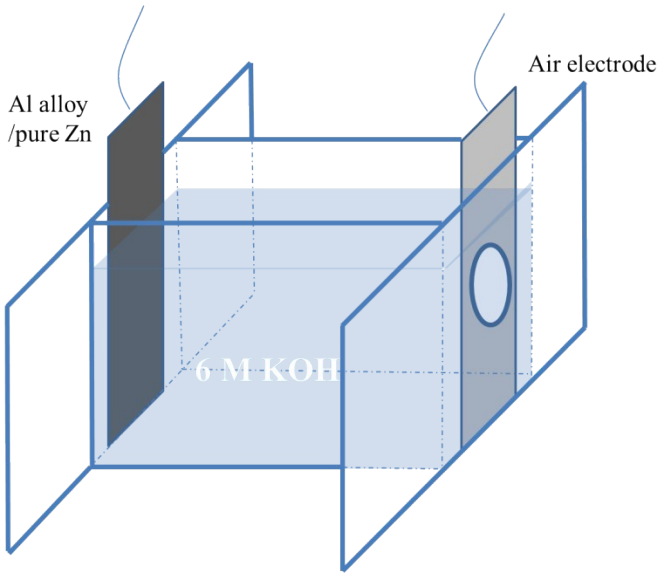
In order to better describe the electrochemical performance of the $NiCo_2S_4$, the as-prepared sample was evaluated by loading the sample onto the air electrode. The fabrication process of air cathode is same for both zinc/air battery and aluminium/air battery, which is shown in Fig 1(b). The air electrode contained three layers: air diffusion layer, nickel mesh and catalytic layer. The catalytic layer was fabricated by catalysts, active carbon and acetylene black, as conductive additive, polytetrafluoroethylene emulsion (PTFE, 60 wt %), as binder, were mixed uniformly in a weight ratio of 3:3:1:3.

The aluminium/air batteries are assembled with aluminium alloy plate (anode), aqueous electrolyte which contained 6.00 M KOH and 0.01 M Na_2SnO_3, 0.50 mM $In(OH)_3$, 7.50 mM ZnO as anticorrosives and air electrode (cathode) in a home-made cell model (in ESI). The zinc/air batteries are fabricated with three parts: pure zinc plate (anode), 6.00 M KOH aqueous solution (electrolyte) and air electrode (cathode), in the same model. The air cathode is fixed on the side with a circular hole while the metal plate is fixed on another side. The air diffusion layer is a membrane which is used to prevent electrolyte from leaking and let air go through at the same time. The air diffusion layer is fabricated by rolling press the acetylene black and polytetrafluoroethylene hybrid slurry (mass ratio: 1:5) which are dispersed in ethanol.

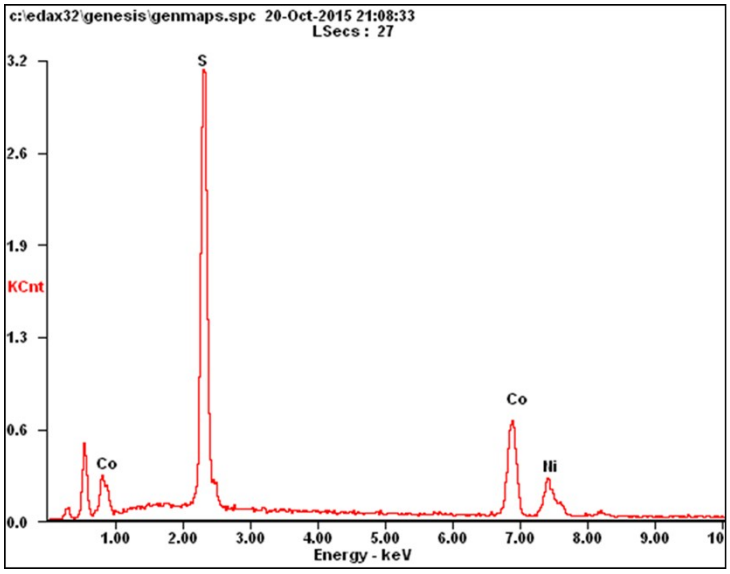
The constant-current discharge measurement was carried out by estimating the electrochemical performance of the air cathode in the application of aluminium/air batteries. And the bifunctional activity of the $NiCo_2S_4$ was evaluated by applying the sample loaded air cathode in rechargeable zinc/air batteries with the constant-current charge-discharge measurement. The charge-discharge measurement is carried out using

a LAND CT2001A battery-testing instrument. All battery testing measurements are operated under atmospheric air.

The electrical conductivities of Co_3S_4, NiS and $NiCo_2S_4$ are tested using a four-point probe conductivity measurement. The membrane which is used to test is fabricated by fully roll pressing the hybrid (tested material: active carbon: PTFE(60wt%)=1:1:5, Mass ratio). The thickness of all membranes is 0.5mm. The sheet resistances of the Co_3S_4, NiS and $NiCo_2S_4$ loaded membrane are listed in Table.1.



Schem.1. The apparatus used for electrochemical measurements for the air electrodes



Element	Wt%	At%
SK	41.03	56.09
CoK	40.49	30.12
NiK	18.47	13.79
Matrix	Correction	ZAF

Fig.1. EDS data of $NiCo_2S_4$

Table.1. Sheet resistence of sample loaded membrane

Sample loaded membrane	Sheet resistence (k Ω /sq)
$NiCo_2S_4$ loaded membrane	4.50
Co_3S_4 loaded membrane	7.48
NiS loaded membrane	44.8

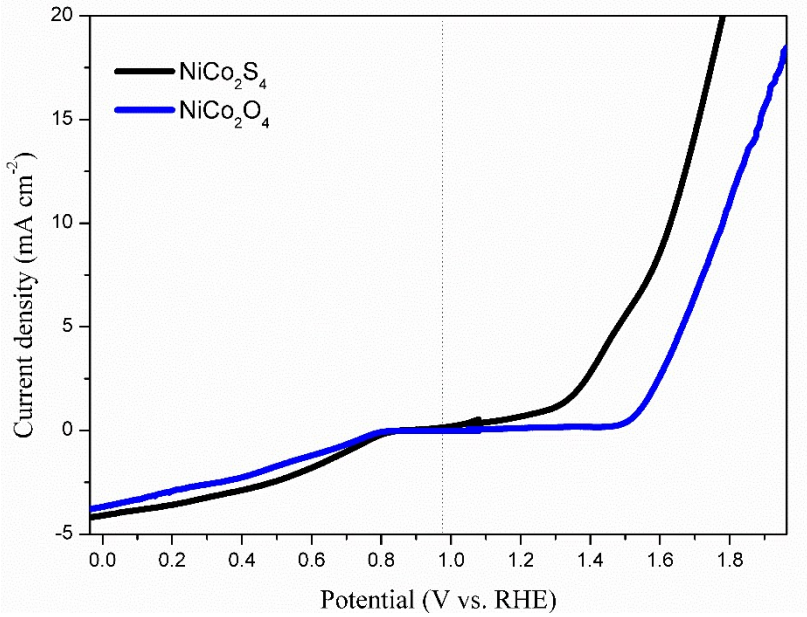


Fig.2. ORR and OER curves of $NiCo_2S_4$ and $NiCo_2O_4$

[1] Q. Wang, B. Liu, X. Wang, S. Ran, L. Wang, D. Chen and G. Shen, Journal of Materials Chemistry, 2012, 22, 21647.