Supplementary Information

CoFe2O4 nanofibers by electrospinning as bifunctional nanocatalysts for oxygen evolution and oxygen reduction reactions in alkaline media.

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**EXPERIMENTAL**

2.1 Reagents

All materials were acquired from Sigma-Aldrich in reagent grade and used as received: iron (III) nitrate nonahydrate (Fe(NO3)3·9H2O; 99.95%), cobalt (II) nitrate hexahydrate (Co(NO3)2·6H2O; 99.99%), polyvinylpyrrolidone (PVP, Mw=1300000), N,N-dimethylformamide (DMF, 99.8%, anhydrous), 2-Propanol (99.5%, anhydrous), potassium hydroxide (KOH, 90%), and Nafion® solution (~5% in aliphatic alcohols). Additionally, the following materials were used: Vulcan XC-72 (Cabot), 20 wt. % Pt/C (E-Tek), ultra-high purity (UHP) nitrogen (N2, 99.999%, Infra), UHP oxygen (99.999 %, AOC), and deionized water (Jalmek).

2.2 Synthesis of the nanocatalysts

CoFe2O4 nanofibers were synthesized by the electrospinning method as follows: first 0.6 g of PVP were dissolved in 5 mL of DMF; separately, a second solution with 0.294 g of Fe(NO3)3·9H2O and 0.106 g of Co(NO3)2·6H2O (molar ratio of 1:2) was dissolved in 5 mL of DMF. Then, the second mixture was added to the PVP solution and stirred for 12 h at room temperature. The resulting solution had a polymer:metal salts weight ratio of 60:40, and a weight/volume ratio of 20.

For the synthesis process, the solution was loaded into a syringe and electrospun with an applied voltage of 10 kV, a distance between the syringe needle and the collector of 10 cm, and a flow rate of 0.3 mL h−1. The collected fibers (CoFe2O4-PTT; PTT= prior to thermal treatment) were annealed at 300 (CoFe2O4-300), 600 (CoFe2O4-600), and 900°C (CoFe2O4-900) in air atmosphere, with a heating rate of 2°C min-1.

2.3 Physicochemical characterization

The thermal properties were characterized by thermogravimetric (TGA) and Differential Scanning Calorimetry (DSC) analyses in a T.A. Instrument U600 apparatus, with a heating rate of 3°C min−1 in air atmosphere. The morphology and chemical elemental composition were analyzed by FE-SEM (JEOL JSM-7800F Prime), by SEM-EDS (Philips XL30-ESEM with an EDAX detector), and HRTEM (FEI Talos F200X). High Angle Annular Dark Field (HAADF) images were obtained in STEM mode for chemical mapping. The structural properties were analyzed by powder X-ray diffraction (XRD) in a Bruker D2 Phaser 2nd Gen diffractometer. The crystallite size (D) was determined from data of the (311) reflection of the nanofibers, with the aid of the Scherrer equation. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha+ device. The carbon 1s peak was adjusted to 284.8 eV for calibrations purposes. Raman spectroscopy characterization was performed in a Raman Thermo Scientific DXR2 (633 nm, He-Ne laser).

2.4 Electrochemical measurements

The catalytic activity for the ORR and the OER was evaluated using the rotating ring-disk electrode (RRDE) technique in a standard three-electrode cell, using a Pine WaveDriver 20 potentiostat. The working electrode (geometric area= 0.196 cm2) was prepared by dropping 10 μL of catalyst ink (2 mg of nanocatalyst, 8 mg of Vulcan, 1 mL of 2-propanol, and 5 μL of Nafion). A platinum wire in a separate compartment was used as counter electrode. An Ag/AgCl (3M NaCl) electrode also in a separate chamber was the reference. The measurements were carried out at room temperature in alkaline electrolyte (0.1 M KOH solution), while the potentials were reported vs. the Reversible Hydrogen Electrode (RHE).

The catalytic activity for the ORR was studied at different electrode rotation rates (ω= 200, 400, 800, 1200, and 1600 rpm) in O2-saturated electrolyte. Cyclic voltammograms (CVs) curves were obtained in a potential range between 1.2 and 0.05 V vs. RHE at scan rate of 5 mV s-1. Only the negative scans were shown here. The percentage of hydrogen peroxide (%𝐻𝑂2−) and the electron transfer number (n) were calculated with equations (1) and (2), respectively [1]:



where *ID* and *IR* are the disk and the ring currents, respectively, and *N* is the current collection efficiency of the RRDE in alkaline media (*N* = 0.37).

Meanwhile, the catalytic activity for the OER was evaluated in O2-saturated electrolyte in the potential range between 1.2 and 1.9 V vs. RHE. CVs were obtained at a scan rate of 5 mV s-1 and ω= 1600 rpm. Only the positive scans were shown in this work.

Accelerated Degradation Tests(ADT) were performed according to the recommendations by the US Department of Energy (DOE) [2]: the nanocatalyst were polarized in the 0.6 - 1.0 V vs RHE potential range for 3000 cycles, at a scan rate of 50 mV s-1. For comparison purposes, a commercial 20 wt. % Pt/C nanocatalyst was evaluated under the same conditions.

**References**

[1] I. L. Alonso-Lemus, M.Z. Figueroa-Torres, D. Lardizabal-Gutíerrez, P. Bartolo-Pérez, J. C. Carrillo-Rodríguez and F. J. Rodríguez-Varela, Sustain. Energy Fuels 3, 1307–1316 (2019).

[2] S.M. Alia, C. Ngo, S. Shulda, M.A. Ha, A.A. Dameron, J.N. Weker, ACS Omega. 2, 1408–1418 (2017)

Figure S1. High-resolution XPS spectra of CoFe2O4-PTT and CoFe2O4-300 in the regions a-b) C 1s, c-d) O 1s, e-f) Fe 2p and g-h) Co 2p.



Figure S2. STEM-HAADF micrographs and chemical mapping of a) Pt/C and b) CoFe2O4-300/C.

Table S1. Parameters of the ORR at the nanocatalysts at 1600 rpm.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Nanocatalyst | *Eonset**(V vs RHE)* | *E1/2**(V vs RHE)* | *j at* *0.8 V vs RHE**(mA cm-2)* | *%HO2-at 0.4 V vs RHE (%)* | *n at 0.4 V vs RHE* |
| Cycle | Cycle | Cycle | Cycle | Cycle |
| 1 | 3000 | 1 | 3000 | 1 | 3000 | 1 | 3000 | 1 | 3000 |
| **Pt/C** | 0.983 | 0.975 | 0.878 | 0.861 | -3.921 | -3.261 | 1.07 | 0.927 | 3.98 | 3.97 |
| **CoFe2O4-300/C** | 0.801 | 0.819 | 0.716 | 0.739 | -0.114 | -0.209 | 21.14 | 27.77 | 3.56 | 3.43 |
| **CoFe2O4-600/C** | 0.806 | 0.821 | 0.719 | 0.740 | -0.114 | -0.208 | 29.37 | 36.88 | 3.39 | 3.21 |
| **CoFe2O4-900/C** | 0.791 | 0.806 | 0.685 | 0.700 | -0.061 | -0.100 | 39.78 | 47.02 | 3.17 | 2.98 |

Table S2. Parameters of the OER at the nanocatalysts at 1600 rpm.

|  |  |  |
| --- | --- | --- |
| Nanocatalyst | *Eonset**(V vs RHE)* | *E at* *10 mA cm-2**(V vs RHE)* |
| Cycle | Cycle |
| 1 | 3000 | 1 | 3000 |
| Pt/C | 1.673 | 1.690 | 1.904\* | 1.932\* |
| CoFe2O4-300/C | 1.547 | 1.558 | 1.754 | 1.785 |
| CoFe2O4-600/C | 1.612 | 1.656 | 1.843 | 1.936\* |
| CoFe2O4-900/C | 1.644 | 1.683 | 1.864 | 1.965\* |
| \*Extrapolated data |  |  |  |  |

Table S3. DE of the OER and the ORR at the nanocatalysts.

|  |  |
| --- | --- |
| Nanocatalyst | *DE (V)* |
| Cycle |
| 1 | 3000 |
| Pt/C | 1.055 | 1.119 |
| CoFe2O4-300/C | 1.440 | 1.600 |
| CoFe2O4-600/C | 1.565 | 1.761 |
| CoFe2O4-900/C | n/d | n/d |
| n/d: not determined |  |  |