# Initiating A Mild Aqueous Electrolyte Co<sub>3</sub>O<sub>4</sub>/Zn Battery with 2.2 V-High Voltage and 5000-Cycle Lifespan by a Co(III) Rich-electrode

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## Experiment

## Materials

Cobaltous nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) is purchased from Alfa. Urea (CH<sub>4</sub>N<sub>2</sub>O), Ammonium fluoride (NH<sub>4</sub>F), Cobalt Sulfate (CoSO<sub>4</sub>·7H<sub>2</sub>O), Zinc sulfate (ZnSO<sub>4</sub>), acrylamide (C<sub>3</sub>H<sub>5</sub>NO), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and N, N'-methylenebisacrylamide (C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>), and Potassium hydroxide

(KOH) are purchased from Aladdin. All chemicals are analytically pure and used as received without any further purification.

#### The pre-treatment of carbon cloth

Firstly, the carbon clothes are cleaned using acetone and distilled water under ultrasonic condition for 5 min. Secondly, the carbon clothes are immersed into mixture solution of concentrated  $H_2SO_4$ (96%) and concentrated HNO<sub>3</sub> (65%) with ratio of 2:1 for 30 min. Thirdly, 6 g KMnO<sub>4</sub> is added into above mixture solution and stirred vigorously for 1h at room temperature. Then, 100 mL distilled water is slowly mixed in ice bath and further stirring for 2h. After that,  $H_2O_2$  is added into the mixture solution drop by drop until the solution become clear. Finally, the treated carbon clothes is washed with distilled water and in vacuum overnight. After calcining at 950 °C for 1h at rate of 5 °C/min, the pretreated carbon clothes are obtained.

#### The preparation of freestanding Co(III) rich-Co<sub>3</sub>O<sub>4</sub> on carbon cloth electrode

In a typical synthetic process, 7 mmol of cobaltous nitrate ( $Co(NO_3)_2 \cdot 6H_2O$ ), 11.5 mmol urea ( $CH_4N_2O$ ) and 7 mmol ammonium fluoride ( $NH_4F$ ) is dissolved in 25 mL distilled water under vigorously stirring at room temperature. For well-balanced  $Co_3O_4$ , instead of 4 mmol Cobaltous nitrate as added without other modification. After stirring for 2 h, the homogeneous solution is transferred into 25 mL hydrothermal reactor and the pre-treated carbon clothes are immersed into the solution around the reactor wall. The hydrothermal reactor is sealed and heated at 120 °C for 8 h in an electric oven. After the hydrothermal reactor is cooled to room temperature, the carbon clothes coated with pink precursor is picked out and washed with distilled water and ethanol for three times, respectively. After that, the carbon clothes with pink precursor is dried at 60 °C for 12 h. The freestanding Co(III) rich-Co<sub>3</sub>O<sub>4</sub> nanorod on carbon cloth electrode is obtained after

annealed precursor at 350 °C for 3h. The loading mass of active materials on electrode is around 1.05 mg per square centimeter. The loading mass is evaluated by measuring the difference of mass before and after Co(III) rich-Co<sub>3</sub>O<sub>4</sub> growing on carbon cloth.

#### The preparation of deposited-Zn on carbon cloth electrode

The deposited-Zn on carbon cloth is prepared by a facile electrochemical deposition method using two-electrode setup. In detail, the Zn plate is used as counter electrode, pre-treated carbon cloth is used as working electrode and 1 M ZnSO<sub>4</sub> is used as electrolyte. Electroplating is conducted at 5 mA·cm<sup>-2</sup> for 3000 s using an electrochemical workstation (CHI 760D, Chenhua).

## The synthesis of polyacrylamide hydrogel electrolyte

The PAM hydrogel electrolyte is synthesized by in-situ polymerization method. Firstly, 80 mM ZnSO<sub>4</sub> and 8 mM CoSO<sub>4</sub> are dissolved in to 40 mL distilled water under vigorous stirring. Then, 10 g acrylamide is added in above mixture solution under vigorously magnetic stirring at 40 °C. After that 2 mg N, N'-methylenebisacrylamide as cross-linkers and 50 mg potassium persulfate as initiator are added into the above solution and maintain at 40 °C for 2 hours. To remove dissolved oxygen, the mixture solution is degassed and sealed under nitrogen for 30 min. Finally, the PAM film is obtained through free-radical polymerization at 70 °C for 2 hours.

## Assembly of the solid-state Zn/Co<sub>3</sub>O<sub>4</sub> battery

The solid-state  $Zn/Co_3O_4$  battery is assembled using  $Co_3O_4$  nanorod on carbon cloth electrode, deposited-Zn on carbon cloth electrode and PAM hydrogel electrolyte directly without any further treatment. In detail, the  $Co_3O_4$  nanorod on carbon cloth electrode and electro-deposited Zn on carbon cloth electrode are directly coated on each side of the as-fabricated PAM film to assemble solid-state  $Zn/Co_3O_4$  battery without any separator.

#### Characterization

The crystal structure is evaluated by utilizing a Bruker D2 Phaser X-ray diffractometer with radiation from a Cu target ( $\lambda$  =0.154 nm) operating at 30 kV and 10 mA, respectively. And Raman scattering characterization were conducted with a multichannel modular triple Raman system (Renishaw Co.) with confocal microscopy at room temperature using the 633 nm laser. The morphology and microstructure of samples is investigated by using field emission scanning electron microscopy (FESEM; JEOL JSM-6700F, 5 kV) and JEOL-2001F field-emission transmission electron microscopy (FESEM), and the accessory EELS was used to determine to composite elements. The chemical state and composition are analyzed using an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scienctific) at  $1.2 \times 10^{-9}$  mbar using Al K $\alpha$  X-ray beam (1486.6 eV). All XPS spectra are calibrated by shifting the detected adventitious carbon C 1s peak to 284.4 eV.

#### The measurement of electrochemical performance

The electrochemical performance is tested using freestanding  $Co_3O_4$  nanorods on carbon cloth electrode as cathode, freestanding deposited-Zn nannosheets on carbon cloth as anode and 2 M ZnSO<sub>4</sub> with 0.2 M CoSO<sub>4</sub> additives aqueous solution as electrolyte. The loading mass of active materials is around 1 mg·cm<sup>-2</sup>. Galvanostatic charge-discharge measurements is conducted between 0.8 and 2.2 V utilizing a land 2001A battery testing system with two-electrode configuration at room temperature. Calculation of specific capacity is based on the mass of initial  $Co_3O_4$  nanorods on carbon cloth. Cyclic voltammetry curves (CV) and electrochemical impedance spectroscopy (EIS, 100 kHz to 0.01 Hz, 5 mV amplitude) are examined using an electrochemical workstation (CHI 760D, Chenhua). The energy density (E) of the  $Zn-Co_3O_4$  battery is calculated by using the following equation:

$$E = \int_{0}^{t} IV_{(t)} dt/m$$

where *t* is the time, *I* is the discharge current,  $V_{(t)}$  is the discharge voltage at t, dt is time differential and m is the total mass of the device.



Figure S1. Schematic illustration of the procedure for Co(III) rich-Co<sub>3</sub>O<sub>4</sub> grown *in-situ* on

carbon cloth.



Figure S2 SEM images of precursor. It is shown that the entire surface of carbon cloth is covered by densely ordered nanorods clusters. Each cluster consists of around tens of nanorods with a length of about  $2 \mu m$ .



**Figure S3.** Crystal structure of a cubic spine Co<sub>3</sub>O<sub>4</sub> viewed along b axis.



Figure S4. Raman shift spectra of well-balanced Co<sub>3</sub>O<sub>4</sub> and Co(III) rich-Co<sub>3</sub>O<sub>4</sub>.



**Figure S5.** (a) The HRTEM images of Co(III) rich-Co<sub>3</sub>O<sub>4</sub> nanorod composed of nanocrystals and (b) the nanocrystal size distribution obtained by statistical analysis of the HRTEM image.



Figure S6. High-resolution O 1s XPS spectra of (a) well-balanced Co<sub>3</sub>O<sub>4</sub> and (b) Co(III) rich-

Co<sub>3</sub>O<sub>4</sub>.



Figure S7. Linear cyclic voltammetry (LSV) of Zn/Co(III) rich- $Co_3O_4$  battery in alkaline and aqueous electrolyte to evaluate the voltage of oxygen production.



**Figure S8.** Schematic illustration of Zn/Co(III) rich-Co<sub>3</sub>O<sub>4</sub> battery in alkaline and mild solution.



Figure S9. ICP characterization to measure Co concentration in the charge-discharge process.



**Figure S10**. Electrochemical performance of Co(III) rich-Co<sub>3</sub>O<sub>4</sub> batteries in optimal aqueous electrolyte. (a) Comparison of CV scanning (0.1 mV s<sup>-1</sup>, second cycle) and (b) the cycling performance of Zn/Co(III) rich-Co<sub>3</sub>O<sub>4</sub> batteries in 2 M aqueous ZnSO<sub>4</sub> electrolyte and 2 M aqueous ZnSO<sub>4</sub> electrolyte with different CoSO<sub>4</sub> additive at current density of 1 A·g<sup>-1</sup>, respectively.

Cathode	Anode	Electrolyte	Voltage	Cycling stability	Reference
Co(III) rich-Co <sub>3</sub> O <sub>4</sub> nanorods on CFC	Zn	2 M ZnSO <sub>4</sub> +0.2 M CoSO <sub>4</sub>	~2.2 V	92 % after 5000 cycles	Our work
Co <sub>3</sub> O <sub>4</sub> on Ni foam	Zn	1 М КОН	~1.9 V	80 % after 2000 cycles	<i>Adv. Mater.</i> 2016, 28, 4904–4911.
NiO/Ni(OH)2 nanoflakes	Zn	0.1 M KOH	~1.3 V	70 cycles	Nano Lett. 16, 3, 1794- 1802
MnO <sub>2</sub> nanorods	Zn	2 M ZnSO <sub>4</sub> +0.1 M MnSO <sub>4</sub>	~1.4 V	92% after 5000 cycles	Nature Energy. 2016, 1, 16039-160076.
MnO <sub>2</sub>	Zn	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> +0.1 M Mn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	~1.6	94% after 3000 cycles	Nat. Commun., 2017, 8, 405-414.
$V_2O_5 \cdot nH_2O$	Zn	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	~1.0 V	71% after 900 cycles	Adv. Mater. 2017, 1703725-1703731.
Zn <sub>3</sub> V <sub>2</sub> O <sub>7</sub> (OH) <sub>2</sub> ·2H <sub>2</sub> O	Zn	1 M ZnSO <sub>4</sub>	~1.5 V	68% after 300 cycles	Adv. Mater. 2017, 1705580-1705587.
$\mathrm{H}_2\mathrm{V}_3\mathrm{O}_8$	Zn	3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	~1.0 V	94.3% after 1000 cycles	Small. 2017, 13, 1702551- 1702558.
VS <sub>2</sub> Nanosheet	Zn	1 M ZnSO <sub>4</sub>	~0.9 V	98.0% after 200 cycles	Adv. Energy Mater. 2017, 7, 1601920-1601927.
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> (nano arrays)/CNFs	β-Ni(OH) <sub>2</sub>	1 M LiOH + 3 M KOH	~1.5 V	92% after 100 cycles	Chem. Commun., 2011, 47, 12473-12475
Co <sub>3</sub> O <sub>4</sub> @Ni–Co–O nanoarray	hierarchical Co <sub>x</sub> Fe <sub>3-x</sub> O <sub>4</sub> nanoarray on Cu foam	6 М КОН	~1.0 V	88% after 500 cycles	Nano Energy, 2014, 10, 229-234
Ni(OH) <sub>2</sub> /MWCNT	FeO <sub>x</sub> /graphe ne	1M KOH	~1.1 V	80% after 800 cycles	Nat. Commun.,2012, 3, 917-925.
LiMn <sub>0.05</sub> Ni <sub>0.05</sub> Fe <sub>0.9</sub> PO <sub>4</sub>	LiTi <sub>2</sub> (PO4) <sub>3</sub>	saturated Li <sub>2</sub> SO <sub>4</sub>	~0.92 V	63.2% after 50 cycles	J Power Sources, 2009, 1, 706-710.

**Table S1.** Comparison of our developed Zn/Co(III) rich-Co<sub>3</sub>O<sub>4</sub> battery with other reported aqueous batteries.



Figure S11. SEM images of Co(III) rich-Co<sub>3</sub>O<sub>4</sub> electrode after 5000 cycles.



**Figure S12**. Zn stripping/plating from Zn/Zn symmetrical cells at 0.2mA cm<sup>-2</sup> in a 6 M KOH alkaline solution electrolyte and in a mild 2 M ZnSO<sub>4</sub> with 0.2 M CoSO<sub>4</sub> aqueous electrolyte, respectively.



**Figure S13**. SEM image of a pristine Zn anode, Zn anode electrode after 6 cycles (24 h) in KOH electrolyte and Zn anode electrode after 140 cycles (280 h) in 2 M ZnSO<sub>4</sub> with 0.2 M CoSO<sub>4</sub> additives aqueous electrolyte after Zn plating/stripping test.



**Figure S14.** The XRD patterns of cycled Zn anodes in 2 M ZnSO<sub>4</sub> with 0.2 M CoSO<sub>4</sub> aqueous electrolyte and 1M KOH electrolytes after Zn plating/stripping test.



Figure S15. Characterization of Zn anode of Zn/Co(III) rich-Co<sub>3</sub>O<sub>4</sub> battery in mild aqueous electrolyte. (a) SEM image and (b) XRD pattern of cycled Zn anode in 2 M ZnSO<sub>4</sub> + 0.2 M CoSO<sub>4</sub> electrolyte after 5000 cycles of stability test.



Figure S16. Characterization of Zn anode of Zn/Co(III) rich- $Co_3O_4$  battery in alkaline electrolyte. (a) SEM image and (b) XRD pattern of cycled Zn anode in 1 M KOH electrolyte after 500 cycles of stability test.



Figure S17. Cyclic voltammograms (CV) curves of Zn/Co(III) rich-Co<sub>3</sub>O<sub>4</sub> batteries in the first and second cycles in 2 M ZnSO<sub>4</sub> + 0.2 M CoSO<sub>4</sub> electrolyte.



**Figure S18.** High-resolution O 1s XPS spectrum of Co(III) rich- $Co_3O_4$  electrode at (a) initial status, (b) discharge to 0.8 V and (c) charge to 2.2 V.



Figure S19. SEM images of Co(III) rich-Co<sub>3</sub>O<sub>4</sub> electrode during charge-discharge process.



Figure S20. XRD patterns of Co(III) rich-Co<sub>3</sub>O<sub>4</sub> electrode during charge-discharge process.



**Figure S21.** The TEM images of Co(III) rich-Co<sub>3</sub>O<sub>4</sub> cathode discharged to 0.8 V in the first cycle. The new flake-like on the surface of Co(III) rich-Co<sub>3</sub>O<sub>4</sub>



Figure S22. The XRD patterns collected from Co(III) rich-Co<sub>3</sub>O<sub>4</sub> electrodes discharged to 0.8 V.



Figure S23. Schematic illustration of the process for Co(III) rich-Co<sub>3</sub>O<sub>4</sub> on carbon cloth,

metallic Zn on carbon cloth and Zn/Co(III) rich-Co $_3O_4$  battery.



Figure S24. XRD pattern of deposited-Zn on carbon cloth.



Figure S25. SEM images of deposited-Zn on carbon cloth at different magnification

As shown in Figure S24, the deposited-Zn on the carbon cloth exhibits a morphology of uniform nanosheets with porous structure on carbon cloth, which help facilitate the electrolyte/ion accessibility and fast charge transport.



Figure S26. SEM Image of polyacrylamide (PAM) hydrogel electrolyte.

Polyacrylamide (PAM) hydrogel is promising to host water and contribute electrolyte ions to move freely, owing to its high absorbency and macro-porous structure. The driving force is an osmotic pressure difference arising from the concentration of ionic groups inside the hydrogel network. Hence, PAM hydrogel is potential candidate as polyelectrolyte for energy conversion and storage device.



Figure S27. Ions conductivity of PAM hydrogel electrolyte.

The testing system is assembled with sandwich structure. In detail, the ionic conductor (PAM hydrogel) is in middle of two FTO glasses with the dimension: width  $\times$  length  $\times$  thickness=1.2 cm  $\times$  1.0 cm  $\times$  0.06 cm.

Resistance of the ionic conductor is investigated by measuring the high-frequency intercept of the semi-circle in the Nyquist plot. Resistivity of the ionic conductor is calculated by the equation:

$$\rho = {^{R \times A}/_{d}}$$

where  $\rho$  is the resistivity of ionic conductor, R is the resistance, A is the area of ionic conductor, and d is the thickness of the ionic conductor respectively



Figure S28. Ion conductivity versus swelling ratio of PAM hydrogel.



**Figure S29**. Electrochemical performance of solid-state Zn/Co(III) rich-Co<sub>3</sub>O<sub>4</sub> battery at a bending angle of 90°.



**Figure S30**. SEM images of freestanding Co(III) rich-Co<sub>3</sub>O<sub>4</sub> nanorod on carbon cloth electrode under 60°, 90°, 120°, 150° and after 1000 times bending at 90°.



**Figure S31**. SEM images of freestanding deposited-Zn on carbon cloth electrode under 60°, 90°, 120°, 150° and after 1000 times bending at 90°.



**Figure S32.** (a) Galvanostatic charge-discharge curves of two Zn/Co(III) rich-Co<sub>3</sub>O<sub>4</sub> battery connected in series. (b) Galvanostatic charge/discharge curves of two Zn/Co(III) rich-Co<sub>3</sub>O<sub>4</sub> battery connected in parallel.