

Recycling of iron from vanadium titanium magnetite tailings and its application in asymmetric supercapacitor

Jiale Chen^a, Lei Qian^{a*}, Zongyao Fu^a, Guanfeng Li^a, Ying Zeng^a

^a College of Materials and Chemistry & Chemical Engineering, Chengdu
University of Technology, Chengdu, Sichuan, 610059, China

* Corresponding authors. qianlei13@cdu.cn.

Supporting Information

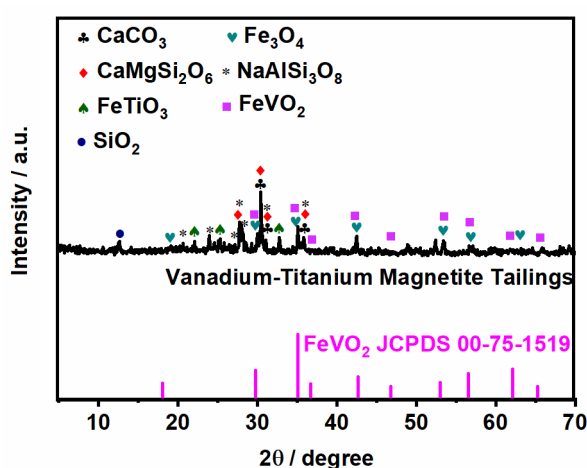


Fig S1 XRD pattern of VTMT.

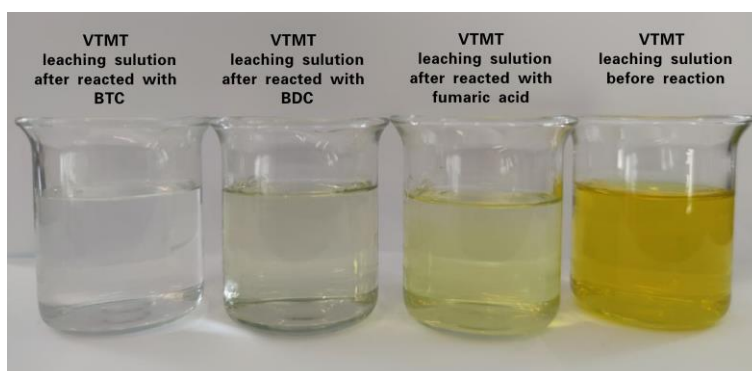


Fig.S2 The photograph of VTMT leaching solution before and after reacted with fumaric acid, BDC and BTC.

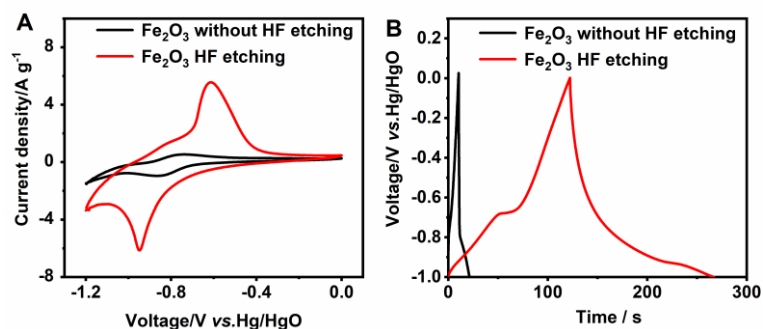


Fig S3 the CV and GCD curves of MIL-100(Fe) derived Fe₂O₃ with and without HF etching.

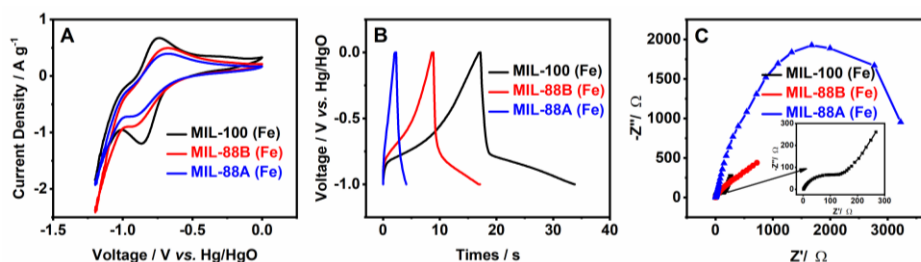


Fig S4 The CV(A), GCD (B) and EIS curves (C) of MIL-100 (Fe), MIL-88A (Fe), MIL-88B (Fe), the scan rate was 10 mV s^{-1} , the current density was 1 A g^{-1} .

Preparation of NiCo(O)S

NiCo(O)S was prepared two-steps method containing ion exchange and calcination using ZIF-67 as precursor. ZIF-67 NCs were synthesized according to previous report with some modification [1]. In a typical synthesis, 292 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 mL deionized water (DIW) containing 4 mg cetyltrimethylammonium bromide (CTAB). Then this solution was rapidly injected into 70 mL an aqueous solution containing 4.54 g 2-methylimidazole and stirred at room temperature for 30 min and then stand for 24 h. The product was collected by centrifugation at 3600 rpm for 5 min, washed with ethanol for several times. The Ni doped ZIF-67 (Ni-ZIF-67) was prepared by the ion exchange reaction between ZIF-67 and $\text{Ni}(\text{NO}_3)_2$ at room temperature in ethanol. Using Ni-ZIF-67 as

precursor and thioacetamide as sulphur sources, the NiCo(O)S was prepared by a two steps method, containing hydrothermal and calcination. First, 60 mg Ni-ZIF-6 nanocube was dispersed in 30 mL ethanol and reacted with 120 mg thioacetamide at 120 °C for 4h. then, the NiCo(O)S was obtained by the calcination of the Ni-ZIF-67 sulfide at 400 °C for 3 h in air.

Characterization of NiCo(O)S

The NiCo(O)S was characterized by XRD, EDS and SEM. From the XRD pattern (Fig S4) we can find that, the crystallinity of NiCo(O)S was poor, the diffraction peaks were difficult to distinguish. From the EDS data we can find that, The S content was lower the metal content, we conclude that, cobalt nickel oxide and sulfide both exist, referring to the previous reports[2], the product was named as NiCo (oxy) sulfide (NiCo(O)S). the morphology of precursor and NiCo(O)S was characterized by SEM images (Fig S5). The ZIF-67 was nanocube with length of about 300 nm, the surface was smooth. After reacted with Ni(NO₃)₂, the morphology of nanocube was existence but the surface was rough, this may be due to the formation of CoNi layer double hydroxides. After hydrothermal and calcination, the morphology of NiCo(O)S was similar with the Ni-ZIF-67.

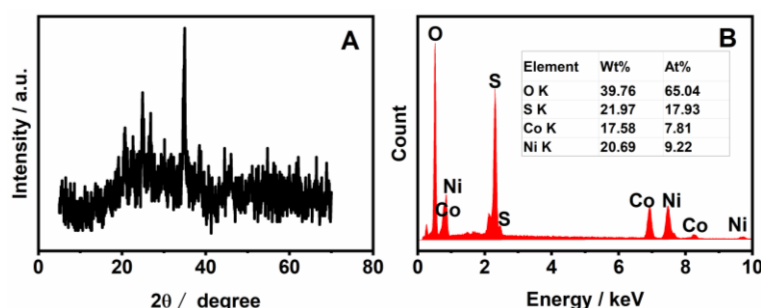


Fig S5 The XRD pattern and EDS of NiCo(O)S

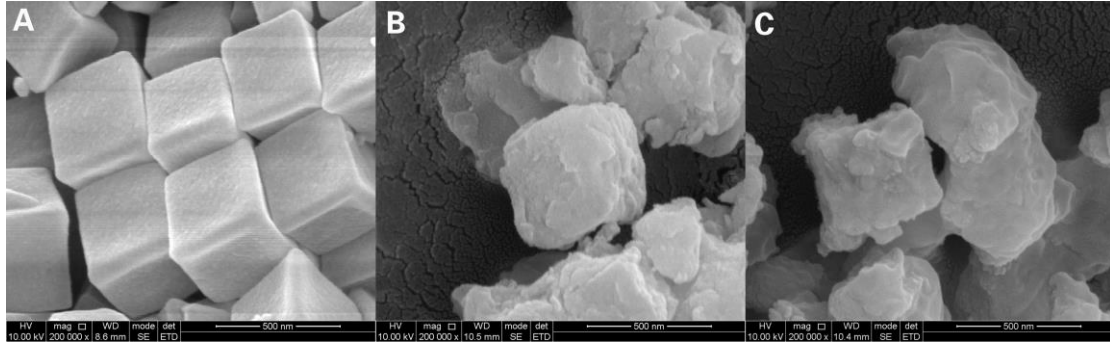


Fig S6 The SEM images of ZIF-67(A), Ni-ZIF-67(B) and NiCo(O)S (C).

Capacitance Performance

The capacitive performance was characterized by CV, GCD and EIS methods. As shown in Fig S6A, a pair of obviously redox peaks at about 0.3 V and 0.41 V (2 mV s^{-1}) was observed, this may be due to the redox reaction between NiCo(O)S and NiCo(O)SOH [3], which is distinct from those of electric double-layer capacitors, implying their capacitance is mainly governed by the redox mechanism.

the rate capability of the NiCo(O)S was discussed by CV and GCD method. Figure S6A displays the CV profiles of NiCo(O)S electrode at different scan rates ranging from 2 to 100 mV s^{-1} . Apparently, a couple of explicit and symmetrical redox peaks can be observed from each CV curve, as the scan rate increased, the redox peaks shifted. The specific capacitance of NiCo(O)S was 808, 648, 532, 414, 266, 173 F g^{-1} at scan rate of 2, 5, 10, 20, 50, 100 mV s^{-1} . The GCD curves in Fig S6B show obvious charge and discharge platforms, which are in good agreement with the redox peaks in CV curves. The specific capacitance of NiCo(O)S was 642, 532, 446, 319, 213 F g^{-1} at current density of 0.5, 1, 2, 5, 10 A g^{-1} . The CV and GCD results indicated that, the rate ability of NiCo(O)S was need to be improved. The cycling stability of NiCo(O)S was investigated by GCD measurements. As shown in Fig. S6C, after 7000 cycles, the specific capacitance retention was 83.5%. The capacitance decay may be due to the decreasing of the

conductivity, this can be confirmed by the EIS measurement, (Fig S6D) after cycles, the electron resistance increased.

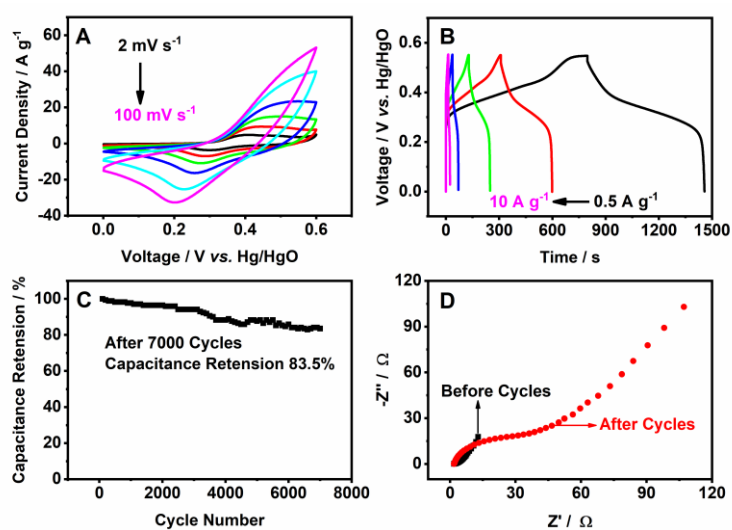


Fig S7 The CV curves at various scan rates (A), GCD profiles at different current density (B), cycling stability of NiCo(O)S (C) and EIS plots of NiCo(O)S before and after 4000 cycles (D)

- [1] P. He, X. Y. Yu and X. W. Lou, Carbon-incorporated nickel-cobalt mixed metal phosphide nanoboxes with enhanced electrocatalytic activity for oxygen evolution, *Angew. Chem. Int. Ed.* 56 (2017) 3897-3900.
- [2] X. Zheng, Y. Cao, Z. Wu, W. Ding, T. Xue, J. Wang, Z. Chen, X. Han, Y. Deng and W. Hu, Rational design and spontaneous sulfurization of NiCo-(oxy)hydroxysulfides nanosheets with modulated local electronic configuration for enhancing oxygen electrocatalysis, *Adv. Energy Mater.* 12 (2022) 2103275.
- [3] Q. Tang, W. Wang and G. Wang, The perfect matching between the low-cost Fe₂O₃ nanowire anode and the NiO nanoflake cathode significantly enhances the energy density of asymmetric supercapacitors, *J. Mater. Chem. A* 3 (2015) 6662-6670.