

Supplementary Information

Room-temperature, one-step synthesis of Mn_3O_4 nanoparticles using morpholine as complexing and precipitating agent: toward cathode material for zinc-ion battery

Saad G. Mohamed^{a,b*}, Jixu Wan^c, and Xuejin Li^c

^aMining and Metallurgy Engineering Department, Tabbin Institute for Metallurgical Studies (TIMS), Tabbin, Helwan 109, Cairo 11421, Egypt.

^bAcademy of Scientific Research & Technology (ASRT), 101 Kasr Al-Ainy St., Cairo, Egypt

^cSchool of Materials Science and Engineering, State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao, 266580 P.R. China

*Corresponding authors: S. G. Mohamed (saadmohamed@tims.gov.eg)

Experimental procedures

Mn₃O₄ Synthesis

Mn₃O₄ nanopowders was synthesized through a one-step, room-temperature method. 4 mmol Mn(NO₃)₂·4H₂O (98% Alfa Aesar) was dissolved in 25 ml deionized water (DIW) until a faint pink solution was formed, then 1 ml morpholine (C₄H₉NO, 98%, Aladdin Scientific) was added dropwise to the Mn²⁺·(2NO₃⁻) aqueous solution, the solution was suddenly converted to beige-white turbid solution. The solution underwent vigorous stirring (1500 rpm) for 24h and turned to brown. The precipitate was collected and cleaned several times using DIW and absolute ethanol using a centrifuge (8000 rpm). The product was dried at 80C in a vacuum for 24h.

Electrochemical measurements

The produced Mn₃O₄ nanoparticles, Super P conductive carbon, and polyvinylidene difluoride (PVDF) binder were combined with N-methyl-2-pyrrolidone (NMP) to form a slurry to produce the electrodes at a weight ratio of 70:20:10, which served as the working cathode. This slurry was uniformly coated onto a graphite foil (0.05 mm thickness, King Carbon Tech, China), functioning as the current collector, and subsequently dried under vacuum. The dried foil was then cut into circular discs with a loading weight of 1.5 ± 0.2 mg per disk. Zinc metal foil (0.1 mm thickness, >99.99%, Dingyuan Metallic Materials, China) was used as the anode, while a combination of 2 M ZnSO₄ and 0.1 M MnSO₄ served as the electrolyte. In assembling the 2032-type coin cells, a glass-fibre separator was placed between the prepared cathode and anode with the addition of a fixed volume of 100 µl of electrolyte under open-air conditions. Electrochemical discharge/charge measurements were subsequently conducted using a battery tester (NEWARE BTS-4000, China) at various current densities within a potential range of 0.8–1.9 V versus Zn²⁺/Zn. Cyclic

voltammetry (CV) scans were performed using a potentiostat model workstation (VSP, BioLogic, France).

Low-temperature performance was performed in a refrigerator (DW-50, Shnghai Yuengia Experimental Equipment Co., Ltd, China) connected temperature controller with a battery tester (BT-2018R, LANBTS, China) at -10°C using 2 M ZnSO_4 and 0.1 M MnSO_4 with the addition of vol 30% of 1,2-dimethoxyethane (DME, 99.5%, Macklin, China).

Physical characterizations

The crystallinity and phase structure of the samples were examined using a range of advanced characterization techniques. Powder X-ray diffraction (XRD) analysis was conducted with a Bruker AXSD8 ADVANCE instrument (Germany) utilizing $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Raman spectra were acquired using a WiTec alpha 300R Raman spectrometer. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Scientific instrument to analyze the surface composition and oxidation states of the UiO-66/Se/PANI sample, employing monochromatized $\text{AlK}\alpha$ radiation. Morphological analysis was carried out using a Thermo Scientific Quattro S Field-emission scanning electron microscope (FE-SEM). High-resolution transmission electron microscopy with selected area electron diffraction (HR-TEM/SAED) was performed using a JEOL JEM-2100 instrument to further explore the morphology of the prepared samples. The specific surface areas and pore size distributions were assessed using a Brunauer-Emmett-Teller (BET) surface area analyzer (Micromeritics ASAP 2460) through adsorption and desorption isotherms.