

Supporting information

Co-substitution of Prussian blue analogue with hollow heterostructures for ultrahigh capacity and rate capability aqueous Zn²⁺ batteries

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Experimental Section

1. Synthesis of H-PBMN

Firstly, 0.396 g MnCl₂·4H₂O, 4.83 g of potassium citrate and 3.0 g of PVP (K30) were added and dissolved into 50 mL deionized water to form A solution. Then, 0.422 g K₄Fe(CN)₆·3H₂O was dissolved in 50 mL of deionized water to form B solution, which was then dropwise added into the A solution at a rate of 2.0 mL/min under vigorous stirring to form mixed solution. Secondly, 50 mL of 0.02 M K₂Ni(CN)₄ solution and the 50 mL of 0.02 M MnCl₂ aqueous solution with 1.0 g PVP and 1.61 g of potassium citrate were dropwise added to the mixed solution at the same dropping rate (2.0 mL/min) under vigorous stirring. The mixture was kept stirring for 6 h at room temperature and then aged for another 24 h. The H-PBMN precipitates were collected by centrifugation after washing with deionized water and ethanol several times, and then dried under vacuum at 60 °C overnight. The synthesis methods for contrast sample H-PBM were similar to that of the H-PBMN, but replaced 0.02 M K₂Ni(CN)₄ solution with 0.02 M K₄Fe(CN)₆·3H₂O solution.

2. Materials characterization

The crystallographic structures of the H-PBMN and electrodes after cycles were analyzed by X-ray diffractometer (XRD) using a Malvern Panalytical PW3040/60 with

a Cu K α radiation source. The element valence states were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA). The morphology, structure, and size of the samples were investigated by the scanning electron microscopy (SEM, JSM-7001F) and the transmission electron microscopy (TEM, JEOL, JEM-2100F) equipped with Energy dispersive X-ray spectroscopy (EDX). The Brunauer Emmett Teller (BET) surface area and the pore size distribution of the samples was obtained by N₂ adsorption-desorption analysis.

3. Electrochemical measurements

The H-PBMN electrode was prepared by casting on a carbon fiber paper a slurry, in which the H-PBMN active material, ketjen black, and polyvinylidene fluoride (PVDF) binder with a weight ratio of 7:2:1 were mixed by N-Methyl-2-pyrrolidone (NMP). Subsequently, the coated fiber paper was dried in a vacuum oven at 60 °C for 12 h. The electrochemical characterizations of H-PBMN were conducted in the CR2032 coin cells consisting of 0.03 mm Zn foils as the anode, Whatman GF/A glass fiber filter as the separator, and the 3 M Zn(CF₃SO₃)₂ electrolyte. The Cyclic voltammogram (CV) was performed on an IVIUMnSTAT multichannel electrochemical analyzer (N66728) in the voltage range of 0.4-1.85 V. The electrochemical impedance spectroscopy (EIS) (10 mHz-100 kHz, 5 mV) was performed on electrochemical working station (CHI660E). The charge/discharge tests and Galvanostatic intermittence titration technique (GITT) were measured by using the Neware CT-4008 test system in a potential range of 0.4-1.85 V.

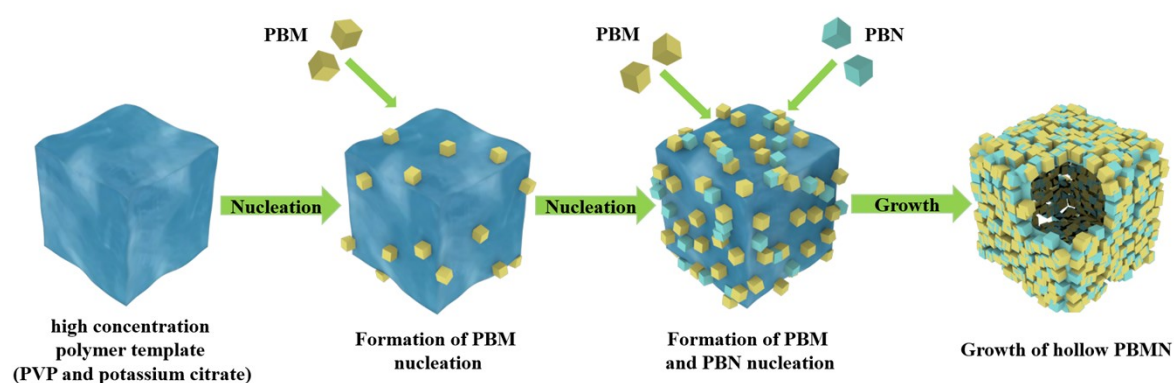


Fig. S1. Schematic diagram of the synthetic process of H-PBMN.

Table S1. Comparison of the cycle performance of the H-PBMN cathode materials in aqueous Zn ion batteries

Electrodes	Capacity mAh g ⁻¹ @A g ⁻¹	Cycling Performance	Ref.
H-PBMN	71.9@0.5	77.9% retained after 400 cycles	This work
KMHCF-PVP-80	140@0.1	60.7% retained after 400 cycles	1
MZHCF-7	41.6@0.05	94% retained after 500 cycles	2
CoMn-PBA	- @1.0	74.6% retained after 1000 cycles	3
ZnHCF	50.6@0.5	71% retained after 1000 cycles	4
Mn-PBA	- @1.0	53.6% retained after 1000 cycles	3

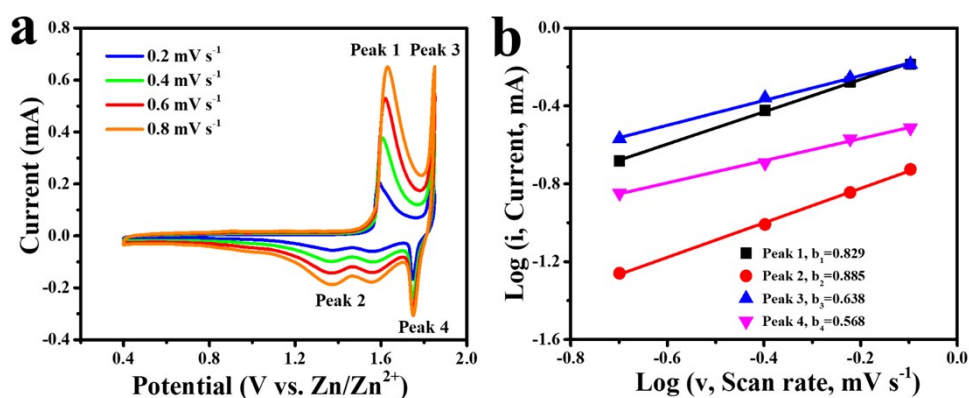


Fig. S2. (a) CV curves of the H-PBMN cathode at different scan rate of 0.2-0.8 mV s⁻¹. (b) log (i, Current) versus log (v, Scan rate) plots at specific peak currents.

References:

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