A new high-performance rechargeable alkaline Zn battery based on mesoporous nitrogen-doped oxygen-deficient hematite

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ABSTRACT Highly efficient, environmentally friendly, and inexpensive cathode materials have been regarded as the core elements in a wide range of rechargeable alkaline zinc batteries (RAZBs). Herein, a three-dimensional ordered mesoporous nitrogen-doped oxygen-deficient iron trioxide nanoarray (denoted as N-Fe₂O_{3-x}) has been developed as a new kind of cathode material for RAZBs, with great promise. The N-Fe₂O_{3-x} nanoarray is prepared *via* a unique high-isostatic pressure-assisted nanocasting process and N₂ plasma activation, which endow the N-Fe₂O_{3-x} material with highly effective areas, abundant active sites, fast electrolyte diffusion channels, and shortened charge transport pathways. Consequently, a high capacity of 288 mA h g⁻¹ (at 1.0 A g⁻¹) and an excellent energy density of 135 W h kg⁻¹ (based on the weights of N-Fe₂O_{3-x}) are achieved for the Zn battery composed of N-Fe₂O_{3-x}//Zn by using the optimized N-Fe₂O_{3-x} material as the cathode and Zn metal as the anode. Moreover, the rechargeable Zn battery possesses excellent stability; at 10 A g⁻¹, the battery retains 73% capacitance after 1000 cycles. The excellent electrochemical performance of the N-Fe₂O_{3-x}//Zn battery is much higher than those of the current Zn batteries based on iron oxides and hydroxides. This is the first example of using iron trioxide as a cathode for RAZBs, which may be of intense interest to later researchers.

Keywords: zinc battery, oxygen-deficient, Fe₂O₃, mesoporous, nitrogen doping

INTRODUCTION

With the impending global energy and environmental crisis, as well as the fast growth of electric vehicle and smart electronic equipment use, superior energy storage devices with low cost, high safety, environmental friendliness, and excellent energy storage performance are urgently required. Rechargeable multivalent battery technologies, such as those based on Al [1,2], Mg [3,4], Zn [5,6], Ni [7,8], or Ca [9], have gradually attracted extensive attention due to the increasing demand for the use and storage of clean energy. In comparison with other energy storage

technologies, aqueous rechargeable zinc batteries (RZBs) have obvious advantages for clean energy storage due to the intrinsic merits of zinc anodes, such as high capacity (820 mA h g⁻¹), high abundance, water compatibility, benign environmental impacts, intrinsic safety, and low oxidation–reduction potential (–0.76 V vs. a standard hydrogen electrode SHE) [10,11]. Given the prominently high capacity of a Zn anode, the main limiting factor for high-energy RZBs is the cathode [12,13]. Most reported cathodes such as Zn–manganese-based, Zn–vanadium-based, Zn–molybdenum-based, or Zn–Prussian blue analogs-based compounds mainly operate on the principle of a Zn²⁺ insertion/extraction energy storage mechanism [10,13]. Unfortunately, the insertion/extraction of large hydrated Zn²⁺ can easily cause significant structural changes, which usually result in a poor charge/discharge cycle. Besides, at higher charge/discharge current densities, the barriers to charge transfer and ion diffusion are obviously enhanced, leading to poor rate capability [12,14].

Rechargeable alkaline zinc battery (RAZB) is another type of RZB, which is commercially successful and seen as potential alternatives to lithium-ion batteries (LIBs) [15]. Unlike the Zn²⁺ (de)intercalation mechanism of zinc ion batteries (ZIBs), the protonation/deprotonation mechanism controls the charge transfer in RAZBs [13]. Over the past few decades, great efforts have been made to improve the electrochemical performance of RAZBs. However, the limited cathode materials, which are mainly nickel-based, cobalt-based, and air-based materials, greatly hinder the rapid development of RAZBs [10,13]. The exploitation of new cathode materials is crucial to further development. Owing to their abundant reserves (iron is the most abundant metal in the Earth's crust), low cost [16], nontoxicity, and high theoretical capacity (~336 mA h g⁻¹), iron oxides have been widely investigated in supercapacitors (SCs) [16,17], LIBs [18,19], and sodium-ion batteries (SIBs) [20,21]. However, to the best of our knowledge, their use in RAZBs has been barely reported. Recently, Xu *et al.* [22] demonstrated a Zn//Fe₃O₄ battery by coupling a three-dimensional (3D)-structured Fe₃O₄ cathode with a metallic Zn anode, which delivered a capacity of 45 mA h g⁻¹ at 100 mA g⁻¹ with about 30% capacity remaining

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after 50 cycles. However, the capacity and stability of the Zn//Fe₃O₄ battery are far from sufficient because of the natural poor conductivity and easy structural destruction of Fe-based electrodes during electrochemical reactions.

In this work, we report a 3D mesoporous nitrogen-doped Fe₂O₃ with rich oxygen vacancies (N-Fe₂O_{3-x}) as a new cathode for alkaline Zn batteries. The as-prepared N-Fe₂O_{3-x} is easily obtained by a unique synthesis method of high-isostatic pressure-assisted nanocasting and N₂ plasma activation. Plasma technology, with its high-energy and low-operating temperature conditions, has recently appeared as an extremely effective strategy for material preparation/modification [23]. The N₂ plasma treatment on porous Fe₂O₃ nanoarrays can simultaneously introduce nitrogen heteroatoms and oxygen vacancies without changing the bulk structure and phase. The high-porosity texture with rich N heteroatoms and oxygen-vacancy not only enables effective electron transport and rapid ion diffusion within the electrode but also improves active sites and conductivity, offering significantly enhanced capacity and charge/discharge rates. As a demonstration, an alkaline Zn//N-Fe₂O_{3-x} battery is fabricated, which achieves an excellent capacity of 288 mA h g⁻¹ at 1.0 A g⁻¹ and a high energy density of 135 W h kg⁻¹ at the power density of 0.47 kW kg⁻¹ (based on the mass of N-Fe₂O_{3-x}). Besides, the rechargeable Zn//Fe₂O_{3-x} battery shows excellent stability, cycling up to 1000 cycles with 73% capacity retention. Our work implies that 3D porous nitrogen-doped oxygen-deficient Fe₂O₃ (hematite) may hold great promise for actual application in RAZBs.

EXPERIMENTAL SECTION

Synthesis

The KIT-6 was prepared according to the procedure reported by Ryoo and coworkers [24].

Synthesis of the ordered mesoporous Fe₂O₃: In a typical synthesis of pristine ordered mesoporous Fe₂O₃, 1 g of dry mesoporous silica KIT-6 was added to Fe(NO₃)₃ (analytic reagent (AR), Sigma-Aldrich) solution (60 wt%, 30 mL) and sonicated for 20 min. Afterward, the mixtures were sealed into isostatic-pressurizing equipment for several minutes at 300 MPa. The superfluous Fe(NO₃)₃ solution was filtered and then sealed into a nickel dry pan and heat-treated in a muffle furnace at 600°C for 6 h. The heating rate was 5°C min⁻¹. Finally, to remove the KIT-6 template, the resulting mixture (KIT-6@Fe₂O₃) was treated in 2 mol L⁻¹ NaOH at 60°C thrice. Then, the obtained products were collected by centrifugation, washed with deionized water and ethyl alcohol thrice, respectively, and dried at 60°C.

Synthesis of nitrogen-doped and oxygen-deficient Fe₂O₃ (N-Fe₂O_{3-x}): Nitrogen-doped and oxygen-deficient Fe₂O₃ was obtained by plasma technology. In a typical procedure, the obtained pure mesoporous Fe₂O₃ was activated by N₂ plasma (radio frequency: 13.56 MHz) in a plasma-enhanced chemical vapor deposition (PECVD) process equipment (OTF-1500X-4CV-PE-SL) with N₂ flux of 15 sccm (standard cubic centimeter per minute) and base pressure of 1800 mTorr (1 Torr = 133.3 Pa), at various irradiation times (0.5, 1 and 1.5 h), power levels (150, 200 and 250 W), and temperatures (30, 100 and 200°C). The resulting samples are denoted as N-Fe₂O_{3-x} (X, Y, Z), where X, Y, Z represent the treatment time, power, and temperature, respectively. The sample treated at 1 h, 200 W, and

30°C was denoted as N-Fe₂O_{3-x} in the text and was studied in detail.

Characterizations

The phase and chemical composition properties of the samples were analyzed *via* X-ray photoelectron spectroscopy (XPS, ESCALab250, Thermo VG, USA), X-ray powder diffraction (XRD, SmartLab, Japan), Raman spectroscopy (HR800, France), energy-dispersive X-ray spectroscopy (EDS) (JEM-ARM200P, Japan), and electron paramagnetic resonance (EPR, Bruker, A300-10-12, Bruker, at 77 K, Germany). The microstructure and morphology were investigated with spherical aberration-corrected transmission electron microscopy (TEM, JEM-ARM200P, Japan), scanning electron microscopy (SEM, Zeiss/Bruker, Gemini500, Germany), and N₂ adsorption-desorption (Micromeritics ASAP 2020 PLUS HD88, USA).

Electrochemical measurement

The electrochemical properties of the alkaline Zn battery were studied in a two-electrode cell with the as-prepared iron trioxide materials as the cathode, Zn foil (0.5 cm × 2.0 cm; 1 mm in thickness) as the anode, and 2 mol L⁻¹ KOH as the electrolyte solution. The Fe₂O₃ and N-Fe₂O_{3-x} cathodes were prepared by mixing Fe₂O₃ or N-Fe₂O_{3-x} (80 wt%) with acetylene black (10 wt%, AR, Sigma-Aldrich) and polyvinylidene fluoride binder (10 wt%, AR, Sigma-Aldrich) in 1-methyl-2-pyrrolidinone (AR, Sigma-Aldrich), and then vigorously stirred to form a homogeneous slurry at 30°C. Afterward, the slurry was coated on a clean nickel foam current collector (0.5 cm × 2 cm) with about 1.4 mg cm⁻² of active material and dried at 60°C in vacuum. The weight of the zinc anode was overdosed compared with that of the cathode material (wt% 160:1). The electrochemical properties of the batteries were investigated by galvanostatic charge-discharge (GCD), cyclic voltammetry (CV), and alternating current (AC) impedance measurements with a CHI 760E electrochemical workstation (Chenhua, Shanghai).

RESULTS AND DISCUSSION

The ordered mesoporous nitrogen-doped oxygen-deficient N-Fe₂O_{3-x} nanoarrays were prepared *via* a two-step approach, which involves a hard-template synthesis and plasma treatment (Fig. 1). First, the ordered mesoporous Fe₂O₃ nanoarrays were fabricated by a high-pressure nanocasting technology (Fig. S1) with KIT-6 as the hard template and Fe(NO₃)₃ as the precursor and then calcined in a closed system consisting of a dry pan with a lid (Fig. S2a). Then, to introduce N heteroatoms and oxygen vacancies, the as-prepared ordered mesoporous Fe₂O₃ was further treated with N₂ plasma.

The morphology and microstructure of the as-obtained N-Fe₂O_{3-x} were investigated by SEM and TEM. Typical SEM and TEM images of the N-Fe₂O_{3-x} sample are presented in Fig. 2a, b, which clearly show that the as-prepared N-Fe₂O_{3-x} have round pie-like morphology with diameters of 100–250 nm and numerous regular mesopores of about 5 nm throughout the whole structure. The 3D orderly porous nanoarray structure can facilitate rapid ion transport on the N-Fe₂O_{3-x} electrode during the electrochemical reaction processes. Compared with the pristine Fe₂O₃ (Fig. S3a), the surface of N-Fe₂O_{3-x} is much rougher, and the color turns black (Fig. 1), indicating the morphology and bandgap of the material have mildly changed after high-energy plasma bombardment. The obvious electron

Figure 1 Schematic synthesis of Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$ samples.

diffraction spots (the inset of Fig. 2b) and well-resolved lattice fringes (Fig. 2c) signify the polycrystalline nature of the $\text{N-Fe}_2\text{O}_{3-x}$ nanoarrays. Whereas an approximately 0.4-nm thick amorphous layer is observed on the surface of $\text{N-Fe}_2\text{O}_{3-x}$ (Fig. 2c), indicating the surface of the Fe_2O_3 has become amorphous after high-energy N_2 plasma treatment. In $\text{N-Fe}_2\text{O}_{3-x}$ nanoarrays, well-resolved lattice fringes with a spacing of 0.367 nm are clearly observed, consistent with the characteristic (110) planes of hematite Fe_2O_3 (PDF#33-0664) [25] (Fig. 2c), signifying their hematite structure. Fig. 2d shows the high-angle annular dark-field (HAADF) image and the corresponding high-resolution EDS element mappings of $\text{N-Fe}_2\text{O}_{3-x}$, which clearly show the ordered mesoporous nanoarray structure of the $\text{N-Fe}_2\text{O}_{3-x}$ in which the Fe, O, and N elements are distributed homogeneously, demonstrating that N species are successfully introduced into $\text{N-Fe}_2\text{O}_{3-x}$. Additionally, the N atomic ratio of $\text{N-Fe}_2\text{O}_{3-x}$, measured by elemental analysis, is about 0.387% (Table S1).

It is worth noting that the calcination environment has a significant influence on the structure and crystallinity of the

products. When the mixture was calcined in a dry pan without a lid (denoted as an open system; Fig. S2b), the resulting products were nanospheres rather than ordered mesoporous nanoarrays (Fig. S3b), for the low migration rate of Fe^{3+} . In the closed system, the NO_2 , O_2 , and H_2O byproducts promote the movement of Fe^{3+} to form a continuous structure. Such differences in the synthesis conditions are sufficient to significantly change the atomic ordering within the walls, which has a profound influence on the electrochemical performance. In addition, the closed-system calcination favors the formation of products with high crystallinity. XRD results indicate that the products obtained in the closed system are typical $\alpha\text{-Fe}_2\text{O}_3$, which show much higher crystallinity than those of the open system (Fig. S4).

The XRD results of the Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$ are collected in Fig. 2e. All the characteristic diffraction peaks of the two samples match with the hexagonal Fe_2O_3 (PDF#33-0664), indicating their hematite structure. This result also confirms that there are no phase transitions during the plasma process. Fig. S5 shows the corresponding low-angle powder XRD patterns of Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$.

Figure 2 (a) SEM images of the $\text{N-Fe}_2\text{O}_{3-x}$; (b) TEM image and the corresponding selected area electron diffraction pattern (inset) for the $\text{N-Fe}_2\text{O}_{3-x}$ sample; (c) high-resolution TEM image of the $\text{N-Fe}_2\text{O}_{3-x}$ sample; (d) HAADF image of the $\text{N-Fe}_2\text{O}_{3-x}$ and its related EDS mappings of Fe, O, and N elements in a selected area; (e) XRD patterns of the as-synthesized Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$ samples; and (f) N_2 sorption-desorption isotherms and pore size distribution curves (inset) for the Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$ samples.

$\text{Fe}_2\text{O}_{3-x}$. The peaks at 2θ values of $\sim 1^\circ$ and $\sim 1.85^\circ$ are close to the (211) and (332) reflections of KIT-6 [6], suggesting that the as-prepared samples successfully inherited the ordered mesoporous structure of KIT-6, which is further proved by N_2 sorption-desorption analysis (Fig. 2f). The obvious hysteresis loops and concentrated pore size distributions (2–6 nm, by the Barrett-Joyner-Halenda (BJH) method) also clearly support their mesoporous structure. Additionally, high Brunauer-Emmett-Teller (BET) specific surface areas of $130 \text{ m}^2 \text{ g}^{-1}$ and $103 \text{ m}^2 \text{ g}^{-1}$ and pore volumes (PV) of $0.34 \text{ cm}^3 \text{ g}^{-1}$ and $0.32 \text{ cm}^3 \text{ g}^{-1}$ were obtained for the Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$, respectively (Table S1). The relatively lower BET and PV of $\text{N-Fe}_2\text{O}_{3-x}$ are due to the partial pore structure deterioration during the plasma process.

To further study the influence of N_2 plasma treatment on the

composition and oxidation states of the $\text{N-Fe}_2\text{O}_{3-x}$, EPR, XPS, and Raman analyses were carried out. A distinct signal at $g = 2.000$ is shown in the EPR spectra for Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$ samples (Fig. 3a), which can be attributed to the exchange-coupling interaction of Fe^{3+} ions [17]. In addition, an obvious narrow peak located at a magnetic field strength of 3515 G with $g = 2.002$ in the $\text{N-Fe}_2\text{O}_{3-x}$ spectrum, which is the single-electron characteristic signal of oxygen vacancy [26], clearly confirming the formation of oxygen vacancies after plasma treatment. Fig. 3b shows the O 1s core-level XPS spectra of the Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$. The peak at $\sim 531.4 \text{ eV}$ is generally believed to be caused by oxygen defects [27], and that at $\sim 529.5 \text{ eV}$ is ascribed to Fe–O [28]. In comparison with the original Fe_2O_3 , the peak attributed to oxygen defects is sub-

stantially enhanced for $\text{N-Fe}_2\text{O}_{3-x}$, demonstrating that the oxygen vacancies increased after N_2 plasma treatment, which is consistent with the EPR result. In the meantime, the Fe–O peak of the $\text{N-Fe}_2\text{O}_{3-x}$ shifts positively compared with the pristine Fe_2O_3 , suggesting the electron structure of the Fe_2O_3 sample has changed after plasma treatment. The Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$ samples exhibit the typical Fe 2p core-level XPS spectra of hematite with two prominent peaks centered at around 710 and 724 eV (Fig. 3c), which belong to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively [17,29]. However, for the $\text{N-Fe}_2\text{O}_{3-x}$ sample, the two peaks show positive shifts (710.89, 724.40 eV) when compared with those of the pristine Fe_2O_3 (710.64, 724.00 eV), revealing that the Fe valence state decreases after N_2 plasma treatment due to the N doping and introduction of oxygen vacancies. These oxygen defects with many unsaturated sites are commonly considered to be highly reactive sites for electrochemical reactions [30]. Also, the $\text{N-Fe}_2\text{O}_{3-x}$ sample exhibits a distinct N signal (Fig. 3d, e), confirming the presence of N on the $\text{N-Fe}_2\text{O}_{3-x}$. Moreover, the Fe–N signal is found at ~ 397.30 eV, indicating some nitrogen atoms access to the lattice of iron trioxide after N_2 plasma treatment.

All the Raman peaks (Fig. 3f) of the pristine Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$ samples display representative characteristic Raman peaks of $\alpha\text{-Fe}_2\text{O}_3$ [31]. More importantly, the characteristic peaks at 600–700 cm^{-1} of the $\text{N-Fe}_2\text{O}_{3-x}$ sample (inset in Fig. 3f) have positively shifted and become broader than those of the pristine Fe_2O_3 , which indicates the formation of oxygen defects after N_2 plasma treatment [32]. These results demonstrate that N_2 plasma activation can effectively induce oxygen vacancies and N species into Fe_2O_3 without changing the phase and morphology of bulk Fe_2O_3 .

To assess the application of the Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$ samples in alkaline Zn batteries, the electrochemical tests were performed

in a conventional two-electrode cell in 0.02 mol L^{-1} $\text{Zn}(\text{Ac})_2$ –2 mol L^{-1} KOH aqueous electrolyte, with the as-made iron trioxide samples as the cathode and a metallic Zn foil as the anode. Fig. 4a displays the CV curves of the $\text{Fe}_2\text{O}_3//\text{Zn}$ and $\text{N-Fe}_2\text{O}_{3-x}//\text{Zn}$ batteries. The batteries display one pair of well-defined redox peaks, located at about 0.85 V and 0.40 V in the CV curves, which could be ascribed to the reversible oxidation–reduction reaction in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple [29,33–35]. Obviously, the current response of the $\text{N-Fe}_2\text{O}_{3-x}//\text{Zn}$ battery is significantly higher than that of the $\text{Fe}_2\text{O}_3//\text{Zn}$ one, indicating a substantial enhancement after the N_2 plasma activation. Additionally, the CV curves of the $\text{N-Fe}_2\text{O}_{3-x}//\text{Zn}$ battery obtained in the range from 1 to 80 mV s^{-1} show basically similar shapes with little distortion (Fig. S6), revealing its superior electrochemical reversibility and high-rate ability. We further explored the electrochemical kinetics of the $\text{N-Fe}_2\text{O}_{3-x}$ electrode using the power law $i = av^b$. The b value, determined from the slope of a $\log(v) - \log(i)$ plot (Fig. 4b), is about 0.5, meaning that the current changes of the $\text{N-Fe}_2\text{O}_{3-x}//\text{Zn}$ battery in the range of 1 to 80 mV s^{-1} are diffusion-controlled processes.

The typical GCD curves were also collected to investigate the electrochemical performance of $\text{Fe}_2\text{O}_3//\text{Zn}$ and $\text{N-Fe}_2\text{O}_{3-x}//\text{Zn}$ batteries. In comparison with the $\text{Fe}_2\text{O}_3//\text{Zn}$ battery, the $\text{N-Fe}_2\text{O}_{3-x}//\text{Zn}$ battery delivers substantially higher discharge voltages and longer discharge times (Fig. 4c), confirming its enhanced energy storage performance. A decent gravimetric specific capacity of 288 mA h g^{-1} (based on the mass of $\text{N-Fe}_2\text{O}_{3-x}$, 0.288 mA h cm^{-2}) at 1 A g^{-1} is achieved by the $\text{N-Fe}_2\text{O}_{3-x}//\text{Zn}$ battery, which considerably outperforms the $\text{Fe}_2\text{O}_3//\text{Zn}$ battery (90 mA h g^{-1}) and most other previous RAZBs and ZIBs (Table S2), such as Zn/NiO (155 mA h g^{-1} , 1 A g^{-1}) [36], Zn/MnO_2 (258 mA h g^{-1} , 0.65 C) [37], $\text{Zn}/\text{Co}_3\text{O}_4$ (162 mA h g^{-1} , 1 A g^{-1}) [38], $\text{Zn}/\text{Bi}_2\text{O}_3$ (200 mA h g^{-1} , 1 A g^{-1}) [12], $\text{Zn}/\text{V}_2\text{O}_5$

Figure 3 (a) EPR spectra, (b) O 1s core-level XPS spectra, (c) Fe 2p core-level XPS spectra, (d) XPS survey spectra, (e) N 1s core-level XPS spectra, and (f) Raman spectra of Fe_2O_3 and $\text{N-Fe}_2\text{O}_{3-x}$.

Figure 4 (a) CV curves of the N-Fe₂O_{3-x}//Zn and Fe₂O₃//Zn batteries at 10 mV s⁻¹; (b) the relationship between ln(v) and ln(i) of the N-Fe₂O_{3-x}//Zn battery (i: anodic-cathodic peak currents of CV curves, v: scan rates); (c) GCD profiles of the N-Fe₂O_{3-x}//Zn and Fe₂O₃//Zn batteries at 1 A g⁻¹; (d, e) rate performances of the Fe₂O₃//Zn and N-Fe₂O_{3-x}//Zn batteries; (f) EIS of the Fe₂O₃//Zn and N-Fe₂O_{3-x}//Zn batteries.

(224 mA h g⁻¹, 0.1 A g⁻¹) [39], Zn//VS₂ (190.3 mA h g⁻¹, 0.05 A g⁻¹) [40], Zn//polypyrrole (123 mA h g⁻¹, 1.9 A g⁻¹) [41], and Zn//CoHCF (149.53 mA h g⁻¹, 0.2 A g⁻¹) [5]. Meanwhile, the N-Fe₂O_{3-x}//Zn battery has a moderate rate capability, which can maintain values higher than 42 mA h g⁻¹ at a large current density of 10 A g⁻¹ (Fig. 4d, e). All the above results indicate that the existence of N heteroatoms and oxygen deficiencies can significantly improve the electrochemical energy storage capacity of the Fe₂O₃ electrode. Electrochemical impedance spectroscopy (EIS) analyses were also conducted to study the substantive reason for the boosted electrochemical property (Fig. 4f). The charge transfer resistance (*R*_{ct}) for N-Fe₂O_{3-x}//Zn is measured to be 2.0 Ω, which is substantially smaller than that of the Fe₂O₃//Zn battery (5.0 Ω), suggesting the introduction of nitrogen and oxygen vacancies greatly improved the conductivity of Fe₂O₃.

Ex-situ XPS was applied to further explore the electrochemical mechanism of the N-Fe₂O_{3-x}//Zn battery. Fig. S7a shows the *ex-situ* XPS results of the Fe 2p core-level collected at various states (Fig. S7b) of the N-Fe₂O_{3-x} cathode, which clearly shows the formation of Fe²⁺ and FeO(OH) in the process [42,43]. The intensities of the FeO(OH) in the charge states (State 2 and State 3) are higher than those in the discharge states (State 4 and State 5), which confirms the formation of FeO(OH) in the charging process. Meanwhile, the Fe²⁺ in the discharge process is more abundant than those of charge states, suggesting the formation of Fe²⁺ in the discharge process. Therefore, based on these results and previous studies [10,33–35,44–46], the electrode reactions could be described by the following:

Anode:

We also investigated the influence of the plasma treatment conditions of power, temperature, and time on the composition, morphology evolution, and electrochemical properties of N-Fe₂O_{3-x}. The samples of Fe₂O₃ plasma-treated at different power levels (X: 150, 200, 250 W), temperatures (Y: 30, 100 and 200°C) and times (Z: 0.5, 1 and 2 h), are denoted as N-Fe₂O_{3-x} (X, Y, Z), whereas the sample treated at 200 W power, 30°C, and 1 h is denoted as N-Fe₂O_{3-x} in the text. The XRD results indicate that at these N₂ plasma treatment conditions, the samples remain in the hexagonal hematite phase without other new phases (Fig. S8). In comparison with the pristine Fe₂O₃, the BET specific surface area decreases after N₂ plasma treatment, as the high-energy nitrogen plasma bombarded the sample, resulting in slight structural damage (Fig. S9, Table S1). Besides, according to the XPS and Raman analyses results (Figs S10–S12), the sample developed more oxygen defects under high power and high temperature treatment. Fig. S13 compares the capacities (at 1 A g⁻¹) and the charge transfer resistances of N-Fe₂O_{3-x} (X, Y, Z)//Zn batteries. All N-Fe₂O_{3-x} (X, Y, Z)//Zn batteries exhibit higher capacity than the pristine Fe₂O₃//Zn battery (Fig. S14), revealing that structural deficiencies and N heteroatoms can boost the electrochemical energy storage performance of the Fe₂O₃. It is noted that excess oxygen vacancies may result in a decrease in active sites. The N-Fe₂O_{3-x} (X, Y, Z) electrode treated at 200 W power, 30°C, and 1 h N₂ plasma shows the highest capacity and almost the lowest charge transfer resistance (*R*_{ct}, 2 Ω).

Figure 5 (a) Cycling performance of the N-Fe₂O_{3-x}/Zn and Fe₂O₃/Zn batteries; (b) the Ragone plots of the N-Fe₂O_{3-x}/Zn battery with other energy storage devices for comparison.

The charge–discharge cycling stabilities of the N-Fe₂O_{3-x}/Zn and Fe₂O₃/Zn batteries were tested at 10 A g⁻¹. As shown in Fig. 5a, after 1000 cycles, the N-Fe₂O_{3-x}/Zn battery can still maintain 73% capacitance, which is relatively higher than that of the Fe₂O₃/Zn battery (69%) and far superior to that of a previously reported Fe₃O₄/Zn battery [22]. In addition, the charge–discharge platforms of the N-Fe₂O_{3-x}/Zn battery is clearly observed even after 1000 cycles (inset of Fig. 5a), signifying the excellent reversibility of electrochemical reactions. Fig. 5b presents the Ragone plots of our N-Fe₂O_{3-x}/Zn battery. Encouragingly, our battery obtains a high energy density of 135 W h kg⁻¹ at a power density of 0.47 kW kg⁻¹, exceeding many of the previously reported Zn batteries and other aqueous batteries (Table S3), such as Ni//Fe (100.7 W h kg⁻¹, 0.287 kW kg⁻¹) [33], NiCo₂O₄/Bi (85.8 W h kg⁻¹, 1.02 kW kg⁻¹) [47], NiCo₂S₄/rGO/Fe₂O₃ (61.7 W h kg⁻¹, 1.2 kW kg⁻¹) [48], Al//graphite Al ion (40 W h kg⁻¹, 3.0 kW kg⁻¹) [49], Ni//Bi (43.35 W h kg⁻¹) [8], CNH//NNA@Zn battery (138 W h kg⁻¹, 1.72 kW kg⁻¹) [50], Zn//VS₂ battery (123 W h kg⁻¹, 0.0323 kW kg⁻¹) [40], Zn//Zn_{0.2}MnO₂ battery (61 W h kg⁻¹, 0.1 kW kg⁻¹) [51], Na_{0.14}TiS₂/ZnMn₂O₄ battery (51 W h kg⁻¹, 0.024 kW kg⁻¹) [52], and Zn₂Mo₆S₈/ZPB battery (47 W h kg⁻¹) [53].

CONCLUSIONS

In summary, we have developed an efficient method of high-isostatic pressure-assisted nanocasting and N₂ plasma activation to design 3D-ordered mesoporous Fe₂O₃ nanoarrays with rich nitrogen heteroatoms and oxygen vacancies (N-Fe₂O_{3-x}). The special structure and composition significantly enhanced the electrochemical properties of N-Fe₂O_{3-x}, rendering it a new cathode for RAZBs. The as-prepared N-Fe₂O_{3-x}/Zn battery gains a high reversible capacity of 288 mA h g⁻¹ (1 A g⁻¹) and a decent energy density of 135 W h kg⁻¹ at a power density of 0.47 kW kg⁻¹. In addition, this N-Fe₂O_{3-x}/Zn battery possesses good cycling durability, maintaining 73% capacity after 1000 cycles at 10 A g⁻¹. This work, therefore, may open up a new promising prospect for the application of porous N-Fe₂O_{3-x} in alkaline zinc batteries (RAZBs).

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Conflict of interest The authors declare no conflict of interest.

Supplementary information Calculations and supporting data are available in the online version of the paper.

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基于介孔氮掺杂氧缺陷型三氧化二铁正极的新型高性能可充放碱性锌电池

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摘要 高效、环保、廉价的正极材料被认为是可充电碱性锌电池(RAZBs)的核心要素。据此, 本工作开发出一种具有三维有序介孔结构、丰富氮掺杂和氧缺陷的三氧化二铁纳米材料($\text{N-Fe}_2\text{O}_{3-x}$)。该材料作为一种新型碱性锌电池的正极材料, 表现出优异的性能。 $\text{N-Fe}_2\text{O}_{3-x}$ 纳米材料采用独特的高等静压纳米铸造工艺和 N_2 等离子体活化方法制备, 该材料具有高有效面积、丰富的活性位点、快速的电解质扩散通道和短电荷传输途径。以优化后的 $\text{N-Fe}_2\text{O}_{3-x}$ 材料为正极, 金属锌为负极制备的 $\text{N-Fe}_2\text{O}_{3-x}/\text{Zn}$ 碱性锌电池具有高的容量(288 mA h g^{-1})和能量密度(135 W h kg^{-1} , 基于活性物质 $\text{N-Fe}_2\text{O}_{3-x}$ 的重量计算)。此外, 该可充电锌电池具有良好的稳定性, 在 10 A g^{-1} 电流密度下, 1000次循环后仍有73%的电容保持率。该 $\text{N-Fe}_2\text{O}_{3-x}/\text{Zn}$ 电池的电化学性能远远高于目前其他铁基锌电池。本工作首次利用三氧化二铁作为正极材料应用于可充电碱性锌电池的研究, 其优良特性将吸引更多研究者的兴趣。