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Zeolitic imidazolate framework-8 derived zinc oxide/ carbon nanofiber as freestanding electrodes for lithium storage in lithium-ion batteries

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HIGHLIGHTS

- Freestanding carbon nanofibers (CNF) grafted with amorphous ZnO are produced.
- The CNFs are decorated with the rhombic dodecahedral morphology of ZIF8.
- The synergy effect between ZIF8-derived ZnO CNF increased electrochemical performance.
- The freestanding composites showed a stable and higher specific capacity.

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ABSTRACT

Zeolitic imidazolate framework-derived carbon and metal oxide composites are promising for applications in lithium-ion batteries due to their morphology and porous structure. Herein, we report freestanding carbon nanofibers grafted with amorphous ZnO where the rhombic dodecahedral morphology of the parent (ZIF8) is maintained. The impacts of ZIF8 loading temperature on particle size after pyrolysis and on the electrochemical properties of these hybrid structures for LIBs are investigated. Polyacrylonitrile nanofiber loaded with ZIF8 at 45 °C exhibits a perfect sodalite topology and optimized particle size. The carbonized freestanding composite fibers have a high specific capacity of 818 $mAh{\cdot}g^{-1}$ at a current density of 100 $mA{\cdot}g^{-1}$ after 100 cycles. This remarkable performance of ZIF8-derived ZnO is due to its loading and coordination chemistry, which facilitates flexible volume changes and continuity in electrical conductivity through a continuous carbon nanofiber.

1. Introduction

Metal-organic frameworks (MOFs) are porous three-dimensional coordination polymers with metals ions at vertices connecting multiple organic monomers. Carbonization of MOFs can produce multifunctional composites with properties that are superior to those of the individual components (carbon and/or metal) in energy storage devices such as lithium-ion batteries (LIBs) [1]. The initial utilization of as-synthesized MOF-177 for lithium ion battery applications was reported by Li et al. However, without carbonization, the presence of the organic linker resulted in relatively low electrical conductivity [2]. Hence, MOF-derived carbons [3] or metal oxides [4] generated by high-temperature annealing have emerged as alternatives for achieving enhanced conductivity.

The coordination chemistry, uniform cavity tuning, and the ability of MOFs to act as host matrices for metal species offer opportunities for various types of MOFs to be produced for numerous applications [1]. Zeolitic imidazolate frameworks (ZIFs) represent a class of MOFs in which metal centers such as Zn or Co are coordinated to the nitrogen of imidazole ligands in a metal-ligand-metal array with an inter-ligand angle of 145° as shown in Fig. 1a [5]. In the ZIF family, ZIF8 with a sodalite (SOD) topology that consists of zinc ions surrounded by 2-methyl imidazolate (2MI), exhibits exceptional chemical and thermal stability and is widely studied for hydrogen storage [6]. ZIF8 is of particular interest for LIB applications, as the 2MI coordination network can host a large number of Zn ions due to its rhombic dodecahedral morphology [7].

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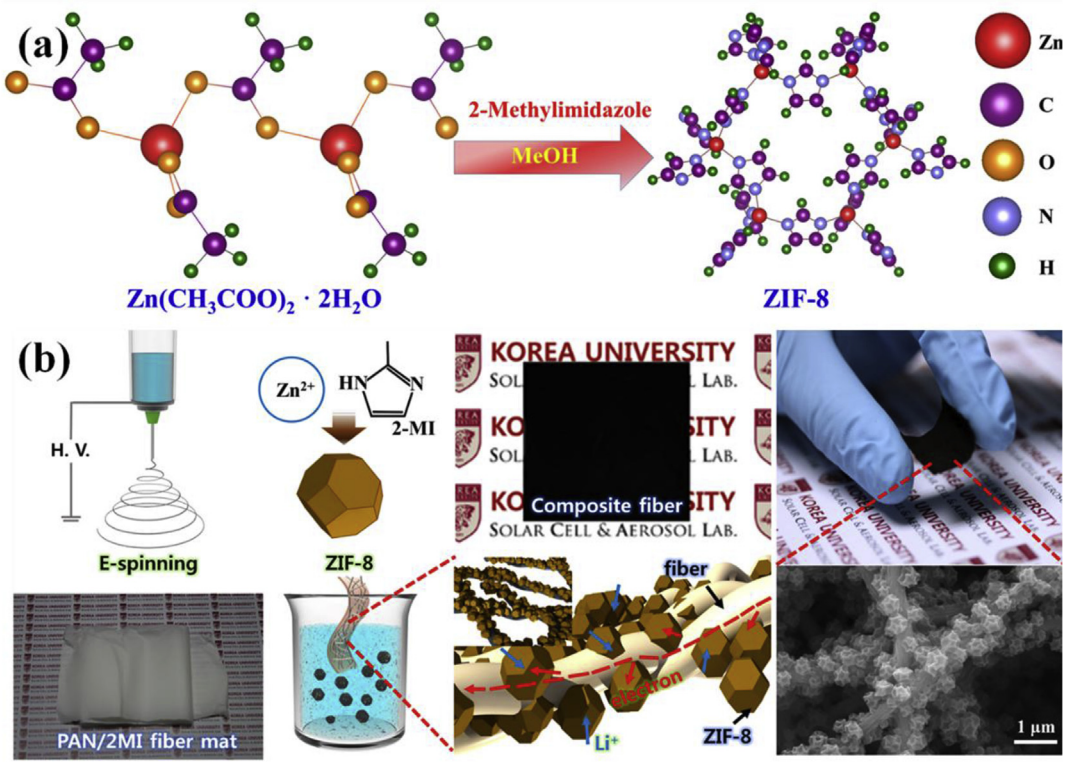

Fig. 1. Schematic depicting: (a) Zinc acetate dihydrate in the presence of 2-methyliimidazole and methanol reacts to form ZIF-8. (b) From left to right: steps illustrating electrospinning of PAN-2MI fiber mat, ZIF8 loading onto fibers, black colored composite fiber mat after carbonization, flexibility test, and morphology of fiber showing rhombic dodecahedral structure of ZIF8-derived ZnO.

The synthesis of ZIF8 has been executed by various approaches, such as liquid-phase diffusion [8], solvothermal [9], sonochemical [10], mechanochemical [11], and steam-assisted hydrothermal techniques [5]. Furthermore, water, dimethylformamide, and methanol are commonly used for the synthesis of ZIF8, with methanol as the most widely used solvent [12,13]. Han and coworkers synthesized ZIF8 by a mechanochemical synthesis process, followed by coating with organic molecules such as glucose, citrate, and chitosan, and then carbonized the coated ZIF8 at different temperatures under nitrogen. The resulting anode showed a capacity of 750 $mAh \cdot g^{-1}$ at 50 $mA \cdot g^{-1}$ after 50 cycles [7]. Zou and coworkers synthesized ZIF8 by a precipitation method using carbon nanotubes. To obtain ZnO, the composite was annealed in air. However, the anode comprising the ZnO/MWCNT composite delivered a lower capacity of 419.8 $mAh \cdot g^{-1}$ at 200 $mA \cdot g^{-1}$ after 100 cycles [14]. Zheng and coworkers utilized nitrogen-containing ZIF-derived carbon, produced by direct pyrolysis of ZIF at 800 °C under nitrogen, as a LIB anode. They prepared ZIF8 by a precipitation process using methanol, followed by carbonization of ZIF8 under N_2 and treatment with 35% concentrated HCl to remove residual Zn. The fabricated ZIF8-derived carbon electrodes exhibited superior lithium storage, which was attributed to their high nitrogen content [3]. These studies demonstrate that ZIF8 can be used as a precursor for preparing ZnO/carbon nanostructures with promising performance as LIB anode materials.

The aforementioned approaches used binders and Cu foil current collectors to fabricate the desired LIB electrode. These binders increase the mass, while decreasing electrical conductivity, and thus hamper the capacity and performance of LIB cells. Furthermore, the use of a Cu foil current collector also adds mass. Thus, to exploit the advantages of the porous nature and metal centers of ZIF8 in freestanding and binder-free LIB anodes, herein we report the synthesis of ZIF8 and its deposition on electrospun PAN-2MI nanofibers (NFs). After carbonization, the ZIF8-loaded NFs are transformed to amorphous ZnO/carbon nanofibers (CNFs) that deliver superior capacity even after 100 cycles. Detailed electrochemical evaluation based on charge-discharge profiles, rate capability, and impedance measurements is also presented.

2. Experimental procedures

2.1. Fiber synthesis

The freestanding fibers were prepared using 8 wt% polyacrylonitrile (PAN, M_w = 150 kDa; Sigma Aldrich) in *N,N*-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), to which 0.8 wt% 2MI was added. The 2MI serves as a seed for loading the ZIF8 particles. The optimal parameters for fiber preparation were as follows: flow rate: 250 $\mu l \cdot h^{-1}$, voltage: 7 kV, needle-to-drum distance: 13 cm, and drum speed: 200 rotations per minute (rpm). The fibers were deposited over the course of 2 h and collected on a drum collector to yield a 30 × 10 cm^2 piece of nonwoven fabric.

2.2. Chemical synthesis of ZIF8

Herein, we used the precipitation synthesis route, which is simpler and less time-consuming than the hydrothermal synthesis process. A ZIF8 precursor solution was prepared by mixing 0.5 mmol of zinc acetate dihydrate and 2 mmol of 2-methyl imidazole in 50 mL of methanol. Formation of the ZIF8 crystals started within 10 min, as evidenced by the change of the transparent solution to a turbid white color. As explained by Lai et al. [15], ZIF8 formation involves deprotonation of 2MI to form the imidazolium ion, while dissolution of the Zn salt furnishes the Zn^{2+} ions. Further, these Zn^{2+} and imidazolium ions react and are linked via a bridging N atom to form six-membered rings that are then further linked to produce particles of overall rhombohedral shape.