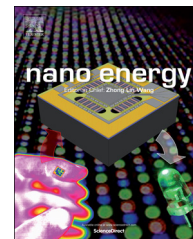




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RAPID COMMUNICATION

Self-supported, binder-free 3D hierarchical iron fluoride flower-like array as high power cathode material for lithium batteries



Bingjiang Li^b, Zhongjun Cheng^c, Naiqing Zhang^{a,c,*},
Kening Sun^{a,c,*}

^aState Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, PR China

^bDepartment of Chemistry, Harbin Institute of Technology, Harbin 150001, PR China

^cAcademy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150090, PR China

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Abstract

We present a tactful and advanced architecture design of self-supported, binder-free 3D hierarchical iron fluoride flower-like array directly growing on Ti foil by a solvothermal approach. The probable growth mechanism of the 3D microflower is explored. The advantages of the porous 3D hierarchical nanostructure materials endow a stable capacity of 123 mAh g^{-1} at 3 C rate, and a good rate capability of 101 mAh g^{-1} at a high current density of 2 A g^{-1} (10 C). The superior electrochemical performance can be ascribed to the synergistic effect of charge transfer expressway, high specific surface area and porous hierarchical structure for electrolyte penetration deriving from the unique porous 3D hierarchical structure. The superior electrochemical performance combined with the unique structure of the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ flower-like array demonstrates its great potential of being utilized as the cathode material in high rate battery application.

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*Corresponding authors at: State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, PR China. Tel./fax: +86 451 86412153.

E-mail addresses: znqmww@163.com (N. Zhang), keningsunhit@126.com (K. Sun).

Introduction

Lithium ion batteries (LIBs) are regarded as promising power sources for portable electronic devices and hybrid electric vehicles due to their high energy density and long lifespan [1,2]. For their practical applications, new technologies

require electrodes with much higher capacity and power density to store and deliver more energy faster [3,4]. Therefore, the development of new electrode materials (currently mainly limited by the cathode side) that meet the requirements mentioned above is of utmost importance. To realize LIBs with higher capacity and power densities, new kinds of cathode materials have been developed recently [5,6]. Among them, iron fluoride has attracted rapidly increasing amount of attention due to its high theoretical capacity of 237 mAh g^{-1} ($1e^{-}$ transfer) and 712 mAh g^{-1} ($3e^{-}$ transfer), abundant sources, and relatively low cost [7-10]. Despite these advantages, the use of iron fluoride has been limited due to intrinsic drawbacks such as the slow diffusion of Li^{+} and low electron conductivity [9-11].

Nowadays, various endeavors have been made to overcome their drawbacks, including reducing the electron and Li^{+} flow path by using nanomaterials, or hybridizing iron fluoride with a conductive additive (graphene, carbon nanotube and conducting polymer) [12-16]. However, it is noteworthy that traditional electrode design for iron fluoride (deriving from pasting homogeneous slurry of nanosized active material, conductive additive and a polymeric binder onto the current collector) has obvious drawbacks including poor electron transport, additional undesirable interfaces, the negligence of the advantages of nanoscale size, and low specific capacity caused by the extra weight of additives [17]. Hence, constructing advanced nanostructure array electrode directly growing on conducting substrate with expressway for charge transfer is a promising strategy to overcome these drawbacks.

In recent years, three-dimensional (3D) hierarchical structures constructed with low dimensional nanoscale building blocks have drawn growing attention [18-22]. Ordered 3D hierarchical structures could inherit the superior characteristics of the pristine building blocks, and more importantly, also possess new physicochemical properties arising from their secondary architecture [18,19]. The advantages of the 3D hierarchical structures electrode endow a short length for electron transport and Li^{+} diffusion determined by the small thickness of nanounits, better interconnection between building blocks, and high porosity for efficient transport of Li^{+} [19]. However, fabrication of self-supported 3D hierarchical nanostructures arrays with desirable architectures still remains a great challenge.

Herein, we first report the synthesis of porous 3D hierarchical iron fluoride flower-like array directly growing on Ti foil by a solvothermal approach. The 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]) ionic liquids acting as a fluoride source are environmentally friendly and operationally safe compared with other erosive fluoride sources (such as HF) [10,11,13]. To the best of our knowledge, there is no report on nanostructure iron fluoride array growing directly on conducting substrate. The advantages of the 3D nanostructure materials endow a stable and high discharge capacity of 123 mAh g^{-1} at 3 C rate after 50 cycles, and a good rate capability of 101 mAh g^{-1} even at a high current density of 2 A g^{-1} (10 C). The superior electrochemical performance can be ascribed to the synergistic effect of charge transfer expressway, high specific surface area and porous hierarchical structure for electrolyte penetration.

Experimental section

Synthesis of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ flower-like array on Ti foil

Titanium foils ($4 \times 5 \text{ cm}^2$) were cleaned by a sonication method in a mixture solution of acetone, alcohol, deionized water (1:1:1 in vol) for 1 h. Afterward, the titanium foils were placed in 200 mL autoclaves with solutions made up of 80 mL alcohol, 30 mL [Bmim][BF₄], 1 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Then the autoclaves were firmly sealed and placed in a 120°C drying oven (2-10 h). The titanium foils were rinsed with acetone and dried at 80°C under vacuum for 8 h after the reaction. The precipitate in solution was also collected and washed sequentially by acetone and dried in an oven.

Materials characterization

Scanning electron microscope (SEM, Hitachi, SU8010), transmission electron microscope (TEM, Tecnai F20, 200 kV), and X-Ray Diffraction (XRD, Rigaku D/max- γ B, Cu K α radiation) were applied to characterize the detailed structure and morphology information of the materials. N_2 adsorption/desorption isotherms were measured by using ASAP 2020 (Micromeritics).

Cell fabrication and electrochemical characterizations

The mass of electrode materials was measured on Mettler Toledo MS105DU (Max: 42 g, $d=0.01 \text{ mg}$). The substrate supporting $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ flower-like array was cut into a disk with a surface area of 1.77 cm^2 and directly used as the working cathode (15 mm diameter, $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ flower-like array on one side of the foil was removed for electrical contacting beforehand). For the comparative study of the electrochemical performance, $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ powder electrode was also prepared. The powders were collected from the precipitation in the solution. The electrode slurry was fabricated by mixing active materials with polyvinylidene fluoride (PVDF was dissolved in N-methyl-2-pyrrolidone NMP with content of 10 wt%) as a binder and carbon black as a conductive agent with a weight ratio of 8:1:1. The obtained slurry was coated by a doctor-blading method. Then the electrodes were cut into discs with diameter of 15 mm and dried at 120°C overnight under vacuum. The coin type (CR-2025) test cells were assembled in an argon-filled glove box (Mbraun, $\text{H}_2\text{O} < 0.1 \text{ ppm}$, $\text{O}_2 < 1 \text{ ppm}$) using 1 M LiPF_6 in diethyl carbonate, ethylene carbonate and ethylmethyl carbonate (EC/EMC/DMC, 1:1:1 in vol) as an electrolyte, two pieces porous polypropylene films (Celgard 2400) as the separator metallic lithium as the counter/reference electrode. All the as prepared cells were stabilized for 12 h before measurements. Over a voltage range of 1.7-4.5 V (vs Li^{+}/Li), the discharge/charge measurements were carried out by using a Neware (Shenzhen Neware Electronic Co., China) battery test system at various current rates (1 C is equivalent to 200 mA g^{-1}). Electrical impedance spectroscopy (EIS) measurements were carried out using an electrochemical workstation (Princeton Applied Research PARSTAT 2273 advanced electrochemical

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