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Flexible textile electrode with high areal capacity from hierarchical V_2O_5 nanosheet arrays

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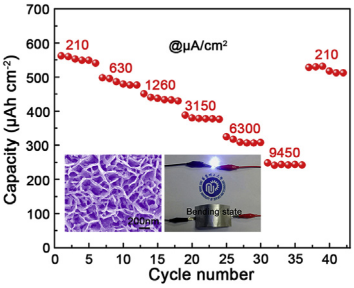
HIGHLIGHTS

- Hierarchical V_2O_5 nanosheets are firmly grown on surface-decorated carbon cloth.
- The polydopamine plays a pivotal role in the formation of robust flexible cathode.
- The flexible cathode exhibits superior mechanical strength and LIBs performances.

GRAPHICAL ABSTRACT



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ABSTRACT

The search for an appropriate flexible cathode is pivotal to expediting the development of flexible and foldable lithium-ion batteries (LIBs). Herein, we demonstrate a simple and scalable synthesis of hierarchical V_2O_5 nanosheet arrays on polydopamine (PDA)-decorated carbon cloth with strong combination between them, which then directly applied as flexible cathode for LIBs. We found this flexible cathode with a loading mass of 2.1 mg cm^{-2} can deliver a high specific capacity of 120 mAh g^{-1} even at 15C (1C = 300 mA g^{-1}) and maintain a long-term cycling stability, *i.e.* simply 0.30% capacity loss per cycle at 2C for 100 cycles without morphology change. More importantly, the corresponding areal capacity can reach as high as 560 μAh cm^{-2} at 210 μA cm^{-2}, favorably comparing with the-state-of-art flexible cathode reported to date. Additionally, a flexible LIBs full cell has been assembled, exhibiting high mechanical strength and superior electrochemical performances.

1. Introduction

The exploitation of flexible and foldable lithium-ion batteries (LIBs) is crucial to meet the increasing demands for portable electronic devices with flexibility, miniaturization and portability [1–4]. The key to obtain such LIBs lies in making satisfied flexible electrodes [5–7]. To date, substantial strategies have been explored for achieving high-capacity and stable flexible anodes, such as directly growing various metal oxides-based materials on flexible substrates [8,9], or hybridizing them with carbonaceous materials to forming free-standing anode [10,11]. Nevertheless, flexible cathodes still lag far behind the corresponding anodes [12]. It is noted that the traditional cathode materials (*e.g.* $LiCoO_2$ [13], $LiFePO_4$ [14], $LiMnO_2$ [15]) are hard to directly grow on flexible

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substrates owing to their intricate preparation process [16]. Moreover, coating cathode materials on flexible substrates (not Al foil) is easy to cause the detachment between them, inevitably resulting in rapid capacity loss [12,17,18]. Therefore, it is crucial to search for novel flexible cathode for developing high-performance flexible LIBs.

With this perspective, orthorhombic V_2O_5 has been shown huge potential as cathode materials of LIBs due to its unique capability of incorporating multiple Li^+ ions (*e.g.* delivering 294 mAh g^{-1} for two Li^+ ions intercalation) as well as low cost and good safety [19–22]. However, its low electrical conductivity and big volume variation during cycling have not yet been effectively solved [20,21,23]. More importantly, unlike other transition metal precursors (ionic salts, M^{n+}: M = Mn, Co, Ni, et al.), most vanadium resources exist in organic vanadates, which causes the difficulty in realizing the grown of V_2O_5 nanostructures on various flexible conductive substrates (*e.g.* carbon fiber, graphite paper). Recently, Gwon et al. [24] deposited a layer of V_2O_5 nanoparticles on graphene paper by pulsed laser deposition. Afterwards, Krishna et al. [25] designed $V_2O_5/Ag/V_2O_5$ sandwich film by the plasma-assisted reactive evaporation technique. Although both of them showed a relatively high gravimetric specific capacity at various rates, their areal specific capacity is still unsatisfactory (only 75 μAh cm^{-2} at 20 μA cm^{-2} for $V_2O_5/Ag/V_2O_5$ film) due to the low loading mass of active materials. It will ineluctably cause higher resistance and easy-detachment of active materials after further increasing the loading mass. Therefore, the strong incorporation of V_2O_5 and flexible substrates is the key to exploit flexible electrodes with high areal capacity and superior stability.

Herein, we successfully realize the synthesis of hierarchical V_2O_5 nanosheet arrays well-grown on polydopamine (PDA)-decorated carbon cloth (donated as V_2O_5 NAs/CC) with strong combination between them, which can be directly applied as a durable cathode for flexible LIBs. Consequently, the V_2O_5 NAs/CC with a loading mass of ~2.1 mg delivers a high specific capacity of 120 mAh g^{-1} even at 15C (1C = 300 mA g^{-1}) with a long-term cycling stability. Impressively, the corresponding areal capacity can also reach as high as 560 μAh cm^{-2} at 210 μA cm^{-2}, outperforming the-state-of-art flexible cathode reported so far. Additionally, a flexible LIBs full cell has been assembled, also exhibiting high mechanical strength and superior electrochemical performances.

2. Experimental section

2.1. Synthesis of the V_2O_5 NAs/CC flexible electrode

The commercial carbon cloth was first treated in concentrated acid of HNO_3/H_2SO_4 (1:3 in volume) for 24 h, washed by deionized water before drying at 60 °C in an electronic oven. And then, a 2 cm × 8 cm the above carbon cloth was immersed in the mixture of 50 mL Tris solution (10 mM) and 48 mg dopamine with stirring for ~ 5 h at room temperature. After washing with distilled water, the well-modified carbon cloth was further immersed in an autoclave containing 30 mL of isopropanol (IPA) and 0.3 mL of vanadium oxytriisopropoxide (VOT), and subsequently heated in an electronic oven at 200 °C for 12 h. Finally, the V_2O_5 NAs/CC electrode was obtained by annealing the solvothermal products at 350 °C for 2 h in air atmosphere.

2.2. Characterization

The crystal phase of the samples was characterized via X-ray powder diffractometer (XRD, Bruker D8 Advance, Cu Kα radiation). The microscopic morphologies were investigated by FESEM (S-4800) and TEM (JEOL-2100, operating at 200 kV). X-ray photoelectron spectroscopy (XPS) spectra were studied by AXIS Ultra DLD spectrometer. Thermogravimetric analysis (TGA) was carried out with a DMA 2980/DS analyzer under flowing air.

2.3. Electrochemical measurements

The V_2O_5 NAs/CC electrode was cut into small round pieces with a diameter of 12 mm, and directly used as the electrode. The loading mass of active materials was about 2.1 mg/cm^2. Each electrochemical test cell was assembled in an argon-filled glovebox with water oxygen contents less than 0.1 ppm. Pure Li foil was used as counter electrode and 1 M $LiPF_6$ in mixed solution (ethylene carbonate/dimethyl carbonate, 1:1 in volume) was used as electrolyte. The separator was polypropylene membrane. For the full cell assembly, the V_2O_5 NAs/CC and pre-lithiated carbon fibers cloth were served as cathode and anode with optimal capacity match. Cyclic voladtammetry (CV) was tested by an Autolab PGSTAT302 N at a scan rate of 0.2 mV s^{-1}. Electrochemical impedance spectra (EIS) were also carried out on PGSTAT302 N electrochemical workstation in the frequency range of 100 kHz to 0.01 Hz under constant voltage mode. Galvanostatical charge/discharge measurements were conducted by the LAND-CT2001A test system at various current densities within the range of 2.0–4.0 V and 2.5–4.0 V, respectively.

3. Results and discussion

Fig. 1a illustrates the fabrication process of the hierarchical V_2O_5 nanosheets on carbon cloth with surface modification. The pristine carbon cloth was first treated in mixed acid to clean its surface, and then decorated a layer of polydopamine (PDA). With the assistance of rich functional groups of PDA [19], the hierarchical V_2O_5 nanosheets are very easy to grow on the surface of carbon cloth by a simple solvothermal treatment of vanadium oxytriisopropoxide (VOT) and the subsequent thermal annealing. Such a fascinating flexible electrode can be directly applied as LIBs cathode without the extra addition of inactive binders and conductive agents. Fig. 1b reveals the typical 3D network morphology of V_2O_5 NAs/CC. With different magnification, it can be observed that the surface of each carbon fiber is uniformly covered by V_2O_5 nanosheets with a thickness of ~20 nm (Fig. 1c–d). It is worth noting that the surface modification of carbon cloth by PDA is the key step for growing hierarchical V_2O_5 nanosheets. Without the PDA decoration even under the same conditions, few V_2O_5 nanosheets will be grown on carbon cloth (Fig. S1). In addition, it shows a strong combination force between them, which will be supported by the fact that the V_2O_5 NAs can be well-maintained after ultrasonic treatment for over 30 min. The abundant porous structure created by interconnected V_2O_5 NAs (Fig. 1d) can also be observed, greatly enhancing electrolyte infiltration capability and electrons/ions mass transport.

To further confirm the crystal structure of the V_2O_5 nanosheets, the X-ray powder diffractometer (XRD) is carried out. As observed in Fig. 2a, except for the broad diffraction peak at ~26° originating from carbon cloth [7,10], other diffraction peaks can be indexed to the orthorhombic V_2O_5 phase (ICDD PDF No. 41–1426), confirming the successful preparation of the V_2O_5 NAs/CC. We further identify its chemical compositions by X-ray photoelectron spectroscopy (XPS), as shown in Fig. 2b, where the two major peaks at ~ 517.1 and ~ 525.2 eV can be attributed to V $2p_{2/3}$ peak and V $2p_{1/2}$ peak of V^{5+} [26,27]. In addition, an extremely small peak appears at 515.6 eV, corresponding to V^{4+} with a content of less than 5%. High magnification TEM image (Fig. 2c) shows a typical sheet-like structure with a size of 110 nm (Fig. S2), being in good agreement with the corresponding SEM observations. Interestingly, the electron beam