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Exploring electrolyte preference of vanadium nitride supercapacitor electrodes

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ABSTRACT

Vanadium nitride hierarchical nanostructures were prepared through an ammonia annealing procedure utilizing vanadium pentoxide nanostructures grown on graphite foam. The electrochemical properties of hierarchical vanadium nitride was tested in aqueous and organic electrolytes. As a result, the vanadium nitride showed better capacitive energy storage property in organic and alkaline electrolytes. This work provides insight into the charge storage process of vanadium nitride and our findings can shed light on other transition metal nitride-based electrochemical energy storage systems.

1. Introduction

The rapid development of electronics markets has required largely increasing energy demands during the last decade. Recently, lithium-ion battery (LIB) and supercapacitor (SC) have been deemed to be the most hopeful energy storage devices [1–3]. Among them, SCs are superior to LIB in terms of fast charging/discharging ability, high power density and long cycling stability. Basically, SCs could be classified to two mechanisms: electrical double-layer capacitor (EDLC) and pseudocapacitor. For the LIB, the energy storage comes from electrostatic capacitance, which is resulted from charge separation at the interface of electrolyte and the electrodes. However, these electrodes with high specific-area including active carbon, carbon nanotubes (CNTs) and graphene, usually produce limited specific capacitance [4]. While pseudocapacitance of redox-active materials arises from a fast reversible faradic process, which can provide much higher specific capacitances up to 1000 F g^{-1} [5]. In this regard, various transition metal oxides, such as MnO_2 [6–10], WO_3 [11–14], VO_x [15,16] and NiO [17], have been widely investigated as possible electrode materials for high performance pseudocapacitors. However, the attempt to utilize the high power density of SCs with high rate capability is limited by their poor electron conductivity. In addition to metal oxide materials, metal nitrides are emerging as a new and hopeful electrode material for high-performance supercapacitors by virtue of their outstanding high capacitance and electrical conductivity [18–26]. On this account, transition metal nitrides like vanadium nitride (VN) are considered as the promising pseudocapacitive candidates for next-generation high performance SCs owing to their excellent electrical conductivity and high specific pseudocapacitance.

In general, the pseudocapacitors have various electrolyte options: aqueous, organic and ionic liquid electrolytes [5]. For aqueous electrolyte, the higher ionic conductivity assures the fast ions transport, resulting in high rate capability. While organic and ionic liquid electrolytes are superior to aqueous in terms of larger potential window which could transfer to higher energy/power density. Hence it is of significance to understand the charge storage process of VN in different electrolyte and find out the most suitable one for both scientific and industrial demands.

Herein, the electrochemical performance of hierarchical VN was tested in aqueous and organic electrolytes. The VN showed better capacitive energy storage property in organic and alkaline electrolytes, for example, the capacitive charge storage is nearly 74% in $LiPF_6$ and 70% in KOH at 50 mV s^{-1}, respectively. As organic electrolytes usually have large voltage window (nearly 3 V), the energy density of electrochemical device based on them will greatly enhanced. Our results reveal that organic electrolyte is probably the most suitable electrolyte for VN supercapacitor device. Overall, this work provides insight into the charge storage process of VN and our findings can shed light on other transition metal nitride-based electrochemical energy storage systems.

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2. Experimental

2.1. Materials and methods

The growth of the graphite foams was achieved by chemical vapor deposition (CVD) using nickel foams as the template as previously reported [27]. Then the above graphite foams were used as the backbone for the growth of V_2O_5 by a hydrothermal synthesis [15]. The solvothermal solution was prepared by dissolving 2 mM V_2O_5 and 6 mM $H_2C_2O_4$ powder with 12 mL of distilled water at 75 °C for about 2 h until VOC_2O_4 was formed. Then 3 mL of 30% H_2O_2 was added and kept continuously stirring for about 20 min to obtain a brown solution, followed by addition of 65 mL ethanol. The obtained solution was transferred into 100 mL teflon-lined stainless steel autoclave liners. The graphite foams were immersed into the reaction solution. The autoclave liners were kept at 180 °C for 90 min, and then the sample was collected and rinsed with distilled water and ethanol in turn for three times. V_2O_5 nanostructures were obtained by annealing the products at 300 °C in air for 2 h. Finally, the V_2O_5 nanostructures were converted to VN by annealing in ammonia at 800 °C for 1 h. The mass loading of VN was determined about 1.2 mg cm^{-2}.

2.2. Characterization and measurements

The microstructure and phase of samples were characterized by scanning electron microscopy (SEM, FEI SIRION) and X-ray diffraction (XRD, Rigaku, MiniFlex600, Cu Kα). The electrochemical performance was investigated by CV, which was performed on a CHI660C electrochemical workstation (Chenhua, Shanghai). All experiments were performed at room temperature. Standard CR2032-type coin cells was assembled in an argon-filled glove box with the as fabricated VN as the working electrode (with diameter of 12 mm, without any binder or additives), the lithium foil as the counter electrode, 1 M $LiPF_6$ in ethylene carbonate-dimethyl carbonate (1:1 in volume) as the electrolyte, and a polypropylene (PP) film (Cellgard 2400) as the separator. Hg/HgO reference electrode and graphite rod counter electrode were used for 1 M KOH test, and Ag/AgCl reference electrode and graphite rod counter electrode were used for 1 M LiCl test.

3. Results and discussion

The VN hierarchical nanostructures were obtained through an ammonia annealing procedure utilizing V_2O_5 nanostructures. The V_2O_5 nanostructures were synthesized on graphite foam, and the graphite foam was fabricated by CVD method as previously reported. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of graphite foam are shown in Fig. 1a. Two characteristic peaks at 1581 cm^{-1} (G peak) and 2725 cm^{-1} (2D peak) are identified for the graphite foam in the Raman results (Fig. 1b). Typical SEM images of the product are given in Fig. 1c and d, showing the morphology of VN grown on graphite foam. Compared to bulk materials, a large interfacial area between electrode and electrolyte for charge transport and a shortened diffusion path for intercalation/de-intercalation of active species could be provided by this hierarchical branching structure. Moreover, this unique structure could lead to enhanced function of the electrode. In addition, the graphite foam can serve as a conducting scaffold for supporting electrochemically active materials. The VN with a diameter of around 100 nm and about 50 nm diameter of each particle are identified in SEM image, with a thickness of about 600 nm. Energy dispersive X-ray spectroscopy (EDS) further confirmed the VN, as shown in Fig. 2a. V, N, O and Cu peaks were clearly observed, in which O signal could be attributed to the surface oxidation of VN, while Cu were obtained from TEM grid. As shown in the X-ray diffraction (XRD) patterns (Fig. 2b), three diffraction peaks at 37.9°, 44.2° and 64.2° can be indexed to cubic VN (PDF 35-0768) [28].

The charge storage properties were investigated in different electrolytes shown in Fig. 3. Using Dunn's analysis [29–32], the potential regions could be determined where the capacitive contributions occur in the CV curves. In the analysis, based on their relationship to the sweep rate of a cyclic voltammetry

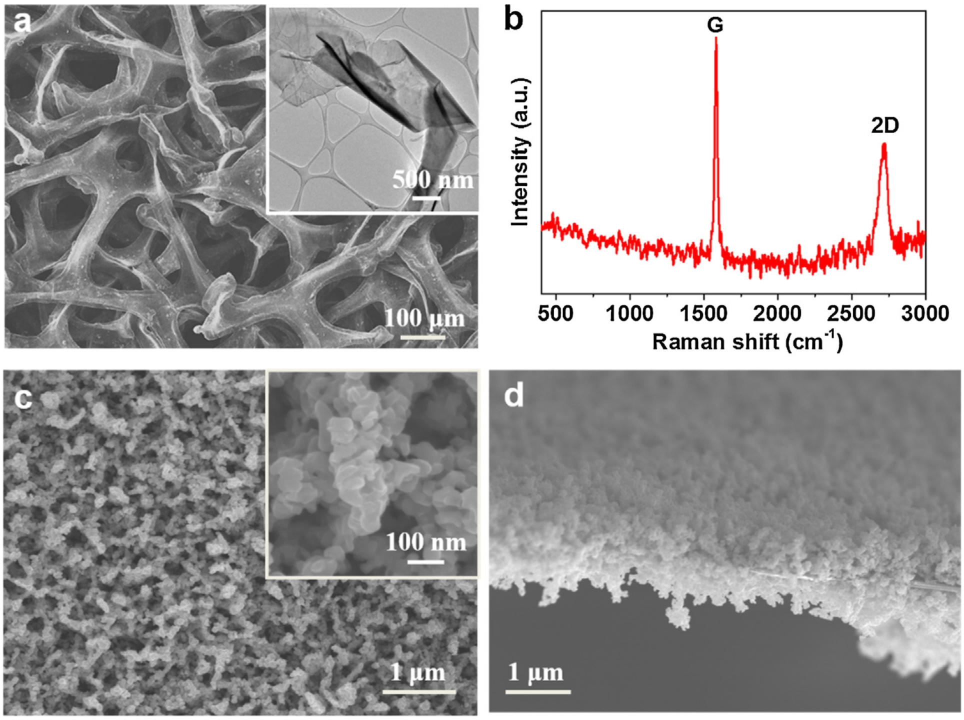

Fig. 1. (a) SEM and TEM images and (b) Raman spectrum of the graphite foam. (c) and (d) SEM images of VN hierarchical structures grown on graphite foam.