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Molybdenum oxide nanowires based supercapacitors with enhanced capacitance and energy density in ethylammonium nitrate electrolyte

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ABSTRACT

Orthorhombic molybdenum trioxide (α-MoO_3) nanowires as an electrode for electrochemical supercapacitors in ethylammonium nitrate (EAN) electrolyte exhibits a high specific capacitance of 288 Fg^{-1}, which is 8 times higher than the specific capacitance obtained from MoO_3 nanowires in water based electrolyte. MoO_3 nanowires in EAN electrolyte exhibit energy density of 46.32 Wh kg^{-1} at a power density of 20.3 kW kg^{-1} with outstanding cycling stability with specific capacitance retention of 96% over 3000 cycles. We believe that the superior performance of the MoO_3 nanowires in EAN based electrolyte is primarily due to its relatively low viscosity (0.28 P at 25 °C), high electrical conductivity (20 mS cm^{-1} at 25 °C) and large working voltage window. The results clearly demonstrate that EAN as electrolyte is one of the most promising electrolyte for high performance large scale energy storage devices.

1. Introduction

During the last few decades, electrochemical energy storage devices such as supercapacitors have gained considerable attention due to their fast charge and discharge rate, high power density, extraordinary cyclic lifetime and high reliability as compared to batteries [1–3]. According to charge storage mechanisms, supercapacitors are divided into two categories, double layer and pseudocapacitors [4–6]. Among these, pseudocapacitors provide very high energy and power density as compared to the double-layer capacitors. However, their energy density is still quite low for their practical applications in electrical vehicles [6]. The energy density can be enhanced either by new electrode materials which can provide very high capacitance or by enhancing the working voltage window of the existing materials as the decomposition of aqueous electrolytes at high voltage is a major obstruction in achieving this goal. Therefore, usage of non-aqueous electrolytes for supercapacitor applications has recently gained immense interest among researches. And among these non-aqueous electrolytes, ionic liquids (ILs) have been used extensively to increase the voltage widow operability with high ionic conductivity. ILs provide unique combination of properties like high ionic conductivity, high stability, non-volatility and wide electrochemical stability, which make them a potential candidate to get desired results [7–10]. The idea of using ILs for higher performance of supercapacitors have recently gained popularity and researchers have tested ILs and their mixtures, most of them belonging to pyrrolidinium and imidazolium cations family, for EDLCs containing different forms of carbon based materials [9–12]. However, there are a very few studies available targeting the enhanced electrochemical window (Ew) for transition metal oxide pseudocapacitors. The challenge of achieving high power density and good cyclability in pseudocapacitors using room temperature ionic liquids (RTILs) is very big and our present work is an attempt to find a suitable RTIL with wide electrochemical window, low viscosity and high conductivity to increase the performance of transition metal oxides such as MoO_3, which not only offers good potential for the intercalation of ions between the crystal layers but also provide multiple oxidation states (faradic capacitance). In the current work, we report for the first time, the use of RTIL (ethylammonium nitrate (EAN) as an electrolyte for MoO_3 nanowires due to its relatively low viscosity (0.28 P at 25 °C) and high electrical conductivity (20 mS cm^{-1} at 25 °C) [12].

2. Experimental methods

Ethylammonium nitrate (EAN) with purity > 97% was purchased

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from io-li-tec Germany and molybdic acid (99.99%), nitric acid (70%), carbon black and polytetrafluoroethylene (PTFE) binder were purchased from Sigma Aldrich and used as received. For the synthesis of MoO_3 nanowires, 20 mmol solution of MoO_2 powder was made in 25 mL of H_2O_2 which was magnetically stirrered for 30 min and pH of the solution was adjusted to 1 by adding HNO3 with constant stirring. After that the solution was transferred into teflon-lined stainless autoclave (25 mL capacity). The autoclave was placed in the oven at 180 °C for 12 h. In the final step the precipitates were filtered, washed many times with distilled water and ethanol, and dried over night in the oven at 90 °C. In order to make the electrode for supercapactor, MoO_3 nanowires, carbon black and polytetrafluoroethylene (PTFE) binder in the ratio of 75:15:10 were dispersed in ethanol and stirred until homogeneous solution was achieved. After that solution was coated onto a conductive carbon-cloth (ELAT, Nuvant systems Inc.) followed by drying at 95 °C for 12 h in a vacuum oven. The morphological and structural properties of the synthesized MoO_3 nanowires were examined by field emission scanning electron microscopy (FE-SEM, JEOL JSM−7401F) and X-ray diffraction (XRD, D8 FOCUS 2200 V, Bruker AXS, Cu Kα radiation (λ) 1.5418 Å), respectively. All electrochemical measurements were carried in a three-electrode assembly consisting of Ag/AgCl, Pt foil and MoO_3 nanowires coated carbon cloth as a reference, counter and working electrode, respectively, in ethylammonium nitrate as electrolyte at room temperature using a Biologic VMP3 potentiostat/galvanostat.

3. Results and discussion

Field emission scanning electron microscopy (FE-SEM) analysis of MoO_3 nanowires synthesized at 180 °C for 12 h was carried out, and the corresponding results are shown in Fig. 1(a). The FE-SEM analysis of MoO_3 nanowires shows that MoO_3 nanowires have an average diameter of 110 nm with a length in the range of tens of micrometers. The crystallographic information of MoO_3 nanowires was examined by X-ray diffraction as shown in Fig. 1(b) which matches with the standard peaks for the orthorhombic phase of MoO_3 (JCPDS card 89−7112).

To evaluate the electrochemical properties of MoO_3 nanowires, electrochemical measurements were conducted in a three-electrode electrochemical cell with MoO_3 nanowires coated carbon cloth, Pt wire, Ag/AgCl (satd. KCl) electrodes as working, counter and reference electrodes in ethylammonium nitrate electrolyte solution. Cyclic voltammograms (CVs) of MoO_3 nanowires electrode at a scan rate of 20 m Vs^{-1} in 1 M H_2SO_4 and ethylammonium nitrate electrolyte solution is shown in Fig. 2(a). It can be seen that MoO_3 nanowires has a very broad potential window of about 1.8 V in ethylammonium nitrate electrolyte as compared to about 1 V in 1 M H_2SO_4 electrolyte solution. Furthermore, MoO_3 nanowires electrode in both 1 M H_2SO_4 and ethylammonium nitrate electrolyte solution show a faradaic reaction at the interface of MoO_3 electrodes with electrolyte ions, which is a distinctive behavior of pseudocapacitors. The CV curve shows the redox peaks in the MoO_3 nanowires electrode in both 1 M H_2SO_4 and ethylammonium nitrate electrolyte solution suggesting a major contribution of redox capacitance to the overall specific capacitance [13–16]. The presence of these redox peaks in ethylammonium nitrate electrolyte system clearly indicates the $[NO_3]^-$ anion insertion and de-insertion reactions at different energy states [10].

To further quantify the rate performance and redox processes, the cyclovoltammetry experiments were carried out for MoO_3 nanowires at various sweep rates in ethylammonium nitrate electrolyte solution at room temperature as shown in Fig. 2(b). As the scan rates increase from 5 to 50 mV s^{-1}, the shape of all these CVs remain same indicating excellent capacitive behavior and high rate capability of MoO_3 nanowires in ethylammonium nitrate electrolyte. The change in the specific capacitance of MoO_3 nanowires in ethylammonium nitrate electrolyte with increasing scan rates is shown in Fig. 2(C) and it was observed that specific capacitance of MoO_3 nanowires in ethylammonium nitrate electrolyte is significantly higher than the MoO_3 nanowires in 1 M H_2SO_4. The MoO_3 nanowires electrode achieve specific capacitance of 288 Fg^{-1} at 5 m Vs^{-1} in ethylammonium nitrate electrolyte which is 8 times higher as compared to the MoO_3 nanowires (36 Fg^{-1}) in 1 M H_2SO_4. The specific capacitance of MoO_3 nanowires in ethylammonium nitrate electrolyte is also higher than MoO_3 nanowires and its composites reported in literature [14–20]. The increase of capacity observed is usually attributed to irreversible decomposition of the electrolyte, relatively low viscosity (0.28 P at 25 °C) and high electrical conductivity (20 $mS \cdot cm^{-1}$ at 25 °C). Here, $[NO_3]^-$ ions are stable in oxidation, as recently shown by Zhang et al. [80] in graphitic carbon electrodes. The long-term electrochemical stability of the MoO_3 in ethylammonium nitrate electrolyte was examined by CV at a scan rate of 20 m Vs^{-1} for 3000 cycles, and the corresponding results are presented in Fig. 2(d). The capacity decay was only 3.4%, even after 3000 cycles, indicating the excellent stability of the electrode material for energy storage applications.

The electrochemical performance of MoO_3 nanowires in ethylammonium nitrate electrolyte was further studied by galvanostatic charge/discharge measurements. Fig. 3(a) show the charge/discharge curves of MoO_3 nanowire electrodes collected at a current density of 0.5 A g^{-1}. It is obvious from the results that MoO_3 nanowires showed a non-linear charge−discharge curve, indicating that the nanowires are pseudocapacitive with specific capacitances

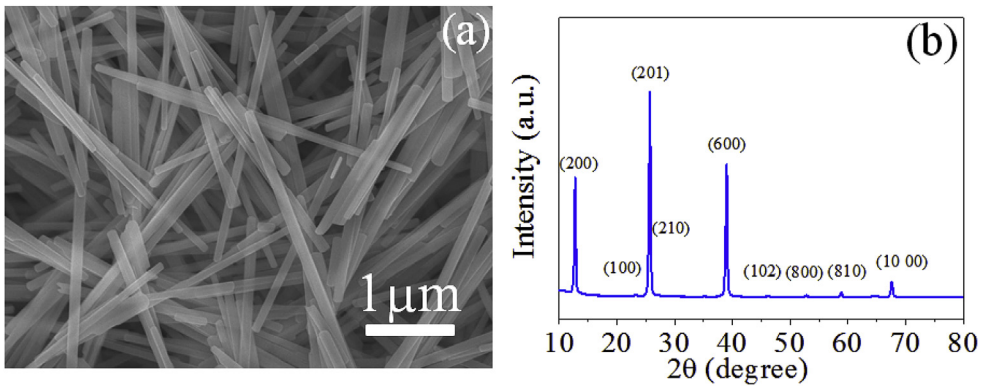

Fig. 1. (a) FE-SEM image of the MoO_3 nanowires synthesized at 180 °C for 12 h, and (b) XRD patterns of MoO_3 nanowires synthesized at 180 °C for 12 h.