Redox-Active Electrolyte based MnWO₄//AC Asymmetric Supercapacitors

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Abstract

Finding supercapacitive materials with high energy and power densities has attracted significant interest in recent years. Herein, we are reporting layered MnWO_4 nanostructure for supercapacitor applications. MnWO_4 //AC asymmetric cell was fabricated by using hydrothermally synthesized MnWO_4 nanostructure as a cathode and activated carbon as an anode. Prior to device fabrication, the structural and electrochemical properties of MnWO_4 were thoroughly studied. MnWO_4 //AC asymmetric cell with KOH electrolyte showed specific capacitance and energy density of 90 F/g (at 1 mA/cm²) and 51 Wh/kg, respectively. Upon addition of redox-active KI into KOH, both the specific capacitance and energy density were significantly enhanced (144 F/g and 90 Wh/Kg, respectively). The enhanced electrochemical properties of MnWO_4 //AC asymmetric cell can be attributed to the high-speed solution-phase Faradic reactions contributed by KI redox species in the KOH electrolyte.

Introduction

Increasing environmental pollution and depletion of traditional energy resources has aroused extensive attention on energy storage and energy conversion devices [1]. Especially, electrochemical energy storage devices are projected to be a vital part of electronic portable devices, electric vehicles, and airplanes [2, 3]. Among all the energy storage systems, supercapacitors (SCs) are the most promising candidates for the above-mentioned applications because they deliver relatively high power, fast charging, good cyclic stability, and low maintenance cost [4-6]. However, SCs possess very low energy density in comparison to fuel cells and batteries [2,3]. The energy density of SCs can be further enhanced by developing asymmetric supercapacitors (AS) where one electrode stores the charges by faradaic redox reactions and the other one stores the charges based on the electrical double layer capacitance (EDLC) mechanism [3]. In AS configuration, different voltage windows of two different electrode materials are added to maximize the resultant operating potential window, which intern increases the resultant energy density according to the equation, $E = 0.5 CV^2$. Typically, carbonaceous materials and their derivatives such as graphene, activated carbon, or CNTs [7-9] are used as an anode. On the contrary, the pseudo-capacitive materials (e.g. NiO , MnO_2 , Fe_3O_4 , and RuO_2) and conducting polymers, in which high pseudocapacitance comes from reversible surface faradaic redox reactions are used as positive electrodes [10-16].

In recent years, redox-active nanomaterials have gained a lot of interest as positive electrodes. The nano-dimensions and redox behavior of these materials simultaneously offer multiple oxidation states and higher surface area for charge storage. Among different metal oxides, metal tungstate is interesting candidate because of its reversible electrochemical redox reactions, good electrical conductivity, good theoretical specific capacitance, and low cost [17-19]. Recently, manganese tungstate (MnWO_4) has gained a lot of attention due to its outstanding physicochemical properties [20-23]. MnWO_4 has indeed been reported as a good supercapacitor electrode since Mn and W species are electrochemically active [24-25]. Moreover, the additional W metal helps to improve the conductivity of the MnO_2 electrode [26].

However, these reports are focused on the preliminary study of MnWO_4 as the SC electrode and not an SC device.

Another approach to enhancing the specific capacity of the SC cell in terms of enhancing the potential window is to modify the electrolyte by the addition of redox-rich species like halides (KI, KBr), quinones, sodium vanadium complexes, and phenylenediamine, etc. in conventional electrolyte systems [2,3]. The redox-active species enhance the pseudocapacitive contribution of the electrolyte which helps to enhance the potential window of SC cell [3]. KI is found to be one of the best candidates due to its low cost, eco-friendly and iodide can produce redox pairs (like I^-/I_3^- and I_2/IO_3^-) during the electrochemical process [3].

Hereby, we have designed MnWO_4 nanostructures by the facile hydrothermal method. We have designed $\text{MnWO}_4//\text{AC}$ asymmetric cells and investigated their electrochemical performance in pristine KOH and KOH with KI added species. The $\text{MnWO}_4//\text{AC}$ asymmetric cells show significant enhancement in energy density owing to the extended voltage window contribute by KI modified KOH electrolyte.

Experimental

In a typical synthesis of MnWO_4 nanoparticles by hydrothermal method, 5 mM of sodium tungstate ($\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$, SD fine chemicals) and manganese acetate anhydrous ($\text{Mn}(\text{CH}_3\text{COO})_2$, Alfa Aesar) were dissolved in DI water under magnetic stirring to make a homogeneous mixture. The mixture was then transferred to a Teflon liner having 100 ml capacity and put in bomb autoclave. The bomb autoclave was then placed in an oven and heated at 180 °C for 12 hours. Finally, the prepared powder was removed and washed thoroughly by using DI water and ethanol and dried at 60 °C for 2 hours.

The structural and morphological analyses were carried out by using XRD (Rigaku-Ultima III) FESEM (FEI Quanta 650 F) and TEM (Tecnai G2 F20 STWINHR(S)) techniques. The XPS (SPECS Germany, PHOIBOS) was used to confirm the oxidation states of the ions. The electrochemical properties such as galvanostatic charge-discharge (GCD), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were studied by using a Biologic VMP3 potentiostat. The MnWO_4 electrodes were fabricated by making a slurry of MnWO_4 powder with binder and carbon black in a ratio of 90:5:5. The prepared slurry was screen printed on the carbon cloth and dried at 130 °C for 2h. The active material coated carbon cloth was then used as working electrodes with Ag/AgCl reference electrode and Pt counter electrode in 2M KOH electrolyte. The asymmetric device was fabricated by using MnWO_4 as cathode and AC as anode electrodes separated polypropylene film soaked in KOH. Similarly, $\text{MnWO}_4//\text{AC}$ asymmetric device was fabricated with KI added KOH electrolyte.

Result And Discussion

Figure 1a shows a powder XRD pattern of MnWO_4 sample. The XRD pattern confirms single phase formation of crystalline monoclinic phase without any impurity peaks. The XRD pattern well matched

with the standard XRD pattern of MnWO_4 (JCPDS#010720478). The lattice parameter values were found to be $a = 4.8300 \text{ \AA}$, $b = 5.7603 \text{ \AA}$, $c = 4.9940 \text{ \AA}$ with a β value of 91.14° . The XPS analysis was used to investigate the surface composition of the ions present in the MnWO_4 sample. XPS confirms the surface composition and states of the ions. Figure 1b-d depicts the XPS spectra of as-prepared MnWO_4 nanorods. Fig. 1b-d show the XPS spectra of Mn 2p, W 4f, and O 1s, respectively. Fig 1b shows the deconvoluted Mn 2p spectrum which consists of two peaks at the binding energies of 641.4 and 653.5 eV could be assigned to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively [27]. The Mn ions are presented in the form of divalent (+2) oxidation state. Figure 3c shows the XPS spectra of W 4f in which two peaks appearing at the binding energies of 34.58 eV and 36.71 eV were corresponded to the W 4f_{7/2} and W 4f_{5/2}, respectively which confirms the +6 valence state of W in MnWO_4 [27]. The O 1s peak was associated with the binding energy of 529.57 eV (Fig. 4d), which could be assigned to Mn-O-W bond in MnWO_4 [27]. The presence of all the characteristic peaks further proves the single phase formation of MnWO_4 .

The morphology of the SC electrode strongly influences the performance of supercapacitors. In particular, hierarchical nanostructures such as nanorods, nanosheets, and nanoplates undoubtedly contribute to enhance the performance of the supercapacitors because of their high surface areas, and short electron- and ion-transport pathways. The FESEM images of the MnWO_4 nanostructures (Fig 2a,b) show edge-curved nanorods piled up together to form an aggregated morphology. The average diameter and length of the nanorods were found to be 70 nm and length of 200 nm; respectively. The edge curved nanorods are highly favorable for electrochemical performance. The morphological details of MnWO_4 nanorods were further investigated by using HRTEM analysis (Fig. 2c). The HRTEM images further confirm the formation of agglomerated MnWO_4 nanorod morphology consistent with FESEM data. The HRTEM image of the MnWO_4 clearly showed two distinct lattice fringes with d-spacing of 0.48 nm and 0.29 nm corresponding to (100) and (111) lattice planes, respectively, and well-matched with the XRD data. Moreover, SAED pattern reveals bright diffraction rings corresponding to the lattice planes of (100), (011), and (111) indicating the nanocrystalline nature and formation of the monoclinic crystal structure of the MnWO_4 sample (Fig. 3d).

Figure 3a exhibits the typical CV plots of the MnWO_4 single electrode with a scan rate ranging from 5 to 100 mV/s with a potential window between -0.6 to 1 V. The pseudo-rectangular shapes of the CV curves of the MnWO_4 electrode indicate the pseudo-capacitive behavior. Moreover, the shape of the curves did not change remarkably indicating the superior rate capability of MnWO_4 . Figure 3b shows the GCD curves of the MnWO_4 electrode recorded at different current densities. The charging and discharging curves are nonlinear at all current densities, which might be due to the absorption/desorption process at electrode and electrolyte interface, and faradic redox reaction of MnWO_4 ($\text{Mn}^{2+}/\text{Mn}^{3+}$) with the electrolyte [27]. The specific capacitance as well as areal capacitance were calculated and presented in Fig. 3c. MnWO_4 electrode showed maximum specific (areal) capacitance of 430 F/g (320 mF/cm²) at a current density of 6 mA/cm² and it is retained to 70 F/g (50 mF/cm²) even at 20 mA/cm². Comparably high values of capacitances at high current densities confirm the good rate capability of the MnWO_4 electrode. Further,

the MnWO₄ electrode showed about 90 % of capacitance even for 5000 cycles, suggesting good cyclic stability (Fig. 3d).

For practical relevance, an asymmetric cell MnWO₄//AC was fabricated using 2 M KOH electrolyte and KI added KOH electrolyte. The CV curves of the MnWO₄//AC asymmetric cell in KOH electrolyte were studied at different scan rates of 10 to 100 mV/s as shown in Fig 4a. The CV curves show quasi-rectangular shapes even at high scan rates of 100 mV/s, revealing good rate capability and excellent reversibility of the device. Similarly, GCD curves of the MnWO₄//AC asymmetric cell show nearly linear variation within the potential window of 0 to 1.6 V (Fig. 4b). The specific capacitance as a function of current density was estimated using the following equation.

$$C = \frac{2 \cdot I \cdot \int V \cdot dt}{m \cdot V^2} \quad \dots (1)$$

where I is the discharge current, V is the potential window, dt is the discharge time and m is the mass of the material on electrodes (both electrodes, 5.9 mg). Figure 4c represents the specific capacitance of MnWO₄//AC asymmetric cell at various current densities. MnWO₄//AC asymmetric cell showed a maximum specific capacitance value of 90 F/g at a lower current density of 1 mA/cm². Figure 4d shows the Nyquist plots (EIS measurement), which clearly showed a straight line at low frequencies indicating capacitive characteristics of MnWO₄//AC asymmetric cell. The inset of fig. 4d shows the frequency dependent impedances of Bode plots. The plots remain at small resistances at high frequency, and show slant lines at low frequency, indicating ideal capacitive behaviour of the MnWO₄//AC asymmetric cell. The obtained specific capacitance and also the operative voltage window are still smaller than that of other asymmetric supercapacitors.

To further enhance the electrochemical performance of the device, redox-active additive KI (0.02 M) was added in the pristine 2 M KOH. Both the CV and CD were studied for MnWO₄//AC asymmetric cell with a modified electrolyte. Figure 5a shows the CV curves for MnWO₄//AC cell with and without KI redox additive at a fixed scan rate of 40 mV/s. The MnWO₄//AC asymmetric cell with and without KI added electrolytes show clear difference in CV curves. The CV curve for MnWO₄//AC asymmetric cell with KI added electrolyte showed a large current area as compared to MnWO₄//AC asymmetric cell with pristine electrolyte indicating an enhancement in pseudocapacitance of MnWO₄//AC asymmetric cell. Moreover, MnWO₄//AC asymmetric cell with KI added electrolytes showed weak additional redox peaks possibly due to the reversible redox reactions of KI. Most interestingly, MnWO₄//AC asymmetric cell showed extended voltage window by 0.4 V, making a total voltage window of 2.0 V which is quite large. The increased area under the curve and extended voltage window confirm the enhancement of specific energy density. Figure 5b shows the CV curves for MnWO₄//AC asymmetric cell with KI added electrolyte at different scan rates. The weak redox peaks are well sustained even at high scan rates, indicating better rate capability behavior of MnWO₄//AC asymmetric cell. However, MnWO₄//AC asymmetric cell with KI

added KOH electrolyte did not show much change in the shape of GCD curves (Fig. 5c). The maximum specific capacitance calculated from GCD curves for $\text{MnWO}_4//\text{AC}$ asymmetric cell for KI added electrolyte was obtained to be 140 F/g (Fig. 5d), which is almost 1.5 times higher than the one obtained for $\text{MnWO}_4//\text{AC}$ asymmetric cell without redox additive (90 F/g). The enhancement in specific capacitance is due to the addition of redox active species from KI, which not only improved the ionic conductivity of the electrolyte but also enhanced the electron transfer redox reactions.

We have further calculated the specific energy and specific power for both the asymmetric cells and presented in Fig. 6a as a Ragone plot. The specific energy of $\text{MnWO}_4//\text{AC}$ asymmetric cell with KI additive showed a maximum of 90 Wh/kg at a specific power of 2000 W/kg. Interestingly, the energy density of $\text{MnWO}_4//\text{AC}$ asymmetric cell is reasonably high even at a high power density (of 30 Wh/kg at 10000 W/kg). The obtained values of energy density are 3 fold higher than that of $\text{MnWO}_4//\text{AC}$ asymmetric cell with KOH (35 Wh/kg at 600 W/kg). Importantly, the values obtained for the present $\text{MnWO}_4//\text{AC}$ asymmetric cell are comparable to the other reported asymmetric devices (Table 1). Figure 6b shows the cyclic stability of the $\text{FeWO}_4//\text{AC}$ asymmetric cells for 3500 cycles. Both the $\text{FeWO}_4//\text{AC}$ asymmetric cells showed great cyclic stability ($\approx$ 5% capacity loss) even at 3500 cycles, suggesting excellent rate capability for $\text{FeWO}_4//\text{AC}$ asymmetric cells.

We have synthesized MnWO_4 edge-shaped nanorods by a simple hydrothermal method. $\text{MnWO}_4//\text{AC}$ asymmetric cell was then fabricated by using MnWO_4 nanostructure as a cathode and commercially obtained AC as an anode. The electrochemical performance of $\text{MnWO}_4//\text{AC}$ asymmetric cells was investigated in pristine KOH and KI added KOH electrolytes. $\text{MnWO}_4//\text{AC}$ asymmetric cell with pristine KOH showed a specific capacitance of 90 F/g and an energy density of 35 Wh/kg, respectively. Upon addition of redox-active KI into KOH, both the specific capacitance and energy density values were significantly enhanced (144 F/g and 90 Wh/Kg, respectively). The enhancement in supercapacitive properties can be attributed to increased ionic conductivity and reversible redox reactions by KI species in the KOH electrolyte.

Declarations

Acknowledgment

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Tables

Table I. Comparative study of electrochemical performance of different Asymmetric supercapacitors

Sr. No.	Supercapacitor	Electrolyte	Energy Density (Wh/kg)	Ref.
1.	MWCNTs/MnO ₂ //Fe ₂ O ₃	K ₃ Fe(CN) ₆	54.39	28
2.	VO _x -3DG//AC	VOSO ₄ /KCl	16	29
3.	MWCNTs// MWCNTs	KI	100.8	30
4.	Ni-Co-LDH//AC	K ₃ Fe(CN) ₆	38.7	31
5.	Co(OH) ₂ /GNS//AC/CFP	K ₃ Fe(CN) ₆	114	32
6.	Ni-Co-O@RGO//AC	K ₃ Fe(CN) ₆	39	33
7.	Bi ₂ O ₃ //AC	KI	35.4	34
8.	TN-NPCs//AQ-NPCs	KI	23	35
9.	Ni ₃ Se ₂ @CF//AC	K ₃ Fe(CN) ₆	32.8	36

Figures

Figure 1

a. XRD pattern of MnWO₄ sample. b–d. High-resolution XPS spectra for Mn 2p, W 4f, and O 1s of MnWO₄ sample, respectively

Figure 2

a, b. SEM images at different magnifications with. c-d. HRTEM and SAED patterns for MnWO₄ sample, respectively

Figure 3

a. Cyclic voltammogram of the MnWO₄ electrode in a conventional KOH electrolyte. b. CD profiles at different current densities. c Areal and specific capacitances at different current density. d. Corresponding specific capacitance at 5000 charge-discharge cycles for MnWO₄ electrode in KOH electrolyte.

Figure 4

a. CV curves. b. CD curves. c. Specific capacitances d. Nyquist plot for MnWO₄/AC asymmetric cell in KOH electrolyte.

Figure 5

a. CV curves for MnWO₄/AC asymmetric cell with and without KI-additive in KOH electrolyte at a scan rate of 40 mV/s. b, c. CV and CD curves for MnWO₄/AC asymmetric cell with KI-additive in KOH electrolyte at different scan rates and current densities, respectively. d. Variation of specific capacitances MnWO₄/AC asymmetric cell with KI-additives.

Figure 6

a. Comparative Ragone plot. b. Cyclic stability up to 3500 cycles of MnWO₄/AC asymmetric cell with KI-additives with and without KI-additive in KOH electrolyte.