#### RESEARCH



# Hydrated and non-hydrated rGO-MnMoO<sub>4</sub> nanocomposites as supercapacitor electrodes

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#### Abstract

Hydrated and non-hydrated rGO-MnMoO<sub>4</sub> nanocomposites (rGO-MnMoO<sub>4</sub> and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O) are synthesized by an easy hydrothermal method for use as supercapacitor electrodes. These nanocomposites are in situ grown onto the nickel foam. These nanocomposites are characterized via their structure, morphology, and chemical bonding. The electrochemical performance of these nanocomposites was measured as the supercapacitor electrodes. The morphological study of the samples reveals that the calcination process changes the morphology of nanocomposites from nanoflakes to cross-nanosheets for the hydrated and non-hydrated nanocomposites, respectively. The results showed that the cooperation of both the GO and the hydrated compound has a synergistic effect on the electrochemical performance of nanocomposites. The rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite at a scan rate of 5 mV s<sup>-1</sup> in 1 M KOH electrolyte shows the highest specific capacitance of 855.6 F g<sup>-1</sup>. It was found that the diffusion-limited process has a main contribution (than the capacitive process) to the storage mechanism of hydrated and non-hydrated rGO-MnMoO<sub>4</sub> nanocomposites. Also, the investigation of the storage mechanism contribution reveals that this mechanism depends on the scan rate. The designed quasi-solid-state symmetric supercapacitor device of rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O with KOH/PVA gel electrolyte can deliver a high energy density of 7.81 Wh kg<sup>-1</sup> and a high power density of 2500 W kg<sup>-1</sup>. Also, the assembled quasi-solid-state symmetric supercapacitor (SSC) exhibits a capacitance retention of 77.7% after 5000 cycles.

**Keywords** Electrochemical supercapacitor  $\cdot$  Binary metal oxide  $\cdot$  Manganese molybdate  $\cdot$  Graphene oxide nanocomposite  $\cdot$  Symmetric supercapacitor

# Introduction

One of the most significant technological and social challenges today is figuring out how to convert and store sustainable and renewable energy, such as full cells, rechargeable batteries, and supercapacitors. Meanwhile, supercapacitors (SCs) have proved to be one of the utmost important portable energy storage systems due to their fast charge/discharge process, long cycle life, high power density, and higher energy density compared with conventional capacitor [1–3].

The charge storage mechanism in SCs can be assorted into two classes, including electrical double-layer capacitance (EDLC) and pseudocapacitance. The EDLC mechanism is the physical adsorption/desorption of ions at the electrode/ electrolyte interface, and the pseudocapacitance mechanism refers to the reversible Faradaic redox reactions between the active material of the electrode and electrolyte [1, 4]. Typically, the pseudocapacitors, including transition metal compounds [5–7] and conducting polymers [8, 9], increase stored energy compared with EDLCs, including carbonaceous materials [10, 11].

Binary metal oxides, due to their various oxidation states and high electrochemical activity compared with single metal oxides, have attracted significant interest as pseudocapacitor materials [3, 12]. Manganese- and molybdenum-based metal oxides (such as MnO<sub>2</sub>, MoO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, and MoO<sub>3</sub> [13–16]) have much potential to be utilized as supercapacitor electrode active materials due to their high electrochemical activity and large working voltage window [17]. MnMoO<sub>4</sub>, as a

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binary metal oxide, has attracted much attention as an electrode material for supercapacitors [18–20]. For example, MnMoO<sub>4</sub> nanorods were synthesized by Veerasubramani et al., showing a maximum specific capacitance of 168.32 F g<sup>-1</sup> at 0.5 mA cm<sup>-2</sup> current density [18]. Wang et al. reported hierarchical 3D-MnMoO<sub>4</sub> fanlike with a specific capacitance of 562 F g<sup>-1</sup> at 1 A g<sup>-1</sup> [19].  $\alpha$ -MnMoO<sub>4</sub> nanorod was synthesized by a microwave-hydrothermal route, which showed a specific capacitance of 551 F g<sup>-1</sup> at 1 A g<sup>-1</sup> in a 2 M NaOH electrolyte [20].

To overcome the low electrical conductivity of the transition metal oxides, their carbonaceous nanocomposites can be used for EDLC supercapacitors. Graphene, due to its high surface area, unique electrical properties, and good electrochemical stability, was used as a part of a metal oxide graphene composite for a supercapacitor electrode [21, 22]. As an example,  $\alpha$ -MnMoO<sub>4</sub>/graphene hybrid was prepared as the electrode of a supercapacitor by Ghosh et al., showing a high specific capacitance of 364 F g<sup>-1</sup> at 2 A g<sup>-1</sup> [23]. MnMoO<sub>4</sub>. 4H<sub>2</sub>O composite nanoplates were decorated on nickel foam by Hu et al., showing a maximum specific capacitance of 1.15 F cm<sup>-2</sup> at 4 mA cm<sup>-2</sup> [24].

Herein, a facile hydrothermal method is presented for synthesizing rGO-MnMoO<sub>4</sub> and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposites. These nanocomposites are in situ grown onto a nickel foam (NF). The structure, morphology, and chemical bond of these samples are characterized. The electrochemical performance of hydrated and non-hydrated rGO-MnMoO<sub>4</sub> nanocomposites has been measured as a supercapacitor electrode. In this work, the effects of hydration and synergistic properties of manganese molybdate with graphene oxide have been investigated by analyzing the results of different characterizations and the electrochemical behavior of the samples and investigating the contribution of each of the charge storage mechanisms. The highest specific capacitance of 855.6 Fg<sup>-1</sup> was obtained for the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite at 5 mV s<sup>-1</sup>. Results shown that the diffusion-limited process had the main contribution to the storage mechanism of hydrated and non-hydrated rGO-MnMoO<sub>4</sub> nanocomposites. Also, electrochemical impedance spectroscopy (EIS) measurement clearly presents low resistance in the electrode/electrolyte system. In addition, the assembled quasi-solid-state symmetric supercapacitor (SSC) device has shown high energy density at higher power densities and good cycle stability.

#### Experiment

# Preparation of the rGO-MnMoO<sub>4</sub> and rGO-MnMoO<sub>4</sub>. $H_2O$ electrodes

The nickel foam pieces (5, 30, and 0.3 mm in size, 95–98% porosity, obtained from Nanosize Co., Iran) were washed with 1 M HCL solution and then with deionized (DI) water

and dried at 70 °C for 6 h. The graphene oxide powder was synthesized by the modified Hummers procedure explained in our previous work [22, 25]. A total of 0.05 g of the synthesized graphene oxide was dispersed in 15 mL of DI water with 30 min of magnetic stirring and 15 min of probe ultrasonication. Also, 0.60 g of hydrated sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>.2H<sub>2</sub>O, obtained from Merck) and 0.63 g of manganese nitrate tetrahydrate (Mn(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O, obtained from Merck) were dissolved in 8 mL of DI water separately. Then, the solutions were mixed and continuously stirred for 30 min, and 15-min ultrasonic probe for further segregation. Then, the obtained mixture was poured into the 50-mL Teflon-lined stainless-steel autoclave along with NF pieces and was kept at 150 °C for 6 h in the oven. After reaching room temperature, the coated NF was washed out several times with DI water and ethanol respectively, and then dehumidified in an oven at 150 °C for 24 h. It leads to the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite. The obtained product (powder and the coated NFs) was placed inside a muffle furnace for calcination at 400 °C temperature for 1 h, resulting in rGO-MnMoO<sub>4</sub>. The pure MnMoO<sub>4</sub>.1H<sub>2</sub>O and MnMoO<sub>4</sub> were synthesized in the same conditions without GO. The mass loading of active material on the electrode was  $\approx 0.8 \text{ mg cm}^{-2}$ . The illustration of rGO-MnMoO<sub>4</sub> and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O syntheses is schematically shown in

#### Fabrication of quasi-solid-symmetric supercapacitor

The electrodes of a symmetric supercapacitor cell were prepared using rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O@NF, while the electrolyte and separator were made of KOH/PVA gel. To prepare the KOH/PVA gel electrolyte, 6 g of KOH was dissolved in 60 mL of DI water with magnetic stirring. Then, 6 g of PVA was gradually added to the solution while being vigorously stirred and heated at 90 °C. After obtaining a clear gel, the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O@NF electrodes were immersed in the gel solution for 5 min and dried at 50 °C for 15 min. This process was repeated three times. The soaked, coated NFs were then aligned in parallel and re-immersed in the gel solution. Finally, the gel was solidified at ambient conditions to form a quasi-solid supercapacitor cell. The mass loading of active material and the active area for positive and negative electrodes are about 1.2 mg cm<sup>-2</sup> and  $2 \times 2$  cm<sup>2</sup>, respectively. Fig. 1

#### **Measurements and characterization**

X-ray powder diffractions (XRD) were collected by a GNR explorer system ( $\lambda = 0.15405$  nm). The morphological characterizations were studied by field emission scanning electron microscopy (FE-SEM, MIRA3 TESCAN). Fourier-transform

**Fig. 1** The schematic illustration of rGO-MnMoO<sub>4</sub>, rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O electrode preparation, and quasi-solidstate symmetric supercapacitor



infrared spectroscopy (FTIR) was recorded using the Thermo Nicolet AVATAR 370-FT-IR (USA) with KBr pellets at room temperature. Raman spectra were collected by Confocal Raman Spectroscopy-Lab Ram HR (Horiba, Japan) with a laser beam at a wavelength of 532 nm in the range of 250–2300 cm<sup>-1</sup>.

The electrochemical performance of the samples was measured using a PGSTAT302N electrochemical at room temperature. A three-electrode configuration was applied for measuring the electrochemical properties. The different coated NFs were used as the working electrodes, and the counter and reference electrodes were platinum wire and Ag/ AgCl, respectively. Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) tests were carried out in aqueous 1 M KOH at various scan rates and applied currents. The specific capacitance  $C_s$  (F g<sup>-1</sup>) is expressed by Eqs. (1) and (2) from the CV and GCD curves, respectively [26, 27]:

$$C_s = \frac{\int I(V) \, dV}{m \left(\Delta V\right) \,\vartheta} \tag{1}$$

$$C_s^{\rm dis} = \frac{I}{m \frac{\Delta V}{\Delta t}} \tag{2}$$

where I, m,  $\vartheta$ , and  $\Delta V$  are the current response, the mass of the active electrode material, the voltage scan rate, and the potential window, respectively, and  $\Delta t$  is the discharge time. EIS measurement was done in the frequency range of 10 mHz to 100 kHz at an open circuit potential of 5 mV.

In order to determine the capacitance properties of the symmetric supercapacitor device, the two-electrode configuration was used at room temperature. The specific capacitance of the device can be calculated using Eqs. (1) and (2), where *m* represents the total mass loading of both electrodes.

# **Results and discussion**

The FE-SEM images were used to evaluate the morphology of the samples. Figure 2 shows the FE-SEM images of the coated active materials on the NF. Figure 2a presents the NF arms on which  $MnMoO_4$  has grown. The magnified image of  $MnMoO_4$  is shown in Fig. 2b, which illustrates a cross-nanosheet morphology on the NF arms.

Figure 2c shows the FE-SEM image of the rGO- $MnMoO_4$  nanocomposite; it can be seen that the size of the cross-linked nanosheet has been increased in the presence of GO. Figure 2d presents the Fe-SEM image of the MnMoO<sub>4</sub>.1H<sub>2</sub>O sample showing the morphology of the nanoflakes. By comparison, in Fig. 2b, d, one can easily deduce that the morphology changes from flake (in  $MnMoO_4$ .1H<sub>2</sub>O) to cross sheet (in  $MnMoO_4$ ) due to the calcination process. The FE-SEM images of the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite are shown in Fig. 2e, f in different magnifications. As shown in these figures, it is clear that the presence of GO also caused the further growth of cross-sheets and changed the morphology from flake (in MnMoO<sub>4</sub>.1H<sub>2</sub>O) to cross-sheet (in rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O). Moreover, the GO sheets are observed in this nanocomposite (Fig. 2c, f), indicating that the morphology changes from nanoflake to crossnanosheet with the calcination process. In addition, it can be found that the effect of increasing graphene oxide in the composites is similar to the effect of sample heating in the calcination process. That is, the morphology of the composite sample is very similar to the morphology of the composite sample without calcination. Therefore, it is suggested that perhaps the increase in graphene oxide may have increased the temperature of the hydrothermal process.

Fig. 2 FE-SEM images of the prepared a  $MnMoO_4$ and b its magnified, c rGO-MnMoO<sub>4</sub> nanocomposite, d MnMoO<sub>4</sub>.1H<sub>2</sub>O, e rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O, and f its magnified



The presence and distribution of the elements in our samples were studied by elemental mapping images. The SEM image of the coated rGo-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite on the NF arms and their elemental mapping images are shown in Fig. 3a, b–f, respectively. Figure 3b–f illustrates the distribution of Mo, Mn, C, and O elements, respectively. These images demonstrate a uniform distribution of those elements on the NF.

The structure of the samples was examined by XRD. The XRD pattern of rGO-MnMoO<sub>4</sub> and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O

is illustrated in Fig. 4. The synthesized sample without calcination illustrates hydrated manganese molybdate (MnMoO<sub>4</sub>.1H<sub>2</sub>O) according to the JCPDS 039-0085 reference code. In addition, the observed peak at  $2\theta = 26.40^{\circ}$  (inset Fig. 4a) is attributed to (002) planes of rGO, which attribute to the formation of rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite. After calcination of this sample at 400 °C, its XRD pattern shows the structure of rGO-MnMoO<sub>4</sub> according to the reference code of JCPDS 01-072-0285. The peaks at 2 $\theta$  = 22.48, 26.00, 31.34, 33.05, 39.14, 45.64, 52.05, 58.89, and



**Fig. 3** a The FE-SEM image of coated rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite on the NF arms and their elemental mapping images of **b** Mo, **c** Mn, **d** C, **e** O elements, and **f** all elements



Fig. 4 The XRD patterns of the rGO-MnMoO<sub>4</sub> and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposites

62.98° are related to (021), (220), (022), (-222), (-511), (150), (004), (-424), and (-711) planes of MnMoO<sub>4</sub>, respectively, and the peak at  $2\theta = 26.75^{\circ}$  is attributed to rGO (002) planes. The temperature behavior of the hydrated sample, MnMoO<sub>4</sub>.1H<sub>2</sub>O, demonstrates that during the exit of intra-structural water from the structure at temperatures above 400 °C, the sample's structure is re-formed.

The chemical bonds of the samples are studied by the FTIR technique. Figure 5a illustrates the FTIR spectra of  $MnMoO_4$  and  $MnMoO_4$ .1H<sub>2</sub>O. The peaks at 936, 864, 779, and 713  $\text{cm}^{-1}$  are related to the MnMoO<sub>4</sub> structure. The absorption peaks at 936 and 864 cm<sup>-1</sup> are ascribed to the stretching vibrations of the Mo = O bond. Also, the peaks at 779 and 713  $\rm cm^{-1}$  are assigned to the bending vibrations of the Mo-O-Mo group [28, 29]. In the MnMoO<sub>4</sub>.1H<sub>2</sub>O FTIR spectrum, the peak at 893 is also related to Mo-O-Mo the bending vibrations, and this shift in wavenumber is related to the presence of the OH group in the structure. Also, the strong peak at 596 cm<sup>-1</sup> can be ascribed to the O-H stretching vibration of the water molecules [30]. Two absorption peaks at 1616 and 3429 cm<sup>-1</sup> are associated with the vibration of the OH groups [31]. The low intensity of these peaks in the spectrum of MnMoO<sub>4</sub> can be attributed to the water group adsorbed on the surface of the samples. While in the spectrum of MnMoO<sub>4</sub>.1H<sub>2</sub>O, the higher intensity of these peaks corresponds to the hydrated structure. The FTIR spectra of rGO-MnMoO<sub>4</sub> and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O are shown in Fig. 1S in the supporting information (SI).

The Raman spectra of the  $MnMoO_4.1H_2O$  and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite are presented in Fig. 5b. (The Raman spectra of the MnMoO<sub>4</sub> and rGO-MnMoO<sub>4</sub> nanocomposites are illustrated in Fig. 2S in the SI.) The characteristic peaks at 916 and 858 cm<sup>-1</sup> can be ascribed to the stretching vibrations of (MoO<sub>4</sub>) ions. In addition, the



Fig.5 a The FTIR spectra of  $MnMoO_4$  and  $MnMoO_4.1H_2O$  and b the Raman spectra of  $MnMoO_4.1H_2O$  and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposites

observed peaks at 804 and 323 cm<sup>-1</sup> are related to the bending vibrations of  $(MoO_4)$  groups. Also, in the spectra of graphene oxide nanocomposites, rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O and rGO-MnMoO<sub>4</sub> nanocomposites (as shown in Fig. 2S), the observed characteristic bands at 1581 and 1334 cm<sup>-1</sup> are ascribed to the G- and D-bands of carbonaceous materials, respectively [7]. The G- and D-bands are imputed to  $E_{2g}$  mode from the in-plane vibration of sp<sup>2</sup> carbon and A<sub>1g</sub> phonons of sp<sup>3</sup> carbon atoms in disordered graphite, respectively [32, 33]. The ratio of the intensity of the D-band to the G-band (I<sub>D</sub>/I<sub>G</sub>) is 1.085. This ratio, which is attributed to the degree of graphitization and the density of defects in carbonaceous materials, can show the reduction of GO during the hydrothermal treatment [32, 34].

The cyclic voltammetry of the samples was performed at a potential scan rate of 5 mV s<sup>-1</sup> in a potential range of 0–0.45 V. The cyclic voltammogram of the samples is illustrated in Fig. 6a. The observed anodic and cathodic redox peaks in CV curves reveal a pseudocapacitance (faradaic) behavior for these samples. The anodic peaks are found out at 0.394 and 0.360 V for MnMoO<sub>4</sub> and rGO-MnMoO<sub>4</sub>, and at 0.352 and 0.348 V for MnMoO<sub>4</sub>.1H<sub>2</sub>O and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O, respectively. It was found that the addition of GO to manganese molybdate reduces redox reaction potential. It can be attributed to the increment in electrochemical activity due to the GO functional groups. Moreover, the redox reaction potential of hydrated samples is lower than that of non-hydrated samples. This is probably caused by hydrated metal oxides due to the presence of the OH or/ and OH<sub>2</sub> groups, which are more electrochemically active in aqueous electrolytes [35]. The specific capacitances of 226.7, 524.4, 284.4, and 855.6 F  $g^{-1}$  were obtained using Eq. (1) for MnMoO<sub>4</sub>, rGO-MnMoO<sub>4</sub>, MnMoO<sub>4</sub>.1H<sub>2</sub>O, and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O, respectively. The results show that the specific capacitance of the hydrated manganese molybdate is higher than that of the non-hydrated. In fact, it can be attributed to the hydrated groups that can provide a layer or/and tunnel structures that allow ions and solvent molecules to permeate the active materials [35]. In addition, the hydrated structure could provide more appropriate charge transport [36]. The results showed that compositing the rGO with manganese molybdate increased the capacitance by a factor of more than 2. It can be ascribed to an increment of surface area and conductivity of the composites [36].

For comparison, the GCD curves were measured for  $MnMoO_4$ , rGO- $MnMoO_4$ ,  $MnMoO_4$ .1H<sub>2</sub>O, and rGO- $MnMoO_4$ .1H<sub>2</sub>O at a constant current density of 1 A g<sup>-1</sup>

in a potential range of 0-0.38 V. The GCD curves of the samples are illustrated in Fig. 6b. In the GCD tests, it was observed that the saturation potential value was 0.38 V in an applied constant current (Fig. 6b) which is different from the potential range. In accordance with the CV curves, a derivation from the triangular shapes in the GCD curves offers the pseudocapacitive treatment. Using Eq. (2), the specific capacitances of 208.2, 441.1, 323.2, and 526.3 F  $g^{-1}$  were obtained for MnMoO<sub>4</sub>, rGO-MnMoO<sub>4</sub>, MnMoO<sub>4</sub>.1H<sub>2</sub>O, and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O, respectively. The obtained specific capacitances from GCD curves demonstrate the improvement of the capacitance values for the hydrated samples composited with rGO. As can be seen from the obtained results of CV and GCD measurements, the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite has the maximum specific capacitance (855.6 F  $g^{-1}$  at 5 mV  $s^{-1}$ ).

Figure 6c illustrates the CV curves of rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O for different scan rates. It is observed that when the scan rate increases, the area of the closed curves increases, and the anodic and cathodic peaks are shifted to more and fewer potentials, respectively. At the scan rate of 5 mV s<sup>-1</sup>, the highest specific capacitance of 855.6 F g<sup>-1</sup> was obtained for rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O. At scan rates of 10, 20, 50, and 100 mV s<sup>-1</sup>, the specific capacitance decreases to 695.6, 567.8, 469.8, and 343.9 F g<sup>-1</sup>, respectively.

The GCD curves of the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite are illustrated in Fig. 6d for different applied constant current densities. According to the GCD curve (and Eq. (2)),

Fig. 6 a The CV and b GCD curves of  $MnMoO_4$ , rGO- $MnMoO_4$ ,  $MnMoO_4$ ,  $H_2O$ , and rGO- $MnMoO_4$ . $1H_2O$ , and rGO- $MnMoO_4$ . $1H_2O$  c The CV and d GCD curves of the rGO- $MnMoO_4$ . $1H_2O$  nanocomposite at different scan rates and applied constant current densities, respectively



at a current density of 1, 2, 3, 5, and 10 A  $g^{-1}$ , the specific capacitances of 526.3, 501.1, 466.6, 414.5, and 300 F  $g^{-1}$  were obtained for the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite, respectively.

The relationship between peak current and potential scan rate in CV curves can be assumed to be the sum of the currents for capacitive (EDLC and pseudocapacitance) and diffusionlimited processes, which are proportional to the linear and square root of scan rate. It is given by

$$I_p = K_1 \vartheta + K_2 \vartheta^{\frac{1}{2}} \tag{3}$$

or

$$\frac{I_p}{\vartheta^{\frac{1}{2}}} = K_1 \vartheta^{\frac{1}{2}} + K_2 \tag{4}$$

where  $\vartheta$  is the potential scan rate and  $K_1$  and  $K_2$  are adjustable coefficients. Figure 7a shows  $\frac{I_p}{\vartheta^{\frac{1}{2}}}$  as a function of  $\vartheta^{\frac{1}{2}}$  and its linear fitting for the anodic and cathodic processes. The slope and intercept of this line determine  $K_1$  and  $K_2$ , respectively, and therefore,  $K_1\vartheta$  and  $K_2\vartheta^{\frac{1}{2}}$  represent the capacitive and diffusion-controlled current. The *R*-square (COD) in the linear fitting was 0.9117 and 0.9624 for the anodic and cathodic processes, respectively. The values of 0.11, 0.04, -0.06, and -0.03 were obtained for the coefficients of  $K_1$  and  $K_2$  in the anodic and cathodic processes, respectively. The capacitive and diffusion-limited contributions are shown in Fig. 7b for various scan rates. It was found in Fig. 7b that in the anodic process at the scan rate of 5 mV s<sup>-1</sup>, the capacitive and diffusion-limited processes contributions were 16% and 84%, respectively. It was found that the capacitive contribution increases to 47% at 100 mV s<sup>-1</sup>. Therefore, the investigation of storage mechanism contributions reveals that the diffusion-limited process has a majority contribution than the capacitive process, which decreases with the increase in the scan rate. It can be attributed to reducing the ability of ions to penetrate the pores of the active material at higher scan rates [22]. The change in the ratio of the capacitive and diffusion-limited contributions in the anodic and cathodic processes is almost the same.

The specific capacitances of rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O are illustrated as a function of the scan rate and applied current density in Fig. 7c. The specific capacitance decreases with the increase in scan rate and applied current density. It can be attributed to the sufficient time provided for redox reactions at low scan rates and current densities, which leads to better charge storage [37]. In addition, this decrease is approximately linear in the specific capacities smaller than 550 F g<sup>-1</sup>.

The specific energy density (*E*) and specific power density (*P*) are given by the equation of  $E = \frac{1}{2}C_s^{\text{dis}}V^2$  and  $P = \frac{E}{t}$ , respectively, where  $C_s^{\text{dis}}$  (in F g<sup>-1</sup>) is the GCD mode-specific capacitance and *V* (in V) and *t* (in s) are the potential window and discharge time, respectively.

Fig. 7 a The peak current vs. scan rate, b the contribution of capacitive and diffusionlimited processes, c the specific capacitance behavior vs. scan rates and current density, and d the Nyquist plot of the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite. The inset shows the equivalent circuit used to describe the impedance spectra



The frequency response of the sample was evaluated by EIS. The Nyquist plot, described as the imaginary part of impedance (Z'') versus its real part (Z'), can reveal the frequency treatments of the electrode/electrolyte system. Figure 8 shows the Nyquist plot of the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite. The equivalent circuit used to describe the impedance spectra is demonstrated in the inset of Fig. 7d. It includes the series resistance  $(R_s)$ , charge-transfer resistance  $(R_{ct})$ , Warburg's impedance  $(Z_w)$ , and constant phase element (CPE). In the Nyquist plot, the intercept of the real axis corresponds to equivalent series resistance at high frequencies, and the half-semicircle curve is related to the  $R_{ct}$  of the electrode [38, 39]. The solid line in Fig. 7d shows the fitted curve to the experiment data. A value of 1.84 and 0.39  $\Omega$  was obtained for  $R_s$  and  $R_{ct}$ , respectively. These values clearly present low resistance in the electrode/electrolyte system. Also, the small diameter of the semicircle curve of the electrodes shows the good electrochemical activity of the electrode materials. In the middle-frequency region, the observed 45° diagonal line is related to the Warburg impedance, describing the frequency dependence of ion diffusion/transport in the electrolyte.

The electrochemical performance of the prepared electrodes in the current work is compared with previously reported materials in Table 1. As can be seen in Table 1, the specific capacitance of  $168 \text{ F g}^{-1}$  at 0.5 mA cm<sup>-2</sup> was reported for the MnMoO<sub>4</sub> nanorods by Veerasubramani et al. [18]. A specific capacitance of 215 F g<sup>-1</sup> at 1 mA cm<sup>-2</sup> was obtained for the MnMoO<sub>4</sub>.0.9H<sub>2</sub>O compound by Nti et al. [40]. These results show that the specific capacitance of 526 F g<sup>-1</sup> for rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O exhibits a good enhancement compared to the current work electrodes of MnMoO<sub>4</sub>, rGO-MnMoO<sub>4</sub>, MnMoO<sub>4</sub>.1H<sub>2</sub>O, and previously reported works.

To analyze the performance of the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite in full-cell configuration, a symmetric supercapacitor is prepared. CV tests are conducted at different scan rates ranging from 5 to 100 mV s<sup>-1</sup> at a potential range of -0.5–0.5 V, as presented in Fig. 8a. The quasi-rectangular shape of CVs reveals the capacitive behavior of electrode materials. In addition, the CV profiles maintain their shapes as the scan rate increases, indicating excellent electrochemical reversibility.

The GCD curves are measured for the SSC device at different current densities from 1 to 5 A  $g^{-1}$  in a potential window of 0–1 V, as shown in Fig. 8b. The specific capacitance of the SSC device is calculated based on Eqs. (1) and (2) from the CV and GCD curves as a function of scan rate and applied current densities, respectively, as shown in Fig. 8c, d. It was found that the SSC can provide a specific capacitance of 65.63 F  $g^{-1}$  at 5 mV s<sup>-1</sup> and 56.26 F  $g^{-1}$  at 1 A  $g^{-1}$ .



Fig. 8 a The CV and b GCD curves of SSC at different scan rates and applied constant current density, respectively. The specific capacitance behavior vs. c scan rates and d current density, e Ragone's plot, and f the cycle life of the SSC. The inset of f shows the SSC photograph

Figure 8e illustrates the Ragone plot describing the relationship between energy density and power density. A specific energy density of 7.81 Wh kg<sup>-1</sup> is obtained for the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O sample with a specific power density of 500



Fig. 8 (continued)

W kg<sup>-1</sup> at 1 A g<sup>-1</sup>. The specific energy density decreases to 4.13 Wh kg<sup>-1</sup> at 5 A g<sup>-1</sup> with a specific power density

of 2500 W kg<sup>-1</sup>, which shows the good performance of the assembled SSC compared with other reports in Table 1.

To verify the long-term electrochemical cycling stability of SSC, 5000 GCD cycles were carried out at a current density of 5 A  $g^{-1}$ . The capacitance retention values are obtained, as shown in Fig. 8f. The calculated capacitance retention value after 5000 cycles is 77.7%, which shows the long-term stability of the fabricated device. The photograph of SSC is shown in the inset of Fig. 8f.

## Conclusion

In summary, facile hydrothermal synthesis of the rGO-MnMoO<sub>4</sub> and rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposites is reported as the supercapacitor electrodes. These nanocomposites are in situ grown onto the nickel foam. These electrode materials are characterized in terms of structure, morphology, and chemical bonding. Also, their electrochemical performances, as supercapacitor electrodes, are measured in a 1 M KOH solution. The morphological study of the samples reveals that morphology changes from nanoflakes for the hydrated sample to cross-nanosheets for the nonhydrated sample with the calcination process. In addition, it seems that the presence of GO in the raw material may increase the hydrothermal reaction temperature. The highest specific capacitance of 855.6 F  $g^{-1}$  is obtained for the rGO-MnMoO<sub>4</sub>.1H<sub>2</sub>O nanocomposite at a scan rate of 5 mV  $s^{-1}$ . The investigation of storage mechanism contributions reveals that the diffusion-limited process has a majority contribution (than the capacitive process), which decreases with increasing the scan rate. Moreover, a quasi-solid-state SSC device is designed. It delivers 65.63 F  $g^{-1}$  at a scan rate of 5 mV s<sup>-1</sup>, a high energy density of 7.81 Wh kg<sup>-1</sup>, and a high

Sample	Specific capacitance	Electrolyte	Energy den- sity (Wh/ kg)	Power density (W/kg)	Ref.
Mn-MoO <sub>4</sub> /graphene	302 F/g at 0.1 A/g	1 M Na <sub>2</sub> SO <sub>4</sub>	41.9	208	[41]
Amorphized MnMoO <sub>4</sub>	373 F/g at 5 mV/s	1 M KOH	-	-	[42]
MnMoO4 nanorods	551 F/g at 1 A/g	2 M NaOH	15.5	224.9	[20]
MnMoO <sub>4</sub> .0.9H <sub>2</sub> O	215 F/g at 1 mA/cm <sup>2</sup>	1 M KOH	-	-	[40]
MnMoO <sub>4</sub> /CoMoO <sub>4</sub>	187 F/g at 1 A/g	2 M NaOH	9.6	-	[43]
MnMoO <sub>4</sub> nanorods	168 F/g at 0.5 mA/cm <sup>2</sup>	2 M NaOH	9.87	95.58	[44]
MnMoO4 nanoparticle	200 F/g at 1.6 A/g	2 M NaOH	11	100	[45]
MnMoO <sub>4</sub>	208 at 1A/g	1 M KOH	-	-	Current work
rGO-MnMoO <sub>4</sub>	441 at 1A/g	1 M KOH	-	-	Current work
MnMoO <sub>4</sub> .1H <sub>2</sub> O	323 at 1A/g	1 M KOH	-	-	Current work
rGO-MnMoO <sub>4</sub> .1H <sub>2</sub> O	526 F/g at 1A/g	1 M KOH	-	-	Current work
rGO-MnMoO <sub>4</sub> .1H <sub>2</sub> O symmetric superca- pacitor	56.26 F/g at 1 A/g	KOH/PVA	7.81	500	Current work

Table 1Electrochemicalperformance of current workcompared with similar reportedmaterials

power density of 2500 W kg<sup>-1</sup>. Also, the SSC shows capacity retention of 77.7% after 5000 GCD cycles.

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Author contributions S. R. Ghorbani and R. Ghanbari defined the project and designed the experiments. S. M. Jawad and R. Ghanbari performed measurements and wrote the main manuscript text. S. R. Ghorbani, H. Arabi, R. Ghanbari, and S. M. Jawad contributed to the discussions and analysis of the data. S. R. Ghorbani and H. Arabi reviewed the manuscript.

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**Data availability** The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Declarations

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Competing interests The authors declare no competing interests.

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