High energy density and enhanced stability of asymmetric supercapacitors with mesoporous MnO₂@CNT and nanodot MoO₃@CNT free-standing films

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ARTICLE INFO

Keywords: MnO₂ MoO₃ Carbon nanotubes Asymmetric supercapacitors Enhanced electrochemical stability

ABSTRACT

Asymmetric supercapacitors employ two different electrode materials with different working potentials and charge-storage mechanisms. One is for redox reactions or pseudocapacitance, similar to batteries, and the other for electric double-layer capacitance, similar to supercapacitors. This helps improve both energy density and power density. The choice of materials and control of nanostructures are the keys to enhancing electrochemical performance. Use of an aqueous electrolyte is desired for safety issues but the operating voltage window remains a challenge. We chose MoO₃ and MnO₂ for the two electrodes, where both exhibited pseudocapacitance with a high voltage window of 2 V. Each material was further nanostructured with carbon nanotubes to form MoO₃ nanodots on CNT surfaces (MoO₃@CNT) and mesoporous MnO₂ embedded in CNT networks (MnO₂@CNT). Therefore, the specific surface area improved to 68 m²/g for MoO₃@CNT and 343 m²/g for MnO₂@CNT, while the conductivity increased to 2.27 and 10.82 S/cm, respectively. For full-cell asymmetric supercapacitors with Na₂SO₄ as the electrolyte, a high energy density of 27.8 Wh/kg at a power density 524 W/kg or 9.8 Wh/kg at a high power density 10,000 W/kg was observed, where the power density was increased by a factor of 4 relative to the value reported with graphene oxide composites. Our ASCs exhibited excellent cycle stability with a capacitance retention of 96.8% after 10,000 cycles at 5 A/g. The simple self-assembly approach and free-standing nature of these metal oxide@CNT hybrid films offer high potential for the development of safe, low-cost, and wearable energy storage devices in the near future.

1. Introduction

The rapid growth of renewable energy technologies, hybrid electric vehicles, and consumer electronic devices in today’s society motivates researchers to develop sustainable energy power sources such as lithium ion batteries and supercapacitors [1–3]. Unlike batteries—which show a high energy density but a low power density and have short cycle-lives—supercapacitors can deliver high power density with an almost unlimited number of cycles, but suffer from low energy densities [4–6]. To overcome this constraint, researchers are interested in developing asymmetric supercapacitors (ASCs) in which two different types of electrode materials are coupled together (one is the positive electrode and another is the negative electrode) [7–10]. ASCs exhibit large voltage windows, particularly with aqueous electrolytes, owing to the different working potentials of the two electrodes, enhancing the energy density while maintaining high power density, safety, and environmental friendliness.

The choice of electrode materials is an important factor in ASCs. ASCs with electrode materials that have a large work function difference exhibit large voltage windows. MnO₂ as the positive electrode and MoO₃ as the negative electrode provide the largest work function difference (~ 2.5 V) among the transition metal oxides [11]. MnO₂ possesses high theoretical specific capacitance (1370 F/g), environmental friendliness, and low cost [12,13]. MoO₃ is non-toxic and a low-cost material with high electrochemical activity (can reach 512 F/g at 1 A/g) [14,15]. These metal oxides, however, exhibit poor electrical conductivities (10⁻⁹ to 10⁻⁸ S/cm) owing to their intrinsic insulating nature [16,17]. Carbon materials such as carbon nanotubes (CNTs), graphene (Gr), reduced graphene oxide (rGO), and carbon fibers have high conductivities and are usually combined with these...
metal oxides to improve their electrical conductivities, which in turn increases the overall electrochemical performance [18–29]. rGO/MnO2 and rGO/MoO3 composites show high specific capacitances of 320 F/g and 291 F/g at 2 mV/s, respectively [11], which are much higher than those of bare MnO2 (240 F/g at 2 mV/s) and MoO3 (230 F/g at 2 mV/s). However, rGO/MnO2 and rGO/MoO3 electrodes exhibited poor rate capability and cycle stability (large capacitance degradation after 1000 cycles). MnO2/carbon fiber composite delivered a high specific capacitance of 713 F/g at 0.5 A/g, but had poor cycle stability (only 86.8% capacitance retention after 1200 cycles) [21]. Another study on the MnO2/CNTs composite reported good rate capability and cycle stability (no obvious capacitance decay after 10,000 cycles) but moderate specific capacitance (201 F/g at 1 A/g) [19]. Some MoO3- and MWNT composites are reported to have improved electrochemical properties compared to bare MoO3 [22,23]. However, they suffer from a low specific capacitance (<150 F/g) and short cycle-life (1000 cycles). Reported MnO2- and MoO3-based composites suffer from either low porosity or poorly defined nanostructure of the electrode composite. A highly porous structure ensures easy access of electrolyte ions into electrodes, leading to increases in capacitance and rate capability. The use of CNTs coupled with metal oxides thus enhances electrochemical performance as CNT-based networks have more appropriate mesopores than graphene-based composites. A well-defined nanostructure of metal oxides can provide shorter diffusion pathways, which increases power performance.

We suggest a method for fabricating an asymmetric supercapacitor with high electrochemical performance and long cycle stability by taking advantage of the electrostatic interaction between CNTs and metal oxides decorated using cationic surfactants. This led to strong adhesion and uniform distribution of nanostructure metal oxides on the CNT surface, followed by hydrothermal treatment for MoO3@CNT (negative electrode) and thermal annealing for MnO2@CNT (positive electrode). Because of hydrothermal treatment and annealing, metal oxides having intrinsically large sizes were uniformly embedded in the CNT network with size ~10 nm (called nanodots in both metal oxide@CNT composites). Consequently, specific surface areas improved to 68 m2/g for MoO3@CNT and 343 m2/g for MnO2@CNT with well-developed pore size distribution in the mesoporous region in MnO2@CNT. We demonstrate that full-cell asymmetric supercapacitors with Na2SO4 electrolyte display excellent electrochemical performances with high cycle stability.

2. Experimental section

2.1. Synthesis of nanodot MoO3@CNT composite for negative electrodes

Single-walled carbon nanotubes (SWCNTs, > 75 wt%, TUBALL™, Russia) were dispersed in deionized water using cetyltrimethylammonium bromide (CTAB, > 99%, Sigma-Aldrich) as the surfactant (0.1 wt % of CTAB in deionized water). The initial SWCNT concentration was 1 mg/mL. The CTAB-SWCNT solution was sonicated for 2 h using a homogenizer with a power of 350 W. After removing undispersed SWCNT bundles by centrifuging for 10 min at 7191G (8000 rpm), the final CTAB-SWCNT solution had a concentration of 0.6 mg/mL.

MoO3 powder (200 mg, 100 nm, orthorhombic crystal, Sigma-Aldrich) was dispersed in 100 mL ethanol through sonication. MoO3 solution was then mixed with controlled amount of CTAB-SWCNT solution and stirred overnight. The SWCNT ratio was controlled between 10% and 30%. A simple hydrothermal method was followed to prepare the MoO3@CNT composite following previous work [30]. In detail, 75 mL of dispersed solution was transferred into a 100 mL Teflon-lined autoclave and then placed in an oven at 180 °C for 24 h. After hydrothermal treatment, the samples were naturally cooled to room temperature. The samples were filtered to form the film, followed by freeze drying.

2.2. Synthesis of mesoporous MnO2@carbon nanotube composite for positive electrodes

MnO2 was prepared by co-precipitation following previous reports [31]. Mn(NO3)2·4H2O (0.346 g) and 0.1 g poly(ethylene glycol)-block-poly (propylene glycol)-block-poly(ethylene glycol) were dissolved in 20 mL deionized water. The as-obtained transparent solution was cooled in an ice bath with intermittent dropping of liquid nitrogen to maintain the freezing point of water. KMnO4 (0.1 M, 20 mL) was slowly added dropwise into the above mixture. The final MnO2 powder was obtained by filtering the black precipitate from solution, followed by water washing and freeze drying.

MnO2 powder (200 mg) was dispersed in 100 mL ethanol through sonication. MnO2 solution was mixed with controlled amount of CTAB-SWCNT solution and stirred overnight. The SWCNT ratio was controlled between 20% and 70%. The mixture was filtered to get the film, followed by freeze drying. To remove CTAB linkers, the MnO2@CNT sample was annealed at 350 °C for 1 h in an Ar atmosphere at a heating rate of 2 °C/min.

2.3. Physicochemical characterization of electrode materials

The surface morphology and nanostructure of each sample was examined by FE-SEM (JSM 7000 F, JEOL) and HR-TEM (JEM-ARM-200F). Elemental analyses were conducted by energy dispersive X-ray spectroscopy (EDS, Oxford-Horiba Inca Xmax50). The powder sample was taken during filtration and dispersed in ethanol. The suspension was dropped on a 200 mesh Cu grid. Crystallographic structure analysis was performed using XRD (Rigaku SmartLab X-ray diffractometer) with Cu-Kα radiation (λ = 0.15406 nm). Raman spectroscopy was performed using a micro-Raman system (Renishaw, RM1000-In Via, UK) with a laser of wavelength 532 nm. Functional groups were examined by XPS (ESCA2000, VG Microtech, England) on an instrument equipped with an Al-Kα radiation source (1486.6 eV). High-resolution spectra were collected at a fixed pass of 20 eV, and the C1s peak at 284.6 eV was used as the charge reference. Micropore and mesopore size distributions were estimated via the Horváth–Kawazoe and Barrett–Joyner–Halenda methods, respectively. Electrical resistivity was measured with a 4-point probe system. The size and thickness of each sample were confirmed by FE-SEM and the conductivity of each sample was calculated using the following formula:

\[ R = \frac{\rho L}{l \ t} = R_s \frac{L}{l} \]

where \( R \) is the electrical resistance, \( \rho \) the resistivity, \( L \) the length, \( l \) the width, and \( t \) the sheet thickness. \( R_s \) is the sheet resistance. The bulk resistivity \( \rho \) (in Ω-cm) was calculated by multiplying the sheet resistence and the film thickness,

\[ \rho = R_s \times t \]

Finally, conductivity \( \sigma \) is defined as the inverse of resistivity,

\[ \sigma = \frac{1}{\rho} \]

2.4. Fabrication of asymmetric supercapacitor device

To construct an ASC, the loading mass ratio of active materials (MoO3@CNT and MnO2@CNT) was controlled to be 1:3:1 (for charge balance) to optimize the total capacitance. This will be discussed later. Free-standing metal oxide@CNT samples were employed as electrodes in a coin-cell configuration (CR2032) without binders or conductive additives. Two electrodes were isolated using an ion-porous separator (Grade GF/C, Whatman, Korea). Neat 1 M Na2SO4 (Sigma-Aldrich) was used as aqueous electrolyte.
2.5. Electrochemical measurement

The electrochemical test was carried out on a Biologic VMP3 electrochemical workstation. The MoO₃@CNT negative electrode and MnO₂@CNT positive electrode were assembled in a three-electrode cell. Platinum net and Ag/AgCl electrode were used as counter and reference electrodes in 1 M Na₂SO₄ electrolyte at room temperature. Electrochemical impedance was measured in the frequency range 10 kHz to 10 mHz.

The gravimetric specific capacitance \( (C_s) \) was calculated from CV measurements using the following formula:

\[
C_s = \frac{2}{m_s} \times \frac{|Q_s|}{2V},
\]

where \(|Q_s|\) and \(|Q_p|\) are charges stored during negative and positive cycles, respectively, \(m_s\) is the active mass of each electrode and \(V\) is the potential window. \(C_s\) was also calculated from CD measurements as follows:

\[
C_s = \frac{2I}{M_s \Delta t},
\]

where \(I\) is the constant current applied, \(\Delta t\) is the slope obtained by fitting a straight line to the discharge curve, \(M_s\) is the active mass of each electrode, and \(I_s\) is the current density.

The gravimetric energy density \( (E) \) and gravimetric average power density \( (P_{av}) \) were calculated from CD measurements using the following formula:

\[
E = \frac{C_s \times V^2}{8} \quad \text{and} \quad P_{av} = \frac{E}{\Delta t},
\]

where \(V\) is the operating voltage and \(\Delta t\) the discharge time.

3. Results and discussion

The process for preparing electrode materials for asymmetric supercapacitors is schematically illustrated in Fig. 1. The SWCNTs were positively charged by the cationic surfactant (CTAB) [5,32]. The positively charged CTAB-grafted SWCNT solution was stirred with negatively charged MoO₃ dispersed in ethanol to prepare the negative electrode. For the positive electrode, the CTAB-SWCNT solution was mixed with negatively charged mesoporous MnO₂ dispersed in ethanol.

Fig. 2a and b show the morphology of the MoO₃@CNT composite. The HR-TEM images show that MoO₃ nanodots of diameter ~ 10 nm were uniformly embedded on the surfaces of CNT bundles (Fig. 2c, d and Fig. S1a–d). The as-prepared MoO₃@CNT composites had smaller diameter MoO₃ nanoparticles than pristine MoO₃ (Fig. S1e) owing to strong interactions between CTAB-CNTs and the metal oxide, as well as the harsh conditions of the hydrothermal process. Fig. 2e and f show MnO₂ clusters that were covered and trapped by CNT channels in the MnO₂@CNT composite. HR-TEM micrographs (Fig. 2g, h and Fig. S2a–d) reveal that MnO₂ nanoparticles (~ 30 nm) were partially distributed on and embedded in the CNT network. SEM images of pristine MnO₂ are shown in Fig. S2e, revealing large clusters due to aggregation. Two different fringe spacings were observed in both the metal oxide@CNT composites (Fig. 2d, h), indicating the formation of highly resistive metal oxides and highly conductive CNTs, leading to the easy transport of electrons through the whole structure.

Raman spectra of the composites and bare SWCNT are shown in Fig. 3a. The D-band/G-band intensity ratios of MoO₃@CNT, MnO₂@CNT, and SWCNT were 0.208, 0.04, and 0.028, respectively. The higher intensity ratio of MoO₃@CNT relative to MnO₂@CNT was attributed to highly defective CNTs, perhaps ascribed to the low hydrothermal treatment of the composite. The hydrothermal process (for the MoO₃@CNT sample) gave rise to more defective CNTs because of harsh conditions such as a high pressure (9 bar) and temperature (180 °C), developing a high D-band intensity (Fig. 3a). In the MnO₂@CNT sample, high-temperature treatment (350 °C) annealed defects in CNTs and generated fewer defects than those generated in the hydrothermal-treated MoO₃@CNT sample owing to the reduction of oxygen-functional groups and increase in the graphitic structure. Structural characterization of the composite was performed by XRD spectral analysis. Fig. 3b shows typical X-ray diffraction (XRD) patterns of pristine MoO₃, MoO₃@CNT, pristine MnO₂, and MnO₂@CNT. Pristine MoO₃ presented very sharp diffraction peaks, which indicated a highly crystalline orthorhombic structure (α-MoO₃, green line). The XRD pattern of the MoO₃@CNT composite (black line) consisted of both MoO₃ and hexagonal MoO₂ peaks (ICDD No. 00-050-0739), which indicated a partial change in the phase of MoO₃ to MoO₂ during the hydrothermal reaction [14,33]. Pristine MnO₂ (orange line) and MnO₂@CNT composite (red line) showed widened and weak (400) peaks at ~ 36°, suggesting the amorphous nature of MnO₂.

Nitrogen adsorption and desorption isotherms of the metal oxide@CNT composite showed typical H₁/H₄ characteristics (Fig. 3c). The Brunauer–Emmett–Teller specific surface areas (SSAs) of MoO₃@CNT and MnO₂@CNT were 68 and 343 m²/g, respectively. Our MoO₃@CNT composite exhibited a higher SSA than pristine MoO₂ (~ 6 m²/g) and other MnO₂@carbon composites such as α-MoO₃/multi-walled CNT composite.
Fig. 2. SEM images (a, b) and TEM images (c, d) of MoO$_3$@CNT. SEM images (e, f) and TEM images (g, h) of MnO$_2$@CNT.

Fig. 3. (a) Raman spectra of MoO$_3$@CNT, MnO$_2$@CNT, and SWCNT. (b) XRD patterns of MoO$_3$, MoO$_3$@CNT, MnO$_2$, and MnO$_2$@CNT. Nitrogen adsorption/desorption isotherms (c) and pore size distributions (inset: micropore size distribution) (d) of MoO$_3$@CNT and MnO$_2$@CNT. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article).
nanocomposites (21.7 m²/g) [14] and GrMoO₃ nanosheets (~ 10 m²/g) [11]. The SSA of the MnO₂@CNT composite (343 m²/g) decreased slightly compared to that of pristine MnO₂ (370 m²/g) (Fig. S5). This was attributed to MnO₂ nanoparticles embedded in CNTs, which reduced the active surface for N₂ adsorption/desorption, as shown in SEM and HR-TEM images (Fig. 2 and Fig. S2). Although the SSA decrease led to reduced electrolyte-ion adsorption, rate capability was improved owing to increased conductivity. The MnO₂@CNT composite possessed a higher SSA value than other MnO₂@carbon composites such as GrMnO₂ (152 m²/g) [11] and MnO₂/CNT (160 m²/g) [34].

Fig. 3d shows the pore size distributions of the two composites. MoO₃@CNT possessed a high proportion of macropores (around 65.5 nm) and mesopores, but few micropores. MnO₂@CNT was dominated by mesopores (around 29.4 nm), a reasonable number of micropores, and few macropores. The SSA and pore size distribution differences between MoO₃@CNT and MnO₂@CNT came from the intrinsic porous properties of the metal oxides. A high portion of mesopores was desirable in both hybrid electrodes for fast ion diffusion and use in high power density devices. In the MnO₂@CNT sample, micropores at 0.5 nm and 1.8 nm increased the capacitance while mesopores at 29 nm allowed efficient ion diffusion. The micropore volume of the MoO₃@CNT sample was smaller than that of the MnO₂@CNT sample.

The surface chemistries of MoO₃@CNT and MnO₂@CNT composites were analyzed using XPS. Fig. S6a shows elemental presence via a wide scan (survey) of each composite. It was observed that the binding energies of Mo 3d₅/₂ and Mo 3d₃/₂ in the MoO₃@CNT composite were 232.9 eV and 236 eV, respectively (Fig. 4a). Three lower satellite peaks at 237.4 eV, 234.5 eV, and 231.4 eV can be assigned to MoOₓ, MoO₂ + MoOₓ complex, and MoO₂, respectively. The area percentage ratio of MoO₂ to other phases of molybdenum oxides in the MoO₃@CNT composite was 3.9:1 (Table S1). The O 1s XPS spectrum exhibited three characteristic peaks at 530.7 eV, 532 eV, and 533.3 eV, corresponding to Mo-O, C-O, and C-OH groups, respectively (Fig. 4b).

The binding energies of Mn 2p₃/₂ and Mn 2p₁/₂ in the MnO₂@CNT composite were 641.2 and 652.9 eV, respectively. The peak separation of 11.7 eV between Mn 2p₃/₂ and Mn 2p₁/₂ in the composite indicated that Mn was present in the composite in the Mn⁴⁺ state (Fig. 4e) [34]. The lower satellite peaks at 643.1 eV, 654.8 eV, and 645.5 eV reflected two Mn-O states and one MnO₂ state, respectively. The O 1s XPS spectrum presented three components at 529.9 eV, 532.2 eV, and 533.8 eV corresponding to the Mn-O bond, C-O, and C-OH groups, respectively (Fig. 4d). The intensity ratios between C-OH, C-O, and Mn-O groups in MnO₂@CNT were higher than those of C-OH, C-O, and Mo-O groups in MoO₃@CNT. This was due to the higher mass ratio of CNTs in MnO₂@CNT (50%) than in MoO₃@CNT (20%).

The electrochemical performances of both metal oxide@CNT composites were evaluated in a three-electrode system with 1 M Na₂SO₄ aqueous solution. The MoO₃@CNT electrode was measured in the potential window −1.0 to 0 V (vs. Ag/AgCl) while the MnO₂@CNT electrode was measured in the potential window −0.1 to 0.9 V (vs. Ag/AgCl). In neutral electrolyte, the electrochemical reduction and oxidation of water occur via the following reactions:

\[
\text{reduction : } 2H^+ + 2e^- \rightarrow H_2(g) \\
\text{oxidation : } 2H_2O \rightarrow 4H^+ + 4e^- + O_2(g)
\]

The corresponding Nernst equations are as follows:

Fig. 4. XPS spectra of MoO₃@CNT and MnO₂@CNT showing Mo 3d (a), O 1s (b), Mn 2p (c), and O 1s (d) fitted peaks.
In the present case, the pH of the electrolyte (Na2SO4 in aqueous medium) was ~ 7 and thus, the thermodynamic reduction and oxidation potentials of water were -0.41 V and 0.817 V, respectively. Experimentally, the potential windows were from -1 V to 0 V for the negative electrode and -0.1 to 0.9 V for the positive electrode. In both cases, the potential windows were beyond the thermodynamic limit. However, the kinetic barriers are high for the hydrogen evolution reaction at MoO3 surface and oxidation evaluation reaction at MnO2 surface [11,35]. We can determine these kinetic barriers by measuring the onset potential for water reduction and oxidation. The onset potential for hydrogen evolution reaction is -0.985 V (vs Ag/AgCl) at the MoO3@CNT surface and the onset potential for oxygen evolution reaction is 1.146 V (vs Ag/AgCl) at the MnO2@CNT surface (Fig. S8). This clearly justifies the stability of the potential window of 2 V (1.146 V + 0.985 V = 2.131 V) in our asymmetric device.

Fig. 5a and b show CV curves of MoO3@CNT (1.33 mg/cm2; 16.8 µm in thickness) and MnO2@CNT (1 mg/cm2; 12.6 µm in thickness), respectively, at different scan rates from 1 to 200 mV/s. CV curves of both electrodes exhibited quasi-rectangular shapes, indicating the contributions of pseudocapacitance in addition to electrical double-layered capacitance. The as-observed redox peaks in CV curves of the MnO2@CNT sample corresponded to the redox process between Mn4+ and Mn3+ [36]. In the case of MnO2, maximization of the polarization potential occurred owing to irreversible reactions from Mn4+ to Mn7+. At a neutral pH (6.4) and an alkaline pH (10), the potential of the reaction from Mn4+ to Mn7+ was 1.19 V and 0.98 V, respectively (vs. NHE) [37]. In our case, we used Na2SO4 (pH ~ 7) and the operating voltage window was -0.1 to 0.9 V (vs. Ag/AgCl), or 0.097–1.097 V (vs. NHE), which was lower than 1.19 V. The rate performances of both electrodes are shown in Fig. 5c. The MoO3@CNT and MnO2@CNT electrodes had excellent specific capacitances of 281 F/g and 337 F/g, respectively at 1 mV/s. At a high scan rate of 200 mV/s, they retained high capacitances of 79 F/g (MoO3@CNT) and 150 F/g (MnO2@CNT). CV tests of CNT samples for both positive and negative electrodes are shown in Fig. S9. While the contribution of CNTs was mostly electric double-layer capacitance, the primary contribution to the total capacitance resulted from the pseudocapacitance of metal oxides. Both electrodes exhibited high cycle stability with capacitance retention of 84% for MoO3@CNT and 92% for MnO2@CNT after 9000 cycles at a large discharging current density (5 A/g). The charge-discharge curves of both electrodes at 5 A/g are shown in Fig. S10. The loading mass dependence and CNT mass ratio optimization of the composites are shown in Fig. S11. The high rate performance and cycle stability of both samples were attributed to highly porous conductive structures and robust architectures of the metal oxide@CNT composites.

To further evaluate the potential of these metal oxide@CNT composites in practical applications, an asymmetric supercapacitor was fabricated using an MoO3@CNT (1.33 mg/cm2; 16.8 µm in thickness) negative electrode and MnO2@CNT (1 mg/cm2; 12.6 µm in thickness) positive electrode (Fig. 6a). The actual mass loadings of MoO3@CNT and MnO2@CNT were 2.37 and 1.92 mg, respectively. The operating voltage of the ASC (basically the sum of the potential ranges of MoO3@CNT and MnO2@CNT) was extended up to 2 V since the hydrogen and oxygen evolution reactions were kinetically restricted on these transition metal oxide@CNT composites [11]. To further confirm the stable working voltage window of 2 V, we tested the electrolyte stability by measuring CV curves of the asymmetric device in the voltage window range from 1.4 to 2.2 V (with scan rate of 50 mV/s), as shown in Fig. S12. Charge balance was necessary to...
optimize the total capacitance of the asymmetric device: \( q_+ = q_- \) (where \( q_+ \) is the positive electrode charge and \( q_- \) is the negative electrode charge). As \( q = C \times \Delta E \times m \) (where \( C \) is the specific capacitance, \( \Delta E \) the potential window, and \( m \) the mass of the electrode), the mass balance is given by \( \frac{n_+}{n_-} = \frac{C^+ \times \Delta E^+}{C^- \times \Delta E^-} \). The choice of capacitance at different scan rate seems to be arbitrary. Since we focus on improving energy density, we chose low scan rate of 10 mV/s (See Fig. 5c), the ASC was assembled with the optimized mass ratio (MoO3@CNT)/(MnO2@CNT) 1.3:1.

CV curves of MoO3@CNT//MnO2@CNT ASCs at different scan rates from 5 to 200 mV/s are presented in Fig. 6b. The CV curves had
quasi-rectangular shapes, reflecting their nearly ideal capacitive behaviors, high rate capabilities, and low internal resistances. CD curves at various current densities are shown in Fig. 6d. The CD plots were almost symmetric, indicating good coulombic efficiency and excellent reversibility of the MoO$_3@$CNT//MnO$_2@$CNT ASC. Fig. 6c and e illustrate the scan rate and current density dependences of the total capacitance, respectively, of the ASC. The device exhibited maximum capacitance of 54 F/g at 5 mV/s and 61 F/g at 0.2 A/g. Fig. 7a shows a Ragone plot of the MoO$_3@$CNT//MnO$_2@$CNT ASC compared to those of previously reported GrMnO$_2$/GrMoO$_3$ ASC and MnO$_2$/MoO$_3$ ASC [11]. The MoO$_3@$CNT/MnO$_2@$CNT device had a high energy density of 27.8 Wh/kg at a power density of 524 W/kg. Its energy density remained at 9.8 Wh/kg at a high power density of 10,000 W/kg. Our ASC device outperformed ASCs with bare metal oxides and metal oxide@graphene composites [11]. A high capacitance retention of 96.8% was observed after 10,000 cycles at a discharge current density of 5 A/g (Fig. 7b). The excellent cycle stability was ascribed to the highly porous conductive and well-defined robust nanostructures of both electrodes. The capacitance of the ASC increased (~ 11%) during the first 4520 charge/discharge cycles. This could have been caused by insufficient wetting hours overnight, which varied depending on the electrode material. In addition, energy efficiency of ~ 42.2% and Coulombic efficiency of 98.9% of the MoO$_3@$CNT/MnO$_2@$CNT ASC are shown in Fig. S14. The low energy efficiency is related to the irreversibility of faradaic processes and possibly the rapid self-discharge at the initial stage. Electrochemical impedance spectroscopy was performed to measure the impedance of the MoO$_3@$CNT/MnO$_2@$CNT ASC. The as-obtained Nyquist plot shows a nearly perpendicular line in the low-frequency region, indicating fast ion diffusion in the asymmetric device (Fig. 7c). The low equivalent series resistance (ESR) (~ 0.26 Ω) was attributed to the high electrical conductivities of the electrodes (2.27 S/cm of MoO$_3@$CNT and 10.82 S/cm of MnO$_2@$CNT). The charge-transfer resistance ($R_{ct}$) was ~ 14 Ω, which was comparable to other ASC reports [11,13,18,38–40].

The self-discharge curve obtained immediately after charging to a $V_{\text{max}}$ of 2 V (open-circuit voltage) is shown in Fig. 7a. Most supercapacitors are operated in the range $V_{\text{max}}$ to 1/2 $V_{\text{max}}$ for self-discharge test. The self-discharge time required for the voltage across the device to drop from $V_{\text{max}}$ to 1/2$V_{\text{max}}$ was measured to be 52 h, which was higher than those of commercial supercapacitors and those mentioned in other previous reports [41–44]. Our ASC exhibited a rapid self-discharge rate in the initial stage, which saturated around 1 V. The curve can be fit into two regions: i) fast potential driven region and ii) slow diffusion controlled region [42,45]. The first part represents the potential drop between inter-particles in each electrode. Since we have two asymmetric cathode and anode electrodes in the full cell, two time constants ($\tau_1$ and $\tau_2$) can be used to fit the curve (Fig. S16). An additional slow-fitting parameter ($\tau_3$) could be attributed to a hybrid effect but requires a detailed study. The second part represents the potential drop by ion diffusion across two electrodes.

4. Conclusions

Our ASC was successfully developed using MoO$_3@$CNT and MnO$_2@$CNT composites as negative and positive electrodes, respectively. These two transition metal oxide@CNT nanocomposites are highly flexible, conductive, and free-standing with three-dimensional
porous and robust structures. The as-prepared ASC device exhibited high energy and power densities, and excellent cycle stability at an operation voltage window of 2 V in the Na2SO4 aqueous electrolyte. The self-assembly of metal oxide/CNT hybrids in solution and use of simple hydrothermal and annealing methods can lead to low-cost and mass production. These hybrid films and the cell configuration of the ASC are also promising for the development of flexible and wearable energy storage devices in the near future.

Acknowledgements

This work was supported by the Institute for Basic Science of Korea (IBS-R011-D1).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ensm.2017.12.009.

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