Chemical Engineering Journal 309 (2017) 151–158

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Advanced electrochemical energy storage supercapacitors based on the flexible carbon fiber fabric-coated with uniform coral-like MnO_2 structured electrodes

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HIGHLIGHTS

- Novel coral-structured MnO_2 on carbon fiber fabric (CFF) was first time fabricated.
- Solid-state highly flexible CFF/MnO_2 based supercapacitor device is fabricated.
- The device exhibits an outstanding specific capacitance of 467 F/g.
- The device displays outstanding capacitance retention of 99.7% after 5000 cycles.
- Coulombic efficiency close to 100% is achieved for device with high energy density.

ARTICLE INFO

Article history:
Received 26 July 2016
Received in revised form 3 October 2016
Accepted 4 October 2016
Available online 5 October 2016

Keywords:
Coral-like MnO_2 nanostructures
Carbon fabric
Hydrothermal reaction
Hybrid devices
Supercapacitors

ABSTRACT

The novel and efficient electrode materials have been developed for supercapacitor applications based on carbon fiber fabric/MnO_2 hybrid materials, in which MnO_2 was uniformly coated on the surface of carbon fiber fabric (CFF). A green hybrothermal method was used to functionalize CFF with coral-like MnO_2 nanostructures to improve the pseudocapacitance properties of the hybrid composites. These CFF/MnO_2 composites are used as excellent flexible electrodes for high-performance electrochemical supercapacitors applications. The morphological, structural and crystalline properties of composites were analysed by using various techniques such as FE-SEM, XRD, XPS, and Raman spectroscopy, respectively. The electrochemical performance was examined by cyclic voltammetry (CV), galvanostatic charge-discharge tests and electrochemical impedance spectroscopy (EIS). In a three-electrode system, the CV tests reveal the superior specific capacitance of 467 F/g at a current density of 1 A/g with capacitance retention of 99.7% and the columbic efficiency remains as high as 99.3% after 5000 cycles, demonstrating an outstanding electrochemical cyclic stability. In addition, high-performance device fabricated with CFF/MnO_2 demonstrated excellent energy density of 20 W h/kg at a power density of 0.175 kW h/kg. These novel electrode materials could be potential candidate for applications in practical and large-scale energy storage systems.

1. Introduction

Recently, the development of novel energy conversion and storage systems have been received a great research interest in nanoscience and nanotechnology as alternative energy sources to achieve a clean and sustainable world due to the limitation of fuels and environmental issues [1–4]. In this regard, electrochemical energy technologies such as rechargeable batteries, fuel cells, solar cells and supercapacitors have been recognised as the most important part of various energy storage technologies [5–10]. Among many technologies in energy storage systems, the electrochemical supercapacitors are safe and efficient devices that possess high energy density, powder density, excellent specific capacitance, long charge-discharge cycle life with highest reversibility, cell design flexibility, environmental and chemical stability, which enables them to find potential applications in the portable electronics, electric vehicles, large scale energy storage grids, etc. [11–14].

In general, electrochemical supercapacitors can be divided into electric double layer capacitors (EDLC) and pseudocapacitors according to the materials and electrochemical charge-discharge

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http://dx.doi.org/10.1016/j.cej.2016.10.012
1385-8947/

mechanism. Energy storage capacity of the double layer capacitors is limited and in order to increase the electrochemical properties (e.g. specific capacitance, power density) of electric double layer capacitors, large specific surface-area electrode needs to be used, such as nanostructured carbon materials (graphene, nanotubes, etc.) [15–17]. On other hand, the psedocapacitors shows faradic electrochemical reactions at the surface of electroactive nanomaterials have mainly used nanostructured metal oxides with the combination of carbon materials, which leads to increase of energy storage and specific capacitance of hybrid materials through the redox reactions between an inorganic and the organic components in the composite system [18–20].

Nanostructured carbon-based electrode materials are commonly used for the electrochemical applications due to low cost, thermal, chemical and environmental stability, and good electrical property with facile electron transport pathways for protons and electrons, and good reversible redox reactions [21,22]. However, their reversible redox processes, energy density, specific capacitance and cycle life stability are poor. To overcome these major challenges and drawbacks, the electrochemical properties of these materials can be improved by the combining them with nanostructured metal oxides. Among different metal oxides, manganese oxide (MnO_2) has been recognized as one of promising inorganic materials due to its easy synthesis process, low cost and excellent electrochemical properties [23]. Thus, this cutting edge research is most important topic and it is necessary to develop alternative low cost and novel electrode materials as next generation of supercapacitors that can charge and discharge in less time while delivering enhanced power density. The cost-effective and poor electrochemical properties (specific capacitance, high energy density and cycle life) of hybrid devices can be overcome by designing an electrode with flexible carbon fiber fabric (CFF) and MnO_2 that contribute an electrochemical behavior during charge and discharge.

Among various carbon-based materials, CFF was chosen in this study because it is one of the most widely used current collectors for energy storage devices due to its one-dimensional structure, high corrosion resistance, high electrical conductivity, low cost and easy fabrication process. The coral-like structured MnO_2 were directly vertically grown on surface of an horizontal 1D structured CFF collectors, enabling one-step fabrication process of supercapacitor electrodes without using any binders or conductive additives. For supercapacitor application, in particular, such unique structures endows the active electrode hybrid materials with a high proportion of surface atoms and active sites on the exposed surfaces and sufficient contact with the electrolyte, short ion and electron diffusion path, benefiting fast charge transfer and electrochemical reactions which proceed at room temperature without requiring any special equipment. These advantages render it an industrially feasible and promising strategy for large-scale production of high-performance energy storage materials. Also, to the best of our knowledge, the reports in the literature on coral-like MnO_2/CFF hybrid solid-state flexible devices as the efficient electrodes with versatile electrochemical properties for the high-performance electrochemical supercapacitor applications are scarce.

In this work, after consideration of the problems described above, highly flexible and warp-proof CFF well covered with uniform coral-like MnO_2 structures have been successfully fabricated for the first time through the green hydrothermal process at different reaction conditions and investigated CFF/MnO_2 flexible electrodes for their morphological, structural and electrochemical properties by using FE-SEM, XRD, XPS, Raman, cyclic voltammetry, galvanostatic charge-discharge and impedance spectroscopy, respectively. Flexible CFF present in the composite system act as an ideal template as it can enable to gradually grow MnO_2 coral-structures on the outer surface of the carbon fabric, as well as current collector of the device. The fabricated CFF/MnO_2 hybrid flexible solid-state electrodes without binder and any additives possessed outstanding electrochemical supercapacitive properties. This device shows an outstanding specific capacitance of 467 F/g in an environmentally friendly 1 M Na_2SO_4 aqueous electrolyte and superb cycle performance to maintain almost 100% of the initial capacitance after 5000 cycles, indicating excellent electrochemical cycle stability, which can be ascribed to the unique structure of the electrode for fast ion diffusion. They also show an excellent energy density of 20 W h/kg, low charge transfer resistance and faster charge/discharge rates. The formation mechanism of the coral-like MnO_2 nanostructures on the surface of carbon fiber fabric is also presented. In addition, the green process and novel electrode materials reported in this study can be simpler and more economical. These unique structured novel electrodes are alternative and promising materials for development of next-generation electrochemical energy storage systems, such as advanced supercapacitors and batteries.

2. Experimental

2.1. Fabrication of CFF/MnO_2 composite electrodes

A commercially available carbon fiber fabric (CFF) (GDL-CT, FuelCellsEtc, USA) was used as supporting material for coating with MnO_2 nanostructures through a hydrothermal method. Prior to the synthesis, polymer sizing on the surface of carbon fabric was removed by heating the fabric at 450 °C for 15 min in argon atmosphere. After the removal of sizing, carbon fabric was cut to a size of 3.0 × 3.0 cm and placed standing inside the liner of a Teflon-lined autoclave. In a typical synthesis procedure, 56.9 mg of potassium permanganate ($KMnO_4$) (Sigma-Aldrich) was dissolved in 60 mL of deionized water under constant magnetic stirring for 30 min, forming a 6 mM $KMnO_4$ solution. Then, the fully dissolved solution was transferred into an 80 mL capacity Teflon-lined stainless steel autoclave liner and the liner was sealed in a stainless steel autoclave. Finally, the reaction was kept at 175 °C for 4 h. After the autoclave was cooled down to room temperature, the sample was removed, washed with distilled water and ethanol several times, and dried at 60 °C for 10 h under vacuum. To investigate the effect of the reaction time on the growth process of MnO_2 structures on the surface of carbon fiber fabric, similar procedures were also conducted under the hydrothermal process at 175 °C for 1 and 7 h.

2.2. Characterization

The morphology of CFF and CFF/MnO_2 hybrids were investigated by the field emission scanning electron microscopy (FE-SEM, JEOL6701) without coating of gold or platinum before FE-SEM analysis. X-ray diffraction (XRD) patterns were recorded using Cu Kα radiation (GBC MMA diffractometer). The surface composition of the samples was examined by X-ray photo electron microscopy (XPS, Thermo-Scientific 2000) using monochromated Mg Kα radiation. Raman spectroscopy of the samples was recorded using a Invia Raman spectrophotometer (Renishaw plc, UK).

2.3. Electrochemical property measurements using three-electrode and two-electrode systems

Electrochemical property measurements of cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were conducted with a potentiostat on an electrochemical workstation (CH1, 660 E, Shangai Chenhua) at room temperature within a voltage window of 0–1.0 V at various

sweep rates. The electrochemical measurements were carried out using a three electrode electrochemical cell containing 1 M Na_2SO_4 aqueous solution as the electrolyte, an Ag/AgCl electrode as reference electrode, and a platinum coil as counter electrode, respectively. CFF/MnO_2 fabric (1.0 × 1.0 cm) was directly used as the working electrode. The specific capacitances were calculated from the CV curves of three-electrode system. Electrochemical impedance spectroscopy (EIS) was performed by applying an alternating voltage (5 mV) in the frequency range between 0.01 Hz and 100 kHz. The specific capacitance of an electrode was calculated from the galvanostatic charge-discharge (GCD) curves of three-electrode system at different current densities 1, 3, 6 and 10 A/g, using an equation $Cs = It/mV$, where Cs [F/g] represents the galvanostatic charge-discharge specific capacitance, I [A] is the discharge current, t [s] is the discharge time, V [V] is the potential change during the discharge, and m (g) is the total mass of the active materials in two electrodes. The energy densities E [W h/kg] of the solid-state flexible device were calculated from the GCD curves of two-electrode system using an equation $E = 0.5CV^2$, where C [F/g] is the specific capacitance of the device, and V [V] is the potential change during the discharge. The power densities P [W/kg] of the device were calculated from the GCD curves of two-electrode system using an equation $P = E/t$, where E [W h/kg] is the energy density of the device, and t [s] is the discharge time.

3. Results and discussion

To fabricate the MnO_2-coated CFF hybrid, the polymer present on the carbon fiber fabric was initially removed by heating it at 450 °C. CFF and MnO_4^- are negatively and positively charged in an aqueous solution. Therefore, when CFF reacted with $KMnO_4$ solution under high pressure and temperature inside the autoclave, CFF/MnO_2 hybrid was formed by the electrostatic interaction between CFF and MnO_2. Morphology was analysed for thermally aged CFF and CFF/MnO_2 hybrids prepared after reaction at 175 °C for different processing time such as 1, 4 and 7 h. As seen in the Fig. 1a, after removal of the polymer present on the surface of carbon fiber fabric, it contains carbon fibers with smooth surface having a length of several hundreds of micro meters. After 1 h calcination time, MnO_2 started growing on the surface of CFF and MnO_2 was tightly attached with CFF (Fig. 1b). It was found that the morphology of CFF/MnO_2 hybrid prepared at 4 h is entirely different from pristine CFF and CFF/MnO_2 hybrid prepared at 1 h. When the hydrothermal reaction time was increased from 1 to 4 h, more MnO_2 was grown and it was uniformly distributed on the entire surface of carbon fiber with coral structures of MnO_2 having a uniform length and diameter (Fig. 1c). From the image, it can also be noted that growth of MnO_2 occurred vertically on CFF surface and MnO_2 was not separated from CFF. In the morphology of CFF/MnO_2 hybrid, absence of any MnO_2 from CFF in any other structures indicates that MnO_2 was successfully grown only on the surface of CFF, resulting in coral-like MnO_2 well-coated on CFF surface. These observations support that CFF serve as good substrate for the controlled growth of MnO_2 corals and the interactions between CFF and MnO_2 was strong. In the hierarchal structures of CFF/MnO_2, the inner part of fiber-shaped structure in the horizontal direction is corresponding to the CFF, and the outer coating in the vertical direction throughout the CFF corresponds to the coral-like MnO_2 unique structure. When hydrothermal reaction time was further increased from 4 to 7 h, MnO_2 was started aggregating on the surface of CFF (Fig. 1d). In this paper, coral-like MnO_2 coated CFF prepared at 4 h was directly used for further structural and electrochemical analysis.

The growth mechanism of coral-like MnO_2 structures on CFF surface is explained as follows. When CFF is inside the potassium permanganate solution, positive charges present on the CFF interact with negatively charged manganese ions and form complex. CFF can function as both the supporting substrate and the sacrificial reductant to yield the CFF/MnO_2 composite because the carbon atoms of CFF can convert Mn^{7+} to Mn^{4+}. This reduction leads to the initial formation of MnO_2 nanostructures on CFF surface, which, in

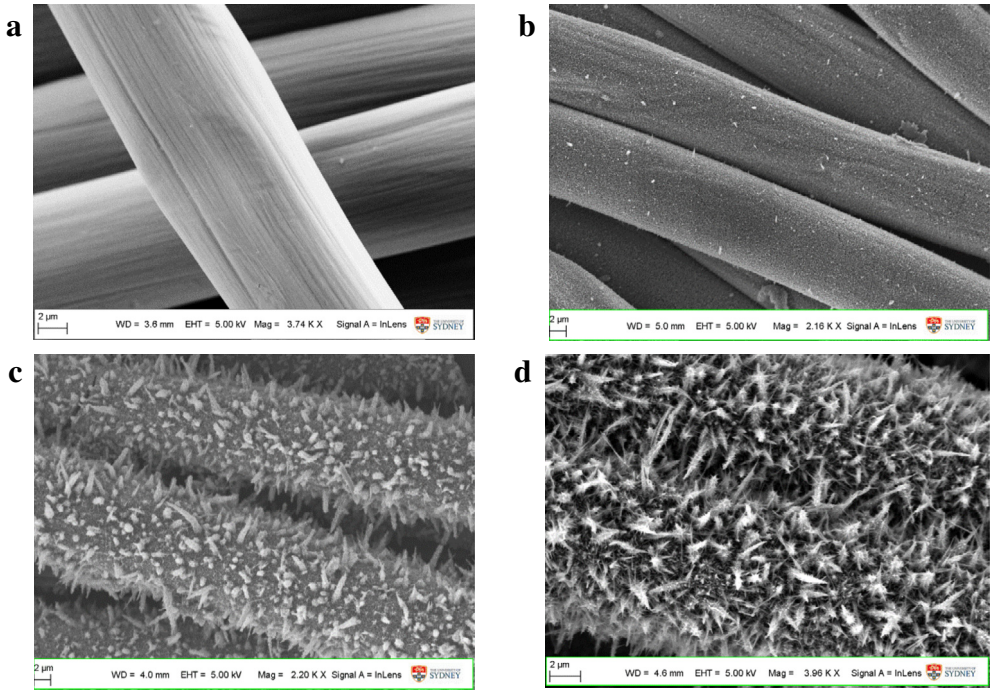

Fig. 1. FE-SEM images of CFF/MnO_2 composites which were prepared at different reaction time, showing the effect of time on the growth of MnO_2 on the carbon fiber fabric. (a) FE-SEM images of thermally aged-CFF, (b) small amount of MnO_2 grown on the CFF surface after 1 h, (c) Coral-like structures of MnO_2 were grown on the CFF surface after 4 h, and (d) Coral-structure of MnO_2 starts to get agglomerated on the CFF surface at 7 h.

turn, function as seeds for further growth to form the coral structures of MnO_2 on the CFF surface as observed on Fig. 1b, and the morphology of the composite can be controlled by varying the hydrothermal reaction time. Thus, after treating the CFF with $KMnO_4$ solution under hydrothermal conditions for 4 h, coral-like MnO_2 structures were densely produced on the CFF surface. Pure CFF was greyish colour and it was changed to dark brown after forming CFF/MnO_2 composite. As seen in Fig. 1c, 4 h is the optimized hydrothermal reaction time to prepare the hierarchical structured CFF/MnO_2 composites. Optimized CFF/MnO_2 hybrid material was further characterized for structural and electrochemical properties to test as supercapacitor.

The XRD patterns obtained from CFF/MnO_2 sample is presented in Fig. 2a. The X-ray diffraction peaks at 12.89°, 29.78°, 36.82°, 39.73°, 43.37°, 47.63°, 54.32°, 57.69°, 61.48°, 65.92°, and 79.44° are attributed to the (110), (310), (211), (330), (301), (510), (411), (600), (521), (002), and (402) crystal planes of α-MnO_2 (JCPDS No. 44-0141). The diffraction peak at 25.24° is ascribed to the carbon fabric, which is marked with an asterisk symbol (*). This characteristic peak is the reflection of graphitic carbon of CFF (JCPDS75-1621). XRD results indicate that the product formed with pure phase without any impurities. The surface composition of the sample was analysed using XPS spectra which is shown in Fig. 2b. As seen in the Figure, the binding energies Mn 2p3/2 and Mn 2p1/2 located at 642.5 and 653.7 eV [24] and the spin energy separation of the two peaks is 11.8 eV, which suggest that the elemental manganese is existed in the sample. The structural features of the composite are further confirmed by Raman measurements. As shown in Fig. 2c, the two strong Raman bands located at 576 and 643 cm^{-1} are induced by the scattering of the different phonons of MnO_2 and Mn-O lattice vibrations in MnO_2 [25], and the strong peaks at 1324 and 1595 cm^{-1} are D and G bands of graphitic carbon of CFF [26]. The Raman bands showed in the spectrum are good agreement with vibrational features of MnO_2 and carbon based materials. These results demonstrate the CFF/MnO_2 hybrid is of high degree of purity and crystallinity. All the above results prove that MnO_2 successfully formed on the surface of carbon fiber fabric. Thermogravimetric analysis showed that the amount of MnO_2 in the CFF/MnO_2 composite was 7.6 wt%.

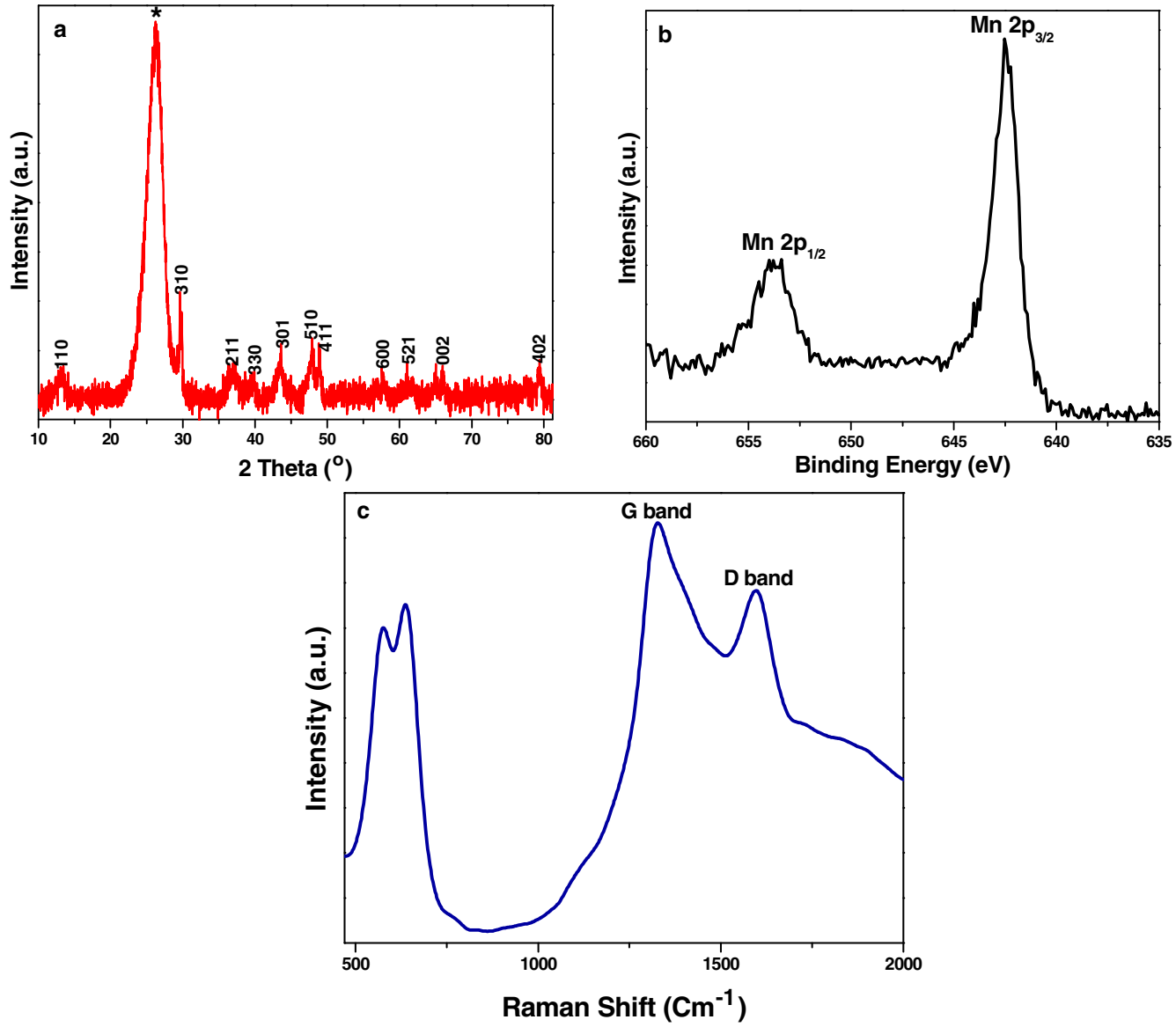

Fig. 2. (a) XRD spectra of CFF/MnO_2 composite, (b) XPS spectra of Mn 2p in the composite, and (c) Raman spectra of CFF/MnO_2 composite prepared with 4 h reaction time.

Cyclic voltammetry (CV) and galvanostatic charge-discharge measurement were conducted in a three-electrode configuration to characterize the capacitive performance of CFF/MnO_2 composites used as supercapacitor electrodes. The CV curve of CFF/MnO_2 composite prepared at 4 h reaction time was showed a typical rectangular box shape in the voltage range of 1 V (Fig. 3a), indicating good charge propagations at the electrode interfaces following the EDLC mechanism. It is noted that the maximal integral area of the CV loop for CFF/MnO_2 composite is much larger than that of thermally aged CFF, indicating that composite formation by combination CFF with MnO_2 produce the synergistic effect in the electrochemical capacitive properties. The current increased with increasing scan rate. When the scan rate was increased from 5 to 200 mV s^{-1}, the CV curve of composite electrode maintained a quasi-rectangular shape with a small distortion (Fig. 3b), indicating good capacitive behavior. According to CV measurements, specific capacitances of 467 F/g were obtained at scan rate of 5 mV/s for CFF/MnO_2 (prepared with 4 h reaction time) in 1.0 M Na_2SO_4 electrolyte, respectively (Fig. 3b), whereas the capacitance of thermally aged CFF was negligible.

The galvanostatic charge-discharge curves of CFF/MnO_2 composite electrode at different current densities are shown in Fig. 3c for the voltage window of 1 V. The shapes of charge-discharge curves are triangular that indicates the electrodes have good capacitive behaviour. According to galvanostatic charge-discharge tests, the specific capacitance of CFF/MnO_2 composite electrode was 463 F/g at current density of 1 A/g (Fig. 3c). The specific capacitance of electrode is 379, 324 and 267 F/g at the current density of 3, 6 and 10 A/g (Fig. 3d). All the above results suggested that the hierarchical structured carbon fiber fabric/MnO_2 hybrid is a potential candidate electrode material with good rate capability, which is due to unique coral-like structure of MnO_2 present on CFF surface. CFF/MnO_2 composite also shows the nearly rectangular feature of CV curves, indicating the combination of double layer and pseudocapacitance behavior that were caused by the synergistic effect between MnO_2 and CFF. The charging curve is nearly symmetric to its corresponding discharging counterpart, indicating good capacitive performance and a highly reversible faradic reaction. CFF/MnO_2 composite electrode possess high specific capacitances (463 F/g), which is due to the synergistic effect between the carbon fibres present in the carbon fabric and the high specific capacitance of coral-like structured MnO_2.

The electrochemical stability of the CFF/MnO_2 composite electrode was examined via cycling tests, and the cycle performance. The cyclability of the electrode is crucial criteria for the practical industrial applications. Fig. 4a shows EIS curves of composite electrode before 1st cycle and after 5000 cycles and the Nyquist plot data shows a steep line at low frequency region, indicating that the fast ion diffusion in the electrode material due to its large charge transfer resistance. The ESR values of composite electrode before and after cycling tests were measured to be 4.1–4.8 Ω. The very low ESR value suggests the electrode has an easy access to

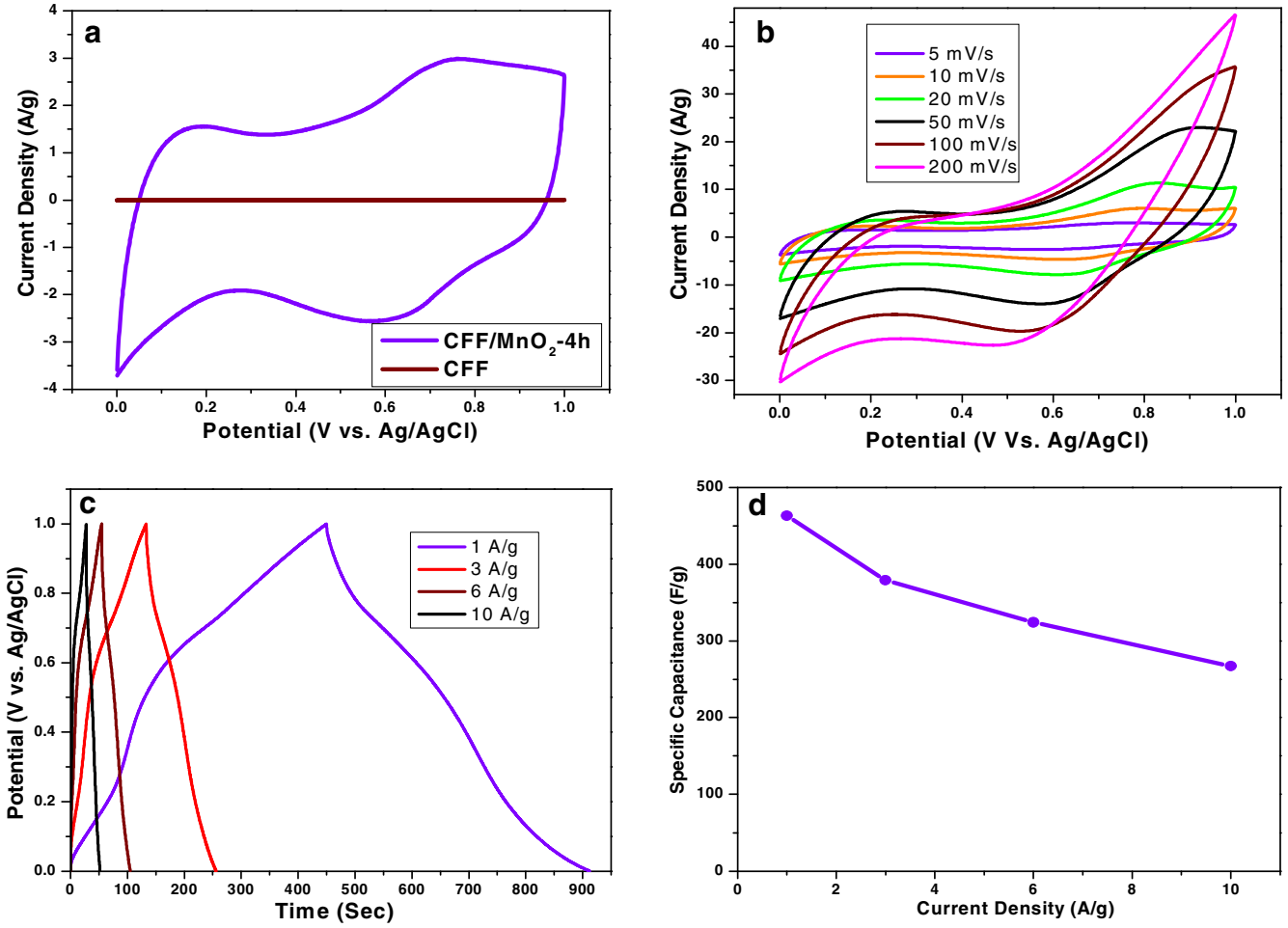

Fig. 3. The electrochemical properties were tested using three-electrode system for CFF and CFF/MnO_2 composite electrode that synthesized with 4 h reaction time. (a) CV curves of CFF and CFF/MnO_2 composite electrode, (b) CV curves of CFF/MnO_2 composite electrode at various scan rates, (c) Galvanostatic charge-discharge curve of CFF/MnO_2 composite electrode at 1 A/g, 3 A/g, 6 A/g and 10 A/g, and (d) the specific capacitance as a function of current density for the composite electrode.

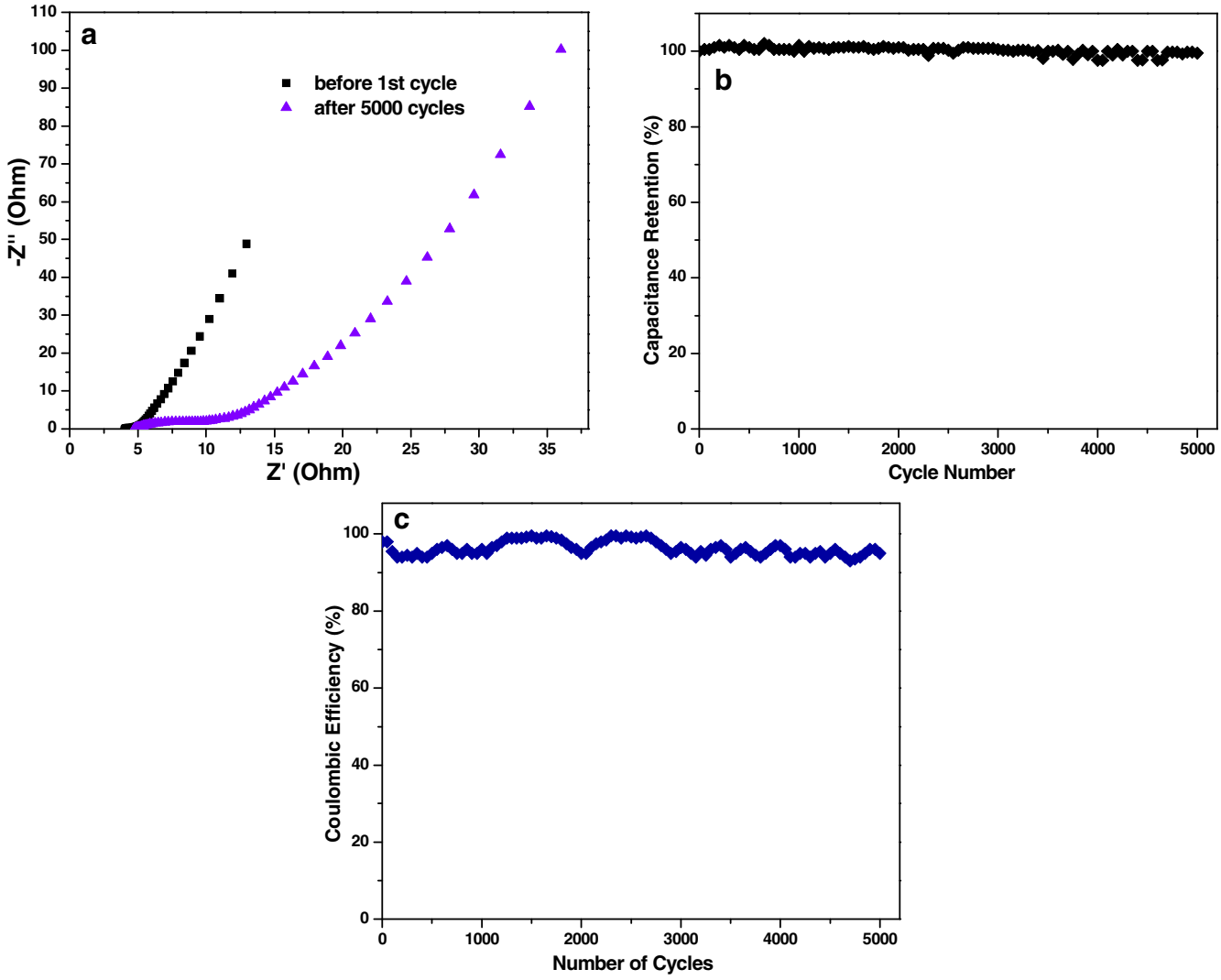

Fig. 4. (a) EIS curve of CFF/MnO_2 composite electrode before and after 5000 cycles, (b) the capacitance retention of composite electrode, and (c) the coulombic efficiency (%) of the electrode. The cyclic stability of electrode was tested for the running cycles of 5000 cycles.

ions for the intercalation and deintercalation. ESR results reveal that low ionic resistance and steeper nature of the slope in the lower frequency region demonstrate the good rate capacitive performance as observed from Fig. 3d. Fig. 4b reveals the outstanding cycling performance of the electrode. After consecutive 5000 cycles, it was found that the charge-discharge capacitance remains equivalent to its initial value (461 F/g) and the retention of capacitance of CFF/MnO_2 hybrid device was 99.7% and the coulombic efficiency remains at 99.3%, indicating that the device is highly stable and no degradation occurs in the sample. The slight reduction in the capacitance can be due to changes in the surface and transport properties of composite electrode during the cycling process.

Energy density is a critical parameter that determines the ability to store the energy of electrochemical devices, which act as a power source for a longer timer. Power density is the rate of energy transfer per mass or area and it determines how fast the energy could be discharged or charged. In order to establish an energy storage device for practical applications, the device is demonstrated in the voltage window of 1.4 V (Fig. 5a) at different scan rates from 2 to 50 mV/s (Fig. 5b) using the two-electrode system. It is found that the CV curves keep their characteristic profile without any polarization at a full voltage, revealing an outstanding electrochemical capacitive performance. Fig. 5c shows the galvanostatic charge-discharge curves of the CFF/MnO_2 hybrid electrode with linear shapes and nearly symmetric charge and discharge curves reveals a fast and reversible Faradic reaction between the electrolyte and MnO_2 nanostructures. Fig. 5d shows the Ragone plots (energy density vs. power density) of the as-fabricated device. It is clearly seen that the device displays an excellent energy density of 20 W h/kg at 175 W/kg, approximately. More remarkably, even when the power density of device reaches 3500 W/kg, the energy density still remains 10 W h/kg, which demonstrates that these devices are promising materials for the fabricating commercial supercapacitors. The superior performance is achieved for the device mainly owing to the high electrochemical capacitive properties of the electrodes and excellent rate capability. The results on the electrochemical studies highlight excellent charge efficiency, high-rate capability and long-cycle lifetime of the CFF/MnO_2 electrode material. Therefore, the electrochemical capacitive results presented here can provide very useful information to take full advantages of MnO_2 coral structures and carbon fiber fabric for high-rate electrochemical capacitors with new designed electrode structures. The outstanding electrochemical performance of as-fabricated CFF/MnO_2-based device indicates its potential application in the energy storage systems.

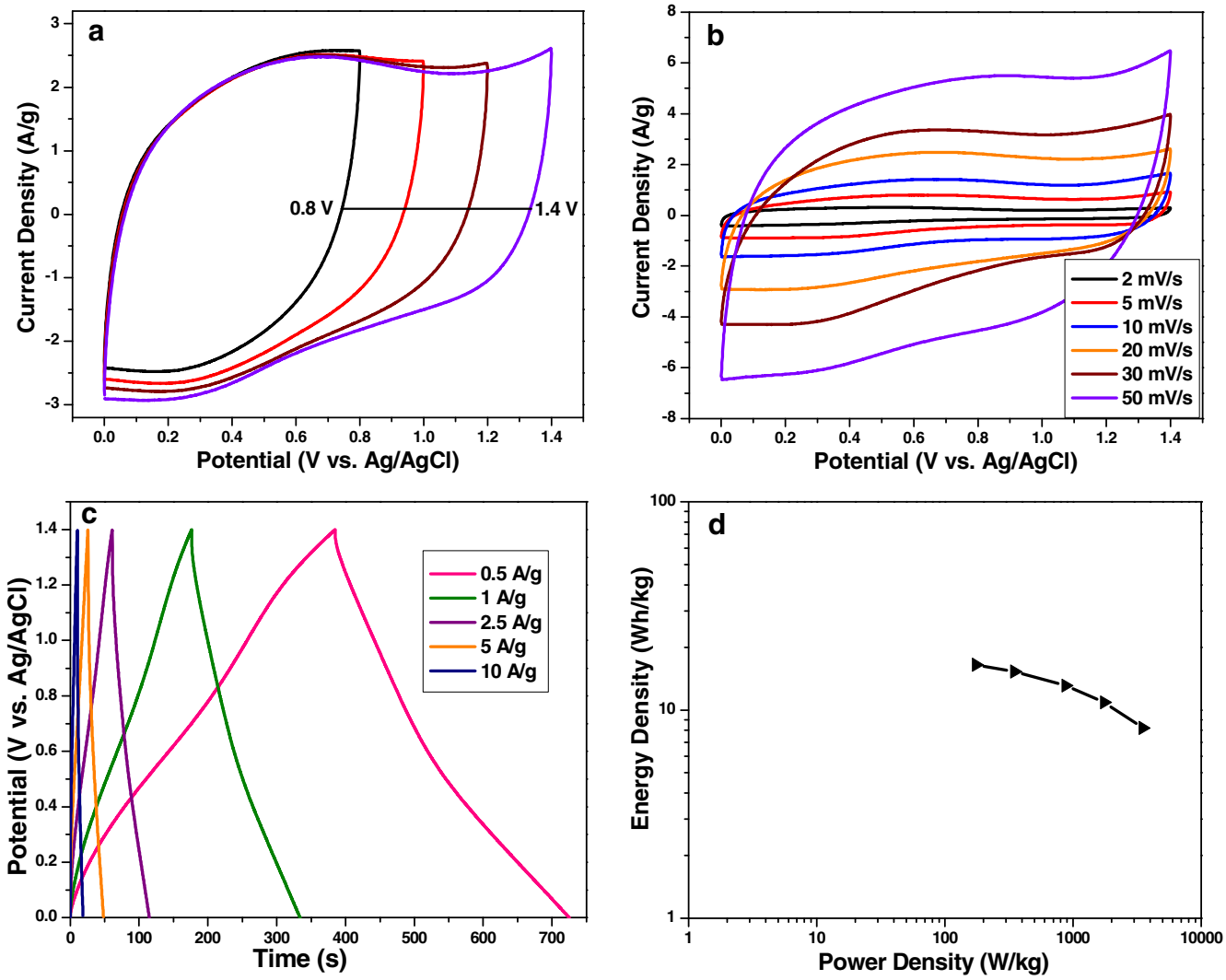

Fig. 5. The electrochemical properties of the device were tested using two-electrode system for the CFF/MnO_2 composite that synthesized with 4 h reaction time. (a) CV curves of the device collected in different scan voltage windows, (b) CV curves at different scan rate, and (c) Ragone plots of the fabricated device.

The results on the capacitive properties of CFF/MnO_2 based device were compared with the supercapacitor properties of some of the carbon-based composite electrodes that have been reported in the literature [27–30]. Hollow spherical porous carbon black based composites were prepared as supercapacitor electrode materials through the in-situ chemical oxidation at by Liu et al. [27]. The prepared porous carbon composite electrodes possessed a specific capacitance of 29 F/g in 1 mol/L H_2SO_4 electrolyte at a current density of 0.1 A/g. The surpercapacitor device was fabricated based on nitrogen-doped activated carbon/carbon nanotubes (N-AC/MWCNTs) by carbonization of polymer-dispersed MWCNTs in a tubular furnace under the nitrogen atmosphere at 700 °C, followed by chemical activation, and N-AC/MWCNTs based electrode displayed the specific capacitance of 103.1 F/g [28]. Caron based composites have been fabricated by growing vertically aligned 1D carbon nanotubes (CNTs) on the surface of 1D carbon nanofibers (CNFs) through an electrospinning method, followed by a calcination process [29], and CNTs/CNFs composite electrode exhibited the specific capacitance of 213.6 F/g in 1 M NaOH electrolyte at a current density of 0.5 A/g and the energy density of 7.42 W h/kg and 60% of rate capability. Pristine CNFs has the specific capacitance of 46 F/g. The effective functionalization of CNTs with CNFs in a vertical direction can provide high electroactive sites that enhance the electron mobility and charge capacitance. Sulfur-doped porous reduced graphene oxide (rGO) was prepared by annealing of graphene oxide-functionalized SiO_2 nanoparticles, and followed by etching with HF [30]. Sulfur-doped porous rGO electrode exhibited the enhanced specific capacitance of 343 F/g at a current density of 0.2 A/g due to the synergistic effect of the hollow framework nanostructure and the effect of sulfur-doping. Hassan et al. reported graphene quantum dots (GQDs), combining porous structure and large surface area to improve the electrochemical capacitive performance of supercapacitors (236 F/g) at a current density of 0.5 A/g, along with photoluminescent properties [22]. Among above carbon-based composite electrochemical capacitors, CFF/MnO_2 electrode demonstrated superior specific capacitance with the stable cycle stability and high energy density and columbic efficiency. These excellent electrochemical properties can be attributed to the well-designed structural advantages and synergistic effect between 1D long CFF and dense uniform-coral structured MnO_2 and they are beneficial to construct free-standing electrodes for the high-performance flexible supercapacitors.

4. Conclusion

CFF was treated under thermal aging process and reacted with $KMnO_4$ solution to fabricate coral-like MnO_2/CFF composite in

which CFF can function as both supporting substrate and sacrificial reductant under hydrothermal conditions. Formation of unique structured MnO_2 on the carbon fiber fabric was proven by FE-SEM, XRD, XPS and Raman investigations. The electrode material containing CFF, coated with coral-like MnO_2 structures, showed a specific capacitance (from GCD) of 463 F/g at 1 A/g in a 1.0 M Na_2SO_4 electrolyte, outstanding retention of capacitance at high charge and discharge rates and good cycling stability. After 5000 cycles, the specific capacitance retention is 99.7%. The newly designed and fabricated durable solid-state flexible device demonstrated excellent stability in a large potential window of 1.4 V and exhibited excellent energy density of 20 W h/kg. In addition to that, our device is low cost with excellent flexibility and high rate capability. The excellent electrochemical properties of the CFF/MnO_2 composite electrode device can be ascribed to the synergistic effect of the unique carbon fibers and high specific capacitance of coral-structured MnO_2. This novel low-cost and high performance device is potential candidate for next-generation electrochemical energy storage systems.

Acknowledgements

The authors wish to acknowledge support from The University of Sydney, Australia for providing research funding to carry out this work.

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