High energy density supercapacitors using macroporous kitchen sponges

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Macroporous, low-cost and recyclable kitchen sponges are explored as effective electrode platforms for supercapacitor devices. A simple and scalable process has been developed to fabricate MnO2–carbon nanotube (CNT)–sponge supercapacitor electrodes using ordinary kitchen sponges. Two organic electrolytes (1 M of tetraethylammonium tetrafluoroborate (Et4NBF4) in propylene carbonate (PC), 1 M of LiClO4 in PC) are utilized with the sponge-based electrodes to improve the energy density of the symmetrical supercapacitors. Compared to aqueous electrolyte (1 M of Na2SO4 in H2O), the energy density of supercapacitors tripled in Et4NBF4 electrolyte, and further increased by six times in LiClO4 electrolyte. The long-term cycling performance in different electrolytes was examined and the morphology changes of the electrode materials were also studied. The good electrochemical performance in both aqueous and organic electrolytes indicates that the MnO2–CNT–sponge is a promising low-cost electrode for energy storage systems.

1. Introduction

Electrical energy storage device usage has seen tremendous growth recently in portable electronic applications. Yet, significant improvement is still needed in the performance of energy storage devices to meet the demand of new applications such as hybrid electric vehicles and grid support applications. Batteries and supercapacitors are two promising energy storage devices that may potentially meet the requirements of future systems. In terms of electrical energy storage, batteries can provide higher energy density than supercapacitors, but their low power density and long-term electrochemical stability are still two major problems that must be overcome. Supercapacitors, on the other hand, have much higher power densities than batteries. However, their relatively low energy density is an obstacle to their widespread use in several potential applications. There are two general approaches to improve the energy density of supercapacitors, according to the equation of \( E = 0.5CV^2 \), where \( C \) and \( V \) are the capacitance and operation voltage window, respectively. One is to enhance the device capacitance. Carbon based materials, such as activated carbon, mesoporous carbon, carbon nanotubes and graphene are among the most frequently used electrode materials for double-layer capacitors due to their stable electrochemical performance. But their capacitances are limited by the electrical charge accumulation at the interface between the electrode and the electrolyte (double-layer capacitance). By incorporating materials that undergo redox reactions in the electrode, the capacitance of these devices can be significantly enhanced. This enhancement is often realized by utilizing transition metal oxides (RuO2, MnO2, SnO2, Co3O4, V2O5, etc.) or electrically conducting polymers (polyaniline, polypyrrole, poly(3,4-ethylenedioxythiophene), etc.) as the electrode materials. Among these materials, MnO2 has received the most attention due to its low cost, large theoretical capacity, and environmental friendliness. As the fast and reversible pseudocapacitive reactions occur mainly at the surface of the electrode active materials, the capacitance of MnO2 is largely dependent on the surface morphology, crystallographic structure and specific surface area. Recently, porous MnO2 with high surface area was reported to contribute to increased specific capacitance for MnO2 based supercapacitors. Lu et al. reported large-area MnO2 for supercapacitor with high specific capacitance. Another more effective strategy to obtain high energy is to enhance the working voltage window of the devices by applying organic electrolytes or ionic liquids, since the energy is related to the square of the working voltage. Ionic liquids are considered as green electrolytes for the future energy storage devices, but their high costs need to be decreased for commercial applications. Nonaqueous organic electrolytes are widely used in commercial energy storage devices by virtue of high voltage range. Most of the organic electrolytes (e.g. tetraethylammonium tetrafluoroborate (Et4NBF4) in propylene carbonate (PC) or acetonitrile, LiClO4 in PC, LiPF6 in ethylene carbonate–dimethyl carbonate (EC–EDC)) are stable even at voltage up to 4 V. Recently, Izadi-Najafabadi et al. reported a stable supercapacitor with high voltage range of 4 V by using 1 M Et4NBF4 in propylene carbonate as electrolyte. Pech et al. studied high-power micro-supercapacitors based on carbon onion by using the same electrolyte. Nam et al. demonstrated the electrochemical behaviors of MnO2 and carbon nanotube composite by using 1 M LiClO4 in PC in the three-electrode configuration.
However, it is well accepted that measurements in three-electrode configuration give higher values of specific capacitance compared to the typical two-electrode configuration.22 Stoller and Ruoff pointed out that the two-electrode configuration is more practical to assess the electrochemical performance of supercapacitors.23

There has been tremendous research on developing low-cost, flexible electrodes for supercapacitor applications.24 Pushparaj et al. reported paper based nanocomposites for energy storage devices.24 Hu et al. investigated energy storage devices on highly conductive paper and textile.26–28 Zhou et al. presented a transparent supercapacitor based on In2O3 and carbon nanotube film.29 Meng et al. synthesized a paper-like polymer supercapacitor for flexible and wearable electronic devices.30

Previously, our group reported supercapacitors based on carbon cloth, textile and sponge in aqueous electrolytes.8,31–34 Sea sponges are aquatic animals that are full of pores and channels on their multicellular bodies. Inspired by their porous nature, synthetic sponges are made of cellulose or polyester, used commonly for packing, household cleaning and personal care. In particular, we found that the commercially available synthetic sponge acted as an excellent substrate for the fabrication of supercapacitor devices.34 In this article we have combined macroporous household-sponges with organic electrolytes to fabricate supercapacitor devices with high energy density. The macroporous nature of the sponges is attractive because it permits facile electrolyte flow to the entire electrode surface where redox reactions can take place. At the same time, organic electrolytes permit larger voltage window compared to aqueous electrolytes. We show that by combining these effects, significant improvement in energy density can be achieved.

2. Experimental

2.1. Materials

The kitchen sponge used in this study is commercially available (Tamimi supermarket, Saudi Arabia). Single walled carbon nanotubes (P3-SWNTs) were purchased from Carbon Solutions, Inc. Manganese nitrate (Mn(NO3)2·4H2O), sodium nitrate (NaNO3), sodium sulfate (Na2SO4), sodium dodecylbenzenesulfonate (SDBS) and lithium perchlorate (LiClO4) were all obtained from Sigma Aldrich. Tetraethylammonium tetrafluoroborate (Et4NBF4) and anhydride propylene carbonate (PC) were acquired from Novolyte. High purity deionized water (18.2 MΩ cm, Milli Q) was used throughout the whole experiment. All chemicals were used without further purification.

2.2. Fabrication process of MnO2–CNT–sponge supercapacitors

The fabrication process of the MnO2–CNT–sponge electrode is similar to our previous reports,31,34 which is schematically illustrated in Fig. 1. Briefly, CNT ink with concentration of 0.8 mg ml−1 in 10 mg ml−1 of SDBS water solution was prepared by applying a 5 min bath sonication (Branson 2510) followed by a 30 min tip sonication (UP400S, Ultrasonic Processor, Hielser; 400 W, 24 kHz). A piece of kitchen sponge cleaned using water and ethanol was then dipped into the CNT ink and removed. A typical photograph of the sponge used in this study is shown in Fig. 1a. The CNT–sponge was washed with an abundant amount of water to get rid of the surfactant after drying in an electrical oven for 1 hour. Then the surfactant-free CNT–sponge was put in a vacuum oven for another three hours to remove the water completely (Fig. 1b). After CNT coating, the sponge becomes highly conductive. Subsequently, a three-electrode configuration was set up in a beaker to electodeposit nanoflower-like porous MnO2 onto the surface of the CNT–sponge. CNT–sponge with an area of 1 cm × 2 cm, Pt wire and Ag/AgCl (Bio logic) were used as the working, counter and reference electrodes, respectively. The electrochemical deposition solution consists of 20 mM of Mn(NO3)2 and 100 mM of NaNO3. The nanoflower-like MnO2 was obtained by applying a galvanostatic deposition with a current density of 500 µA cm−2 for different durations in an electrochemical workstation (CH Instruments 660D). The residual electodeposition solution on the MnO2–CNT–sponge electrodes was carefully washed away by water and the electrodes were dried in a vacuum oven for 10 hours to remove the water completely. Fig. 1c shows that the top half of the CNT–sponge working electrode has been covered by MnO2, which can be clearly identified by its darker color compared to the bottom half of the CNT–sponge electrode. A schematic illustration of the structure of the MnO2–CNT–sponge electrode at this stage of the process (Fig. 1c) is shown in the middle of Fig. 1. The schematic depicts the flower-like morphology of the MnO2 nanoparticles uniformly deposited on the skeleton of 3D macroporous CNT–sponge. All samples were measured in the typical two-electrode coin cells (CR2032, MTI) with MnO2–CNT–sponge (1 cm × 1 cm) used as both the cathode and anode electrodes. The two electrodes were sandwiched by a polypropylene separator (25 µm thick, Celgard 3401) and assembled into a coin cell. Fig. 1d demonstrates the assembled coin cell supercapacitor using two identical MnO2–CNT–sponge binder-free electrodes. No binder or conductive agent was needed in the full cell preparation. The material’s mass loading on the sponge is obtained by measuring the weight difference before and after CNT coating and MnO2 deposition by using a microbalance (Mettler Toledo XP26, resolution of 1 µg). The CNT–sponge plays the role of conductive current collector. The electrolytes used in this study include 1 M of Na2SO4 in H2O, 1 M of Et4NBF4 in PC and 1 M of LiClO4 in PC. For the organic electrolytes, the coin cells were sealed in an Argon-filled glove box (MBRAUN MB200G; H2O < 1 ppm, O2 < 1 ppm).

2.3. Material characterization

The crystallographic structure of our samples was identified by X-ray diffraction (XRD; D8 Advance bulk power XRD, Bruker). The microstructure and morphology were characterized with scanning electron microscopy (SEM; Quanta 600 and Nova Nano 630, FEI), transmission electron microscopy (TEM; Titan 80–300 kV (ST) TEM, FEI). The elemental information of MnO2 was carried out by X-ray photoelectron spectroscopy (XPS; Kratos AXIS Ultra DLD). BET surface area measurement (ASAP 2420, surface area and pore size analyzer, Micromeritics) was conducted by Argon adsorption and desorption at a bath temperature of −185.86 °C.
2.4. Electrochemical measurements

Cyclic voltammetry (CV) was carried out over the scan rates from 1 mV s\(^{-1}\) to 100 mV s\(^{-1}\). Galvanostatic charge and discharge (CD) was tested with the current density from 0.5 A g\(^{-1}\) to 10 A g\(^{-1}\). The working voltage windows were between 0 and 0.85 V for aqueous electrolyte, and between 0 and 2.5 V for organic electrolytes. All measurements were taken at room temperature using VMP3 multichannel electrochemical workstation (Biologic).

The equations used to calculate the specific capacitance\(^3\) from CV and CD are given in the following:

\[
C = \frac{I}{dV/dt} \quad (1)
\]
where \(C\) is the capacitance, \(I\) is the current, and \(dV/dt\) is the potential scan rate.

\[
C_s = \frac{4C}{M} \quad (2)
\]
where \(C_s\) is the specific capacitance, \(M\) is the total mass of active materials in the two electrodes.

The maximum energy density\(^\text{44-46}\) was obtained by using eqn (3):

\[
E = \frac{1}{2}C_sV^2 \quad (3)
\]
3. Results and discussion

The porous structure of the sponge allows excellent water uptake and provides large surface area. The simple and low-cost process provides an effective approach to fabricate flexible supercapacitor electrodes based on a variety of substrates. The sponge-based electrode offers several advantages over other substrates. First, the 3D macroporous nature of the sponge electrode allows facile electrolyte flow to the entire surface of the electrodes where redox reactions can take place. Second, the 3D macroporous structure of the sponge allows CNTs coating and MnO₂ deposition on the skeleton of the sponge easily and uniformly. Third, the smooth inner and outer sides of the skeleton make the sponge virtually free of junctions, which enhances the electrical conductivity of the CNT–sponge. Fourth, the macropores (ranging from 100 to 500 μm) of the sponge provide enough space for the heavy deposition of electrode materials. Fifth, the soft, lightweight and flexible nature of the sponge makes it ideal for wearable and flexible devices. Sixth, the low cost of the sponge substrates may contribute to the future low-cost energy storage applications. The macroporous hierarchical nature of the sponge is retained even after the uniform coating of CNTs and heavy deposition of MnO₂ (Fig. 2a). The MnO₂ deposited on the CNT–sponge has a porous flower-like morphology, as shown in Fig. 2b. After a 10 min deposition of MnO₂, the skeleton of the sponge can be fully covered by the MnO₂, with almost no CNT exposed to the surface. A thick layer of MnO₂ (~1.1 μm) has been formed after a 30 min electrodeposition process, which can be identified by the cross-section scanning electron microscopy (SEM) image in Fig. 2c, and the thickness of the MnO₂ layer is increased with the deposition time. Transmission electron microscopy (TEM) images in Fig. 2d indicate that the MnO₂ flower-like nanoparticles have a polycrystalline nature, which consist of many nanoflakes. X-ray diffraction (XRD) patterns of MnO₂–CNT–sponge electrode show that the polycrystalline MnO₂ has the ε-MnO₂ structure (JCPDS 00-030-0820) (Fig. 3a). The MnO₂ is further characterized by X-ray photoelectron spectroscopy (XPS) to identify the oxidation state of Mn (Fig. 3b). The two characteristic peaks located at binding energy of 654 eV and 642 eV belong to the Mn 2P₁/₂ and Mn 2P₃/₂, respectively. The typical Mn 2P spectra revealed that the oxidation state of Mn is +4, which agrees well with literature.⁶,₃₅ Since the electrochemical performance is partly dependent on the surface condition of active materials, it is important to conduct Brunauer–Emmett–Teller (BET) surface analysis to the deposited MnO₂ on the electrode. The BET surface area measurement results shown in Fig. 3c was conducted by Argon adsorption and desorption at bath temperature of −185.86 °C.
The measured value of BET specific surface area (SSA) is 174 m$^2$ g$^{-1}$, which is among one of the highest reported values for different morphologies of MnO$_2$ nanomaterials.$^9$ For example, Brousse et al. prepared various structures of crystalline MnO$_2$ with SSA larger than 125 m$^2$ g$^{-1}$, reaching a maximal specific capacitance of 150 F g$^{-1}$. Ni et al. synthesized MnO$_2$ nanowires and nanoflowers by hydrothermal method with high SSA up to 226 m$^2$ g$^{-1}$ and specific capacitance of 121.5 F g$^{-1}$. Yu et al. demonstrated spherical o-MnO$_2$ by using a combustion process, with an SSA of 43 m$^2$ g$^{-1}$ and specific capacitance of 123 F g$^{-1}$. Fig. 3d indicates that the average pore size of MnO$_2$ is about 3.2 nm. The large SSA and porous open structure of MnO$_2$ on macroporous CNT–sponge will contribute to the fast ion adsorption–desorption and reversible redox reactions as discussed in the next section.

The electrochemical properties of the MnO$_2$–CNT–sponge supercapacitors in different electrolytes were characterized by cyclic voltammetry (CV) and galvanostatic charge–discharge (CD) measurements. The CV curves of devices of 20 min electrodeposition of MnO$_2$ (Fig. 4a) exhibit nearly rectangular shapes for a wide scan range from 1 mV s$^{-1}$ to 100 mV s$^{-1}$ in 1 M of Na$_2$SO$_4$ in H$_2$O; (c and d) 1 M of Et$_4$NBF$_4$ in PC; and (e and f) 1 M of LiClO$_4$ in PC, respectively.

The symmetrical nature of the CD curves indicates ideal
By replacing aqueous electrolyte with organic electrolytes, the working voltages of supercapacitors can be steadily increased to 2.5 V, almost three times higher than the voltage in aqueous electrolyte (Fig. 4c–f). However, compared to aqueous electrolyte, the shapes of the CV curves in organic electrolytes deviated from rectangular, especially at high scan rates (Fig. 4c). The currents were lower than the ones in aqueous electrolyte for the same scan rates. This is partly because the electroconductivity of the organic electrolyte is lower than that of aqueous electrolyte. It is well known that the viscosity of water is much lower than that of organic solvents. Thus, the electrolyte ions move slower in organic electrolytes. It is interesting that the obtained currents in 1 M of LiClO4 are higher than that in 1 M of Et4NBF4 for the same scan rates in CV (Fig. 4e), which leads to longer charge–discharge time for the same current density in CD curves (Fig. 4f).

To study the performance of devices with different deposition times per mass loadings, we conducted CV measurements and the comparison was made for all supercapacitor devices, as shown in Fig. 5. At the same scan rate of 20 mV s⁻¹, the current increased with the electrodeposition time, indicating that more electroactive materials are involved in the electrochemical charge storage. In 1 M of Na2SO4 electrolyte, the CV curves of the supercapacitors changed from a perfect rectangular shape to a quasi-rectangular shape, when the sample deposition time increased from 20 min to 60 min (Fig. 5a). Similarly, the CV curves deviated from a rectangular shape with the MnO2 mass loading on the electrodes in organic electrolytes (Fig. 5b and c). The fully and heavily coated semiconducting MnO2 on the CNT–sponge reduced the conductivity of the electrode, hence limited the charge storage capability. It is also worth noting that the device currents in the organic electrolytes were lower than the currents in the aqueous electrolyte for the same electrode material, indicating a lower capacitance in both organic electrolytes. In addition, it was found that the current density in 1 M of LiClO4 electrolyte was much higher and the CV curve more rectangular than that in 1 M of Et4NBF4 at the same scan rate (Fig. 5d), showing that the specific capacitance in LiClO4 was higher than that in Et4NBF4.

Fig. 6 summarizes the relationship between specific capacitance and scan rate for the three electrolytes. Generally, the specific capacitance decreased with the scan rate and the mass loading of active materials, as expected. For supercapacitors in 1 M of Na2SO4, the specific capacitance decreased gradually with the scan rate. Symmetric supercapacitor based on MnO2–CNT–sponge electrodes prepared by 20 minute electrodeposition of MnO2 exhibited a specific capacitance of 240 F g⁻¹ at a scan rate of 1 mV s⁻¹. The specific capacitance decreased to 120 F g⁻¹ at...
100 mV s$^{-1}$ (Fig. 6a). In comparison, the specific capacitances decreased quickly at low scan rates in organic electrolytes, but then became stable at high scan rates (Fig. 6b and c). This is mainly caused by the difference in viscosity of the solvents and the resulting ion diffusion rates. The viscosity of PC (2.512 x 10$^{-3}$ Pa s at room temperature) is higher than that of H$_2$O (8.9 x 10$^{-4}$ Pa s at room temperature), resulting in slower cation movement in PC compared to H$_2$O. Therefore, the stored electrical charges depended strongly on the rates of charge-discharge for organic electrolytes. It is interesting that the specific capacitance in 1 M of LiClO$_4$ is almost two times higher than that in 1 M of Et$_4$NBF$_4$ for the same device. Et$_4$NBF$_4$ and LiClO$_4$ are two widely used organic electrolytes for the energy storage devices. It is proposed that the difference of specific capacitance in these two organic electrolytes was determined by the electrode materials and the electrolytes. It was reported that the electroconductivity of 1 M Et$_4$NBF$_4$ in PC is higher than that of 1 M LiClO$_4$ in PC at room temperature. However, the crystallographic radii of cation Et$_4$N$^+$ (0.337 nm) and anion BF$_4^-$ (0.232 nm) are much larger than that of Li$^+$ (0.09 nm) and ClO$_4^-$ (0.215 nm), respectively. Considering that the average pore size for MnO$_2$ is 3.2 nm, the small size of Li$^+$ may diffuse more quickly and absorb more easily onto the pore walls of porous MnO$_2$ compared to the larger size of Et$_4$N$. This agrees well with the traditional point of view on the charge storage mechanism for porous supercapacitor electrodes. Therefore, the supercapacitors in Et$_4$NBF$_4$ behave more like a double layer energy storage device, resulting in low specific capacitance. In contrast, the pseudocapacitive energy storage mechanism is more dominant in supercapacitors with LiClO$_4$ electrolyte, leading to higher specific capacitance.

A key performance metric in this study is the stored energy density in supercapacitors using the three electrolytes. Fig. 6d shows that compared to the aqueous electrolyte, the energy densities in 1 M of Et$_4$NBF$_4$ were three times as high as the aqueous electrolyte (1 M of Na$_2$SO$_4$) despite its lower specific
capacitance. Moreover, the energy densities in 1 M of LiClO$_4$ were six times higher than that in 1 M of Na$_2$SO$_4$, which significantly improved the energy density of the supercapacitors. The maximal energy density value of 152 W h kg$^{-1}$ obtained in 1 M of LiClO$_4$ electrolyte was comparable to some of the highest reported values.$^{44-46}$ At the high scan rate of 50 mV s$^{-1}$, the energy density was still high around 72 W h kg$^{-1}$. However, the energy density of the full device is only one fourth of the maximal energy density based on the single electrode material, meaning that the energy density of the supercapacitors still needs to be improved a lot to compete with the high energy density of batteries.

The long cycling tests were utilized to evaluate the electrochemical stability of the supercapacitors in these three different electrolytes (Fig. 7). The excellent electrochemical stability of supercapacitors with 60 minute deposition of MnO$_2$ in 1 M of Na$_2$SO$_4$ under 10 A g$^{-1}$ showed that about 91.8% of the initial capacitance has been retained after 10 000 cycles of charge–discharge. The cycling performance of supercapacitors in organic electrolytes was not as good as that in aqueous electrolyte. Results revealed that 75.5% and 61.6% of initial capacitance can be retained after 10 000 cycles for the same materials in 1 M of Et$_4$NBF$_4$ and 1 M of LiClO$_4$, respectively. The stability curves of supercapacitors in organic electrolytes showed a fast initial drop in the first 2000 cycles, but then started to stabilize. It is believed that the cycling performance of supercapacitors in organic electrolytes suffers from the degradation of the reversible reactions at the electrolyte–electrode material interface. In order to further understand the long-term cycling behaviors in different electrolytes, we disassembled the cell to examine the morphology changes of the electrode materials after the 10 000 cycles, as shown in Fig. 8. The SEM images showed that the overall morphologies of the 3D porous structures of the electrode materials were retained. Specifically, the porous nature of the MnO$_2$ in Na$_2$SO$_4$ did not change much, which confirmed the excellent stability of the supercapacitor in aqueous electrolytes (Fig. 8a and b). However, some cracking in the electrode material can be observed after cycling in Et$_4$NBF$_4$, although the individual flower-like nanoparticle morphology has been retained (Fig. 8c and d). Some micro-cracking took place after cycling in LiClO$_4$ based supercapacitors (Fig. 8e). Moreover, the surface of the individual MnO$_2$ nanoparticles collapsed gently and formed a continuous less porous film (Fig. 8f). The morphology changes of MnO$_2$ layer caused the drop in cycling performance for supercapacitors in organic electrolytes. However, it has been reported that the stability can be enhanced significantly by a thin layer of conductive wrapping on the surface of the electrodes.$^{47}$

4. Conclusion

In summary, we have demonstrated a simple and scalable process to prepare supercapacitor devices using macroporous sponge electrodes and organic electrolytes. The fabricated supercapacitors exhibited reasonably good electrochemical performance in both aqueous and organic electrolytes. Importantly, compared to aqueous electrolyte, the energy density of supercapacitors in 1 M of Et$_4$NBF$_4$ tripled and the value was further improved by six times when using 1 M of LiClO$_4$ as the electrolyte. The cycling performance of supercapacitors in organic electrolytes was inferior to aqueous electrolytes, but the devices in organic electrolytes retained a significant energy density advantage even after 10 000 cycles.

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References


Fig. 8 Morphology of the electrodes after 10 000 cycles of charge–discharge in (a and b) 1 M of Na$_2$SO$_4$; (c and d) 1 M of Et$_4$NBF$_4$ and (e and f) 1 M of LiClO$_4$. 

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