Highly Dense CeO$_2$ Nano-fibers and MnO$_2$ Nanoflowers Composite Electrode for Energy Storage Application

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Abstract

A high demand of energy storage devices has boosted research for fabricating ultra-efficient supercapacitors with better energy density and cycling stability. Most of metal oxide-based supercapacitors have limited performance because metal oxides are poor electrical conductors, which hinder the optimal output of the device. In this work, we adopted a novel approach to improve the conductivity of the electrodes and charge storing capability of the device by making a hybrid composite structure. Both CeO$_2$ nanofibers and MnO$_2$ nano-flower-like structure are developed using low temperature based hydrothermal synthesis route. The structure and morphology of MnO$_2$ nano-flower-like and CeO$_2$ nanofibers were characterized by field emission scanning electron microscopy (FESEM). FESEM confirmed highly dense CeO$_2$ nanofibers that were ultra-thin in diameter and reproducible nanoflowers are formed during MnO$_2$ synthesis. This composite metal oxide nanostructured electrode made out of CeO$_2$ and different weight percentage of MnO$_2$ is a promising material that can operate at higher voltage due to its superior oxidation performance and shows larger specific capacitance value that enables it to hold more charge during operation. This approach boosts the charge storage capability of the composite electrode materials electrochemically as well as by the pseudo-capacitive effect obtained from MnO$_2$ nano-flower-like and CeO$_2$ nanofibers. Electrochemical measurement of CeO$_2$ nanofibers and MnO$_2$ nano-flowers-hybrid composite shows improved specific capacitance value with very large cycling stability.

Introduction

Energy has been predicted to be one of the biggest problems that the human race is expected to face within the next 50 years. With the advancement in technologies and industries, there is a very large depletion in the fossil fuel reserves which leaves a void in the sustainable and consistent source of energy. Therefore, it makes it imperative to improve on the existing renewable sources of energy as well as in the energy storage devices (Maheswari and Muralidharan, 2015). Scientists, all across the world, have put in a lot of efforts in finding new materials to improve energy storage devices such as batteries, capacitors and super-capacitors (Shovo et al., 2015).

Super-capacitors have unique properties of fast charging times without being overcharged, a high specific power density and virtually endless cycle life. Moreover, the low resistances in the super-capacitors allow high load currents as well as an excellent low temperature charge-discharge performance. All these properties make super-capacitor to be an ideal candidate for applications in computer systems, medical systems, regenerative braking in automobiles, power supplies, inverters, cameras, welders, uninterruptible power Supply (UPS) systems, audio systems and emergency lighting. However, despite all these advantages, super-capacitors still have limitations in terms of their specific energy, operational voltage window, self-discharge and cycling stability.

Super-capacitors can be classified into two different categories: electrical double layer capacitors (EDLC) and pseudo-capacitors. In electrical double layer capacitors, the charge storing capability comes from the electrostatic charge accumulation at the electrode-electrolyte interface which is a non-faradic
process; while the pseudo-capacitors are able to store energy through a fast and reversible faradic reaction, which originate from transition metal oxides or conducting polymers present in the electrode materials (Shuvo et al., 2015).

Common metal oxides that have been researched as possible candidates to be used as electrodes in super-capacitors include: RuO₂, MnO₂, NiO, Co₃O₄, SnO₂, ZnO, TiO₂, V₂O₅, CuO, Fe₂O₃, WO₃, etc. (Jadhav et al., 2015). CeO₂ nano-structures have shown a superior oxidation performance and therefore a high specific capacitance (Maheswari and Muralidharan, 2015; Rajib et al., 2015). Although CeO₂ has good redox characteristics, it suffers from poor conductivity and structure stability. Its lattice always expanded when Ce⁴⁺ was reduced to Ce³⁺. Consequently, it is not to be used alone for electrode material. To meet the requirement of high-performance super-capacitors, good capacitance performance, rate capability, energy density and cycle stability simultaneously, it is essential to combine CeO₂ with carbon materials or MnO₂ (Maheswari and Muralidharan, 2015; Rajib et al., 2015; Gao et al., 2012). Carbon materials can largely compensate for CeO₂ deficiencies in view of their fine conductivity, developed porosity and large specific surface area (Shuvo et al., 2013). On the other hand, MnO₂ is a highly attractive positive electrode material, benefiting from its low cost, abundance, and remarkable electrochemical performance in aqueous electrolytes. In this study, CeO₂ nano-flowers and MnO₂ nano-structures were grown using a low temperature hydrothermal synthesis route. The electrode for the super-capacitor was fabricated using a hybrid composite of the nano-flowers, conductive porous carbon and long chain polymers. The hybrid composite helps in improving the conductivity of the electrodes as opposed to transition metal oxide and thereby improves the specific capacitance of the super-capacitor.

**Materials and Methods**

**Synthesis of Cerium Oxide Nano-Fibers**

Cerium oxide nano-fibers (CeO₂ nano-fibers) were prepared using a one-step hydrothermal method. 6.4 g of sodium hydroxide (NaOH, Sigma-Aldrich, 97%) was dissolved in 16 mL of deionized (DI) water. When solution was clear, 0.5 g of cerium (III) sulfate hydrate Ce₂(SO₄)₃ (Alfa-Aesar, 99.999%) and 16 mL ethylene glycol (TCI America, >99.0%) were added to the solution under continuous stirring for 2 mins. The solution was then transferred into a Teflon-lined stainless steel autoclave (100 mL). The autoclave was sealed and maintained at 140°C for 12 h. After the reaction was completed, the autoclave was allowed to cool to room temperature naturally. The solid grey precipitate was filtered, washed three times with distilled water and ethanol to removes impurities. Finally the black precipitate was dried in a furnace at 80°C (Bugayeva et al., 2007).

**Synthesis MnO₂ Nano-Structures**

MnO₂ nano-structures were prepared using a facile hydrothermal route. In typical 1.71 g of MnSO₄ (Alfa-Aesar, 99.99%) and 2.72 g of KMnO₄ (Home Science Tools, 99.99%) were dissolved in distilled water (35 mL) in room temperature and followed by adding 2mL of H₂SO₄ (Fischer Scientific). Stirring the solution for 3 mins in room temperature, the solution was then transferred into a Teflon-lined stainless steel autoclave (100 mL). The autoclave was sealed and maintained at 140°C for 6 h. After the reaction was completed, the autoclave was allowed to cool to room temperature naturally. The solid black precipitate was filtered, washed three times with distilled water and ethanol to removes impurities. Finally the black precipitate was dried in a furnace at 80°C (Bugayeva et al., 2007).

**Electrode Fabrication**

To fabricate the working CeO₂ electrode, polyvinylidene fluoride (PVDF) (Alfa-Aesar) was used as binding material. Slurry consisting of CeO₂ nano-flowers, PVDF and conductive carbon (Alfa-Aesar, 99%) in a weight ratio of 9:1:1 dissolved in N-Methyl-2-Pyrrolidone (NMP) (Alfa-Aesar, 99%) was formed. The slurry was coated on a stainless-steel disk using Doctor Blade’s technique and dried at 125°C for 12 h. Similarly, electrodes with CeO₂/MnO₂ composite was prepared by preparing a slurry with CeO₂ nano-flowers and MnO₂ nano-flowers mixed in a ratio of 1:2 (Lin and Chowdhury, 2010; Terribile et al., 1998).

**Super-Capacitor Assembly**

The super-capacitors were assembled in a coin cell (CR2032) using the electrodes. A 6 M solution of potassium hydroxide (KOH) (Sigma-Aldrich, 99.99%) was used as an electrolyte and commercially available paper towels cut into the size of the coin cell as a separator (Azam et al., 2013).

**Surface Morphology**

FESEM by Hitachi SU8010 was used to investigate the surface morphology of all the electrodes prior to assembly into the coin cells to verify the grown nanomaterials.

**Electrochemical characterization**

The fabricated coin cell was characterized for its electrochemical properties using a CH Instruments electrochemical workstation to determine the cyclic voltammetry (CV) and charge-discharge performance.

**Results and Discussion**

FESEM was used to determine the size and the morphology of the fabricated CeO₂ nano-flowers and electrodes, as shown in Figure 1. As seen from these images, CeO₂ nano-flowers were interconnected between the porous carbons. It was also found
that the nano-fibers have a diameter less than 30 nm.

Scheme 1 shows the possible reaction scheme with ceria nano-fibers Ce$_2$(SO$_4$)$_4$ used as the precursor. Ethyl glycol is adsorbed on the surface of CeO$_2$ nanoparticles (equation (1)). The surfactant plays an important role in the preparation of ceria nano-structure (Lin et al.; 2010). Sodium hydroxide and deionized water (D.I.) water were added into precursor (equation (3, 3a, 3b)). Nucleation and growth occurred under hydrothermal conditions at 140°C for 12 h. The solid grey precipitate was washed three times with distilled water and ethanol to remove any impurities. The gray powder was dried at 60°C for 12 h (equation (4)). The size and shape of nano-fibers are influenced through the reaction time, reaction temperature and ratio in the initial solution. According to Kuen-Song Lin et al., 2010, the first complete reaction scheme for 1-D ceria preparation in 1998 reported by Terribile et al., 1998.

\[ \text{CeOH} \rightarrow \text{CeO}^- + H^+ \leftrightarrow \text{CeO}^- \text{EG}^+ \]  \hspace{1cm} (1)

According to Terribile et al. (1998), the soluble isolated Ce$^{3+}$, under basic conditions, oxidizes to a hydrated Ce$^{4+}$ formulated as Ce(H$_2$O)$_x$(OH)$_{4-y}$, (equation (2))

\[ 2\text{Ce}^{3+} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Ce}^4 \text{(H}_2\text{O})_x(\text{OH})_{4-y}^+ \]  \hspace{1cm} (2)

Which then readily combines with the surfactant in accordance with reaction, (equation (3a and 3b)),

\[ n\text{Ce}^4 \text{(H}_2\text{O})_x(\text{OH})_{4-y}^+ \leftrightarrow (-\text{CeH}_2\text{O}_0\text{CeH}_0\text{H}_x)_n \cdot m\text{H}_2\text{O} + \text{H}_2\text{O} \]  \hspace{1cm} (3a)

This step can also be viewed as the two individual steps for the formation of polymeric hydroxide, which then reacts with the soft template as cationic surfactants (ethylene glycol) (equations (3a) and (3b)) at a pH value well above that of the isoelectric point of ceria.

\[ (-\text{CeH}_2\text{O}_0\text{CeH}_0\text{H}_x)_n \cdot m\text{H}_2\text{O} + \text{surf} \leftrightarrow n\text{CeO}_2(0-\text{surf})_x \cdot m\text{H}_2\text{O} \]  \hspace{1cm} (3b)

Under these conditions, surfactant and the deprotonated hydroxyl group form an inorganic/organic composite, which upon drying and calcination (equations (4) and (5)) originates pure mesoporous cerium oxide with high surface area,

\[ n\text{CeO}_2(0-\text{surf})_x \cdot m\text{H}_2\text{O} \rightarrow n\text{CeO}_2(0-\text{surf})_x + m\text{H}_2\text{O} \]  \hspace{1cm} (4)

\[ \text{CeO}_2(0-\text{surf})_x \rightarrow \text{CeO}_2 + \text{org} + \text{CO}_2 \]  \hspace{1cm} (5)

According to reaction (3), Terribile et al. observed that the surfactant is able to promote oxidation of Ce$^{3+}$ to Ce$^{4+}$ and form of hydroxide oxide in solution, before drying. The presence of more surface Ce$^{4+}$ atoms is a consequence of the smaller particles formed with the surfactants with a higher number of exposed Ce$^{3+}$ atom (Terribile et al., 1998; Li et al., 2010).

The SEM of MnO$_2$ nano-structures are displayed in Figure 2. As shown in Figure 2, the morphology of MnO$_2$ were nanoflowers-like shape with approximately 3 µm, which contains nanorods with uniform length approximately to 2 µm, Figure 2 (a). Figure 2 (b) shows hybrid porous carbon of CeO$_2$ nano-fibers with between MnO$_2$ nano-structures.

The scheme 2 illustrates the possible formation process of
the MnO$_2$ nano-structures (Feng et al., 2014). During the preparation of the MnO$_2$ nano-structures, KMnO$_4$ plays the role in oxidating Mn$^{2+}$ ion to MnO$_2$. Firstly, the tiny crystalline nuclei of MnO$_2$ are generated from Mn$^{2+}$ by the oxidation in the supersaturated solution and grow into nanoparticles. The nucleation process could be represented as:

\[
3\text{MnSO}_4 + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 + 4\text{H}_2\text{O} \xrightarrow{\text{calcination}} 5\text{Mn(SO}_4)_2 + 2\text{K}_2\text{SO}_4 + 9\text{H}_2\text{O} \quad (6)
\]

Therefore, sulfuric acid is added to decrease the reaction rate, and the morphology can be modulated. The tiny nanoparticles spontaneously aggregate into long nanowires. With minimizing interfacial energies, the nanowires wrap with each other incompactly to form a flowers-shaped MnO$_2$ nano-structures.

CV and galvanostatic charge/discharge were used to understand the electrochemical behavior for the CeO$_2$ nano-fibers with porous carbon. 6 M KOH in DI water was used as the electrolyte solution. Coin cell was assembled using CeO$_2$ nanofibers with porous carbon electrode. Figure 3 (a-c) show CV at different scan rates of 1 V/s, 2 V/s, 3 V/s, 4 V/s and 5 V/s with voltage windows between 1 to 3 V. The area under each CV curve suggests that super-capacitor have a good electrochemical stability (Mendoza et al., 2012; Chena et al., 2011).

Specific capacitance, $C_s$ (Fg-1) for super-capacitor was calculated by the following equation:

\[
C_s = \frac{4I}{m \Delta V} \quad (7)
\]

Where I is the discharge current (A), m is the mass of active material (g), $\Delta t$ is the discharge time (secs), and $\Delta V$ is the...
Figure 4. Galvanostatic charge discharge for CeO$_2$ at a potential window of 3 V with a discharge current of 0.25 A/g.

Figure 6. Galvanostatic charge discharge of CeO$_2$ nano-fibers and MnO$_2$ nano-structures (1:1 ratio) with porous carbon at a potential window of 2 V with a discharge current of 0.25 A/g.

Figure 5. (a-c) Cyclic voltammetry of CeO$_2$ nano-fibers and MnO$_2$ nanoflowers (1:2 ratio) with porous carbon at scan rates of 1 V/s - 5 V/s in an electrolyte of 6 M KOH in D.I. water.

discharge voltage (V).

Figure 4. Shows the galvanostatic charge discharge curves for CeO$_2$ nano-fibers with porous carbon with potential voltage window of 1 V, 2 V and 3 V. The charge and discharge showed a symmetrical behavior which indicates the good electrochemical capacitive property and high reversibility (Shovo et al 2013; Chena et al., 2011; Gao et al., 2012).

CeO$_2$ nano-fibers and MnO$_2$ nano-structures were used to understand the role of CeO$_2$ nano-fibers in electrochemical performance. Fig 5 (a-c), 6, 7 (a-c) and 8 show the CV and galvanostatic charge/discharge of CeO$_2$ nano-fibers and MnO$_2$ nano-structures with porous carbon with 3:9:1 ratio. A 6 M KOH in D.I. water was used as the electrolyte solution for assembling electrode testing set up as coin cells. Figure 5 (a-c) shows cyclic voltammetry at different scan rates of 1 V/s, 2 V/s, 3 V/s, 4 V/s and 5 V/s with a voltage window between 1 to 3V.

The specific capacitance of CeO$_2$ nano-fibers and MnO$_2$ nano-structures (1:1 ratio) with porous carbon was found to be 4.81 F/g at 2 V, compared to the specific capacitance of CeO$_2$ nano-fibers with porous carbon, which was 23.7 F/g at 3 V.

The specific capacitance of CeO$_2$ nano-fibers and MnO$_2$ nano-structures (1:2) with porous carbon were 162.6 F/g at 1.48 V compared to the specific capacitance of CeO$_2$ nano-fibers with porous carbon which were 23.7 F/g at 3 V. Figure 8 shows the galvanostatic charge discharge of CeO$_2$ nano-fibers and MnO$_2$ nano-structures (1:2 ratio) with porous carbon.
Conclusion

We report on a novel approach to improve the conductivity of the electrodes and charge storing capability of the device by making a hybrid composite structure with conducting porous carbon and long chain polymers through a simple, efficient and low temperature based hydrothermal synthesis route. The formation of thin (less than 30 nm in diameter) nano-fibers with long length enabled us to improve on the charge storage efficiency of the device as confirmed by the FESEM images. The simplicity and the efficiency of the process still leaves room for improvement to the nano-structure of the hydrothermally grown CeO$_2$ that can, possibly, lead to an improvement to the specific capacitance and operating voltage window of the super-capacitors.

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References


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