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Nanostructured MnO_2 for Electrochemical Capacitor

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1. Introduction

Energy is always a priority issue for human beings. In the 21st century, pollution due to combustion of fossil fuel, which has triggered the biggest environmental issue "global warming", has become a worldwide problem. The renewable and clean energy sources as well as efficient use of energy are highly necessary to make our economy, environment, society, and human species sustainable (Simon & Gogotsi, 2008; Xu et al., 2010). Energy storage, an intermediate step to energy, creates a new approach to use energy versatility, cleanly, and efficiently. Electrochemical capacitors (ECs) or supercapacitors (SCs), as a new energy storage/conversion device, have gained enormous attention owing to their higher power density and longer cycle life compared to secondary batteries and higher energy density than conventional electrical double-layer capacitors (EDLC). It is also characterized by environmental friendliness, high safety, and good efficiency and can be operated in a wide temperature range with a nearly infinitely long cycle life. Therefore, supercapacitors have been applied in and are showing potential application in communications, transportation, consumer electronics, aviation, and related technologies (Siegwart, 2001; Burke, 2000; Yoda & Lshihara, 1997; Becker, 1957; Yoshino et al., 2004).

Supercapacitors or ultracapacitors, ECs can be fully charged or discharged in seconds. Their energy density (about 5 Wh/kg) is lower than in batteries, but a much higher power delivery or uptake (10 kW/kg) can be achieved for shorter times (a few seconds) (Simon & Gogotsi, 2008; Siegwart, 2001). They have had an important role in complementing or replacing batteries in the energy storage field, such as for uninterruptible power supplies and load-levelling. A recent report by the US Department of Energy assigns equal importance to supercapacitors and batteries for future energy storage systems and articles on supercapacitors appearing in business and popular magazines show increasing interest by the general public in this topic (Simon & Gogotsi, 2008; Whittingham et al., 2004).

Depending on the charge storage mechanism as well as the active materials used, several types of ECs can be distinguished. One group, Electric double layer capacitor (EDLC) uses carbon as the electrodes and stores charge in the electric field at the interface. A second group, known as pseudo-capacitors or redox supercapacitors, uses fast and reversible surface or near-surface reactions for charge storage, which use transition metal oxides and conducting polymers as active materials. Hybrid capacitors, combining a capacitive or pseudo-capacitive electrode with a battery electrode, are the latest kind of EC, which benefit from both the capacitor and the battery properties.

As pseudocapacitors electrode materials, metal oxides, which store energy through highly reversible surface redox (faradic) reactions in addition to the electric double-layer storage, attracted increasing attention in recent years. Among the available metal oxides materials, RuO_2 shows the best performance with high specific capacitance (720 F/g) and 1.4 V potential window, but it is very expensive and toxic, which greatly limits its commercialization (Toupin et al., 2002; Wang et al., 2008; Reddy et al., 2009). Other metal oxides have also been tested as possible candidates for electrochemical supercapacitor devices. Interesting capacitance values have been reported for IrO_2 or CoOx electrodes but they are still expensive compounds (Conway 1997; Lin, 1998). On the other hand, NiO, $Ni(OH)_2$, MnO_2 systems seem more promising due to their lower cost. However, NiO and $Ni(OH)_2$ cannot be used at voltage windows above 0.6 V (Xing et al., 2004). Extensive studies have been conducted to explore alternative economic supercapacitor materials with good performance. Among of the being studied metal oxides, manganese oxide is an attractive candidate for supercapacitor designs due to its availability, low cost, low toxicity and wide voltage windows (Jeong & Manthiram, 2002; Reddy & Reddy, 2003; Reddy & Reddy, 2004). Then, one potential disadvantage of MnOx relative to RuO_2 as a psuedocapacitive material is its lack of metallic conductivity (Long et al., 2003).

It is well known that the theoretical value of specific capacitance of MnO_2 is ~1380 F/g. At present, only 30% or even lower of theoretical value can be obtained (Xu et al., 2010). To further improve the performance of MnO_2-based supercapacitor, it is necessary to design new MnO_2 materials with excellent performance and further understand its charge storage mechanism as electrode of Ecs. In this chapter, the physicochemical features, synthesis methods, and charge storage mechanism of MnO_2 as well as the current status of MnO_2-based supercapacitors are summarized and discussed in detail. The future opportunities and challenges related to MnO_2-based supercapacitors have also been proposed.

2. Crystalline structures of different MnO_2

As an important functional metal oxide, manganese dioxide is one of the most attractive inorganic materials because of its physical and chemical properties and wide applications in catalysis, ion exchange, molecular adsorption, biosensor, and particularly, energy storage (Qi et al.1999; Shen et al., 1993; Cao & Suib,1994). MnO_2 is a best representation of a general class of materials exhibiting a rich chemistry. MnO_2 is a very interesting and attractive material because it is diverse in crystalline structure and rich in Mn valence. Normally, MnO_2 is a complex and nonstoichiometric oxide and often contains foreign cations, physisorbed and structural water molecular, and structural vacancies. Because of the presence of foreign species, the average valence of Mn in MnO_2 generally locates between 3 and 4. However, the variety of MnO_2 in structure and valence comes from only one basic structural unit, MnO_6 octahedron. It acts likes string in a string theory world. In a MnO_2 world, this little tiny MnO_6 octahedron enables the buildup of a colorful and diverse world, in which every version is just one combination of MnO_6 octahedra (Qi et al., 1999; Tsuj & Abe, 1985). The combination of MnO_6 octahedra provides a veritable “toolbox” , from which to design, optimize, and synthesize specific MnO_2 for a specific purpose. Therefore, it is necessary to give a brief review on crystalline structures of MnO_2.

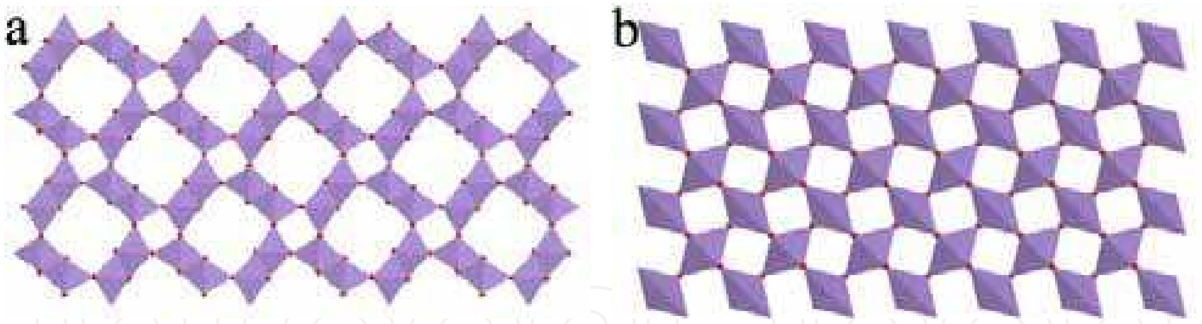

Fig. 1. The structure of α-MnO_2 with double chains of [MnO_6] octahedron (a) and β- MnO_2 with single chains of [MnO_6] octahedron (b).

Fig. 1 illustrates the schematic structure of a-MnO_2 and β-MnO_2. As shown in Fig. 1a, a-MnO_2 is consist of interlinking double chains of octahedral MnO_6 and an interstitial space comprised of one-dimensional channels of relative dimensions (2×2) and (1×1) that extend in a direction parallel to the c axis of a tetragonal unit cell (Wang & Li, 2002). The schematic structure of β-MnO_2 is different to that of a-MnO_2, which is composed of single chains of the octahedral [MnO_6] (Fig. 1b).

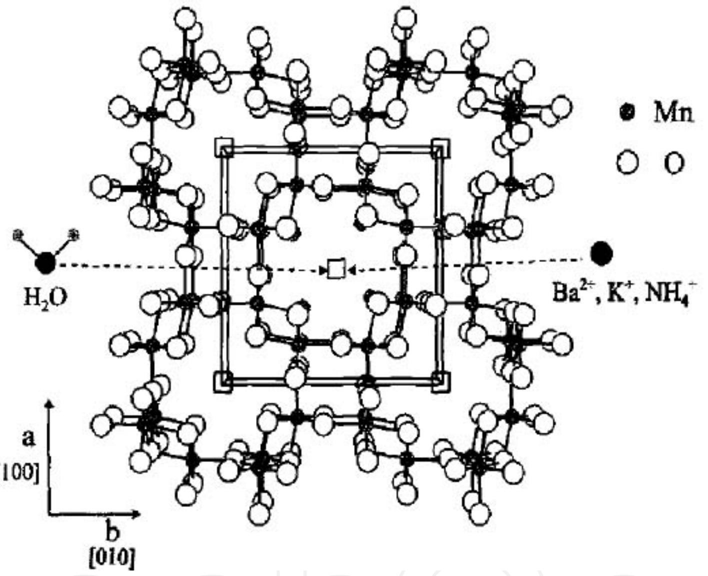

Fig. 2. Schematic structure of a-MnO_2 structure as viewed down the c-unit cell axis (Johnson et al., 1997).

In order further understand the structure of a-MnO_2 more clearly, a [001] projection of the a-MnO_2 framework structure is given in Fig. 2. The structure has tetragonal symmetry with space group I4/m. The framework has an interstitial space consisting of unidimensional channels of relative size (1 ×1) and (2 ×2). The (1 ×1) channels represent the interstitial space that is found in β-MnO_2 (rutile-type structure). Cations such as Ba^{2+} (hollandite), and K^+ (cryptomelane) and NH_4^+ or O^{2-} anions [from H_2O (or H_3O^+) and Li_2O] that stabilize the a-MnO_2 framework partially occupy sites at the center of the (2×2) channels at a special position (0, 0, z), usually close to (0, 0, 1/2) (Johnson et al., 1997; Rossouw et al., 1992). If oxygen occupies this site, the structure adopts a distorted close-packed oxygen array, with the close-packed oxygen layers parallel to the (110) planes. The α-MnO_2 framework structure in natural (mineral) form is stabilized by large cations such as Ba^{2+} (hollandite) and

K^+ (cryptomelane) or by NH_4^+ ions located within the large (2×2) channels of the structure (Brock et al.,1998).

The intergrowth of two or more tunnel phases occurs also in the manganese oxides. An irregular intergrowth of (1×1) tunnels (pyrolusite) and (1×2) tunnels (ramsdellite) in the structure of γ-MnO_2 (nsutite) is well known to electrochemists (Devaraj & Munichandraiah, 2008). Fig. 3 is the structure of γ-MnO_2. This intergrowth structure can be described in terms of De Wolff disorder and microtwinning. Ramsdellite is composed of double MnO_6 chains (Fig. 3b) linked together to form tunnels with a (1×2) octahedra cross-section. Ramsdellite is only observed in nature while the synthetic product γ-MnO_2 contains pyrolusite (1×1) tunnels intergrowths (de Wolff defects) and microtwinnings (Johnson et al., 1997; Portehault et al., 2009; Hill &Verbaere, 2004;. Wolff & P, 1959).

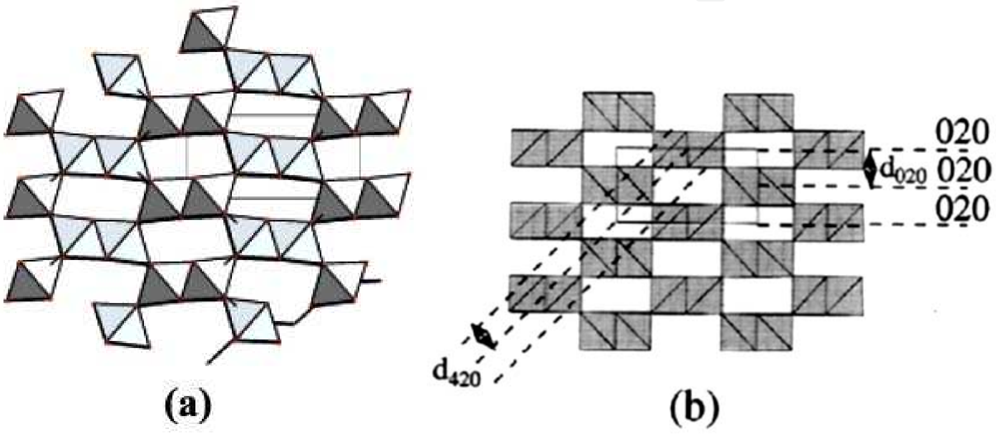

Fig. 3. a. The structure of γ-MnO_2 with irregular intergrowth of (1×1) tunnels (pyrolusite) and (1×2) tunnels (ramsdellite), b, ramsdellite-MnO_2 (Johnson et al., . 1997; Devaraj & Munichandraiah, 2008).

δ- MnO_2 (Fig. 4) is a 2D layered structure with an interlayer separation of ~7 Å. It has a significant amount of water and stabilizing cations such as Na^+ or K^+ between the sheets of MnO_6 octahedra (Devaraj & Munichandraiah, 2008; Ma et al., 2004).

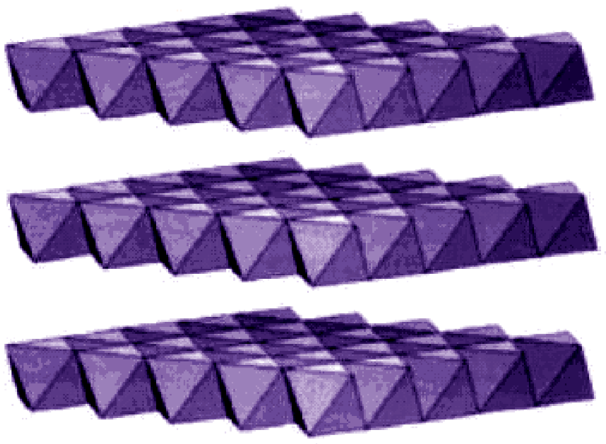

Fig. 4. The structure of δ- MnO_2 with 2D layered structure.

In the spinel structure of λ-MnO_2, the Mn ions occupy the 16d sites in *Fd*3*m* and form a three-dimensional (3D) array of corner-sharing tetrahedra as shown in Fig. 5.

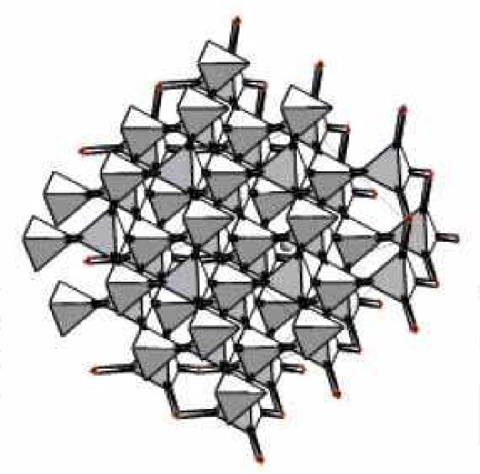

Fig. 5. The structure of λ- MnO_2 with spinel structure (Devaraj & Munichandraiah, 2008).

XRD patterns of MnO_2 listed above are shown in Fig. 6. The curves marked α and α(m) exhibit the patterns of α-crystallographic form (JCPDS no. 44-0141). The curves marked β and γ displayed the XRD patterns of β- (JCPDS no. 24-0735) and γ- (JCPDS no. 14-0644) crystallographic forms of MnO_2, respectively. Broad peaks at 2θ = 12.2, 24.8, 37.0, and 65.4° in the pattern marked δ correspond to δ-MnO_2 (JCPDS no. 18-0802). This pattern of the sample marked λ was indexed to cubic symmetry with space group *Fd*3*m* of λ-MnO_2 (JCPDS no. 44-0992, $a = b = c = 8.03$ Å).

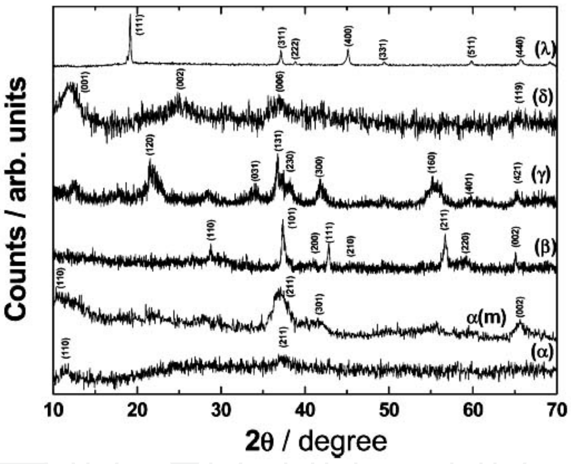

Fig. 6. XRD pattern of α-, β-, γ-, δ- and λ-MnO_2. The data were recorded at a sweep rate of 0.5° min^{-1} using Cu Kα source (Devaraj & Munichandraiah, 2008).

Complex intergrowths of the (2×2) tunnels (hollandite) and the (2×3) tunnel (romanechite) in fibrous manganese oxide minerals and intergrowth of (3×2) tunnels to (3×7) tunnels in natural todorokite have been detected by HRTEM measurements (Qi et al.,1999). However, almost all the intergrowths are random, so that regular periodicity or superstructure may not be apparent. In here, we don't review it again.

3. Synthesis methods of MnO_2

Because of the variety in structures, MnO_2 can be synthesized in dozens of crystalline and disordered forms, each with unique physicochemical properties, which are determined by the synthesis methods and post treatment procedures. The physicochemical properties in turn influence its electrochemical performance. Therefore, it is necessary to give a brief review on the synthesis of MnO_2.

3.1 Hydrothermal process

Hydrothermal process is a very useful and unique method for the preparation of different structured manganese oxides. By controlling the synthesis process, treatment temperature, pH value, post synthesis procedures, etc., different micro-structured MnO_2 could be obtained. Recently, many MnO_2 with different crystal structure and morphology have been successfully prepared by hydrothermal method (Zhou et al., 2011; Zhang et al., 2011; Jiang et al., 2011; Tang et al., 2011; Song et al., 2010; Liu et al., 2006; Yang et al., 2010).

In our previous work (Xu et al., 2007), α-MnO_2 hollow spheres and hollow urchins are synthesized via a simple hydrothermal process without using any template or organic surfactant. Further changing the treatment temperature, polyhedron structured β- MnO_2 be prepared.

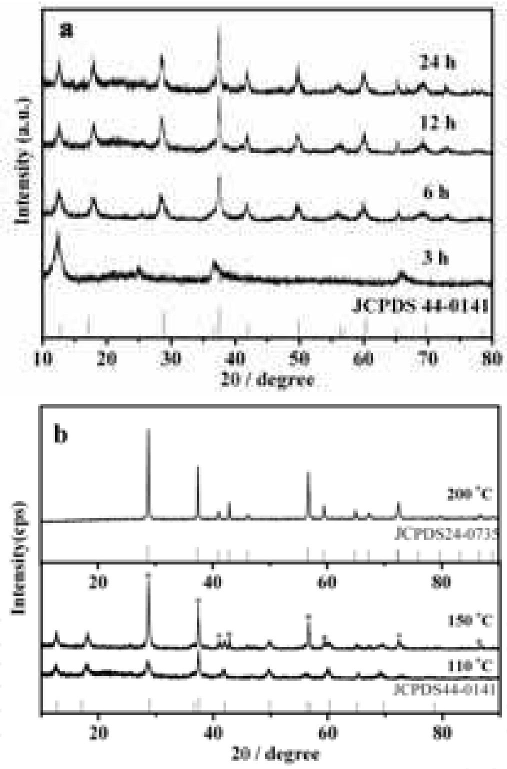

Fig. 7. a. XRD patterns for the standard values and the samples obtained at 110 °C for different reaction time; b, XRD patterns for the standard values and the samples obtained at different reaction temperature for 12 h.

It can be seen from Figure 7a, at 110 °C, after 3 h hydrothermal reaction, only four very weak peaks are observed, and the main peaks can be indexed to α-MnO_2 phase (JCPDS, card no: 44-0141), suggesting the α-MnO_2 forms in the process of hydrothermal treatment for 3h. With increasing of hydrothermal reaction time, all of these peaks intensities increase significantly, with lattice constants of a = 4.399 Å and c = 2.874 Å, which match very well with the standard XRD pattern (Figure 7a, bottom). However, in Figure 7b, for the XRD patterns of the sample obtained at 150 °C for 12 h, the intensive diffraction peaks appeared at 12.68, 18.06, 28.68, 37.36, 49.88, and 60.16 °, respectively, are assigned to the characteristic peaks for α-MnO_2, and the peaks occurred at 28.68, 37.36, 41.04, 42.82, 46.02, 56.65, 59.37, 72.38 and 86.18 °, respectively, should be ascribed to the characteristic peaks for β-MnO_2. Hence, the sample should be composed of α-MnO_2 and β-MnO_2. When the reaction temperature enhanced to 200 °C, the XRD pattern of the obtained sample shows highly crystalline β-MnO_2, all of the diffraction peaks can be indexed to β-MnO_2 (JCPDS 24-0735), which demonstrating the high purity of the β-MnO_2 may obtain in the process of hydrothermal treatment at 200 °C.

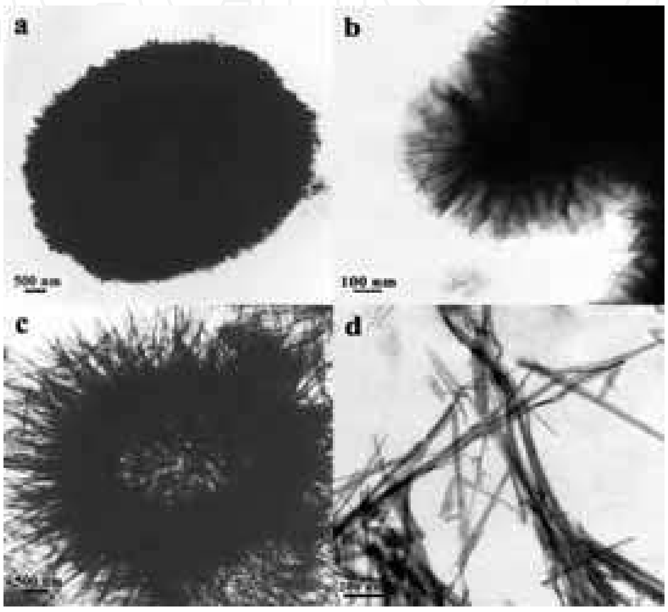

Fig. 8. TEM of α-MnO_2 obtained at 110 °C for different reaction time (a, 3 h; b, 6 h; c, 12 h; d, 24 h).

As shown in Fig. 8, several obvious evolution stages could be clearly observed. In the initial stage (shorter reaction time, 3 h), only a close-grained sphere is observed; after hydrothermal reaction for 6 h, the surface of α-MnO_2 sphere has changed to flower-like nanostructure which consists of nanoflakes and nanowires. When the reaction time was prolonged to 12 h, an interior cavity sphere is easily observed; after reaction for 24 h, the sphere structures disappear completely, only nanorods can be observed.

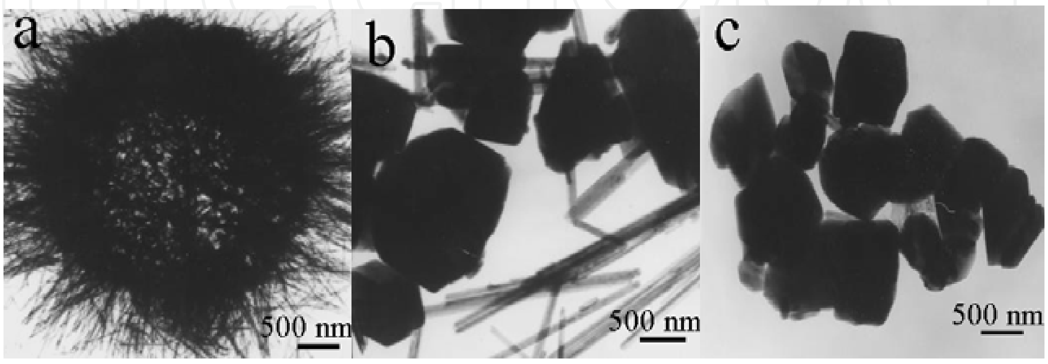

Fig. 9. TEM of MnO_2 obtained at different reaction temperature for 12 h (a, 110 °C; b, 150 °C; c, 200 °C).

The morphology of the products obtained at different temperature for 12 h were also observed by using TEM. Fig. 9a demonstrates the interior cavity spheres of the sample obtained by hydrothermal reaction at 110 °C. Upon increasing the reaction temperature to 150 °C, the sphere structure of the products disappeared completely, as shown in Fig. 9b, a mixture of nanorods and blocks were observed. When the reaction temperature enhanced to 200 °C, the polyhedron structure develops further and becomes the dominant product with good crystallization and regular morphology (in Fig. 9c).

3.2 Template directed synthesis

Since electrolyte diffusion within the bulk electrode materials is a rate-limiting step, a crucial issue to improve the rate capacity of ECs is to optimize the electrolyte transport paths without sacrificing electron transport. Hence, the development of novel synthesis routes to low dimensional and porous manganese oxides attracted increasing attention of scientists, since these compounds offer promising electrochemical properties and a rich application in many field (Wei et al., 2011). Host–guest compounds represent a new and promising class of material that can be used for the controlled preparation of complex organized structures or composites in the nanoscale regime.

3.2.1 Carbon template

CNTs are the most representative nanostructured carbons with one dimensional tubular structure and exhibit outstanding physicochemical properties such as high electrical conductivity, high mechanical strength, high chemical stability, and high activated surface areas. By using CNTs as template and reducing agent, heterogeneous nucleation of MnO_2 were deposited on CNTs, and MnO_2–CNT composite was obtained in literatures (Subramanian et al., 2006; Yan et al., 2009; Ma et al., 2008; Jiang et al., 2009; Xue et al., 2009).

Ordered mesoporous carbon materials are aother attractive type with a nanostructured hierarchy with desirable electrolyte transpnort routes. Dong et al. presented a novel MnO_2/mesoporous carbon composite structure, synthesized by embedding MnO_2 into the mesoporous carbon walls through the redox reaction between permanganate ions and carbons (Dong et al., 2006). A similar process was applied to obtain Mn_2O_3-templated mesoporous carbon composite (Zhang et al., 2009). A kind of MnO_2/mesoporous carbon composite was prepared by Zhu S. M. et al. through incorporating MnO_2 nanoparticles inside the pore channels of CMK-3 ordered mesoporous carbon under sonochemical process (Zhu et al., 2005).

Three dimensional (3D)-assemblies of silica spheres were used as a hard template to synthesize porous carbon materials with large mesopores (~100 nm) and large surface areas reaching up to 900 m^2/ g. Birnessite-type MnO_2 was deposited by a chemical co-precipitation method in the porous network (Lei et al., 2008).

In our past work (Xu et al., 2010), porous MnO_2 was synthesized via a simple and efficient in situ reduction process by using different carbon materials as sacrificed template and reducing agent. It is discovered that the microstructure of the samples has a remarkable effect on the electrochemical capacitive behaviors of the samples, of which the mesoprous MnO_2 prepared by using mesoporous carbon provides good conductivity and high capacitance.

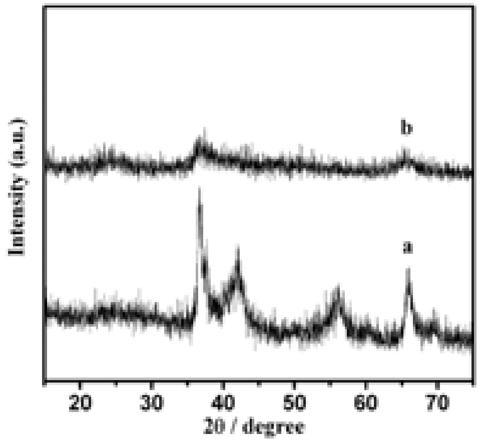

Fig. 10. XRD patterns of the samples obtained by using different carbon sources (a, CNTs; b, Mesoporous carbon)

As shown in Fig. 10, in which all of the diffraction peaks for the sample obtained from CNTs can be indexed to δ-MnO_2. Compared with the XRD peaks of the sample obtained by using CNTs, those of the sample obtained by mesoporous carbon as carbon sources are weak and wide, presents amorphous MnO_2 type, which may be relevant to different raw materials.

Fig. 11 displays the image of the MnO_2 prepared by using CNTs as carbon source is composed of uniform spheres and its built-up interleaving sheets or flakes (Fig. 11b). Interestingly, the MnO_2 prepared by using mesoporous carbon tends to form porous clusters (Fig. 11c). To reveal the actual structure of the cluster, high magnification FESEM were recorded. Fig. 11d clearly shows the surface structure of MnO_2 cluster, which consists of very small nanoparticle and nanowires. The detail structure of the MnO_2 fabricated by using mesoporous carbon was further investigated by TEM.

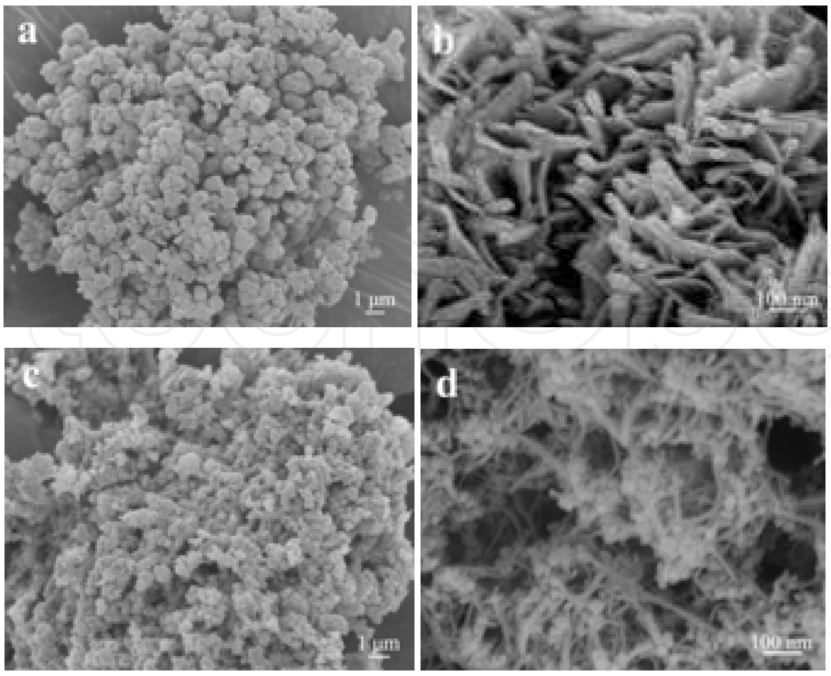

Fig. 11. SEM images of carbon sources and products. (a and b, MnO_2 obtained using CNTs; c and d, MnO_2 obtained using mesoporous carbon.)

A panoramic TEM image of the MnO_2 fabricated by using mesoporous carbon (Fig. 12a) gives more detail structure and morphology, in which lots of nanoflakelets and nanowires intercross with each other to form a slack MnO_2 cluster for a high specific surface area. A high-magnification TEM image (Fig. 11b) further illustrates that the flake has many small pores.

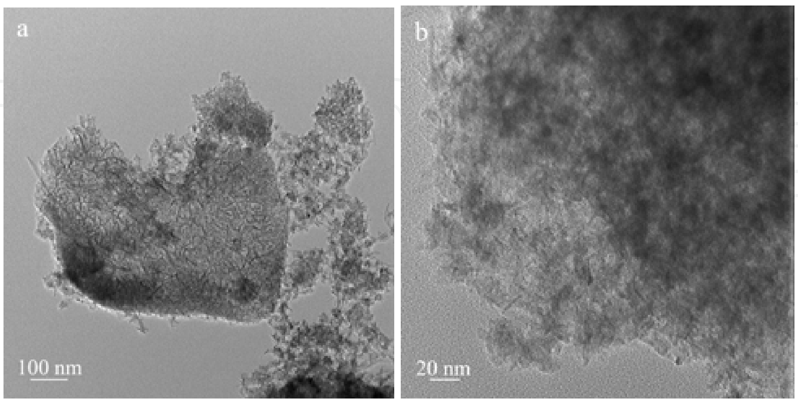

Fig. 12. TEM images of the MnO_2 obtained using mesoporous carbon.

3.2.2 Supramolecular template

In more recently, the discovery of M41S materials by the supramolecular templating mechanism ushered in a new era in synthesis chemistry (Wang et al., 2001; Lee et al., 2002). By using supramolecular template, some materials with high surface area, narrow pore size distribution and large pore volume could be prepared easily.

In our previous work (Xu et al.,2007), a kind of very slack mesoporous amorphous MnO_2 was prepared by using polyacry-lamide (PAM) and polyvinyl-alcohol (PVA) as template. The as synthesized material has large surface area and uniformed pore distribution is expected to favor ion transfer in the pore system and increase the MnO_2-electrolyte interfacial area, respectively.

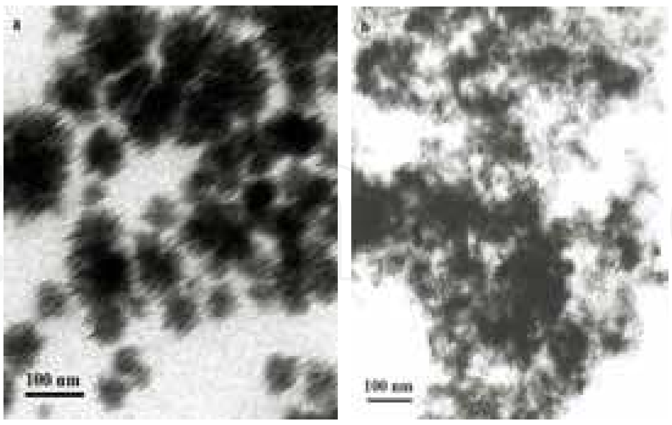

Fig. 13. TEM of MnO_2 obtained by without using supramolecular template (a) and using supramolecular template (b).

The morphology of the samples prepared under different condition was observed by transmission electron microscope (TEM). Figure 13a presents the morphology of the MnO_2 powders obtained without using supramolecular as template. It can be clearly seen that the sample was actually made up of small lamellar nanoparticles that agglomerate with each other to form the clusters. Figure 13b display the morphology of MnO_2 obtained using supramolecular as template. The MnO_2 is very loose and consisted of many small particles. Comparing the morphology of MnO_2 obtained under different conditions, great distinctions could be clearly seen, which indicates that the supramolecular template has played an important role in controlling the morphology of samples. The BET surface areas, calculated from adsorption isotherms, show that the surface area of the MnO_2 obtained using supramolecular template is 171 m^2/g, which increases significantly compared with that of the MnO_2 prepared without using supramolecular template (85 m^2/g).

3.2.3 Modified anodic aluminum oxide (AAO) template

Anodic aluminum oxide (AAO) template offers a promising route to synthesize a high surface area, ordered nanowire electrodes because of its advantages (Zhang et al., 2011; Zhao et al., 2011; Pan et al., 2004; Sui et al., 2001). Recently, amorphous manganese oxide nanowire arrays for high energy and power density electrodes were prepared by the AAO template method (West et al., 2004). But this method is difficult to be used in practical purpose due to the fragility of the AAO template. In our previous work (Xu et al., 2006), AAO films are successfully grown on Ti/Si substrate and is used as a template to synthesize high surface area and ordered MnO_2 nanowire array electrode for electrochemical capacitors. The experimental results indicated that this kind of template has unique electrodeposition properties and can bond well with the deposited materials.

From Fig. 14, we can find that many clusters protrude from the Ti/Si substrate which provide high surface area electrode. The clusters could result from the situation in which the nanowires are uncovered from the framework of the porous anodic alumina template but freestanding incompletely. When the porous anodic alumina template was dissolved away, the nanowires embedded in the template were released gradually and inclined to agglutinate together to minimize the system free energy. Fig. 14 also shows that the nanowires are abundant, uniform and well ordered in the large area.

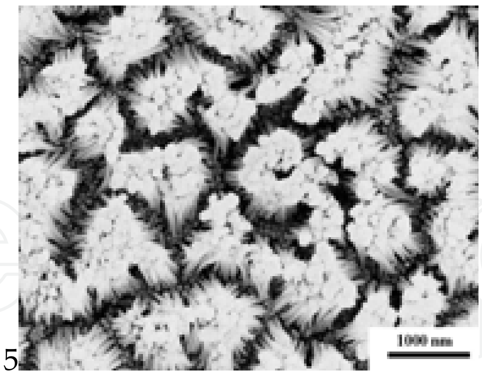

Fig. 14. FESEM image of MnO_2 nanowire arrays grown on AAO/Ti/Si substrate

Since lyotropic liquid crystals (LLCs) have unchanged topology of the phase throughout the process of the reaction and the calcination, it offers the ability to fabricate mesoporous materials with high specific surface areas (Elliott et al., 1999; Yamauchi et al., 2008). In the further work of Xu C. L. et al., lyotropic liquid crystals were introduced as a assisted template to prepared mesoporous MnO_2 (Xu et al., 2009). The mesoporous MnO_2 nanowire array architecture exhibits enhanced capacitance and charge/discharge performance, which is attributed to its intriguing architectures consisting of mesopores and nanowire arrays.

This approach will have potential applications in the fabrication of a wide range of mesoporous nanowire array materials. As can be seen from Fig. 15, the MnO_2 nanowires have uniform mesoporous structures and a continuous porous network is formed. The pores are patterned after the removal of the lyotropic liquid crystals template. The electron diffraction pattern (inset of Fig. 15(B)) demonstrates that the as-synthesized samples are amorphous.

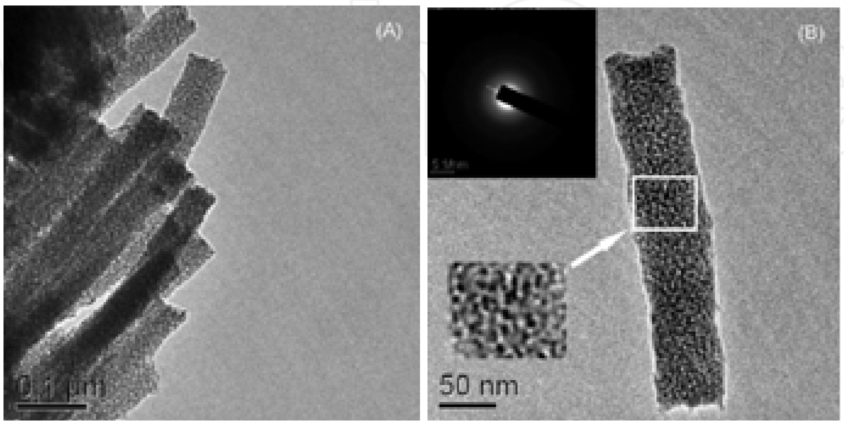

Fig. 15. TEM images of the mesoporous MnO_2 nanowires: (A) low magnification image, and (B) high magnification image. Inset is the electron diffraction pattern of nanowires in TEM.

3.3 Sol-gel process

The sol-gel process offers a number of potential advantages over traditional synthetic procedures. Sol-gel chemistry provides homogeneous mixing of reactants on the molecular level and can also be used to control shape, morphology, and particle size in the resulting products (Choy et al., 1999; Wu et al., 2004. Pang et al. conducted the first research on sol–gel processing of thin film MnO_2 electrodes for EC application in 2000 (Wei et al.2011; Pang et al., 2000; Lide et al., 2009). Stable colloidal MnO_2 was prepared by reducing tetrapropylammonium permanganate with 2-butanol or adding solid fumaric acid to 0.2 M $NaMnO_4$, mixing manganese acetate with a citric acid containing n-propyl alcohol at room temperature, reacting $KMnO_4$ with H_2SO_4 solutions (Wei et al., 2011; Chin et al.2002; Long et al., 2003; Lin et al., 2007; Lin et al., 2009; Lin et al., 2009). Sol–gel-derived nanoparticle MnO_2 thin films were then formed by either dip-coating or ‘’drop-coating’’ colloidal MnO_2 directly onto conductive substrates, followed by calcination at various temperatures. The calcination temperature was found to have significant influence on the surface morphology, specific surface area, and specific capacitance of sol–gel derived MnO_2 thin films, may because the calcination at proper temperatures can generate high porosity and a well-defined pore size distribution through evaporation of the adsorbed water, solvent, and organic molecule (Wei et al., 2011).

4. Charge storage mechanism

The history of MnO_2 for electrochemical energy storage applications can be tracked to more than 100 years ago in a primary Zn/MnO_2 cell, which dominated in primary battery chemistry for centuries (Xu et al., 2010.) In such cells, MnO_2 is used as a cathode in the aqueous electrolytes and stores charge by a so-called double-injection process, which involves the insertion of protons from the aqueous solutions and the reduction of Mn in oxides by electrons from external circuit (Xu et al., 2010; Be´langer et al., 2008; Trasatti, 1991). This double-injection process could be expressed as:

$$MnO_2 + H^+ + e^- \rightarrow MnOOH \tag{1}$$

If the electrode continues to discharge, MnOOH could be further reduced at the second step:

$$MnOOH + 3H^+ + e^- \rightarrow Mn^{2+} + 2H_2O \tag{2}$$

As the ever-increasing needs in energy density of advanced consumer electronics and related technologies, high-voltage secondary lithium ion batteries have attracted more concerns. MnO_2 materials have been studied as cathode materials for lithium ion batteries, and spinel $LiMn_2O_4$ has even been commercialized for mass applications. In this case, the charge storage of MnO_2 in lithium ion batteries is considered to be: (Wu et al., 2004; Armand et al., 1985; Bao et al., 2005).

$$\frac{1}{2}Li^+ + \frac{1}{2}e^- + 2\lambda\text{-}MnO_2 \Leftrightarrow Li_{0.5}Mn_2O_4 \tag{3}$$

$$\frac{1}{2}Li^+ + \frac{1}{2}e^- + Li_{0.5}Mn_2O_4 \Leftrightarrow LiMn_2O_4 \tag{4}$$

Lithium cations from the electrolyte diffuses and stores in the tunnels of MnO_2; meanwhile, electrons travel to the neighboring Mn(IV) sites to balance the charge (Xu et al., 2010; Kadoma et al., 2007; Johnson et al., 2007). Correspondingly, Mn(IV) ions become Mn (III) and electrons are stored. The insertion process of lithium ions and variation of Mn valence between Mn(IV) and Mn(III) are totally reversible.

As soon as capacitive behavior of MnO_2 in the mild aqueous electrolytes was discovered, the researchers began to seriously consider the capacitive charge storage mechanism. An intercalation/chemisorption of proton into the solid phase MnO_2 mechanism was first proposed as following (Pang et al., 2000; Wu et al., 2004; Hu & Tsou, 2002; Bao et al., 2005).

$$MnO_2 + H^+ + e^- \leftrightarrow MnOOH \tag{5}$$

In the process of reversible insertion/desertion of protons (H^+) in MnO_2, Mn valence vary between Mn(IV) and Mn(III).

However, some phenomena, in which the specific capacitance of MnO_2 was directly affected by the species and concentrations of the alkaline metal cations with the same pH value, indicated that the charge storage mechanism is not as simple as expressed by Eq. (5).

It is found that the specific capacitance of MnO_2 electrode were affected by the nature of Li^+, Na^+, or K^+, significantly (Xu et al., 2008; Wen et al., 2004). Hence, a mechanism based on the surface adsorption of electrolyte cations (C^+) on MnO_2 has been proposed subsequently and be described as following: (Xu et al., 2010)

$$(MnO_2)_{surface} + C^+ + e^- \leftrightarrow (MnO_2^-C^+)_{surface} \tag{6}$$

Where $C^+ = H^+, Na^+, K^+, Li^+$.

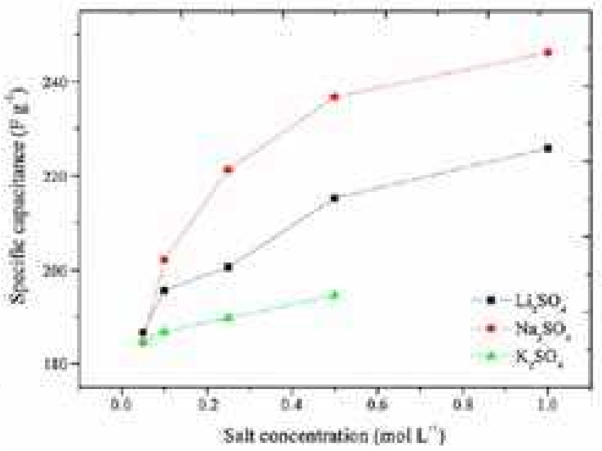

Fig. 16. Dependence of SC values on different electrolytes at sweep rate of 2 mV/s (Xu et al., 2008).

In order to further understand the charge storage mechanism of MnO_2 electrode, Toupin et al. investigated the variation of Mn valence in MnO_2 electrode during charge and discharge process by cyclic voltammetry and X-ray photoelectron spectroscopy (Toupin et al., 2004). A thin MnO_2 films deposited on a platinum substrate and thicker MnO_2 composite electrodes were used. X-ray photoelectron spectroscopy (XPS) measurements (Mn 3s and O 1s) with the thick composite electrodes did not reveal any change that could be assigned to a variation of the manganese valence, and, at this point, the charge storage mechanism could be based on electrostatic effects only. In fact, the charge storage would be similar to that observed for carbon electrodes (Toupin et al., 2004). On the other hand, a completely different XPS behavior was noticed for the thin film electrodes. Both the Mn 3s and O 1s spectra were consistent with manganese oxidation states of +3 and +4 for the reduced and oxidized forms, respectively. The XPS data also show that Na^+ cations from the electrolyte are involved in the charge storage process of MnO_2 thin film electrodes. The Na/Mn ratio for the reduced electrode is much lower than what is anticipated for charge compensation dominated by Na^+ and suggests the involvement of protons. The apparent discrepancy between the XPS data (Mn 3s and O 1s spectra) indicate that only a thin layer of MnO_2 is involved in the redox process and is electrochemically active. The authors think that this thin surface layer cannot be probed for the composite electrode may because this region is brought back to the chemical (oxidation) state of the bulk by internal redox interconversion (Xu et al., 2010; Toupin et al., 2004; Kuo et al., 2006).

In the same paper, a reversible expansion and shrinkage in lattice spacing of the oxide during charge transfer at manganese sites upon reduction/oxidation of MnO_2 was also demonstrated by in situ synchrotron x-ray diffraction. A similar result was also obtained for a layered MnO_2. An increase of the interlayer spacing from 0.70 to 0.72 nm upon electrochemical oxidation indicated that alkaline metal cations, Na^+ ions, intercalated in the 2D tunnels of MnO_2 (Xu et al.,2010; Athouel et al., 2008). The facts of lattice expansion and shrinkage during redox process indicated that the insertion of cations in the electrolytes predominates in the charge storage process of MnO_2.

Hence, based on surface adsorption of electrolyte cations C^+ (K^+, Na^+…) as well as proton incorporation, a more reasonable charge storage mechanism of MnO_2 electrode was proposed (Simon & Gogotsi, 2008).

$$MnO_2 + xC^+ + yH^+ + (x+y)e^- \leftrightarrow MnOOC_xH_y \tag{7}$$

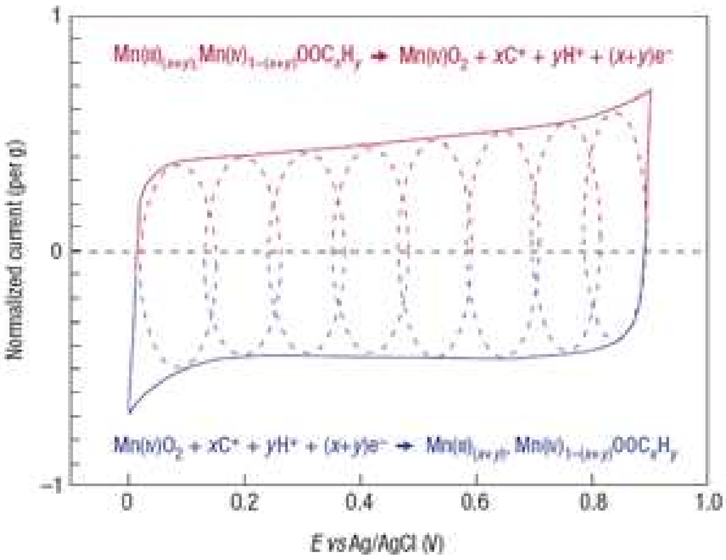

Fig. 17. Cyclic voltammetry of MnO_2-electrode cell in mild aqueous electrolyte (0.1 M K_2SO_4). This schematic of cyclic voltammetry for a MnO_2-electrode cell shows the successive multiple surface redox reactions leading to the pseudo-capacitive charge storage mechanism. The red (upper) part is related to the oxidation from Mn(III) to Mn(IV) and the blue (lower) part refers to the reduction from Mn(IV) to Mn(III) (Simon & Gogotsi, 2008).

As seen in Fig. 17, a cyclic voltammogram of a single MnO_2 electrode in mild aqueous electrolyte, the fast, reversible successive surface redox reactions define the behaviour of the voltammogram, whose shape is close to that of the EDLC.

It is really that the charge storage process of MnO_2 electrode is consists of double layer charging and pseudocapacitive surface redox process according to the research results of many scientists. However, as for the MnO_2 electrode, which process, double layer charging and pseudocapacitive surface redox, give more contribution to its capacitance.

In our previous work (Xu et al., 2007), we found although some double layer charging can significantly contribute to the measured capacitance due to the high surface area of the material, it cannot solely explain the whole capacitance of the electrode. The calculation of the pure double layer capacitance using the BET surface area is far lower than that measured in our work. So it is believed that the main part of the capacitance comes from the pseudocapacitive surface redox process. It may because when the specific surface area of MnO_2 electrode material increases, not only the double layer capacitance will increase, the redox active sites will increase subsequently, so the pseudocapacitance will increase significantly.

The capacitance of MnO_2 electrode also is affected by their microstructure. Ouassim G. et al., study the electrochemical performance of different structured MnO_2 in 0.5 M K_2SO_4 electrolyte (Ghodbane et al., 2009). The various curve shapes in Fig. 18 demonstrate the electrochemical response dependence on the MnO_2 microstructure and indicate that cooperative charge-storage mechanisms may exist. In fact, the typical rectangular shape of pseudocapacitive behaviors is observed for the pyrolusite, Ni-doped todorokitr (Ni-todorokite), ramsdellite, and spinel forms only. For the birnessite, cryptomelane, and octahedral molecular sieves (OMS-5) compounds, the shapes of the CV curves exhibit more or less pronounced redox waves. This behavior suggests that faradic phenomena occur during the charge-storage mechanism. The presence of redox waves during the charge/discharge process was already reported for several MnO_2-based electrodes (Hu & Tsou, 2002; Brousse et al., 2006; Devaraj & Munichandraiah, 2008; Ghodbane & Favier 2009; Chang et al., 2009; Lee et al., 2010). The electrochemical experiments in their work demonstrate that the crystallographic form of MnO_2 influences the electrochemical performance, and the small tunnel of β-MnO_2 was not suitable to store cations, while the large tunnel size of α-MnO_2 favors the storage of cations Devaraj & Munichandraiah, 2008; Cheng et al., 2010). In addition, the presence of other metal cations in the tunnel in advance hinders the diffusion and storage of the electrolyte cations leading to a decrease in capacitance. More recently, further research on the tunnel storage of MnO_2 even revealed that the aprotic ionic liquids anions with the far bigger diameters than that of alkaline metal ion, could also be stored in the tunnels of MnO_2 (Xu et al. 2010 ; Chang et al., 2009; Lee et al., 2010).

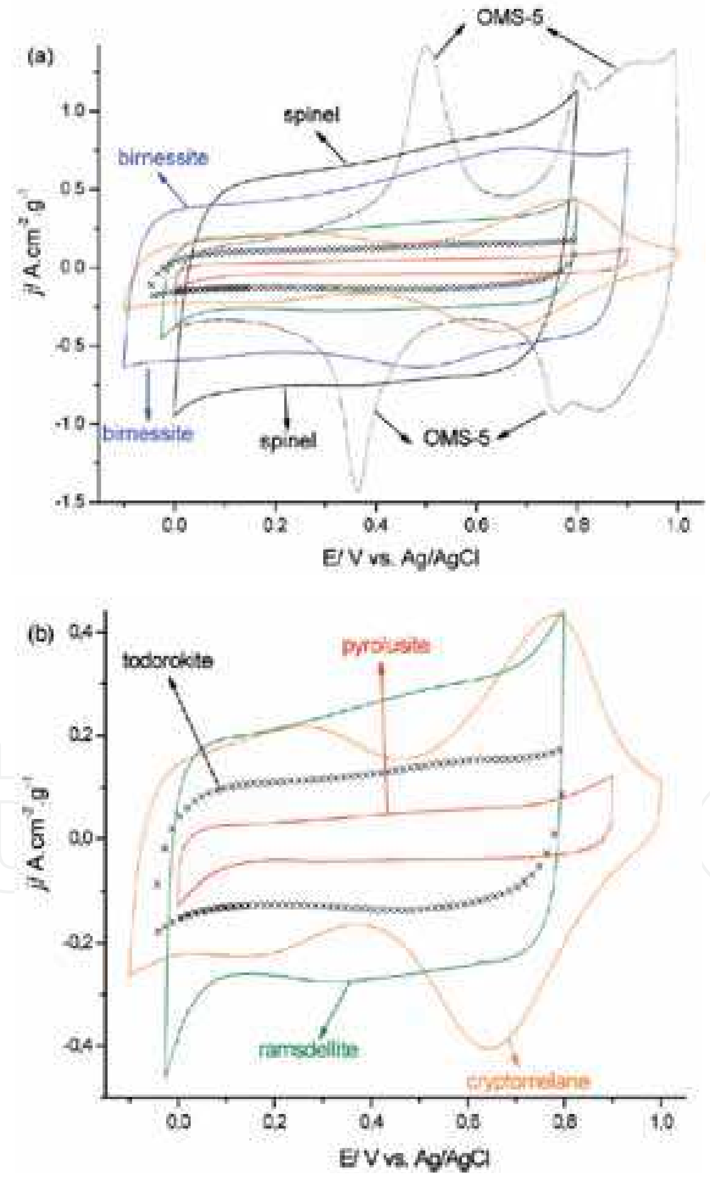

Fig. 18. (a) CV curves (fifth cycle) of different MnO_2 forms recorded in aqueous 0.5 M K_2SO_4 at 5 mV/s. (b) Enlargement of the CV curves of pyrolusite, Ni-todorokite, ramsdellite, and cryptomelane phases (Ghodbane et al., 2009).

More recently, a multivalent cation storage mechanism was proposed by Xu et al., they think not only univalent alkaline metal cations could store in the tunnels of MnO_2, bivalent alkaline-earth metal cations also are present in it (Xu et al., 2009; Xu et al., 2009). The realization of the theoretical capacity of a host material offered by its redox levels is determined by the number of intercalated ions concurrent with the charge transfer of the required number of electrons. From a vacancy viewpoint, polyvalent cations may open up the possibility of electrodes, which exhibit higher gravimetric capacity and energy density, because each multivalent intercalated ions cation will force multiple Mn^{4+} ions to become Mn^{3+} ion and store multiple electrons (Xu et al., 2010). This improvement method may be the most convenient and low cost for enhancing the capacitance of MnO_2-based supercapacitors.

5. Electrolytes system for MnO_2-based supercapacitors

5.1 Aqueous-based electrolytes

For aqueous electrolytes, the maximum operating voltage is theoretically limited by the electrolysis of water to 1.229 V (at 25 ^{o}C). Aqueous electrolytes tend to produce faster rates of charge/discharge due to the relatively high conductivity and low viscosity of concentrated solutions. Further advantages of aqueous electrolytes are their low cost and ease of manufacture in comparison with hygroscopic organic based and ionic liquid electrolytes (Hall et al., 2010).

The most commonly employed aqueous electrolytes for MnO_2-based supercapacitors are Na_2SO_4 and KOH. Other some neutral electrolytes, such as NaCl, KCl, Li_2SO_4, K_2SO_4 also been used as electrolytes. More recently, alkaline-earth metal cations (Mg^{2+}, Ca^{2+}, and Ba^{2+}) are considered for use as charge storage media of MnO_2-based supercapacitors to replace conventional alkaline cations (Li^+, Na^+, and K^+) (Xu et al., 2009). As for electrolytes, relatively concentrated electrolytes are required to minimize the equivalent series resistance and maximize power output. However, the use of concentrated electrolytes also increases the rate of self discharge displayed by the capacitor.

5.2 Organic-based electrolytes

Organic electrolytes allow for increased operating voltages of up to 3 V and a consequent increase in energy density. Typically, the operating voltage is set to 2.5 V to prevent oxidation of the electrolyte through over-charging. To ensure that these electrolytes can operate at the higher voltages they must be handled in an atmosphere free of water and oxygen. This ensures that the evolution of H_2 and O_2 gases at potential differences above 1.23 V does not occur (Hall et al., 2010; K€otz et al., 2000).

The two most common organic solvents used are propylene carbonate (PC) and acetonitrile (AN). AN was often preferred, as its ESR is a factor of three lower than that of PC. However, there is continuing controversy over the safety of AN, in particular in vehicles, due to its high toxicity and flammability. Research aimed at developing a non-toxic electrolyte with low resistivity has proven unsuccessful (Hall et al., 2010; Burke A., 2007). Most organic electrolyte based ECs available commercially utilize PC as the solvent. Tetraalkylammonium salts of anions PF_6^- and BF_4^- are preferred for the production of organic electrolytes due to their high solubility, higher dielectric conductivity, and good conductivity (relative to other organic solutions) (Hall et al., 2010).

5.3 Room temperature ionic liquid electrolytes

Ionic liquids are room-temperature liquid solvent-free electrolytes; their voltage window stability is thus only driven by the electrochemical stability of the ions. A careful choice of both the anion and the cation allows the design of high-voltage supercapacitors, and 3 V, 1,000 F commercial devices are already available (Simon & Gogotsi, 2008; Tsuda & Hussey, 2007). However, the ionic conductivity of these liquids at room temperature is just a few milliSiemens per centimetre, so they are mainly used at higher temperatures. For applications in the temperature range –30 °C to +60 °C, where batteries and supercapacitors are mainly used, and ionic liquids still fail to satisfy the requirements because of their low ionic conductivity. However, the research on ionic liquids for ECs is expected to have an important role in the improvement of capacitor performance in the coming years (Simon & Gogotsi, 2008).

5.4 Solid electrolytes

Replacing liquid electrolytes with solid electrolytes will enhance the safety of ECs, as it can solve problems associated with electrolyte leakage and corrosion. Gel polymer electrolytes (GPE) (Lee et al., 2009; Nagatomo et al., 1987; Peramunage et al., 1995) are capable of giving sufficient rigidity for enhancing device safety and provide much higher ionic conductivity than the polymeric solid electrolytes. There has recently been increasing interest in applying GPE to Ecs (Wada et al., 2004; Wada et al., 2006; Choudhury et al., 2006). More recently, a gel-type electrolyte has been tentatively applied in MnO_2-based systems. The gel electrolyte will prevent leaking of the electrolyte, which is superior to a liquid electrolyte. Although the manufacturing cost of such gel-type device will undoubtedly be high, it will open up a new direction to develop reliable MnO_2-based devices (Lee, et al., 2008).

6. The current status and development of MnO_2-based supercapacitors

Metal oxides present promising potential because of high specific capacitance at low resistance, possibly making it easier to construct high energy, high power supercapacitors. Many metal oxides, such as NiO, $Ni(OH)_2$, MnO_2, Co_3O_4, IrO_2, Fe_3O_4, TiO_2, SnO_2, V_2O_5 and MoO_3 have been studied as SC electrode materials. However, none of these oxides are used in commercial production and they are still in lab-scale research (Jaualakshmi & Balasubramanian, 2008). Among of them, manganese oxide has been paid more attention.

Manganese can be present in three different valence states and its oxides are highly complex. The theoretical capacitance of manganese oxides reaches to ~1380 F/g but the electrochemical reversibility of redox transition of manganese dioxide is usually too low to be applicable and the pure manganese dioxide possess poor capacitive response due to its high resistance of bulk manganese oxide (Xu et al., 2010). In spite of this, manganese oxides are seen to be potential useful materials for pseudocapacitors not only due to their low cost but also to their environmental friendliness (Jaualakshmi & Balasubramanian, 2008).

As reported in literatures, the specific capacitance could reach 600 F/g for thin MnO_2 films (Chin et al., 2002; Pang et al., 2000). It is because thin MnO_2 film significantly reduces the diffusion distances for the solid-state transport of insertion cations and overcomes the limitations of the poor electronic conductivity of MnO_2. However, because of extremely low loading mass, thin films seem to be limited to microsystems for energy storage such as integrated devices or to be used to analyze the charge storage mechanism (Jaualakshmi &

Balasubramanian, 2008). The specific capacitance only reaches 150-300 F/g for MnO_2 powders (Xu et al., 2010). Prasad and Miura reported a capacitance value between 400 and 621 F/g for amorphous electrolytic manganese dioxide and MnO_2-based mixed oxides (Prasad et al., 2004; Prasad & Miura, 2004). But in fact, higher capacitance is expected to obtain. To further improve the performance of MnO_2-based supercapacitor, it is necessary to design MnO_2 materials into nanoarchitectures or composites with other materials, such as porous carbon or polymer.

In order to improve the electrical conductivity, chemical stability, mechanical stability, and flexibility of MnO_2 electrodes, poly (o-phenylenediamine), polyaniline, polypyrrole, and polythiophene and their derivatives have been introduced. The first MnO_2/PANI composite electrode was prepared through a two-step electrochemical route: nanostructured MnO_2 was potentiodynamically deposited on a polyaniline (PANI) matrix synthesized through an electrochemical method. The specific capacitance of the obtained MnO_2/PANI composite electrode reach to 715 F/g, and its energy density is about 200 Wh/ kg at a charge–discharge current density of 5 mA /cm^2 (Prasad & Miura, 2004). Electrochemical co-deposition process and chemical polymerization method were also applied to prepare MnO_2/PANI composite (Sun & Liu, 2008); Zhou et al., 2005). Through addition PANI, the electrochemical performance of MnO_2 as supercapacitor electrode material was enhanced significantly. MnO_2/Ppy nanocomposite electrode materials were also prepared by using different process, and the experimental results indicated that the improvement of composite electrodes was attributed to good conductivity of Ppy (Sharma et al., 2010; Sharma, et al., 2008; Zhang et al., 2009). Polythiophene and its derivatives generally possess excellent electronic conductivity, high chemical stability, and reasonable mechanical flexibility, but they provide low electrochemical energy density (Liu & Lee, 08). The combination of MnO_2 with its high energy storage capacity and highly conductive and flexible. MnO_2/ PThs have advantages over just the sum of the individual components (Sharma & Zhai, 2009). Hence, the conducting polymer and MnO_2 nanoarchitecture are very promising materials with potential applications as ECs, and more efforts have been dedicated to incorporate polyaniline, polypyrrole, and polythiophene conductive polymers to generate MnO2–polymer composite electrodes with desirable morphologies and electrochemical performance (Wei et al., 2011).

It is noted that the nanostructured carbons produced under different synthesizing conditions exhibit a variety of physicochemical features and electrochemical properties (Wei et al., 2011). Nanostructured carbons such as CNTs, nanographites, carbon nanofoams, and ordered mesoporous carbons, especially, grapheme, are widely used as high surface area and excellent electron conducting architectures for MnO_2-based composite electrodes (Dong et al., 2006; Zhang et al., 2009; Lei et al., 2008). The combination of MnO_2 with different carbon is another method to improve the performance of MnO_2 based supercapacitors.

Hybrid systems offer an attractive alternative to conventional pseudocapacitors or EDLCs by combining a battery-like electrode (energy source) with a capacitor-like electrode (power source) in the same cell. An appropriate electrode combination can even increase the cell voltage, further contributing to improvement in energy and power densities (Simon & Gogotsi, 2008). In 2002, Hong et al. initially considered activated carbon (AC) as the negative electrode material for MnO_2-based supercapacitor (Be´guin et al., 2006). Except for the effort to find new negative electrodes, attempts have been made to use the new forms of MnO_2 as new positive electrode materialThese capacitors showed promising performance. Another challenge for this system is to use organic electrolytes to reach higher cell voltage, thus improving the energy density.

7. Opportunities and challenges in future

ECs are being used across a vast swath of commercial and industrial equipment. Future generations of ECs are expected to come close to current Li-ion batteries in energy density, maintaining their high power density. This may be achieved by using ionic liquids with a voltage window of more than 4 V, by discovering new materials that combine double-layer capacitance and pseudo-capacitance, and by developing hybrid devices. ECs will have a key role in energy storage and harvesting, decreasing the total energy consumption and minimizing the use of hydrocarbon fuels. In some instances they will replace batteries, but in many cases they will either complement batteries, increasing their efficiency and lifetime, or serve as energy solutions where an extremely large number of cycles, long lifetime and fast power delivery are required.

Concerning the materials issues, MnO_2 is one of the most studied materials as a low-cost alternative to RuO_2. It has a very high theoretical capacitance of ~1380 F/g but suffer from poor conductivity, only 30% or even lower of theoretical value can be obtained. To further improve the performance of MnO_2-based supercapacitor, it is necessary to design MnO_2 materials into nanoarchitectures with desirable physicochemical features or composites with other materials, such as porous carbon or conductive polymer.

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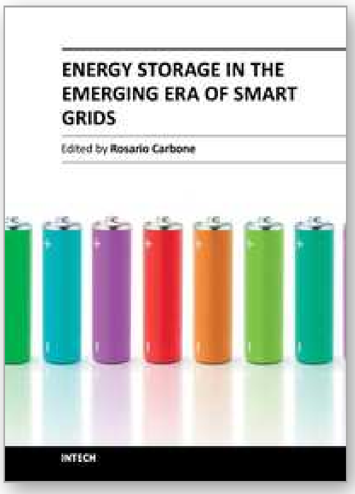

Energy Storage in the Emerging Era of Smart Grids

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Reliable, high-efficient and cost-effective energy storage systems can undoubtedly play a crucial role for a large-scale integration on power systems of the emerging â€œdistributed generationâ€ (DG) and for enabling the starting and the consolidation of the new era of so called smart-grids. A non exhaustive list of benefits of the energy storage properly located on modern power systems with DG could be as follows: it can increase voltage control, frequency control and stability of power systems, it can reduce outages, it can allow the reduction of spinning reserves to meet peak power demands, it can reduce congestion on the transmission and distributions grids, it can release the stored energy when energy is most needed and expensive, it can improve power quality or service reliability for customers with high value processes or critical operations and so on. The main goal of the book is to give a date overview on: (I) basic and well proven energy storage systems, (II) recent advances on technologies for improving the effectiveness of energy storage devices, (III) practical applications of energy storage, in the emerging era of smart grids.

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