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Microstructural characterization of the cycling behavior of electrodeposited manganese oxide supercapacitors using 3D electron tomography

N. Dalili [b], M.P. Clark [a], E. Davari [a], D.G. Ivey [a, *]

[a] Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, T6G 1H9, Canada
[b] NRC-NINT, Edmonton, Alberta, T6G 2M9, Canada

HIGHLIGHTS

- SEM/FIB tomography has been used to study cycling of Mn oxide supercapacitors.
- Mn oxide is anodically deposited as high surface area rods.
- Dissolution/redeposition occurs during cycling near the substrate.
- The redeposited material has a finer morphology and higher capacitance.

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ABSTRACT

Manganese oxide has been investigated extensively as an electrochemical capacitor or supercapacitor electrode material. Manganese oxide is inexpensive to fabricate and exhibits relatively high capacitance values, i.e., in excess of 200 F g^{-1} in many cases; the actual value depends very much on the fabrication method and test conditions. The cycling behavior of Mn oxide, fabricated using anodic electrodeposition, is investigated using slice and view techniques, via a dual scanning electron microscope (SEM) and focused ion beam (FIB) instrument to generate three-dimensional (3D) images, coupled with electrochemical characterization. The initial as-fabricated electrode has a rod-like appearance, with a fine-scale, sheet-like morphology within the rods. The rod-like structure remains after cycling, but there are significant morphological changes. These include partial dissolution of Mn oxide followed by redeposition of Mn oxide in regions close to the substrate. The redeposited material has a finer morphology than the original as-fabricated Mn oxide. The Mn oxide coverage is also better near the substrate. These effects result in an increase in the specific capacitance.

1. Introduction

Electrochemical energy storage devices, such as batteries, fuel cells and electrochemical capacitors (or super capacitors), have generated an increasing amount of interest over the past several years. This interest is fueled largely by the development of hybrid and electric vehicles, as well as the emphasis on renewable energy sources. Electrochemical capacitors are characterized by high power densities, long cycle life and low cost. They are used in conjunction with other energy storage devices to provide a burst of power during periods of high load, such as acceleration of an electric vehicle. Some other applications for electrochemical capacitors are portable electronics, energy grids and emergency power supplies [1,2].

Charge is stored in electrochemical capacitors through the accumulation of ions. The ions are stored either electrostatically in the electrochemical double layer or through Faradaic reactions in the bulk and at the surface. Depending on the electrode material, one of these mechanisms will typically dominate. Electrostatic charge storage allows for fast charge/discharge rates, but overall capacitance is limited by the electrostatic repulsion of the stored ions. Capacitance is typically higher for Faradaic capacitors, but the need for ion diffusion limits their rate capability. For both charge storage mechanisms, the electrode surface area plays an important

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* Corresponding author.
E-mail address: divey@ualberta.ca (D.G. Ivey).

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role in overall capacitance. For double layer capacitors, the amount of charge that can be stored is directly related to the surface area. For Faradaic capacitors, a large surface area allows for easier ion access to the bulk of the material [3].

Manganese oxide (MnO_2) is of particular interest as an electrochemical capacitor because it is inexpensive, environmentally benign and has a high theoretical capacitance (1380 F g^{-1}) [4–6]. Like many transition metal oxides, Mn oxide stores charge in two ways: electrostatically in the double layer and through Faradaic reactions at the surface as well as in the bulk of the electrode. Faradaic processes tend to dominate. The theoretical capacitance of Mn oxide is difficult to achieve because of its relatively poor electronic and ionic conductivity.

Manganese oxide electrodes can be fabricated by a number of ways; e.g., as powders via hydrothermal methods [7], thin films by dip coating and drop coating [8], electrodeposition [8–10] and atomic layer deposition (ALD) [11]. Electrodeposition is commonly utilized, because it is inexpensive, simple and is able to conformally coat complex shapes. In fact, the oxide can be fabricated directly, without subsequent annealing, through anodic electrodeposition. Manganese ions are oxidized at the anode leading to oxide formation on the electrode. Deposition parameters such as temperature, time, current, electrolyte composition and agitation are easily modified and are used to control deposit morphology, structure and properties. Various Mn oxide morphologies have been achieved through electrodeposition, including sheets, rods, fibers and particles. Our group has developed a template-free process to electrodeposit rods with a diameter of ~2 μm and lengths ranging from a few microns to greater than 10 μm [9,10,12,13]. The rods can be deposited on a variety of substrates, such as metallized semiconductors (e.g., Au/Si), Ni foam and carbon. The individual rods have a fibrous structure on the nanoscale, which increases the exposed surface area. The rods also have a “petal-like” shape, i.e., tapered at the base and spread out near the top. This petal shape leads to rod impingement for lengths exceeding 10 μm.

The capacitances for Mn oxide are high, with specific capacitances reaching or even exceeding 200 F g^{-1}. There are conflicting explanations in the literature as to the major factor(s) controlling capacitance, with specific surface area, the crystal structure of Mn oxide, ion conductivity and ion transfer all being cited. Devaraj and Munichandraiah [14] studied MnO_2 nanoparticles, fabricated in a microemulsion medium, that were subsequently annealed at temperatures up to 400 °C. The surface area of the Mn oxide decreased with increasing annealing temperature (from 190 m^2 g^{-1} at 70 °C to 119 m^2 g^{-1} at 400 °C). This correlated to a decrease in capacitance, from ~300 F g^{-1} to ~250 F g^{-1}, over the same temperature range. Ghodbane et al. [15] examined several different allotropic forms of MnO_2 powders. They showed that the crystallographic structure of MnO_2 affects the capacitance. The best performance was achieved for the 3D spinel structure, followed closely by the 2D birnessite structure; both materials had capacitances in the 225–240 F g^{-1} range. They claimed that surface area had only a limited effect on performance, while capacitance could be correlated with ionic conductivity of the Mn oxide powder, i.e., capacitance increased as ionic conductivity increased. Sung et al. [16] also examined different MnO_2 powders, namely δ-MnO_2, α-MnO_2 and γ-MnO_2. They reported less of an effect of structure and more of a correlation with surface area. Capacitance values were highest for δ-MnO_2 nanoplates (up to 213 F g^{-1}), which also had the largest surface area (116 m^2 g^{-1}). The lowest capacitances were obtained for α-MnO_2 nanowires (110 F g^{-1}), with the smallest surface area (53 m^2 g^{-1}). Young and et al. [17] recently compared the capacitance behavior of two MnO_2 materials with vastly different capacitances, i.e., α-MnO_2 (~200 F g^{-1}) and β-MnO_2 (~10 F g^{-1}). A common explanation for the difference in behavior is related to the tunnel or channel sizes in the 3D structures; α-MnO_2 has larger tunnels and is therefore better able to accommodate positive ions during intercalation. Young et al. attributed the capacitance difference to the electronic properties. Specifically, the high capacity for α-MnO_2 was attributed to cation induced charge-switching states in the band gap that overlap with the scanned potential allowed by the electrolyte. The charge switching states come from interstitial and substitutional cations (e.g., H^+, K^+, Na^+) that are incorporated in the material. For β-MnO_2 the scanned potential window does not overlap with its band gap, i.e., it is entirely in the conduction band, so there is no charge switching.

An important consideration when selecting an electrochemical capacitor is its cycling behavior. The electrode should be able to undergo thousands of cycles with little or no capacitance fading. Again, the literature is mixed on the cycling performance of Mn oxide. Our earlier work showed a 25% decrease in capacitance after 250 cycles and the loss was attributed to partial dissolution of Mn oxide [9,10]. Several other studies have shown a capacitance decrease on cycling [8,18]. Pang et al. [8] fabricated MnO_2 electrodes by electrodeposition and dip/drop coating and found that the amount of capacitance loss depended on the processing method with losses ranging from 10 to 38% (over 1500 cycles). They also attributed the loss to partial dissolution of MnO_2 on cycling. Sung et al. [16] observed an increase (<10%) in capacitance for the three different structural types of MnO_2 (δ-MnO_2, α-MnO_2 and γ-MnO_2). α-MnO_2 had the largest increase (~15–20% over 1000 cycles). They attributed the behavior to an improvement in ion transport near the surface of the electrode. Athouel et al. [19] examined Mg-doped MnO_2 Na-birnessite (δ-MnO_2) (original capacitance was ~145 F g^{-1}) over a limited number of cycles (50) and saw a slight increase in the first few cycles followed by stable behavior. The slight increase was attributed to stabilization of the electrode structure.

Chen et al. [7] have studied MnO_2 prepared by hydrothermal methods using electron tomography in a transmission/scanning transmission electron microscope (TEM/STEM). By varying the process time, they generated a variety of structures ranging from nanosheets to nanofibres to nanotubes. The nanosheets were δ-MnO_2, while the nanotubes were α-MnO_2. MnO_2 processed for 1 h (δ-MnO_2 nanosheets) had the highest capacitance (110 F g^{-1} at 0.5 A g^{-1}), while the 12 h sample (α-MnO_2 nanotubes) had the lowest capacitance (<30 F g^{-1} at 0.5 A g^{-1}). There was a very strong correlation between capacitance and surface area; the nanosheets had a surface area of ~200 m^2 g^{-1} compared with a surface area of ~40 m^2 g^{-1} for the nanotubes. The δ-MnO_2 nanosheets exhibited a 20% increase in capacitance on cycling (up to 5000 cycles), with the largest change occurring in the first 1000 cycles. Through their electron tomography work, the authors attributed the capacitance increase to an increase in porosity upon cycling leading to increased surface area and easier access for cations.

As mentioned above, our group has been able to fabricate high surface area Mn oxide rods through electrodeposition. In the original work [9,10,13], the deposits had a defective antifluorite (cubic) nanocrystalline structure and displayed high capacitances (~200 F g^{-1}). In our more recent work, additives have been included in the electrolyte to improve adhesion. Capacitance values were similar, but a different nanocrystalline structure (birnessite-type δ-MnO_2) was obtained. The rod-like morphology was retained, but the capacitance increased on cycling even with partial dissolution of Mn oxide. The purpose of this work is to utilize electron microscopy techniques to characterize the morphology and structure of Mn oxide electrodeposits in detail with the aim of developing an understanding of the capacitive behaviour with cycling. Conventional scanning electron microscopy (SEM), along with slice and view methods using a combination of SEM and focused ion beam