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Improved manganese oxide electrochemical capacitor performance arising from a systematic study of film storage/drying effects on electrochemical properties

Mallory A. Davis, Heather A. Andreas*

Dalhousie University, Department of Chemistry, Halifax, Nova Scotia, B3H 4R2, Canada

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ABSTRACT

This work is the first to systematically relate manganese oxide film storage/drying to a full gamut of electrochemical capacitor (EC) properties, with the aim of enhancing these properties and addressing this oxide's well-known stability issues. Cyclic voltammetry and galvanostatic charging-discharging show that increased film-drying temperatures result in lower resistance and higher power but at the expense of capacitance and energy. Film drying reduces physical stability and cycle life, while undried, electrolyte-stored films exhibit poor long-term aging. Novel electrolyte-stored films show a ~102% capacitance increase, ~75% energy increase and 32% improved film usage compared to 200 °C-dried films, while 200 °C drying results in a ~69% power increase and ~75% decrease in resistance compared to non-heat-treated films.

Using the knowledge acquired from this systematic study, we then strategically design an innovative double-deposition in which an initial manganese oxide layer is oven-dried and subsequently recoated with a second manganese oxide layer before storing the entire electrode in electrolyte. Films made with this novel double-deposition demonstrate the optimal properties achieved from *both* electrolyte-stored films (high energy, capacitance, coulombic efficiency, and physical stability) *and* heat-treated films (low resistance, higher power and rate capability, good aging, and stability in a large potential window); they also demonstrate the smallest degree of self-discharge. This novel synthesis produces films suitable for a wider range of EC applications.

1. Introduction

As the switch to more sustainable energy sources becomes increasingly immediate, improvements in energy storage devices are necessary to achieve efficient storage on multiple time-scales for a full range of applications. For electric vehicles, cell phones or laptops, the slow discharge rate and high energy density of batteries is desirable to maximize the time between recharging. Conversely, for applications requiring rapid movement of charge, such as a camera flash, backup memory or electric vehicle acceleration, electrochemical capacitors (ECs) are advantageous due to their rapid charge/discharge rate and high-power capabilities. To expand the range of potential EC applications, performance improvements are necessary to maximize energy densities, physical and electrochemical stability, and to minimize self-discharge.

ECs store charge through double-layer capacitance and/or pseudocapacitance, i.e. via rapid redox reactions [1–3]. Pseudocapacitance results in a higher energy density and transition metal oxides and conductive polymers have been investigated as EC electrode materials. Recently, manganese oxide has gained prominence due to its abundance, low toxicity, and affordability in comparison to other pseudocapacitive materials such as ruthenium oxide [1]. Manganese oxide also displays capacitive behavior in relatively safe electrolytes, such as Na_2SO_4, avoiding the acidic and basic electrolytes used with other pseudocapacitive materials [4].

Electrodeposition of manganese oxide affords hydrous films [5], with a simple synthesis, film thickness control and substrate flexibility. Electrodeposition also typically ensures a good active material-substrate connection without a binder [6], making these films a good choice for ECs. However, electrodeposited films have stability issues [7,8], particularly on smooth surfaces.

Manganese oxide demonstrates pseudocapacitance through

* Corresponding author.
E-mail address: heather.andreas@dal.ca (H.A. Andreas).

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Faradaic reactions involving changes in the manganese oxidation state with reversible insertion and removal of solution cations [9]. Hydrous areas in the film serve as easy-access sites for the cation diffusion [3,10,11]. Therefore, a greater amount of physisorbed water present in the electrode material is thought to improve the mobility of cations within the oxide film, thereby raising the electrode's capacitance [11]. Clearly the film preparation, particularly the drying procedure, may have a significant impact on the electrochemical properties of manganese oxide.

Increasing the heat-treatment or annealing temperature of both ruthenium oxide and manganese oxide materials removes water, resulting in decreased capacitance [11–16]. Yet, many groups still report elevated-temperature drying of manganese oxide materials [17–20]. Often, the reason for heat-treatment is not specified. Likely, the use of heat-treatment stems from the discovery that proper annealing temperatures can result in increased capacitance retention over long-term cycling at the cost of decreasing the initial capacitance [15,21], or improved oxide conductivity [15,22]. However, the relationship between annealing temperatures and capacitance is not widely agreed upon, since other researchers have reported that annealing at 200 °C can raise capacitance compared to both non-heated samples and those heated at higher temperatures [23,24]. Zhu and coworkers found that capacitance increases with increasing annealing temperature up to 500 °C [25]. Others have found 70 °C to be the ideal heat-treatment temperature for manganese oxide on stainless steel [26], but the majority of literature shows an inverse relationship between capacitance and annealing temperature [11–16].

Of course, capacitance and resistance are not the only critical figures of merit for ECs, and other important properties such as power, coulombic and energy efficiency, physical stability, self-discharge, film usage, and aging have yet to be related to degree of hydration. It is vital to understand how heat-treatment impacts all electrochemical parameters to facilitate the development of new EC materials to produce reliable and practical EC devices.

This work provides a systematic evaluation of the physical and electrochemical properties of electrodeposited manganese oxide films dried using different methods (room temperature in ambient conditions vs. in a desiccator, and oven drying at 100 and 200 °C), and comparing a novel condition – that of undried, wet-stored films. This work also shows for the first time how film hydration influences many other less-studied figures of merit necessary for a good EC, such as efficiency, power, film usage, self-discharge, physical stability, and aging. The 200 °C maximum temperature avoids significant modification of the oxide's crystal structure and oxidation state; by keeping the temperatures low, we focus on the impact of manganese oxide drying and hydration. Through the evaluation of an extensive list of electrochemical and physical properties of manganese oxide thin-films, we identify how specific storage/drying methods improve these parameters. This work is the first of its kind to systematically relate a large range of storage/drying conditions to a full gamut of electrochemical properties that are important for EC materials. The knowledge gained allows for an intelligent choice of storage/drying condition based on the desired electrochemical and physical parameters and can aid in comparing literature that uses different storage/drying conditions. Using the knowledge acquired from this thorough study, we then strategically design an innovative new double-deposition method that demonstrates the optimal properties achieved from heat treatment and wet storage.

2. Materials and methods

Manganese oxide was potentiostatically electrodeposited onto stainless steel (SS304, McMaster-Carr). Prior to deposition, the stainless steel was cleaned by washing thoroughly with 18 MΩ cm water, methanol, and 18 MΩ cm water again, drying with a Kimwipe between each step. The stainless steel was then cut into 1×9 cm strips and wrapped with Parafilm leaving an exposed length of 3 cm (6 cm^2 electrode surface area, deposition on both sides). The electrodes were rinsed with methanol, wiped with a Kimwipe, and rinsed with 18 MΩ cm water again immediately before the deposition. Although it is well-known that manganese oxide has stability issues when coated on smooth surfaces such as stainless steel, we view stainless steel as an ideal substrate for monitoring physical stability since film peeling and flaking can be clearly observed by visual inspection. The single-deposition films were formed using a 1 min potentiostatic deposition at 1.0 V vs. a saturated calomel electrode (SCE) in 0.2 M $MnSO_4$ (made from powder, purity ≥ 99%, Sigma Aldrich, in 18 MΩ cm water) that was at 55–60 °C, deaerated with N_2, and continuously stirred. Following electrodeposition, all electrodes were rinsed with 18 MΩ cm water.

A Bio-Logic VMP3 Multipotentiostat, Ag/AgCl reference electrode (1 M KCl filling solution, ~220 mV vs. SHE, −21 mV vs. SCE) and a large 18 cm^2 geometric area Pt gauze counter electrode were used for all electrochemical depositions and experiments. While a Ag/AgCl reference was used for this work, the potentials herein are reported versus SCE, as this is more common in the literature and allows for facile comparison with literature data.

Initially, manganese oxide films made from a single deposition were investigated using five different storage or drying conditions, including three room-temperature dried/stored conditions: "wet-stored films" were stored in 0.5 M Na_2SO_4 (made from powder, purity ≥ 99%, Sigma Aldrich in 18 MΩ cm water); "humid films" were air-dried in ambient conditions; and, "desiccator-dried films" were stored in a desiccator. Two elevated temperatures were also tested, oven-drying at either 100 °C or 200 °C in air for two hours. At least three replicates were run for each electrochemical experiment and all error bars in figures represent one standard deviation.

Based on the results from the single-deposition films, a double-deposition synthesis was developed. The first deposited manganese oxide layer was rinsed with 18 MΩ cm water and oven-dried at 200 °C for 2 h. After the second deposition, these films were rinsed and stored under "wet-storage" conditions (i.e. in 0.5 M Na_2SO_4) until use. These depositions were carried out under the same conditions described above, but instead of controlling deposition time the total cumulative charge for both depositions (Q_{dep}) was limited to 1.6 C. This value was chosen as it was a rough average of the deposition charges for the single-deposition electrodes. The total Q_{dep} was divided between the two depositions with a 10:90 $Q_{dep}1$:$Q_{dep}2$ ratio (160 mC:1440 mC).

Galvanostatic charge-discharge (GCD) and cyclic voltammetry experiments were conducted in 0.5 M Na_2SO_4 electrolyte using a potential window of either 0.4–0.8 V or 0.0–1.0 V. Cyclic voltammograms (CVs) were collected using a sweep rate of 10 mV s^{-1}. Three GCD cycles were collected at various currents between 0.05 and 30 mA. Because of some film dissolution at low currents (shown below), very low currents were run last. Cycle life and electrode stability were evaluated using up to 4000 CV cycles or 1000 GCD cycles at 1 mA. While capacitance and energy density are often reported in terms of mass or volume, herein the properties are normalized to deposition charge (Q_{dep}) since this provides a measure of the amount of film on the electrode and accurate masses for the wet films could not be measured. As a very rough estimate for the reader, we calculate a mass-loading of 120 μg/cm^2, if we assume 100% of Q_{dep} produces MnO_2; however, as discussed below, other manganese oxides are formed and some Q_{dep} is likely going to non-deposition processes, so this mass-loading should be used with caution.

Self-discharge experiments were performed on films which had