

Surface Area and Morphology of Electrodeposited Manganese Dioxides for Electrochemical Capacitor Applications

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Manganese dioxide thin film electrodes are promising alternative to electrodes based on powdered materials. Thin film electrodes, which are in the order of tens of nanometers thick, have low resistance and good electrical conductivity. They can be prepared by electrodeposition of material directly onto a substrate, which is an advantage over powdered materials since they do not require any additives or binder.

Manganese dioxide thin films have been shown to have much higher specific capacitance than the corresponding powdered material [1]. However, manganese dioxide thin film electrodes are limited by their relatively low specific energy. In thin film electrodes, the surface area and morphology are important factors influencing their performance. Hence, in order to optimize performance, the surfaces of these materials must be tailored for maximum capacitance.

It is known that the deposition conditions can alter the performance of MnO₂ thin films [1]. This is because the deposition conditions determine the oxidation mechanism of Mn(II) ions and also the process of crystal nucleation and growth.

In this work, we have synthesized a range of thin film MnO₂ electrodes using chronoamperometry in an acidic solution of MnSO₄. The current-time profiles for these depositions showed a significant increase in electrode surface area during deposition (Figure 1). This increase allowed us to calculate the electrochemically active surface area of MnO₂ electrodes. By performing depositions for a range of times, we were able to determine how the surface area changes with deposition time, giving insight into the mechanism of crystal nucleation and growth.

We have proposed that the mechanism of MnO₂ formation occurs by the initial oxidation of Mn²⁺_(aq) ions to Mn³⁺ ions. The Mn³⁺ ions begin to nucleate on the surface of the electrode, which increases the electrochemically active surface area. As the deposition continues, the thin film is formed by the continued growth of these crystallites which begin to merge, and decrease the surface area.

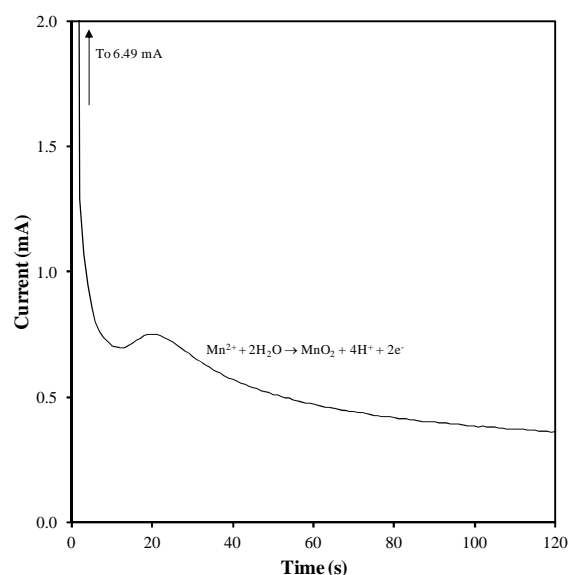


Figure 1. Chronoamperometric response for manganese dioxide deposition.

This hypothesis was supported by characterization of the thin films using TEM and AFM. AFM images show the formation of crystallites on the surface at the start of deposition, followed by the continued growth of these crystallites at longer deposition times. TEM images also indicated that the growth of the film occurs by crystallite nucleation followed by growth of the particles.

1. Cross, A., et al., *Journal of Power Sources*, 196 (2011) 7847-7853.