

# Effect of Electrodeposition Potential on Surface Free Energy and Supercapacitance of MnO<sub>2</sub> Thin Films

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The effect of anodic deposition potential on the supercapacitance of manganese dioxide (MnO<sub>2</sub>) and effect of surface free energy (SFE) on the supercapacitance are discussed. MnO<sub>2</sub> thin films have been synthesized using a potentiostatic electrodeposition method. Their structure, morphology, wettability, electrochemical properties and supercapacitance are discussed. The observed specific capacitance ( $C_s$ ) of MnO<sub>2</sub> thin films is 127 F/g for the deposition potential at 1.20 V/Ag/AgCl. These films also show better stability for over 1000 cycles. The porous MnO<sub>2</sub> thin films lead to high SFE and a corresponding high value of specific capacitance.

**Key words:** Electrodeposition, supercapacitance, surface free energy

## INTRODUCTION

Supercapacitors are being required to store more and more energy. This requirement is because of the miniaturization of electronic gadgets. They possess fast charge–discharge rates and a long cycle life as well as high power density.<sup>1–6</sup> In addition, they are required to enhance their energy density so that it will fulfill future needs. They have a wide scope in day-to-day appliances as well as in hybrid vehicles. Electronic gadgets in daily use also need durable power sources with minimum space. This has resulted in research to improve capacitance values. Improved cell voltage is the critical factor which gives rise to large energy storage in the form of supercapacitors.<sup>3,7</sup> Nowadays, carbon-based electrical double-layer capacitors are being extensively studied for their low cost, larger surface area, better electrical conductivity, high porosity and outstanding cycling stability.<sup>8</sup> However, low capacitance, less than 300 F/g, is not desirable because it limits the energy storage capacity of supercapacitors and

is an obstruction to any further improvement in pseudocapacitance. The pseudocapacitive metal oxides/hydroxides and their binary systems possess high pseudocapacitances from a reversible faradic reaction.<sup>8–13</sup>

Manganese oxides have emerged as important materials for supercapacitor applications.<sup>14–16</sup> They have low toxicity, high abundance, low cost and are eco-friendly, and can be synthesized by many methods.<sup>17–19</sup> Manganese oxides have established their usefulness in energy storage. They were used in the first Leclanche alkaline battery which was developed in the 1860s.<sup>14</sup> Currently, they are being studied as cathode materials for lithium ion batteries.<sup>15,17,20–22</sup> Their application as rapid charging materials for supercapacitors is also being studied.<sup>14,23</sup> To improve the electrochemical behavior of manganese dioxide (MnO<sub>2</sub>), it has to be fabricated in different forms of nanostructure which can be used in batteries and supercapacitors.<sup>24–26</sup> However, MnO<sub>2</sub> electrodes have low capacitances of  $\leq 470$  F/g which is much less than the theoretical capacitance of 1110 F/g.<sup>27–30</sup> Storage of energy, as a surface phenomenon in supercapacitors, can be improved by reducing the size of the structures to nanoscale.<sup>28–32</sup> To maintain the electrochemical

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