Electrochemical Reduction and Deposition of Reduced Graphene Oxide/Manganese Oxide Composite for Supercapacitor Applications via Pulse-Chronoamperometry

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Abstract: The reduced graphene oxide/manganese oxide composite was deposited on the nickel current collector using the Pulse-Chronoamperometry method in a mixture of graphene oxide dispersion and manganese acetate as the precursor. The graphene oxide (GO) was electrochemically reduced to reduced graphene oxide (rGO) and deposited with manganese oxide (MnO_x) at the same time. The effects of manganese acetate ($Mn(Ac)_2$) concentration, deposition temperature, voltage and time on the specific capacitance of rGO/MnO_x electrode were investigated. The electrochemical properties were characterized using galvanostatic charge-discharge and cyclic voltammetry. The effects of electrochemical reduction and deposition parameters on the specific capacitance of rGO/MnO_x electrode were studied using Central Composite Design methodology and a 2 factors interaction model equation was evaluated. The rGO/MnO_x electrode synthesized using 0.2 M of $Mn(Ac)_2$, at 70 °C and -1.0 V versus Saturated Calomel Electrode (SCE) with a total deposition time of 800s exhibited a specific capacitance of 665 F/g was obtained at the current density of 5 A/g. The high specific capacitance of rGO/MnO_x electrode showed its potential application for the fabrication of supercapacitors. This study provides an environmental friendly, time effective and costs efficiency way to reduce graphene oxide and to deposit the rGO/MnO_x composite for electrochemical energy storage application.

Keywords: Reduced graphene oxide; Manganese oxide; Electrochemical reduction; Supercapacitor; Pulse chronoamperometry

1. Introduction

The graphene or reduced graphene oxide (rGO) and metal oxide composite has shown high potential application for energy storage devices such as lithium ion batteries and electrochemical capacitors due to their synergistic effects. Graphene or rGO provides a good conductive porous matrix for metal oxide to enhance its electrical conductivity and reduce the charge transfer resistance, while the metal oxide suppresses the restacking of graphene layers and provides a large capacity for energy storage [1]. Various rGO/metal oxide composites have been reported in the application of electrochemical capacitor or supercapacitor such as rGO/SnO_2 [2], rGO/Co_3O_4 [3], rGO/MnO_2 [4], rGO/Fe_3O_4 [5], rGO/ZnO [6] and rGO/NiO [7] for the past few years. These composites were prepared using sol-gel, hydrothermal, solvothermal and electrochemical reduction and deposition methods [8].

Yao and co-workers [4] prepared the rGO/MnO_2 composite using the hydrothermal method with the reflux process. Potassium permanganate, $KMnO_4$ was used as the precursor and mixed with oxalic acid in the GO dispersion. The resulting mixture was refluxed at 187 °C for 4 hours to obtain MnO_2-GO composite. The composite was further reduced to graphene nanosheet by mixing with sodium borohydride powder which is a strong reductant, refluxed at 207°C for another 4 hours and finally dried for 12 hours in a vacuum oven at 187°C. The specific capacitance of 467 F/g was measured at the current density of 1 A/g. Ezeigwe et al. [9] reported the solvothermal method to produce graphene/MnO_2 composite with 380 F/g at a scan rate of 5 mV/s. The composite was prepared using manganese sulphate and

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