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Spray deposited amorphous RuO_2 for an effective use in electrochemical supercapacitor

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Abstract

The structural, surface morphological and optical properties of sprayed ruthenium oxide thin film were investigated using XRD, SEM and optical absorption measurements. The structural analysis from XRD pattern showed the formation of RuO_2 in amorphous phase. The scanning electron micrographs revealed network-like morphology of ruthenium oxide. The optical studies showed a direct band gap of 2.4 eV for ruthenium oxide films. Ruthenium oxide thin film exhibited a cyclic voltammogram indicative high reversibility of a typical capacitive behavior in 0.5 M H_2SO_4 electrolyte. A specific capacitance of 551 F/g was obtained with ruthenium oxide thin film (electrode) prepared by spray pyrolysis method. The specific capacitances of 551 and 450 F/g at the scan rate of 5 and 125 mV/s, respectively, indicate that the capacitance value varies inversely with scan rate.

Keywords: Ruthenium oxide; Thin films; Spray deposition; Surface morphology; Optical properties; Supercapacitor

1. Introduction

Ruthenium oxide (RuO_2) belong to the family of transition metal oxide with rutile structures, which exhibits interesting properties such as low resistivity, high chemical and thermodynamic stability. Due to such properties, RuO_2 finds great promise in various applications in the very large scale integration (VLSI), as a buffer layer for YBCO superconducting thin films, as an electrochromic material, as catalysts, conductive electrodes and hydrocarbon sensors [1]. The well-known application of RuO_2 is as an electrode in energy storage electrochemical supercapacitors. Electrochemical supercapacitors are the novel energy-storage devices that possess high power density, exhibit excellent pulse charge–discharge property and very long cycle life. During the last decade, supercapacitors have received significant attention to their potential applications in many fields including surge-power delivery devices for electric vehicles, backup-power storage for calculators, starting power for fuel cells, digital mobile telecommunication and memory back-up devices. Supercapacitors are maintenance-free substitutes for batteries in these applications [2–5].

Among the many transition metal oxides, such as RuO_x, NiO_x, and IrO_x, that have been used as an electrode materials for supercapacitors, the most success has been achieved using ruthenium oxide due to its advantages of a wide potential window of highly reversible redox reactions [6], remarkably high specific capacitance [7], and a very long cycle life and metallic type conductivity. Galizzioli et al. [8] first recognized that the current response of thermally prepared anhydrous ruthenium oxide film was similar to that of an ideal capacitor. In recent years, [9,10] the use of hydrous ruthenium oxide as an electrode material was investigated. It was found that powder form of amorphous and hydrous ruthenium oxide formed by

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the sol–gel method was a promising for electrochemical capacitor with high power density and energy density [11,12]. A specific capacitance of 768 F/g has been obtained from an amorphous hydrous ruthenium oxide prepared by sol-gel method [6,13]. In thin film form, Hu et al. [14–16], and Park et al. [17] have successfully employed electrochemically deposited hydrous ruthenium oxide for electrochemical supercapacitors (specific capacitance = 788 F/g). Fang et al. [18] have prepared ruthenium oxide film electrode by organic precursor method and obtained maximum specific capacitance of 593 F/g and interfacial capacitance of 4 F/cm^2. Kim et al. [19] have prepared ruthenium oxide film electrode with an average specific capacitance of 650 F/g and good high rate capability by electrostatic spray deposition. Table 1 shows specific capacitance values of ruthenium oxide electrode deposited by different methods.

Though the hydrous ruthenium oxide exhibits excellent pseudocapacitive behavior with large specific capacitance and good reversibility, the low abundance and high cost of the precious metal are major limitations to commercial application [20]. This has caused the researchers to find new materials like transition metal oxides, or loading of small amount of Ru in other transition metal oxides or in carbon electrode. Alternatively one can fabricate the RuO_2 electrode by a method having high yield, i.e. by a method that can deposit material of large area at expense of small quantity of initial ingredients. One such method is spray pyrolysis, in which a precursor solution is pulverized by means of a neutral gas so that it arrives at the hot substrate in the form of very fine droplets. The constituents react to form a chemical compound onto the substrate. Simplicity and economic viability factors make film formation by spray pyrolysis deposition technique very attractive [21].

In this work, by spraying 20 ml of 10 mM aqueous solution of $RuCl_3$, the RuO_2 films have been deposited on ITO substrates and based on the charge storage purposes, physical and supercapacitive characterization of ruthenium oxide films have been investigated.

2. Experimental

Commercially available corning glass substrates and tin-doped indium oxide (ITO) coated glass (Samsung Corning Co. Ltd., Gumi Korea) were used as substrates. They were sputter coated with thickness of 1650 ± 200 Å, transmittance of 80–92% and resistance of 9 ± 1 Ω/cm. The substrates were ultrasonically cleaned in acetone and then in isopropyl alcohol and finally washed with triple distilled water. Substrates were dried in argon gas before using for film deposition. For deposition of ruthenium oxide thin films, the 10 mM ruthenium chloride solution was prepared in double distilled water and sprayed through a specially designed glass nozzle onto hot glass and ITO substrates [Area 6×2 cm^2]. The deposition parameters like solution concentration, spray rate, nozzle to substrate distance (NSD), carrier gas flow rate, etc., were kept at the optimized values. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) of ruthenium chloride in powder form was carried out for optimization of deposition temperature using TA instrument (USA) SDT 2960 (simultaneous TGA-DTA). The solution was sprayed through a glass nozzle onto substrates kept at 573 K. The spray rate 4 cm^3/min was maintained using air as a carrier gas. The temperature was controlled with an electronic temperature controller. Hazardous fumes evolved were expelled out from deposition chamber by an exhaust system attached to spray pyrolysis unit. To study the structural properties of the films, X-ray diffraction analysis was performed on a X-ray diffractometer (RINT/PMAX 2500, Rigaku, Japan) with copper target ($\lambda = 1.5405$ Å). Surface morphology was examined using scanning electron microscope (Cambridge Stereoscan 250 MK-3 unit). The cross-sectional SEM image was used to estimate the thickness of the film. The optical absorption was measured within the wavelength range 350–850 nm, using a UV–vis spectrophotometer (Varian-Cary 100, Austria). The electrochemical analysis of the RuO_2 films deposited on ITO coated glass substrate was studied by cyclic voltammetry

Table 1
The specific capacitance values of ruthenium oxide electrode deposited by different methods

Serial number	Material	Deposition method	Concentration of H_2SO_4 electrolyte	Scan rate (mV/s)	Specific capacitance (F/g)	Reference number
1	Amorphous $RuO_2 \cdot xH_2O$ powders	Sol–gel	39 wet %	–	768	[11]
2	Amorphous $RuO_2 \cdot xH_2O$ powders	Sol–gel	38 wet %	2	750	[12]
3	Amorphous $RuO_2 \cdot xH_2O$ powders	Sol–gel	0.5 M	2	768	[6]
4	RuO_2	Electrochemical	0.5 M	10	788	[17]
5	RuO_2	Spray	0.5 M	–	593	[18]
6	RuO_2	Spray	0.5 M	20	650	[19]
7	RuO_2	Spray	0.5 M	20	500	[22]
8	Crystalline RuO_2	Non-ionic surfactant templating	0.5 M	2	58	[27]