Supercapacitive performance of hydrous ruthenium oxide ($\text{RuO}_2 \cdot n\text{H}_2\text{O}$) thin films synthesized by chemical route at low temperature

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Abstract. In the present investigation, we report the synthesis of ruthenium oxide ($\text{RuO}_2 \cdot n\text{H}_2\text{O}$) thin films by simple chemical bath deposition (CBD) method at low temperature on the stainless steel substrate. The prepared thin films are characterized for their structural and morphological properties by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The structural study revealed that the ruthenium oxide thin films are amorphous. Scanning electron microscopy study shows compact morphology with small overgrown particles on the surface of the substrate. FT-IR study confirms the formation of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ material. The supercapacitor behaviour of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film was studied using cyclic voltammetry (CV) technique in 0.5 M H_2SO_4 electrolyte. $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ film showed maximum specific capacitance of $192 \text{ F} \cdot \text{g}^{-1}$ at a scan rate of $20 \text{ mV} \cdot \text{s}^{-1}$. The charge–discharge studies of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ carried out at $300 \mu\text{A} \cdot \text{cm}^{-2}$ current density revealed the specific power of $1.5 \text{ kW} \cdot \text{kg}^{-1}$ and specific energy of $41.6 \text{ Wh} \cdot \text{kg}^{-1}$ with 95% coulombic efficiency.

Keywords. Thin films; chemical bath deposition (CBD); supercapacitor; charge–discharge properties.

1. Introduction

In recent years, development of electrochemical supercapacitors had been attracting a pivotal role in micro power source for medical instruments, back-up power source for computer memories, portable electronic systems, digital communication devices and electric vehicles due to their high power density and long cycle life compared with batteries and high energy density compared with conventional capacitors. Electrical energy storage is required for many applications ranging from consumer products and telecommunication devices to electric/hybrid vehicles and stand-by power systems. There are two types of supercapacitors, an electric double layer capacitor (EDLC) and a pseudocapacitor. The charge storage in EDLC is achieved by the formation of a double layer on the surface of the electrode material, whereas, in redox supercapacitors, the charge is stored on both the electrode surface through a double layer and bulk of the material via Faradaic reaction. Hence, the charge stored in redox supercapacitors may be greater than that in double layer counterparts (Ahn *et al* 2006; Yu and Gao 2009).

Many transition metal oxides are under scrutiny for use as electrode materials for supercapacitor applications. For a material to be useful as a pseudocapacitor, it should have several oxidation states, high electrical conductivity and electrochemical stability. Among the various transition metal oxides, ruthenium oxide ($\text{RuO}_2 \cdot n\text{H}_2\text{O}$) fulfils these requirements and it may be one of the most promising pseudocapacitor materials (Park *et al* 2004a;

Gujar *et al* 2007). High specific capacitance of ruthenium oxide resulted from pseudocapacitance, which originated from the Faradic reaction between Ru and H ions in acidic electrolyte. $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ in both crystalline and amorphous forms is of crucial importance for theoretical as well as practical purposes due to the unique combination of characteristics, such as metallic conductivity, high chemical and thermal stabilities, catalytic activities, electrochemical redox properties and field emitting behaviour (Kim and Kim 2001). Usually, various methods such as solution chemistry techniques, reactive sputtering, spray pyrolysis, organometallic chemical vapour deposition, thermal decomposition and sol-gel method have been employed to prepare ruthenium oxide thin films. Recently, ruthenium oxide has been prepared by electrochemical synthesis techniques such as cathodic electrosynthesis or potential cycling method (Huang *et al* 2006; Jow *et al* 2007). Though RuO_2 exhibits excellent pseudocapacitive behaviour with large specific capacitance and good reversibility, the low abundance and high cost of this precious metal are major limitations for its commercial application. Thus, the cost effectiveness and ease of synthesis are the important factors in the successful commercialization of supercapacitor (Mane and Lokhande 2000; Pico *et al* 2008). Alternatively, one can fabricate RuO_2 electrode by a method having high yield, i.e. by a method that can deposit material on large area at the expense of small quantity of initial ingredients. Accordingly, a simple method with high product yield is worthy of being developed. One such method is chemical bath deposition (CBD), which has been well developed to manufacture large-area thin films in view of its numerous advantages: it is effortless, simple, cost effective,

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safe and reproducible. It does not require sophisticated instruments, the preliminary chemicals are generally accessible, cheap and the preparation parameters are easily controlled. The present work describes synthesis of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin films by CBD method and its application for supercapacitor electrodes (Dhawale *et al* 2010; Pawar *et al* 2011).

2. Experimental

Preparation of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin films by CBD method is based on the heating of an acidic bath of ruthenium (III) chloride using 10 mM $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ as a source of ruthenium ions and 0.1 M ammonium persulphate as a complexing agent. The stainless steel substrates were immersed in bath and the bath was placed at 343 K for 2 h. The substrate was plated with ruthenium oxide thin film which was blackish in colour, was then removed from the bath, washed with double-distilled water and dried in air.

Further the films were characterized using different characterization techniques. X-ray diffraction (XRD) pattern was obtained with Philips (PW 3710) diffractometer using $\text{CrK}\alpha$ radiation ($\lambda = 2.29 \text{ \AA}$) for structural characterization of the films. The surface morphology was investigated using JEOL JSM-6360 scanning electron microscope (SEM). FT-IR study was performed to identify the presence of any water bending or stretching vibrations in the synthesized compound. Fourier transform infrared spectroscopy (FT-IR) was recorded between 4000 and 450 cm^{-1} at a spectral resolution of 2 cm^{-1} on a Perkin-Elmer 1710 spectrophotometer using KBr pellets at room temperature in order to identify the characteristic bonding in the material. The electrochemical analysis of the films deposited on stainless steel substrate was studied by cyclic voltammetry (CV) using the potentiostat (263A EG&G, Princeton Applied Research Potentiostat). The electrochemical impedance measurements were conducted with a versastat 3G frequency response analyser (FRA) under Zplot program (Scribner Associates Inc.). The charge-discharge experiments were carried out using WonATech Automatic Battery Cycler WBCS3000 system, interfaced to a computer.

3. Results and discussion

3.1 Thin film formation and reaction mechanism

Figure 1 shows schematic diagram of chemical bath, which is used for the deposition of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film. CBD is based on the formation of solid phase from a solution, which involves two steps as nucleation and particle growth. In nucleation, the clusters of molecules formed undergo rapid decomposition and particles combine to grow up to a certain thickness of the film by heterogeneous reactions at the substrate surface. In the deposition of metal oxides, generally metal ions are complexes in such a way that reaction

Figure 1. Schematic diagram of chemical bath deposition method for preparation of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin films.

takes place between slowly released metal ions to form product in thin film. RuO_2 thin film has been deposited on stainless steel substrates by slow hydrolysis of ruthenium chloride. For deposition of RuO_2 film, RuCl_3 is used as source of ruthenium Ru^{3+} cations. These Ru^{3+} cations get complexed with NH_3 forming ruthenium complexed ions ($\text{Ru}(\text{NH}_3)_n^{3+}$). When this solution is heated, the ionic product exceeds the solubility product precipitation occurs on the substrate and in the solution to form RuO_2 nuclei and thus RuO_2 film forms on the substrate by the following reaction:

In this process, the ammonium persulfate is introduced as a complexing agent and exerts itself to control the release of Ru^{3+} ions for deposition of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin films. The thickness of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film on stainless steel substrate was determined gravimetrically by measuring change in the weight of substrate before and after the film deposition and using the bulk density of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ (6.97 g/cm^3). It is observed that after about 30–40 min, precipitation starts and deposition of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ begins by heterogeneous reaction at substrate surface and film thickness increases with time. The terminal thickness obtained was 0.25 μm for 120 min, after which decrease in the film thickness was observed probably due to the peeling of the powdery material from the substrate surface. Variation in the thickness of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin films as a function of deposition time is shown in figure 2. Inset of figure 2 is a photograph of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film, blackish in colour over $\sim 20 \text{ cm}^2$ area (two sides of substrates) confirming the achievability of CBD method for large area deposition.

Figure 2. Variation in thickness of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin films as a function of deposition time. [Inset is photograph of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film on stainless steel substrate].

Figure 3. XRD pattern of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ on stainless steel substrate.

3.2 Structural study

XRD pattern was recorded in 2θ range of $10\text{--}100^\circ$, in order to study the structural analysis of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film. Figure 3 shows X-ray diffraction pattern of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film deposited on stainless steel substrate. XRD pattern showed the absence of all sharp diffraction lines, indicating that the deposited $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film is amorphous. The peak observed in the pattern is due to the stainless steel substrate. Patake and Lokhande (2007) reported such amorphous type nature of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin films synthesized by M-CBD, i.e. successive ionic layer adsorption and reaction (Patake and Lokhande 2007). Hu and Huang (1999) reported the formation of amorphous ruthenium oxide by cyclic voltammetry (Hu and Huang 1999).

3.3 Surface morphology

Scanning electron microscopy was used to evaluate surface morphology of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film. Figure 4 shows scanning electron micrographs of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film on the stainless steel substrate at two different (a) $5000\times$ and (b) $10,000\times$ magnifications. SEM at lower magnification

showed the total coverage of the substrate surface. The higher magnification SEM image showed compact morphology with ordinary shaped nanograins (size $\sim 33\text{ nm}$) spread over the substrate surface with small cracks on the surface.

3.4 FT-IR study

FT-IR studies were performed in order to identify the presence of bonding or stretching vibrations in the synthesized $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ material. FT-IR absorption spectrum of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ recorded in the range $4000\text{--}400\text{ cm}^{-1}$ is shown in figure 5. The small bond at (ν_1) 466 cm^{-1} , may be influenced by hydrous RuO_2 (Chen *et al* 2009). The strong bond (ν_2) at around 669 cm^{-1} is associated with characteristic vibrational mode of rutile RuO_2 (Mink *et al* 1995). The absorption bond (ν_3) at around 1019 cm^{-1} is assigned for the characteristic stretching vibration of peroxy groups (Wang and Herron 1991). The absorption bond at around (ν_4) 1648 cm^{-1} is due to the vibration of hydroxyl groups of molecular water (Karuppuchamy and Jeong 2006). The sharp absorption band at (ν_5) 3408 cm^{-1} is attributed to the stretching vibrations of OH (Sugimoto *et al* 2004). Thus, FT-IR study clearly confirms the formation of ruthenium oxide with hydrous nature.

3.5 Supercapacitive study

The supercapacitive performance of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film is carried out by cyclic voltammetric technique in the potential range of $0\text{--}+1\text{ V}$ vs SCE in $0.5\text{ M H}_2\text{SO}_4$ electrolyte. The effect of scan rate on the supercapacitive behaviour was studied and is shown in figure 6. It is found that the current under the curve slowly increases with scan rate (Broughton and Brett 2002). The capacitance (c) of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ was calculated by means of the following relation:

$$C = \frac{I}{dv/dt}, \quad (5)$$

where I is the average current in the ampere and dv/dt the voltage scanning rate. The specific capacitance (C_s) of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ was obtained by dividing its respective weight using the relation

$$C_s = \frac{C}{W}, \quad (6)$$

where, W is weight of the active material on the substrate. The interfacial capacitance (C_i) was calculated using the relation

$$C_i = \frac{C}{A}, \quad (7)$$

where A is the area of active material dipped in the electrolyte. $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film showed a maximum specific capacitance of $192\text{ F}\cdot\text{g}^{-1}$ and an interfacial capacitance of $0.0345\text{ F}\cdot\text{cm}^{-2}$ at a scan rate of $20\text{ mV}\cdot\text{s}^{-1}$. The specific and interfacial capacitance values decreased from $192\text{--}140\text{ F}\cdot\text{g}^{-1}$

and $0.0345\text{--}0.0252\text{ F}\cdot\text{cm}^{-2}$, respectively as the scan rate increased from $20\text{--}100\text{ mV}\cdot\text{s}^{-1}$. Ruthenium oxide (RuO_2) is stable in acidic solution and shows a metallic conductivity in the crystalline form. On the other hand, hydrous RuO_2 is a mixed conductor that conducts protons and electrons in acidic solution (as shown in (5)):

During the charging–discharging process, the protons and electrons are transferred between RuO_2 and the electrolyte solution. Thus, it is desirable to have high electronic conductivity as well as high proton conductivity. The higher scan rate leads to either depletion or saturation of protons in the electrolyte inside the electrode during the redox process due to slow transfer of protons. This mainly results in the increase of ionic resistivity leading to a drop in the capacitance of the electrode. The decreasing capacitance suggests that parts of the surface of the electrode are inaccessible at high charging–discharging rates. Hence, the specific capacitance obtained at the slowest scan rate is believed to be the closest to that of full utilization of the electrode material (Conway and Pell Dec 1998; Park et al 2004a). Park et al (2004a) reported

$788\text{ F}\cdot\text{g}^{-1}$ maximum specific capacitance of RuO_2 on the titanium substrate by electrodeposition. The strong influence of high resistivity limits to achieve the maximum specific capacitance (Zheng et al 1995; Park et al 2004b; Kim and Kim 2006).

3.6 Electrochemical impedance studies (EIS)

Electrochemical impedance spectroscopy (EIS) is a powerful, rapid and accurate non-destructive method for the conductivity study as well as to elucidate mechanism and kinetics of chemical and electrochemical reactions on $\text{RuO}_2\cdot n\text{H}_2\text{O}$ films. During EIS experiments, a small amplitude a.c. signal is applied to the system being studied. Therefore, it is a non-destructive method for the evaluation of a wide range of materials, including coatings, anodized films and corrosion inhibitors. As almost all the kinetic parameters of electrode processes depend on the potential and/or film thickness in an electroactive film, the effects of these experimental variables were closely examined over the whole range of frequencies of interest (Komura et al 1995; Mondal et al 2005). In order to investigate the electrochemical characteristics of the electrode and electrolyte in quantitative manner,

Figure 4. Scanning electron micrograph of $\text{RuO}_2\cdot n\text{H}_2\text{O}$ thin film.

Figure 5. FT-IR spectrum of $\text{RuO}_2\cdot n\text{H}_2\text{O}$ thin film.

Figure 6. Scan rate variation of $\text{RuO}_2\cdot n\text{H}_2\text{O}$ thin film measured in potential range of $0\text{--}+1\text{ V}$ in $0.5\text{ M H}_2\text{SO}_4$ electrolyte.

impedance measurements were performed. The electrochemical impedance measurement (at open circuit voltage, in the frequency range 10^5 – 10^{-2} Hz) of RuO₂·nH₂O electrode was carried out in 0.5 M H₂SO₄ electrolyte concentration. The complex-plane plot shown in figure 7 is divided into high and low frequency regions. The frequency at which there is deviation from the semicircle is known as “knee” frequency, which reflects the maximum frequency at which capacitive behaviour is dominant. The presence of semicircle in the high frequency region suggests that there is charge transfer resistance, while straight line in the low frequency region angle of $\sim 45^\circ$ to the real axis can be attributed to the capacitive behaviour. Inset (figure 7) shows expanded high frequency region of the same plot. This implies that the supercapacitor shows a blocking behaviour at high frequencies and capacitive behaviour at low frequencies (Arabale *et al* 2003; Chen *et al* 2003; Dandekar *et al* 2005). ESR of RuO₂·nH₂O film arising from contact resistance of substrate is found to be 22 Ω in the high frequency region and the mid frequency of spectrum revealed electrode/electrolyte interface processes. The relaxation time constant (τ_0) is calculated from plots of $C'(\omega)$ vs frequency (figure 8). It is deduced from the equation that $\tau_0 = 1 / 2\pi f_0$, where f_0 corresponds to the peak frequency in the imaginary capacitance plot and it is found to be 1.98 s. (τ_0) is a very important factor, which decides the applicability of electrode material according to energy demand. Smaller relaxation time constant value exhibits a faster energy release capability of electrode, so as to provide higher power density (Ganesh *et al* 2006).

3.7 Charge–discharge study

The galvanostatic charge–discharge curves of RuO₂·nH₂O were measured by chronopotentiometry technique between

Figure 7. Complex-plane plot of real Z' vs imaginary Z'' of RuO₂·nH₂O electrode in 0.5 M H₂SO₄ electrolyte.

Figure 8. Plot of real capacitance (C') vs frequency ($\log f$) of RuO₂·nH₂O electrode in 0.5 M H₂SO₄ electrolyte.

Figure 9. Charge–discharge curves of thin films measured at $300 \mu\text{A}\cdot\text{cm}^{-2}$ in potential range of 0–0.9 V in 0.5 M H₂SO₄ electrolyte.

0 and +0.9 V (vs SCE) at $300 \mu\text{A}\cdot\text{cm}^{-2}$ in 0.5 M H₂SO₄ electrolyte. The charge–discharge curves in figure 9 shows little iR drop when the sign of applied current is altered. After this ohmic response, the charge–discharge curves are approximately linear with charge and discharge time, signifying that RuO₂·nH₂O behaves as a capacitor. Hence, this material is a suitable electroactive material for supercapacitors (Wang and Hu 2004; Hu and Chen 2004). The supercapacitor parameters such as specific power (SP) and specific energy (SE) are calculated using the following relationship (Prasad and Munichandraiah 2002).

$$\text{SP} = [I \times V]/m, \quad (9)$$

$$\text{SE} = [I \times t \times V]/m, \quad (10)$$

where SP is specific power in $\text{kW}\cdot\text{kg}^{-1}$ and SE is specific energy in $\text{Wh}\cdot\text{kg}^{-1}$. The above expressions show the discharge current (I) in amperes, voltage range (V) in volts, discharge time (t) in seconds and mass of the electroactive material (m) in kilograms. The specific power and specific energy from the charge–discharge curve were found to be

1.5 kW·kg⁻¹ and 41.6 Wh·kg⁻¹, respectively. The coulombic efficiency is calculated using the following (Ganesh *et al* 2006):

$$\eta = [t_D/t_C] \times 100, \quad (11)$$

where, t_C and t_D represent the time of charging and discharging, respectively. The coulombic efficiency for RuO₂·nH₂O was found to be 95%.

4. Conclusions

Amorphous ruthenium oxide (RuO₂·nH₂O) thin films are deposited by chemical bath deposition method. SEM studies showed compact surface with small overgrown particle distributed over the substrate surface. FT-IR confirms the formation of RuO₂·nH₂O. RuO₂·nH₂O thin film shows a maximum specific capacitance of 192 F·g⁻¹ at a scan rate of 20 mV·s⁻¹. The specific power, specific energy and coulombic efficiency estimated from the charge-discharge curve is found to be 1.5 kW·kg⁻¹, 41.6 Wh·kg⁻¹ and 95%, respectively.

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