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# Highly dispersed hydrous ruthenium oxide in poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid) for supercapacitor electrode

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## Abstract

Hydrous $RuO_2$ particles were electrochemically loaded into poly(3,4-ethylenedioxythiophene) doped poly(styrene sulfonic acid), PEDOT-PSS, matrix by employing various potential cycles in cyclic voltammetry and to fabricate the PEDOT-PSS-$RuO_2 \cdot xH_2O$ electrode. The amount of hydrous $RuO_2$ particles loaded into the PEDOT-PSS matrix was easily controlled by varying the number of potential cycles. Scanning electron microscopy photographs reveal a uniform dispersion of hydrous $RuO_2$ particles in the porous structure of PEDOT-PSS matrix. Raman spectrum confirms the incorporation of hydrous $RuO_2$ into PEDOT-PSS matrix. Chronopotentiometry and cyclic voltammetry were employed in 0.5 M $H_2SO_4$ to evaluate the capacitor properties. Specific capacitance values were determined by chronoamperometry. An increasing trend in specific capacitance with loaded amount of hydrous $RuO_2$ particles in PEDOT-PSS was noticed. A maximum specific capacitance of 653 F/g was achieved.

*Keywords:* PEDOT-PSS; Hydrous ruthenium oxide; Electrochemical capacitor; Specific capacitance; Composite electrodes

## 1. Introduction

Growing demands for the generation of power sources with transient high-power density have stimulated great interest in electrochemical capacitors in recent years [1–3]. An electrochemical capacitor of large specific capacitance (supercapacitor) is formed when an electrode material with a large specific surface area is combined with a material that can be reversibly oxidized or reduced over a wide potential range. For an example, the oxides of multivalent metals such as ruthenium and iridium exhibit large faradic pseudocapacitance [4–6].

Among the various transition metal oxide materials that have been investigated over the years, hydrous $RuO_2$ exhibits prominent properties as a pseudocapacitor material [7,8]. It is well known that hydrous $RuO_2$ is an excellent material with a remarkable high specific capacitance value ranging from 720 to 760 F/g (for single electrode system) [9]. Though $RuO_2$ possess advantage in terms of operations over a wide potential range over reversible redox reactions to have high specific capacitance, the expense of $RuO_2$ deters its advantages. Therefore, it is desirable to develop thin film $RuO_2$ electrodes for minimizing the cost of using as capacitors. Thin films of $RuO_2$ have been prepared by using various techniques, including reactive sputtering [10], organometallic chemical vapor deposition [11], sol–gel [12], spray pyrolysis [13], etc. However, the cost effectiveness and case of synthesis are the important factors in the successful commercialization of supercapacitors. For these reasons, conducting polymers such as polyaniline [14], polypyrrole [15] and poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid), PEDOT-PSS [16] are promising matrix materials for embedding metal and metal oxide particles for applications in electronic devices. Niu et al. [17] reported the effect of Pt particles on the electrocatalytic behavior of Pt-modified polyaniline electrode for methanol oxidation. Bensebaaa et al. [18] reported the microwave synthesis of polypyrrole-embedded Pt-Ru catalyst for direct methanol fuel cell. They observed the average particle size of Pt-Ru as around 2.8 nm. Besides that, Ghosh and Inganas [19] reported the use of conducting polymer

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hydrogels as 3D electrodes for application in supercapacitors. They employed PEDOT-PSS as matrix and to form ionically crosslinked conducting networks by treating with $MgSO_4$. Also, polypyrrole was electrochemically loaded into the PEDOT-PSS matrix to improve the mechanical strength. This hydrogel composite electrode exhibits high effective surface area and capacitance.

In this study, hydrous $RuO_2$ particles were electrochemically loaded into the matrix of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrene sulfonic acid), PEDOT-PSS matrix. PEDOT-PSS was selected as a matrix for loading $RuO_2{\cdot}xH_2O$ particles due to the following reasons: (1) PEDOT-PSS has a good compatibility with inorganic materials, good film forming properties, high electrochemical stability and high conductivity [20]; (2) colloidal particles of PEDOT-PSS are negatively charged and expected to serve as a matrix for loading particles of $RuO_2$ particles through steric and electrostatic stabilization mechanisms; (3) PEDOT-PSS can form three-dimensional reaction zones when $RuO_2{\cdot}xH_2O$ particles are loaded into it can have high active surface area.

In this study, the capacitance of PEDOT-PSS-$RuO_2{\cdot}xH_2O$ composite was followed for various amount of loading of $RuO_2{\cdot}xH_2O$ particles in PEDOT-PSS matrix. The change in the morphology of PEDOT-PSS-$RuO_2{\cdot}xH_2O$ composites for the various loading of $RuO_2{\cdot}xH_2O$ particles was followed by scanning electron microscopy (SEM). Electrochemical performance characteristics of the composite electrodes have been evaluated using cyclic voltammetry and chronopotentiometry.

## 2. Experimental

PEDOT-PSS (Alfa, 1.34 wt%) matrix electrode was prepared by spin coating (2000 rpm for 1 min) on indium-tin oxide (ITO) substrate. A thin film of PEDOT-PSS was formed over a cleaned indium tin oxide (ITO) electrode (1.0 cm × 1.0 cm). Before each experiment, ITO coated glass was cleaned in an ultrasonic bath using detergent, double distilled water, and isopropanol, then dried with a dry nitrogen flow and followed by UV-$O_3$ treatments for 20 min.

Cyclic voltammetry was employed to incorporate $RuO_2{\cdot}xH_2O$ deposits into PEDOT-PSS matrix by cycling the potential between 0.0 and 1.0 V for 240 cycles with a scan rate of 50 mV/s. A plating solution consisting 5 mM $RuCl_3{\cdot}xH_2O$, 0.01 M HC1 and 0.1 M KC1 (pH 1.96) was used. After the deposition of $RuO_2{\cdot}xH_2O$ particles into PEDOT-PSS film, the electrode was rinsed with double distilled water for 5 min then dried at 150 °C for 30 min. The amount of $RuO_2{\cdot}xH_2O$ particles loaded into PEDOT-PSS matrix was calculated from the following equation:

$$m = \frac{Q_{\mathrm{dep}} \times M}{\mathrm{F} \times Z}$$

where amount ($m$), amount of $RuO_2{\cdot}xH_2O$ incorporated into PEDOT-PSS was calculated using the deposited charge ($Q_{\mathrm{dep}}$). $M$ is the molecular weight of $RuO_2$, $F$ the Faradic constant and $Z$ is the number of electron involved in the process. Electrochemical formation of $RuO_2{\cdot}xH_2O$ from aqueous solution containing $RuCl_3$ involves a transfer of one-electron as; $\mathrm{Ru(III)} + 2H_2O \leftrightarrow RuO_2 + 4H^+ + e$.

Electrochemical characterization was performed with PGSTAT20 electrochemical analyzer, AUTOLAB Electrochemical Instrument (The Netherlands). All experiments were carried out in a three-component cell. Indium tin oxide coated glass plate (1 $cm^2$ area), Ag/AgCl (in 3 M KC1) and platinum wire were used as working, reference and counter electrodes, respectively. A Luggin capillary, whose tip was set at a distance of 1–2 mm from the surface of the working electrode, was used to minimize errors due to *iR* drop in the electrolytes.

Surface morphology of PEDOT-PSS-$RuO_2{\cdot}xH_2O$ composite was observed by a scanning electron microscopy (SEM) (Philips X1–40 FEG). Raman spectra were taken in the quasi-backscattering geometry using 100 mW of the 514.5 nm line of an Ar ion laser, focused to a line of 5 mm × 100 μm as the excitation source (spectral resolution and the accuracy in the Raman shift in the range ~2 $cm^{-1}$).

## 3. Results and discussion

$RuO_2{\cdot}xH_2O$ particles were electrodeposited into PEDOT-PSS matrix from a solution of 5 mM $RuCl_3{\cdot}xH_2O$ in 0.01 M HC1 and 0.1 M KC1 (pH ~ 1.96) by cyclic voltammetry [21]. Conditions for the electrodeposition of $RuO_2{\cdot}xH_2O$ particles were selected after considering several aspects. Precipitation of ruthenium hydroxide occurred from $RuCl_3$ Above pH values of 4. Also, when the HC1 concentration was beyond 0.01 M, deposition of $RuO_2{\cdot}xH_2O$ was not noticed. Hence, several trial experiments were carried out to optimize the conditions for incorporation of $RuO_2{\cdot}xH_2O$.

Fig. 1 presents the cyclic voltammograms (CVs) recorded during the incorporation of hydrous $RuO_2{\cdot}xH_2O$ into PEDOT-PSS film. The scan rate for the loading of $RuO_2{\cdot}xH_2O$ particles was selected based on few considerations. We presume that scan rate may have influence on the process that is involved in $RuO_2{\cdot}xH_2O$ deposition. PEDOT-PSS is a porous matrix. Hence, diffusion of ruthenium metal ions into the porous matrix and the period of staying of the ruthenium ions at the pores of PEDOT-PSS are expected to be the determining factors for the deposition of $RuO_2{\cdot}xH_2O$ particles. These factors could be controlled through scan rate. A scan rate of 50 mV/s was selected for the deposition of $RuO_2{\cdot}xH_2O$ particles after several trials with different scan rates. In the CVs, one can observe current maximum at two potentials, 0.45 V (peak A) and 1.0 V (peak B) at various cycles. On the cathodic scan of potentials, peaks were observed at ca. 0.78 V (peal B′) and 0.2 V (peak A′). It can be seen that the voltammetric current at ca. 0.45 V (peak A) showed a steady increase with increasing the growth numbers. The results are in accordance with the formation of $RuO_2{\cdot}xH_2O$. Peak A′ is attributed to the reduction of Ru(III) species to Ru(0), and the metallic Ru is thus expected to embed into the PEDOT-PSS matrix [21]. The deposited Ru species, which may be Ru(0) and low oxy-chloro-ruthenium species, are subsequently oxidized to hydrous oxide, $RuO_2{\cdot}xH_2O$ at more positive potentials (peak B) [i.e., hydroxyl/Ru(VI) species]. Ru metallic state may be expected to be stabilized by the sulfonate groups in PEDOT-