



## Cyclic Voltammetric Analysis of Ruthenium Oxide Thin Film Electrodes: Effect of Aqueous Electrolytes†

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The electrolyte is of utmost importance for the determination of electrochemical behaviour of electrodes as the specific capacitance, operating voltage, power density are greatly dependent on the electrolyte. This work focuses on the study of different aqueous electrolytes (KOH, NaOH, KCl, CH<sub>3</sub>COONa, NH<sub>4</sub>Cl) by means of pH, ionic size, molar conductivity, mobility of the ions for the cyclic voltammetry analysis of sol-gel prepared spin coated ruthenium oxide thin film electrodes. The structural study showed the tetragonal formation of ruthenium oxide thin films. Mud-cracked and porous morphologies were clearly found. The electrolytes were of same molarity. Cyclic voltammetric analysis showed the good capacitive behaviour for all the electrolytes but it showed the maximum specific capacitance of 581 F/g for KOH electrolyte. The calculated specific power and specific energy were 36 KW Kg<sup>-1</sup> and 8.25 Wh Kg<sup>-1</sup>, respectively with 71 % efficiency. It may be assumed that the most suitable pore structure of ruthenium oxide was KOH electrolyte.

**Keywords:** Aqueous electrolyte, RuO<sub>2</sub>, Cyclic voltammetry.

### INTRODUCTION

Electrochemical double layer capacitor (EDLC) is a distinctive electrical energy storage device, which can stock up more energy than conventional capacitors and offer much higher power density than batteries. Electrochemical double layer capacitor work on the principle of double layer capacitance at the electrode/electrolyte interface. There are two main types of double layer capacitors according to the charge storage mechanism as electrical double layer capacitor and electrochemical double layer capacitor or supercapacitor. An electrochemical double layer capacitor stores energy in the double layer at the electrode/electrolyte interface, whereas the supercapacitor sustains a Faradaic reaction between the electrode and the electrolyte in a suitable potential window. Among several materials studied for supercapacitors, various forms of carbon, conducting polymers and metal oxides have received enormous interest. Besides carbon and conducting polymers, transition metal oxides are significant materials for supercapacitors, which are being widely studied due to their superior capacitive behaviour [1,2]. Among several studies, most of them reported that in both crystalline and amorphous forms RuO<sub>2</sub> has been considered as the most promising

candidate for electrode materials owing to its reversible charge-discharge process and large capacitance, high chemical and thermal stability, electrochemical redox properties [3,4]. Even though RuO<sub>2</sub> has a great advantage in terms of wide potential range of highly reversible redox reactions with high specific capacitance, it is somewhat expensive for commercial electrodes in bulk type electrochemical capacitors. Hence reducing the amount of RuO<sub>2</sub> to meet energy density and power demands by increasing its utilization efficiency and its specific capacitance is always a key issue for making the devices more cost effective [5]. Thus, there is necessity to develop a thin film process. However, sol-gel spin coating method has characteristic features, which can produce thin bond coating to provide excellent adhesion between the substrate and the top coat [6]. It can provide a simple, economic and effective method to produce high quality coatings. By spin coating, film thickness is easily changed by changing spin speed.

The purpose of this work is to employ a sol-gel spin coating technique to prepare ruthenium oxide thin films from RuCl<sub>3</sub>·nH<sub>2</sub>O precursor and taking it as the electrode material for supercapacitor. The deposited films were studied by means of XRD, SEM and electrochemical behaviour by cyclic voltammetry for different aqueous electrolytes was analyzed.

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## EXPERIMENTAL

**Preparation of RuO<sub>2</sub> electrodes:** The electrode material has to be deposited on a conducting substrate, which will act as a current collector. Stainless steel substrates with area equal to 1 cm<sup>2</sup> were used. The substrates were cleaned by detergent, washed with double distilled water and ultrasonically cleaned and dried at 100 °C. The solution of 0.01 M RuCl<sub>3</sub>·nH<sub>2</sub>O was prepared. The formation of gel and detail synthesis process is explained elsewhere [7]. The process was repeated for multiple coats. In the present work, the films used were of 4 deposition coats.

**Physical characterization:** The structures of thin films were analyzed by X-ray diffraction with a diffractometer Rigaku Ultima IV, Japan using CuK<sub>α</sub> radiation ( $\lambda = 1.54 \text{ \AA}$ ). The surface morphology was analyzed by scanning electron microscopy (SEM JEOLJSM 6360). Since deposited films were found to be porous, the accurate measurement of film thickness was not possible. Therefore deposited weight (g/cm<sup>2</sup>) of a RuO<sub>2</sub> film on substrate was measured in place of film thickness. The weight of the film was measured by a micro-analytical balance (Contech). The pH measurement of different electrolytes were carried out by Digital pH meter model EQ-610 respectively.

**Electrochemical characterization:** Cyclic voltammetry measurements were performed using an electrochemical workstation CH Instruments CH1608E. Measurements were carried out in a 3-electrode cell set up. A saturated calomel electrode (SCE) and a platinum wire electrode were used as reference and counter electrode respectively. The RuO<sub>2</sub> thin films were used as working electrode. The measurements were performed for different scan rates as well as different aqueous electrolytes KOH, NaOH, KCl, CH<sub>3</sub>COONa, NH<sub>4</sub>Cl having 0.1 M molarity each.

## RESULTS AND DISCUSSION

**Physical studies:** The deposited films were uniform, grey in colour and well adherent to the substrate. The thin film electrodes having high surface area, low mass, low cost and strong adhesion between electrode and substrate will result in low interfacial resistance, high power density and long life cycle. These are the important considerations that determine the performance of supercapacitors.

**X-ray diffraction studies:** The structural analysis of the deposited film was carried out using X-ray diffractometer varying diffraction angle  $2\theta$  from 10° to 80°. Fig. 1 shows the X-ray diffraction pattern (XRD) of as deposited RuO<sub>2</sub> thin films. It contains well-defined diffraction peaks of ruthenium oxide and stainless steel substrate, which indicates formation of crystalline and tetragonal ruthenium oxide. Similar results were observed by Fang *et al.* [8] and Park *et al.* [9] by electrodeposition. The calculated values of the lattice parameters are  $a = b = 4.5200 \text{ \AA}$  and  $c = 3.1272 \text{ \AA}$  which are in good agreement with the JCPDS data (65-2824). The peaks having (\*) star mark corresponds to stainless steel.

**Surface morphological studies:** The surface morphological study of the RuO<sub>2</sub> thin film has been carried out from SEM image. Fig. 2 shows scanning electron microscopic photographs of ruthenium oxide thin films at different magni-

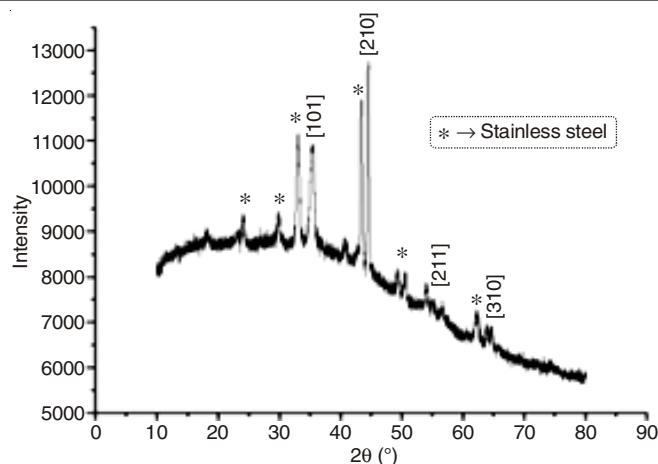


Fig. 1. XRD pattern of as-deposited ruthenium oxide thin film

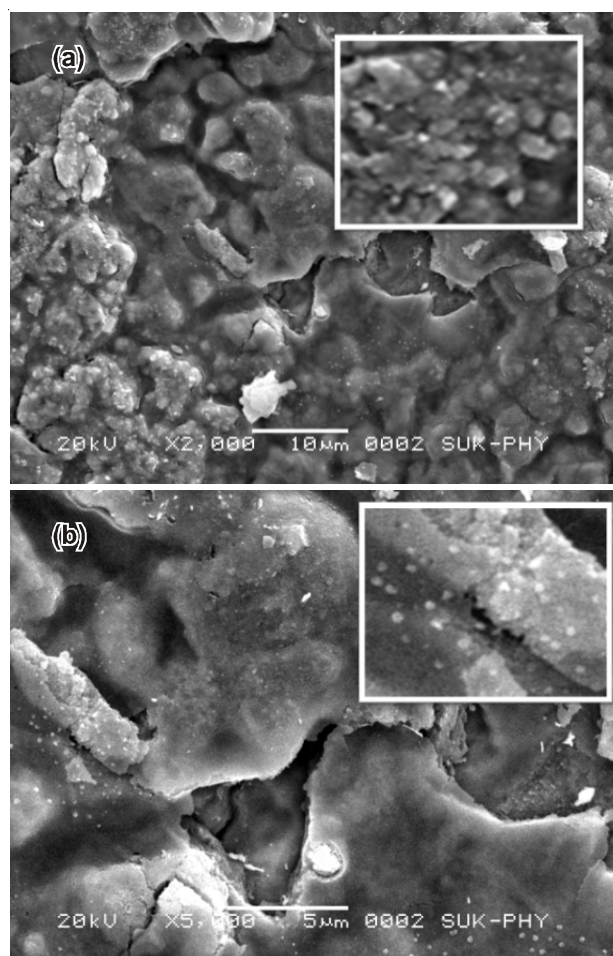


Fig. 2. SEM images of ruthenium oxide thin films (a) X2000 (b) X5000 magnification

fications. It showed that the substrate is well covered with RuO<sub>2</sub> material. The SEM image shows non-uniformly distributed aggregates giving rise to a high surface roughness. The porous and “mud-cracked” morphologies clearly found on these annealed RuO<sub>2</sub> films, which is favourable for penetration of electrolyte. The large cracks are attributed to the presence of inner stress in forming a crystalline RuO<sub>2</sub> film during the high temperature preparation step. In the inset, one can see the particles are well connected yet provide porous structure, which is much required for supercapacitors. The rough texture

represents the grain boundary surfaces. The size of pores laid in the range 40-50 nm. In electrochemical supercapacitors, an increased amount of charge can be stored on the highly extended surface area created by large number of pores within a high surface area electrode material. Nanocrystalline and porous materials as electrode material exhibit good electrochemical performance because these materials possess both a high surface area and pores which are adapted to the size of ions [10-12].

**Electrochemical studies:** Literature indicate that the factors affecting the capacitance are particle size and electrochemical conditions, namely type of electrolyte, concentration of electrolyte, pH of electrolyte, conductivity of the electrolyte, scan rate, *etc.* [13-16]. The electrolyte is the key part of the electrochemical capacitors as the operating voltage, specific capacitance, power density are greatly influenced by the choice of electrolyte. Energy storage in supercapacitor combines pure electrostatic interaction between the charged capacitor plates and the ions from the electrolyte solution and the processes associated with the redox reactions of the electrode material. The resistance of the supercapacitor cell is strongly dependent on the resistivity of the electrolyte used and size of the ions from the electrolyte that diffuse in to and out of the pores of the porous electrode particles. The important criteria for a good electrolyte is that it should possess significant ionic conductivity but negligible electronic conductivity. The attainable cell voltage of a supercapacitor depend on the breakdown voltage of the electrolytes, hence possible energy density will be limited by electrolyte. Power density is dependent on cell's ESR, which is strongly dependent on electrolytes conductivity. The three different types of electrolytes used are organic, aqueous and ionic electrolytes. Organic electrolytes possess higher resistivity than aqueous electrolytes but because of large size of the organic molecules, the requirement of the pore size of the electrode is greater [17]. The commercial usage of ionic electrolytes is limited because of high cost [18]. Aqueous electrolytes are cheaper, easier to purify and have a lower resistance, but they limit the cell voltage to typically 1 V, thereby limiting the maximum achievable power. The most regularly used aqueous electrolytes are acid and alkaline electrolytes because of high conductivity and proton transport mechanism. In aqueous electrolyte, the proton with high mobility and small size chemisorbs to a single oxide ion. The best pore size distribution in the electrode depends upon the size of the ions in the electrolyte, so both electrode and electrolyte must be selected together. To take the benefit of high surface area for high capacitance, it is essential to make sure that the electrolyte is able to enter the pores. The pore size should be large enough for the electrolytic ions to enter the pores. Classification of pores is dependent on the size as micropores, mesopores and macropores. Micro pores are pores with a diameter less than 1 nm. But as the electrolytic ion size is larger than the micro pores, these are not useful. Mesopores are the pores with a diameter between 2 to 50 nm. The traditional view anticipated that mesopores with a size close to twice that of the solvated ions lead to the maximum specific capacitance. The macropores have diameters greater than 50 nm and allow sufficient space for the ions to penetrate. However, they are too large

and hence not able to exploit fully the increased surface area. Here the attempts are made with different aqueous electrolytes NaOH, KOH, KCl, CH<sub>3</sub>COONa and NH<sub>4</sub>Cl, each of 0.1 M concentration for RuO<sub>2</sub> electrode. The capacitive performance of RuO<sub>2</sub> was characterized by using cyclic voltammetry. An ideal capacitive nature of electrode includes a rectangular type of voltammogram, symmetric in anodic and cathodic directions and a large magnitude of the current. Fig. 3 shows the cyclic voltammetry plots for different aqueous electrolytes at 5, 10, 50 and 100 mV/s scan rates.

No redox peaks can be seen on the cyclic voltammetry curves at different scan rates which indicates that the supercapacitive behaviour is purely based on the electrostatic mechanism and charge-discharge process of active materials occurs at a pseudo-constant rate over a whole potential window. It has also been observed from the figure that the optimized potential window and the current density is different for different electrolyte. So it can be seen that molar conductivity, ionic size and pH of the electrolyte and pore size distribution of electrode material, play a key role in the determination of supercapacitive behaviour.

Table-1 shows standard molar conductivity, measured pH and calculated specific capacitance values for different aqueous electrolytes at room temperature [19].

TABLE-1  
STANDARD MOLAR CONDUCTIVITY, pH  
AND SPECIFIC CAPACITANCE VALUES FOR  
DIFFERENT AQUEOUS ELECTROLYTES

Electrolyte (0.1 M)	Standard molar conductivity (cm <sup>2</sup> Ω <sup>-1</sup> mol <sup>-1</sup> ) (0.01 M)	pH	Specific capacitance (F/g)
KOH	258.9	10.34	581
NaOH	234.5	10.12	455
KCl	141.6	9.14	400
NH <sub>4</sub> Cl	–	4.97	140
CH <sub>3</sub> COONa	083.7	6.46	111

The conductivity decreases in the order KOH > NaOH > KCl > CH<sub>3</sub>COONa. It is observed from cyclic voltammetry that potential window and current density are dependent on electrolyte conductivity. For KOH electrolyte, which is having high molar conductivity, the observed current density is high (6 mAmp/cm<sup>2</sup>) and it is minimum (0.8 mAmp/cm<sup>2</sup>) for CH<sub>3</sub>COONa electrolyte, which is having low molar conductivity.

The current flowing through the electrolyte is due to the migration of ions. The ions move towards the oppositely charged electrodes at different speeds. H<sup>+</sup> and OH<sup>-</sup> are unique and move through the solution rapidly and are good charge carriers. Ions such as NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> move through the solution at a slower rate therefore do not conduct electricity as well. Thus conductivity decreases due to decrease in the mobility of the ions. So conductivity and mobility of cations may be the decisive factor for performance of different electrolytes [20].

Table-2 shows the molar conductivity, relative mobility and crystal and ionic radius of cations. In case of CH<sub>3</sub>COONa, Na<sup>+</sup> has low mobility and low conductivity leading to less capacitance. In case of KOH when compared to NaOH, K<sup>+</sup>

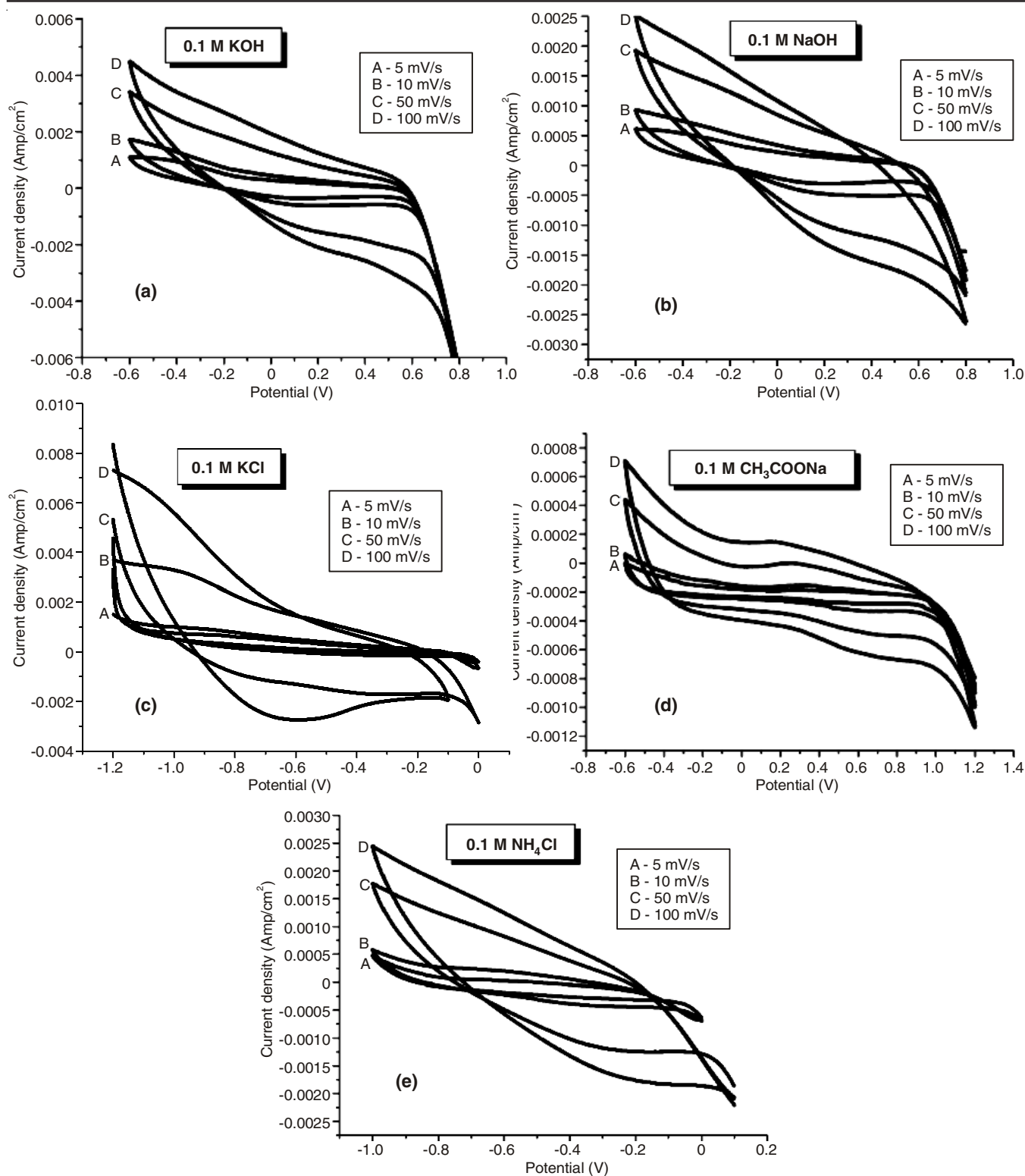


Fig. 3. Cyclic voltammety graphs of ruthenium oxide thin film electrodes for (a) KOH (b) NaOH (c) KCl (d)  $\text{CH}_3\text{COONa}$  (e)  $\text{NH}_4\text{Cl}$  electrolytes

TABLE-2  
MOLAR CONDUCTIVITY, RELATIVE MOBILITY,  
CRYSTAL AND IONIC RADIUS OF CATIONS

Alkali ion	Crystal radius (Å)	Ionic radius (pm)	Relative mobility	Molar conductivity ( $\text{SL mol}^{-1} \text{cm}^{-1}$ )
$\text{K}^+$	1.33	151	1.000	0.0735
$\text{Na}^+$	0.97	102	0.682	0.0501
$\text{NH}_4^+$	1.43	250	1.000	0.0735

ion is bigger than  $\text{Na}^+$  but mobility and conductivity of  $\text{K}^+$  is greater yielding high capacitance. In case of  $\text{NH}_4\text{Cl}$  when compared with KCl, both  $\text{NH}_4^+$  and  $\text{Cl}^-$  have low mobility which decrease the conductivity and in turn capacitance.

Besides it can be seen from cyclic voltammety curve that as the scan rate is increased, the voltammograms window tended to tilt toward vertical axis, thereby becoming quasi rectangle. This is the indication of dominance of the double

layer formation in the energy storage process at lower scan rates [21]. It was found that the current under the curve slowly increased with scan rate. This indicates that the voltammetric currents are directly proportional to the scan rates, indicating an ideal capacitive behaviour [22].

Fig. 4 shows the comparison of specific capacitance at different scan rates and for different electrolyte. It shows maximum observed capacitance of 581 F/g for 0.1 M KOH electrolyte, 405 F/g for 0.1 M NaOH and 350 F/g for 0.1 M KCl, 111 F/g for  $\text{CH}_3\text{COONa}$  and 140 F/g for 0.1 M  $\text{NH}_4\text{Cl}$  at 5 mV/s scan rate. Sodium acetate showed minimum specific capacitance for all the scan rates and maximum capacitance is observed for potassium hydroxide for all scan rates. From the graph, it is also seen that the specific capacitance decreases with increase in scan rate. During the oxidation and reduction process in  $\text{RuO}_2$ , protons are exchanged with the electrolyte and electrode interface. Higher scan rates leads to either depletion or saturation of protons in the electrolyte inside the electrode during the redox process as this proton transfer process is slow. This mainly results a decrease in capacitance of the electrode due to increase of ionic resistivity [23].

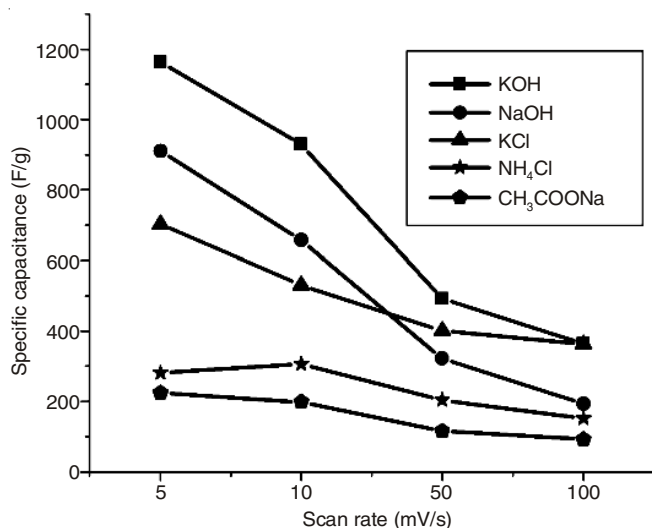


Fig. 4. Comparison of specific capacitance at different scan rates and for different electrolyte

Lowering the scan rate allows more amount of time for the proton access the bulk of the oxide. Hence, the specific capacitance increases with decrease in scan rate [24].

**Stability of electrode:** Stability of  $\text{RuO}_2$  electrode in 1 M KOH was tested by cyclic voltammetry. Fig. 5 shows that the cyclic voltammetry curves of ruthenium oxide electrode at the scan rate of 200 mV s<sup>-1</sup> within the voltage range 0.55 to -0.55 V for 1<sup>st</sup> and 1000<sup>th</sup> number cycle. The current under the curve is decreased by 17 % up to 1000 cycles. We found that our system can withstand about 1000 cycles without a significant decrease in the capacity, illustrating the fairly stable nature of  $\text{RuO}_2$  electrode in energy storage application. The specific and interfacial capacitance values are decreased in small amount with the number of cycles due to the loss of active material. The capacitance decreased from 238 to 196 F/g for 1000<sup>th</sup> cycle.

**Charge-discharge study:** The galvanostatic charge-discharge curves of the  $\text{RuO}_2$  were measured by chronopotentiometry

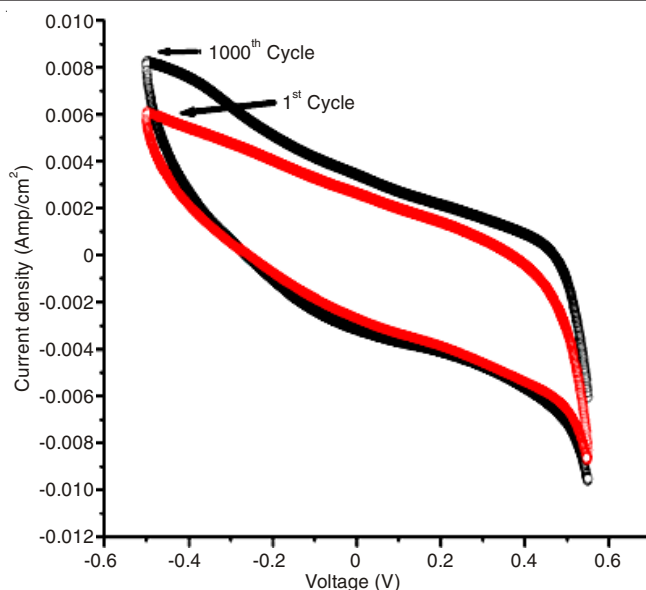


Fig. 5. CV curves of  $\text{RuO}_2$  electrode at 1<sup>st</sup> and 1000<sup>th</sup> cycles for 200 mV/s scan rate in 1 M KOH electrolyte for 4 deposition coats

technique between -1 to +1 V at 5 mA/cm<sup>2</sup> in 1 M KOH electrolyte. The charge-discharge curves (Fig. 6) shows a 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, indicative of  $\text{RuO}_2$  behaves as a capacitor. Hence, this material is a suitable electroactive material for supercapacitors.

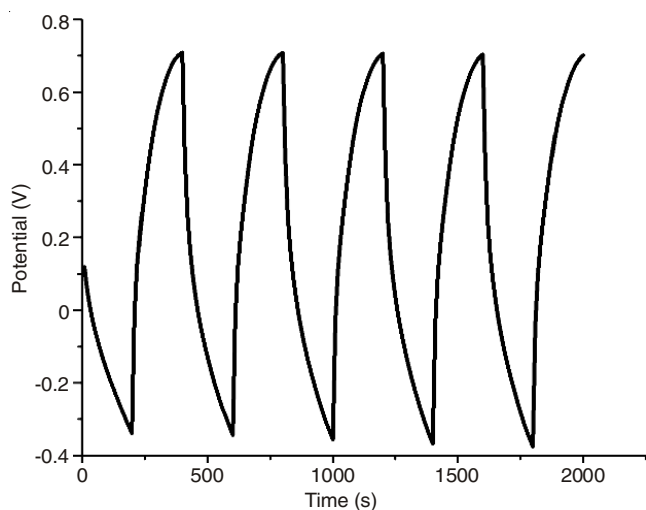


Fig. 6. Charge-discharge curves of thin films measured at 5 mA/cm<sup>2</sup> in the potential range of -1 to +1 V in 1 M KOH electrolyte

The calculated specific power and specific energy were 36 KW Kg<sup>-1</sup> and 8.25 Wh Kg<sup>-1</sup>, respectively. The coulombic efficiency for  $\text{RuO}_2$  was found to be 71.42 %.

## Conclusion

In the conclusion, crystalline ruthenium oxide thin films of non-uniformly distributed aggregates were synthesized by sol-gel spin coating method and successfully applied for electrochemical supercapacitor applications. Aqueous electrolytes used were: KOH, NaOH, KCl,  $\text{NH}_4\text{Cl}$  and  $\text{CH}_3\text{COONa}$ , each of 0.1 M molarity. The electrochemical behaviour of the

electrode depends on molar conductivity, ionic size, mobility of ions and pH value. It may be assumed that the most suitable pore structure of ruthenium oxide was KOH electrolyte. The highest value of capacitance was obtained for KOH electrolyte. It also showed decrease in capacitance with increase in scan rate for every electrolyte. Stability of the electrode was tested for 1000 cycles. The calculated power density and energy density were 36 KW Kg<sup>-1</sup> and 8.25 Wh Kg<sup>-1</sup>, respectively with 71 % efficiency.

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