PREPARATION OF HYDROUS RUTHENIUM OXIDE/ ACTIVATED CARBON ELECTRODE AND ITS SUPERCAPACITIVE PERFORMANCE IN 6 M KOH

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ABSTRACT: Hydrous ruthenium oxide (RuO_2) and activated carbon (AC) denoted as RuO_2/AC composite electrodes were prepared by combining sol–gel and conventional slurry processing techniques. In this paper, several different compositions of composite electrode slurries were fabricated using RuO_2 and AC powders. Benefits from the combined advantages of both RuO2 and AC in such a unique structure were the RuO_2/AC composite electrode supercapacitors exhibited the specific capacitance (5.10 F g^{-1} for RuO_2 50 wt%) and also have good cycling stability. These findings demonstrated the importance and great potential of RuO_2/AC composites in the development of the energy-storage system especially for the high power supercapacitor electrode.

1.0 INTRODUCTION

The study of the energy storage and conversion is very significant due to its limited sources to discover more of this energy and help to drive the cost down for technologies future development [1-2]. In recent years, supercapacitors (SCs) or ultracapacitors have attracted significant attention mainly due to their high rate capability (<1 min charge-discharge) and long cycle life (>100,000 cycles) compared with the conventional capacitors and batteries/fuel cells [3]. Basically, SCs can be classified into three categories according to different charge storage mechanisms [4-5]. Electrochemical double layer capacitors (EDLCs) store energy by the formation of double layer of electrolyte ions on the conductive electrode surface [6]. Pseudocapacitors on the

other hand, are known due to the oxidation-reduction reaction or fast redox reaction causing induces of faradaic current that occurs on the electrode/electrolyte interface as the oxidation state changes [7]. Hybrid capacitors are the combination of two electrodes which store charge electrostatically and faradaically [8].

Various types of transition metal oxides such as ruthenium oxide (RuO_2), manganese oxide (MnO_2) and cobalt oxide (Co_3O_4) [9] have greatly attracted attention to improve the performance of SCs in high power applications. Among them, RuO_2 shows the highest performing pseudocapacitive material to be used as electrode material for SC [10]. In addition, among all carbon materials, activated carbon (AC) has been chosen as an electrode for the SCs from the economical point of view. AC shows high specific capacitance with the high specific surface area and large pore size [11]. Within the structure of AC, there are hierarchically porous carbon called micropores (< 2 nm), mesopores (2-5 nm) and macropores (> 50 nm) [12]. In this work, hydrous RuO_2/AC composites with the different compositions were prepared by combining a sol-gel process and conventional slurry technique. The as-prepared hydrous RuO_2/AC composites were used to investigate their electrochemical performance and to get the best ratio for SC performance.

2.0   METHODOLOGY

2.1   Synthesis of RuO_2/AC composite electrodes

$RuCl_3.xH_2O$ (Sigma Aldrich) and AC (Kuraray) were used to prepare the RuO_2/AC composite electrodes. Amorphous RuO_2 was obtained from sol-gel process. First, the required amount of $RuCl_3 \cdot xH_2O$ was dissolved in distilled water to a 0.1 mol/L $RuCl_3$ solution, at the same time, 0.3mol/L NaOH solution was prepared. Second, the NaOH solution was added into the $RuCl_3 \cdot xH_2O$ solution and stirred continuously until it reached 7 pH value. The black powder of RuO_2 was formed in the NaCl solution. Then, the black powder of RuO_2 was filtered by NaCl solution using filter paper and washed several times in distilled water. Finally, the powder was dried at 150°C for 10 hours to form amorphous hydrous RuO_2 powder. Then the powder was added into AC solution to prepare the six mixtures of compositions using the conventional slurry technique.

2.2 Electrochemical measurements of RuO$_2$/AC composite electrodes

The performance of the SC which consists of RuO$_2$/AC electrode was studied through cyclic voltammetry and galvanostatic charge/discharge analyses. All measurements were performed at room temperature (25°C). The SC was fabricated from two-electrode cell using 25 μm polypropylene (Tonen) separator and 6 M KOH aqueous solution as electrolyte. All electrochemical measurements were carried out using Autolab PGSTAT204 to determine the specific gravimetric capacitance (C$_{sp}$) of the device. The applied voltage ranged from 0.0 V to 1.0 V.

3.0 RESULTS AND DISCUSSION

3.1 Cyclic voltammetry of RuO$_2$/AC composite electrode

In order to further understand the effect of RuO$_2$ content on the electrochemical performance of RuO$_2$/AC electrode, RuO$_2$/AC with different wt% of RuO$_2$ was prepared. Figure 1 shows the typical cyclic voltammetry (CV) curves of RuO$_2$/AC composite electrodes with different ratio of RuO$_2$/AC composite electrode at 1 mV s^{-1}. A gradual change of capacitive behaviour is observed from rectangular-shape CV curves related to EDLC behaviour [13]. The current responses monitored during anodic and cathodic sweep remained almost constant over the entire potential window from 0.0 V to 1.0 V and increased proportionally with an increase of the wt% of RuO$_2$. Hence, there is a synergistic effect of both the EDLC and the improvement in RuO$_2$ dispersion [14]. Referring to [5], C$_{sp}$ is determined such as

$$C_{sp} = \frac{\int_{E1}^{E2} i(E)dE}{2(E_2 - E_1)mv} \qquad (1)$$

where
E$_1$ and E$_2$ are the cut-off potentials in CV;
i(E) is the current value measured at specific voltage;
∫i(E)dE is the total voltammetric charges obtained by integrating the positive (charge) and the negative (discharge) sweeps in CV;
E$_2$-E$_1$ is the width of the cell potential (voltage) window;
m is the average RuO$_2$/AC mass per electrode and
v is the rate of potentiostat scan.

As a result, at 1 mV s^{-1}, the calculated C$_{sp}$ was 1.23, 1.56, 3.43, 3.78, 4.54 and 5.10 F g^{-1} for 0, 10, 20, 30, 40 and 50 wt % of RuO$_2$ respectively.
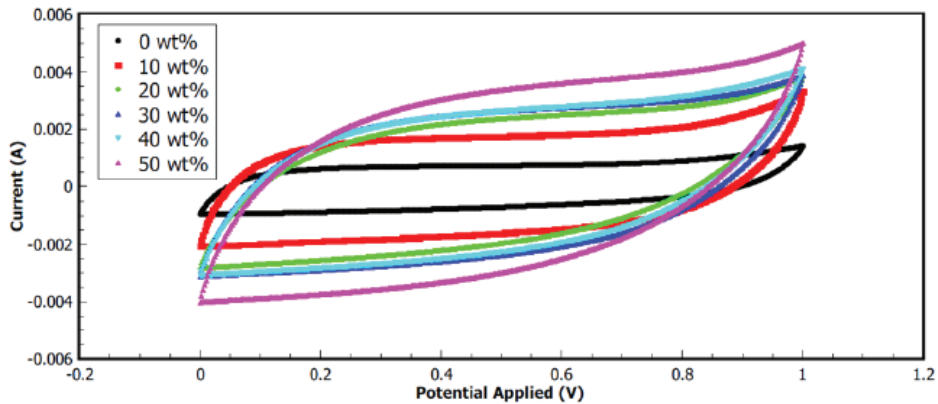

Figure 1: Cyclic voltammetry of RuO$_2$/AC electrode with the different composition ratio at 1 mV s-1

The C$_{sp}$ of RuO$_2$/AC composite electrode based on CV curves is presented in Figure 2. The C$_{sp}$ increased almost linearly with the increase of the RuO$_2$ contents in the composite. This is consistent with previously reported study of similar electrode usage [15]. The C$_{sp}$ of RuO$_2$/AC composite increased from 1.23 (RuO$_2$ 0 wt%) to 5.10 F g^{-1} (RuO$_2$ 50 wt%) with the increase of RuO$_2$ wt%. These results may be attributed to synergistic effect of both the AC and RuO$_2$. Furthermore, the increase of C$_{sp}$ RuO$_2$ from various RuO$_2$ wt% shows that the RuO$_2$ surfaces are fully utilized for ion accessibilities, thus, the electrical charge storage in order to enhance the capacitance performance in 6 M KOH electrolyte [14].
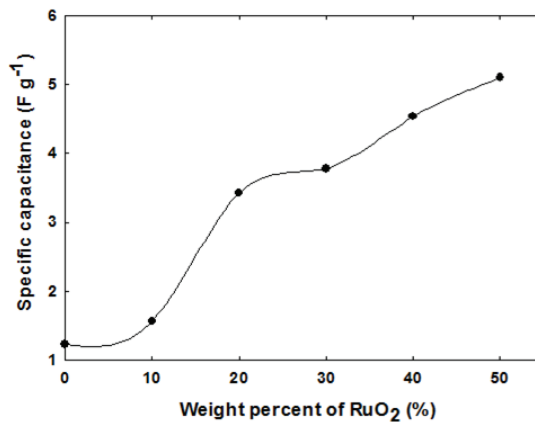

Figure 2: Specific gravimetric capacitance of RuO$_2$/AC composite electrode with the different RuO$_2$ weight percentage

3.2   Cycling Stability of RuO2/AC composite electrode

Figure 3 summarizes the galvanostatic charge/discharge curves for RuO_2 50 wt%/AC composite electrode at applied current of 5 mA. There is a similar trend for discharging time for each cycle indicating a good cycling stability of composite electrode. The galvanostatic charge/discharge curves of RuO_2/AC in Figure 3 resembled symmetric triangular by indicating an ideal capacitive behaviour. IR drop analysis is one of the important factors to consider upon a fabrication of supercapacitor electrode. The observation of IR drops at discharging curve in this work represents the internal resistance of the composite electrode materials. These results show the similar characteristic behaviour of electrode performance with a previous study [16]. Although it is critical to minimize the IR drop, current study proved that the physical interaction and/or contact between both materials was not in good condition. To encounter this problem, additional chemical process should be carried out to enhance the functionality of both RuO_2 and AC. Thus, further analysis of this kind of electrode will become more meaningful for future development of RuO_2 based pseudo-supercapacitor.
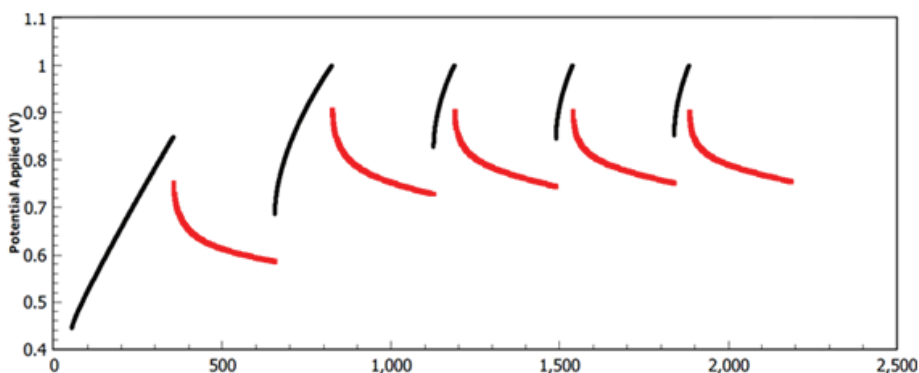

Figure 3: Galvanostatic charge/discharge curves for RuO_2 50 wt%/AC composite electrode at applied current 5 mA

4.0   CONCLUSION

A facile approach is conducted to prepare hydrous RuO_2 for supercapacitor applications by sol-gel method, followed by mixing amorphous hydrous RuO_2/AC composites by conventional slurry technique. The maximum C_{sp} obtained of the electrode in 6 M KOH is 5.10 F g^{-1} from RuO_2 50 wt% at 1 mV s^{-1}. This composite electrode measured from a two-electrode cell configuration which is a very promising potential as electrode material for energy storage device

applications due to the ease of preparation and its good capacitive performance. Increasing RuO_2 wt% will increase the C_{sp} with relatively good cycling stability. Future works entails the use of more than RuO_2 50 wt% and use the different electrolytes with large potential windows to enhance the performance of supercapacitor or probably high power pseudocapacitor.

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