Int. J. Electrochem. Sci., 8 **(2013)** 6574 - 6578

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Synthesis of Active Carbon and Ruthenium Oxide for Electrochemical Performance

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Received: 5 March 2013 / *Accepted:* 17 April 2013 / *Published:* 1 May 2013

Amorphous hydrous active carbon and ruthenium oxide composite electrodes were prepared. Amorphous hydrous Ruthenium oxide was formed by a sol-gel process. In this paper, some different proportions of composite electrodes were fabricated with the RuO_2 and active carbon. The experiment result also shows that the 3:2 of amorphous hydrous active carbon and ruthenium oxide composite electrodes is ideal proportion. The results show that it can improve the impedance characteristic and increase the capacitance of composite electrode by joined them together.

Keywords: electrochemical; sol-gel; amorphous

1. INTRODUCTION

In recent years, electrochemical supercapacitors (ES) or ultracapacitors have attracted significant attention, mainly due to their high power density, long cycle life, and bridging function for the power/energy gap between traditional dielectric capacitors (which have high power output) and batteries/fuel cells (which have high energy storage) [1-4]. Transition metal oxides are a class of important mineral materials that have drawn extensive research attention as electrode materials. Transition metal oxides such as ruthenium oxide [5], manganese oxide [6-8], cobalt oxide [9], and nickel oxide [10-12] are qualified to be electrode materials for electrochemical capacitor [13]. Some of them, such as ruthenium oxide and iridium oxide, exhibit excellent properties for use as pseudo-capacitive electrode materials [14]. Nevertheless, it is also noted that the materials of this class are rare and expensive. Among these materials, ruthenium oxide attracts particular interest due to its high specific capacitance, high chemical/thermal stability, practical availability, environmentally benign nature and lower cost than others [15-19].

In this work, some different proportions of composite electrodes of RuO_2 and active carbon were prepared to investigate their electrochemical performance, and to attain the best ratio of performance and price.

2. EXPERIMENTAL

2.1 Materials preparation

All the chemicals were of analytical reagent and used as received without further purification. In a typical preparation progress, a sol-gel process formed Ruthenium oxide powder as follows. At 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, it was prepared to 0.3mol/L NaOH solution. Secondly, the NaOH solution was added slowly into the $RuCl_3{\cdot}xH_2O$ solution and stirred unceasingly in this process until the PH to a value of 7. The black powder of RuO_2 precipitates in the NaCl solution. Thirdly, the powders were separated from the NaCl solution by a filter, and were washed several times in distilled water. Finally, amorphous hydrous Ruthenium oxide powders were obtained by annealing dry at 150 °C for 10 h in airs and rubbing the powders. Then the powders were added into active carbon to obtain the four mixtures as the proportions of 1:4, 2:3, 3:2, and 4:1, rubbed the mixtures and mixed with proper Teflon binder.

2.2 Materials characterization

Powder x-ray diffraction (XRD) patterns of the sample was recorded on a Philips X'pert diffractometer with Cu Kα radiation (λ=1.5418 Å). The morphology and the structure of the sample were examined with a field-emission scanning electron microscopy (FESEM, JEOL JSM-6300F).

2.3 Electrochemical measurements

The working electrode was prepared by 85 wt% of the active material, 10 wt% of conducting agent (carbon black), and 5 wt% of binder (polyvinylidene difluride, PVDF). Based on the membrane preparation technology it rolled out the film with the thickness of 0.2 mm, and the size of the electrode was about 1×1 cm^2. Then the electrode was pressed on the tantalum plate at adequate pressure. The above four electrodes were marked as A, B, C and D, respectively. These mixtures were pressed onto the glassy carbon electrode (Aida Hengsheng Technology co. td, Tianjin, China) and then dried at 60 °C. The electrolyte used was 3 M KOH aqueous solution. The capacitive performance of the sample was tested on the CHI608A electrochemical workstation with cyclic voltammetry and chronopotentiometry functions using three-electrode system (a saturated calomel electrode (SCE) as the reference electrode, a Pt electrode as the counter electrode).

3. RESULTS AND DISCUSSION

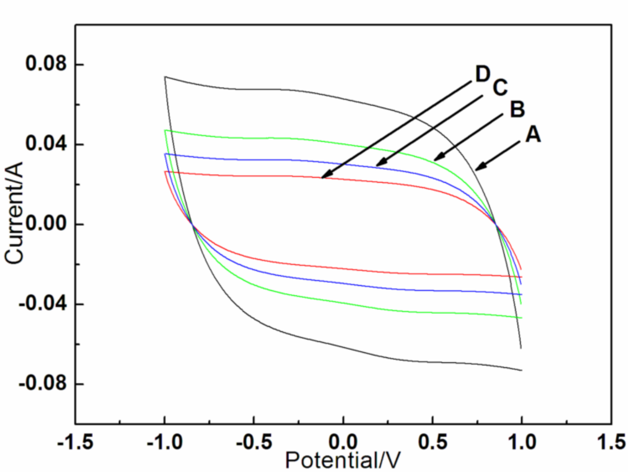

Figure 1. cyclic voltammetry of the composite electrodes materials A: the ratio of active carbon / RuO_2 is 1:4, B: the ratio of active carbon / RuO_2 is 2:3, C: the ratio of active carbon / RuO_2 is 3:2, D: the ratio of active carbon / RuO_2 is 4:1

3.1Electrochemical properties of $RuO_2{\cdot}xH_2O$/ AC composite electrode

Fig.1 is cyclic voltammetry curves of the composite electrodes, shows the influence of different ratio of AC / RuO_2 composite electrode on the capacitance. From Fig.1, the cyclic voltammetry curves of the composite electrodes represents regular inclined ellipse and high reverse, as the percent of the quality of active carbon increases, circuit area decreases, namely specific capacitance gradually decreases.

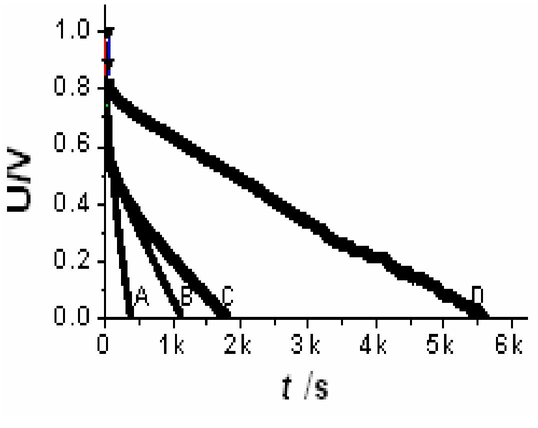

Figure 2. The charge and discharge behavior for composite electrodes materials A: the ratio of active carbon / RuO_2 is 1:4, B: the ratio of active carbon / RuO_2 is 2:3, C: the ratio of active carbon / RuO_2 is 3:2, D: the ratio of active carbon / RuO_2 is 4:1

Fig.2 is the charge and discharge behavior of the four electrodes, the electrode materials behave nicer charge and discharge behavior. The specific capacitance of the four electrodes separately are

618.2F/g, 457.3F/g, 367.2F/g and 194.2F/g. The specific capacitance of pure active carbon and pure RuO_2 powders are 119.3F/g and 705.6F/g, respectively. It shows that the total capacitance of the composite electrode is contributed by the double-layer and faradic capacitance; the surface morphology of the composite electrodes in SEM and the crystalline structures of XRD also approve it. At low percent of the quality of Ruthenium, the double layer from the active carbon mostly effects, but faradic capacitance doesn't distinctly effect; along with the percent of the quality of ruthenium increasing, faradic capacitance gradually strengthens in the total capacitance. Due to faraday capacitance is several times higher than double-layer capacitance, total specific capacitance increase rapidly. It can be seen that specific capacitance approximately decrease linear along with active carbon content joined.

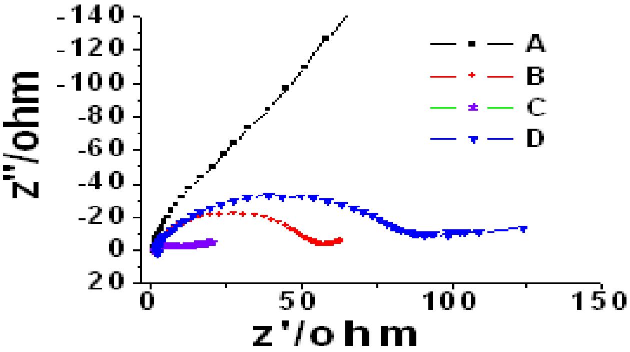

Figure 3. The curve of composite electrode impedance characteristic A: the ratio of active carbon / RuO_2 is 4:1, B: the ratio of active carbon / RuO_2 is 3:2, C: the ratio of active carbon / RuO_2 is 2:3 D: the ratio of active carbon / RuO_2 is 1:4

The AC Impedance characteristics can reflect the synthetic electronic performance of the capacitor. EIS is a routine electrochemical measure. Equivalent series resistance (ESR) of the capacitor is comprised of the resistance of electrode materials, the contact resistance of the particles of electrode material, the contact resistance between the electrode material and collector etc. Fig.3 is the impedance characteristic curves of the composite electrodes. The inner resistances of the four electrodes A, B, C, D are separately 0.8Ω, 1.6Ω, 1.3Ω, 1.8Ω. The resistance of pure active carbon and pure RuO_2 are respectively 0.8Ω and 1.6Ω. According to the above data, we found the relation of the carbon content and electrode resistance by mathematic analyze as shown on Fig.3. We can see that along with the increase of the percent of the quality of active carbon between 20% and 60%, the inner resistance of the composite electrodes decreases rapidly, and that between the initial from 0 to 20% and from 60% to 100%, the rate of inner resistance depressed gently. On the other hand, along with the active carbon joined, faraday impedance decreases rapidly. Active carbon affects the ESR as follows: due to the conductivity of active carbon is rather low, it decreases the resistance of the self electrode materials; as it adheres to RuO_2, the cavity of electrode material and adsorbent electrolyte are obviously increased to decrease the contact resistance of grains of electrode material. As faradic reaction effect decreases, faradic impedance decreases. According to the experiment results, the impedance characteristic of 3:2

ratio composite electrodes is the best. Compared with other sampling, this significantly improves performance especially in the voltage [17-19].

4. CONCLUSIONS

We propose by the investigation that, the ratio of 3:2 active carbon / RuO_2 is relatively appropriate for hybrid super-capacitor. Along with increasing the percent of active carbon in the quality of mixture powders, faraday capacitance in total capacitance and specific capacitance gradually decreases, presented a nearly linear relation in the result of our experiment. With increasing the content of active carbon in 20%~80% in the quality of mixture powders, the impedance performance has been improved.

ACKNOWLEDGEMENTS
The work was supported by the Shandong province Natural Science Foundation of China (No.Y2008F23), Shandong province Science and Technology Development Plan (No. 2011GGB01123) and 863 programme (No.2012AA110407). We thank the anonymous reviewers for their helpful suggestions on the quality improvement of our present paper.

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