The Impedance Properties Analysis of Composite Electrodes for Supercapacitor

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Abstract—Supercapacitor can get high energy density and the ability of quick charging and discharging. In this work, the different mass ratios of composite electrodes mixed with active carbon (AC) based on RuO$_2$·xH$_2$O, were prepared to study the electrical performance parameters of the incorporations. Through Conway’s model and impedance spectroscopy, the composite electrode model has been established, and it is validated by the experiments on their electrochemical performances for different proportions of composite electrodes fabricated with RuO$_2$·xH$_2$O and active carbon. The simulation results show that the composite electrode with 60wt.% amorphous hydrous ruthenium oxide has the lower inner resistance and the higher degree of ruthenium oxide utilization, which are testified by the experiments.

Keywords—Supercapacitor; Impedance; Spectroscopy; Equivalent Circuit Model; Mass Ratio

I. INTRODUCTION

Supercapacitors are widely used in pulse power source as energy storage element, due to their high-power density, long cycle life, and bridging function for the power/energy gap between traditional dielectric capacitors (which have been high-power output) and batteries/fuel cells (which have been high-energy storage) [1-3]. Currently, the electrode material research concentrated on the carbons [4-7], the transition metal oxide [8-10] and conducting polymers [11-13], which all have high specific capacitance in the electrolyte. Transition metal oxides such as ruthenium oxide [14, 15], manganese oxide [16], cobalt oxide [9], and nickel oxide [17], which have drawn extensive research attention as electrode materials, are qualified to be electrode materials for electrochemical capacitor. Ruthenium oxide exhibits excellent properties as pseudo-capacitive electrode materials. However, the expensive price restricts its wider applications [18]. In the ruthenium oxide mixed with other types of electrode materials is a commonly used method. As Mn [15], carbon [19], and Ti [20], and other types of electrode materials [21, 22] are incorporated in a common method of ruthenium oxide. So in the ruthenium oxide with these materials, the material quality in the whole electrode ratio on the electrical performance parameters of the electrode what effect? In this paper, the problem has been solved by established the equivalent circuit models, the element parameters of which were extracted by impedance spectroscopy. The different mass ratios RuO$_2$·xH$_2$O/AC composite electrodes have been prepared to obtain associated electrical properties of experimental parameters. Through simulation and experimental results, we obtain the relationships between the resistance and capacitance change with the mass ratio, the density and other basic parameters of the composite electrodes, such as to prepare corresponding composite electrodes in the different applications.

II. EXPERIMENTS

A. Preparation of the electrodes and the samples

The hydrous ruthenium oxide powder was formed by a Sol-gel process. Then hydrous ruthenium oxide and active carbon powder at the mass ratio \( \alpha \) of hydrous ruthenium oxide in the composite electrodes mixed and skived equability that adding to the proper PTFE. According to the membrane preparation technology, pressed them into the thickness of 0.2mm membrane, intercepted the dimension of 1x1cm$^2$ membranes and pressed it on the tantalum foil current collectors. Then the two above uniform electrodes are separated by the fiberglass cloth, infused in the concentration of 38% vitriol electrolyte to compose of the symmetrical super-capacitor unit as the samples. When the mass ratio of hydrous ruthenium oxide in the composite electrodes \( \alpha=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 \), it fabricates 11 super-capacitors of the same thickness.

B. The Performance Test of Composite Electrodes

The equipment used in the experiments is mainly CHI660A model electrochemistry workstation. The experiment temperature is room temperature.
Charging and discharging test are made for the above samples, the constant current of charging and discharging is 3mA, the range of charge and discharge voltage is 0-1V. According to the measured charge and discharge curve, it can obtain the specific capacitance of the composite electrodes:

Where \( I \) is the discharging current; \( \Delta t \) and \( \Delta V \) are the time difference and voltage difference of corresponding discharging process respectively; \( C_p \) is the specific capacitor of single electrode in Figure; \( m \) is the average mass of two electrodes of super-capacitors.

Added a small magnitude sine AC signal on above samples with the frequency of 0.1Hz ~ 100 kHz and the voltage of 5mV, measurement results can be gotten from Electrical Impedance Spectroscopy (EIS)

III. MODELLING OF COMPOSITE ELECTRODES FOR SUPER-CAPACITORS

Using kinetic parameters to create a supercapacitor equivalent circuit model is one of the main EIS analyses; it can compare the performance of the electrode kinetics intuitively [25]. At present, the common supercapacitor models mainly have a simple model of the ESR [26], Conway’s model [27], transmission line model [28] and neural network model [29], etc. This article used the Conway’s model to establish the model of the composite electrodes.

Conway established the equivalent circuit model of super-capacitor, as seen in Figure 1, where \( R_\Omega \), \( R_s \), \( C_d \) and \( C_s \) represent lead and electrolyte resistance, rate constant, double layer capacitance and Faraday capacitance, respectively. The real part and imaginary part of impedance \( Z_i \), \( Z_j \) are respectively given by:

\[
Z_i = R_\Omega + \frac{R_s}{(1 + \frac{C_d}{C_s})^2 + (\omega C_d R_s)^2} \quad (1)
\]

and

\[
Z_j = \frac{1}{\omega C_s} \left( \frac{1 + \frac{C_d}{C_s}}{C_s} \right) + \omega C_d R_s \left( \frac{1 + \frac{C_d}{C_s}}{C_s} \right)^2 \quad (2)
\]

Here \( \omega \) is angle frequency. Capacitance can be calculated by:

\[
C(\omega) = \text{Re} C = \frac{\text{Im} Y}{\text{Re} Y} = \frac{-\text{Im} Z}{\omega |Z|^2} = \frac{-\text{Im} Z}{\omega ((\text{Re} Z)^2 + (\text{Im} Z)^2)} \quad (3)
\]

Figure 1. The Conway’s model for supercapacitor

For RuO\(_2\)-xH\(_2\)O/active carbon composite electrodes, when \( \alpha = 0 \), it is pure active carbon electrode. The real part and imaginary part of impedance can be expressed in terms of Figure 1 as:

\[
Z_{ic} = R_{ic} + \frac{R_c}{(1 + \frac{C_{ic}}{C_c})^2 + (\omega C_{ic} R_c)^2} \quad (4)
\]

and

\[
Z_{jc} = \frac{1}{\omega C_c} \left( \frac{1 + \frac{C_{ic}}{C_c}}{C_c} \right) + \omega C_c R_c \left( \frac{1 + \frac{C_{ic}}{C_c}}{C_c} \right)^2 \quad (5)
\]

where \( R_{Qc} \), \( Z_iC \), \( Z_jC \), \( R_s \), \( C_d \) and \( C_s \) are the lead and electrolyte resistance, real impedance, imaginary impedance, double layer capacitance and Faraday capacitance of active carbon electrodes, respectively.

When \( \alpha = 1 \), it is pure RuO\(_2\)-xH\(_2\)O electrode. The real part and imaginary part of impedance are obtained from the following equations, respectively.

\[
Z_{ic} = R_{icRu} + \frac{R_{shRu}}{(1 + \frac{C_{icRu}}{C_c})^2 + (\omega C_{icRu} R_{shRu})^2} \quad (6)
\]

and

\[
Z_{jc} = \frac{1}{\omega C_c} \left( \frac{1 + \frac{C_{icRu}}{C_c}}{C_c} \right) + \omega C_c R_{shRu} \left( \frac{1 + \frac{C_{icRu}}{C_c}}{C_c} \right)^2 \quad (7)
\]

Here \( R_{QRu} \), \( Z_iRu \), \( Z_jRu \), \( R_{sRu} \), \( C_{dRu} \) and \( C_{sRu} \) are the lead and electrolyte resistance, real impedance, imaginary impedance, double layer capacitor and Faraday capacitor of pure RuO\(_2\)-xH\(_2\)O electrodes, respectively.

The super-capacitor made in RuO\(_2\)-xH\(_2\)O/C composite electrodes at \( \alpha = 0-1 \) also satisfies the model in Figure 1. As the active carbon and RuO\(_2\)-xH\(_2\)O particulate in the process do not affect their properties, RuO\(_2\)-xH\(_2\)O and active carbon do not influence each other. The electrolyte concentration is assumed to be invariant and side reactions and thermal effects are ignored, the electrolyte resistence is invariant. To remove the part of electrolyte resistance, the equivalent circuit of composite electrodes could be seen as two capacitors of pseudo-capacitor from RuO\(_2\)-xH\(_2\)O and double layer capacitor from active carbon in parallel. Therefore the equivalent circuit can be seen in Figure 2, where \( R_{Qf} \), \( R_{sf} \) and \( R_{sfRu} \), \( C_{df} \) and \( C_{sfRu} \), \( C_{sfC} \) and \( C_{sRu} \) are lead and electrolyte resistance of composite electrodes, rate constant of active carbon and RuO\(_2\)-xH\(_2\)O, double layer capacitors and pseudo-capacitors of active carbon and RuO\(_2\)-xH\(_2\)O, respectively. From Figure 2, it can be seen that the resistance and reactance of the first and second branch are separately written as:

\[
Z'_{ic} = R_{ic} + \frac{R_c}{(1 + \frac{C_{ic}}{C_c})^2 + (\omega C_{ic} R_c)^2} \quad (8)
\]

and

\[
Z'_{jc} = \frac{1}{\omega C_c} \left( \frac{1 + \frac{C_{ic}}{C_c}}{C_c} \right) + \omega C_c R_c \left( \frac{1 + \frac{C_{ic}}{C_c}}{C_c} \right)^2 \quad (9)
\]

The resistance and reactance of the third and fourth branch are separately expressed as:
It is known that \( R = R_o + \frac{\sigma}{\sqrt{j\omega}} \), \( R_o = \frac{RT}{nF_i_o} \), \( C_s = \frac{1}{\sigma \sqrt{j\omega}} \),

\[
\sigma = \frac{1}{nFA\sqrt{\varepsilon \varepsilon_0 D_o}} \left( \beta_o - \beta_o' \right), \quad \beta_o = \frac{RT}{nFC_o}, \quad \beta_o' = \frac{RT}{nFC_o'},
\]

\[
i_o = nFA(\frac{e_o}{\varepsilon_0})^\alpha (\frac{e_o}{\varepsilon_0})^{\alpha'}
\]

Where \( R_{ct} \): charge transmission resistance; \( n \): charge shift number; \( F \): Faraday constant; \( i_0 \): transfer current; \( C_{oxb} \) and \( C_{rdb} \) are the oxide and the reducer concentration of the solution. Due to the area and thickness of each electrode are uniform, the electrolyte concentration is steady and the oxide and reducer concentrations of the solution are steady, \( \beta_o, \beta_o', D_o, D_{rd} \) can be seen as constant. If the variation of the double layer capacitance is along with potential, the double layer capacitance is proportion to the electrode area. It is supposed that the electrode thickness is \( d \), the electrode area is \( A \), the area of RuO\(_2\)-xH\(_2\)O in composite electrode is \( A_fRu \), the area of active carbon in composite electrode is \( A_fC \), the density of RuO\(_2\)-xH\(_2\)O in composite electrode is \( \rho_{Ru} \), the density of active carbon in composite electrode \( \rho_{C} \), the area of electrode thickness is \( d \), the electrode area is \( A \), the area of composite electrodes are respectively the proportion to the electrode area. It is supposed that the electrolyte resistances of composite electrodes is same, if the variation of the double layer capacitance is along with potential, the double layer capacitance is proportion to the electrode area. It is supposed that the electrolyte resistances of composite electrodes is same, namely \( R_{Ω}\Omega = R_{ΩC} = R_{ΩRu} \). It can be reduced that the impedances of the active carbon and RuO\(_2\)-xH\(_2\)O of composite electrodes are respectively the proportion to the pure active carbon and RuO\(_2\)-xH\(_2\)O electrodes. Submitting (12) and (13) into (8)-(11):

\[
\frac{Z'_{dc}}{Z_m-R_{ct}} = \frac{Z'_{dc}}{Z_m} = \frac{Z'_{dc}}{Z_m} = \frac{A_1C}{A}
\]

and

\[
\frac{Z'_{dc}}{Z_m-R_{ct}} = \frac{Z'_{dc}}{Z_m} = \frac{Z'_{dc}}{Z_m} = \frac{A_1C}{A}
\]

Therefore, the resistance and reactance of composite electrodes can be obtained by the following two equations, respectively:

\[
Z_o = \frac{\left(1 - \alpha \right)\rho_o + \rho_C}{\left( \frac{\left(1 - \alpha \right)\rho_o + \rho_C \alpha}{\rho_o + \rho_C} \right) Z_{es}}
\]

and

\[
Z_{oc} = \frac{\left(1 - \alpha \right)\rho_o + \rho_C}{\left( \frac{\left(1 - \alpha \right)\rho_o + \rho_C \alpha}{\rho_o + \rho_C} \right) Z_{es}}
\]

In terms of (3), (16), (17), it can deduce the relationships \( \alpha \) with real resistance, imaginary impedance and capacitance.

**IV. RESULTS AND DISCUSSION**

In order to review the variety of resistance and capacitance of super-capacitors at different ratios \( \alpha \), it need to measure the Impedance Spectroscopy of the super-capacitors fabricated with pure active carbon and pure RuO\(_2\)-xH\(_2\)O electrodes, respectively, as seen in Fig.3 curve A, F. In order to observe the variety rule of inner resistances of super-capacitor with \( \alpha \), it is observed that the change curve of real resistance by (16) at 1.758×10\(^4\)Hz, \( Z_o \approx 0 \); The repeat frequency of charge and discharge used in pulse power source is usually around 0-100Hz, so it selects the resistance of super-capacitor at \( f=1\)Hz and calculated the variety rule of capacitances of composite electrodes at different ratios \( \alpha \) by (3). Table.I is the data involved in models parameters in equations.

![Figure 3. Impedance characteristics of composite electrodes](image)

**TABLE I. PARAMETERS THAT DESCRIBE THE COMPOSITE ELECTRODE**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR (\Omega)</td>
<td>0.332</td>
<td>Assumed</td>
</tr>
<tr>
<td>(\rho_C)</td>
<td>1.09g/cm(^3)</td>
<td>Factory</td>
</tr>
<tr>
<td>(\rho_{Ru})</td>
<td>0.5g/cm(^3)</td>
<td>measured</td>
</tr>
<tr>
<td>(Z_{ic}(f=1Hz))</td>
<td>0.7586 (\Omega)</td>
<td>measured</td>
</tr>
<tr>
<td>(Z_{Ru}(f=1Hz))</td>
<td>0.3987 (\Omega)</td>
<td>measured</td>
</tr>
<tr>
<td>(Z_{ic}(f=1Hz))</td>
<td>-1.8120(\Omega)</td>
<td>measured</td>
</tr>
<tr>
<td>(Z_{Ru}(f=1Hz))</td>
<td>-0.8882(\Omega)</td>
<td>measured</td>
</tr>
<tr>
<td>(Z_{ic}(f=176x104Hz))</td>
<td>0.3819(\Omega)</td>
<td>measured</td>
</tr>
<tr>
<td>(Z_{Ru}(f=176x104Hz))</td>
<td>0.4872(\Omega)</td>
<td>measured</td>
</tr>
</tbody>
</table>

In Fig.4 the solid line is relationship of \( Z_\theta(\omega) \) calculated by (14) and \( \alpha \) at 1.758×10\(^4\)Hz; the dot is the impedance of composite electrodes at different ratios \( \alpha \) by (3). Table.I is the data involved in models parameters in equations.
change is not big. It is obvious that in the range [0.6, 1] reducing the resistance of electrodes has obvious effect. From Fig.3, the above result is also proved, we can see, that after adding to the active carbon, the inner resistance of super-capacitor minishes along with the α. Faraday impedance circularity of pure RuO$_2$·xH$_2$O is smaller than of pure active carbon, namely charge transmission resistance $R_\alpha$ of pure RuO$_2$·xH$_2$O is smaller than of pure active carbon, but when $\alpha = 0.4$, 0.6, 0.8, Faraday resistance circularity of them is smaller than of pure RuO$_2$·xH$_2$O. It shows that pore active carbon adhere to RuO$_2$·xH$_2$O after adding to active carbon, the pores of electrodes and the electrolyte inside the pores of the electrodes increases, as a result the contact resistant between the particles of electrodes minishes to decrease the inner resistance of composite electrodes. On the other hand, when the proportion of the active carbon is not big, as the ions of electrolyte inside the pores of the electrodes is in favor of the transmission of the charge and the concentration of reactant increases, the charge transmission resistance decreases, but when the proportion of active carbon is bigger than a certain value, active carbon of the electrodes takes the main action to increase the charge transmission resistance.

In Fig.5, the solid line is the calculated relationship of $C(\omega)$ and $\alpha$ at 1Hz; the dot is the measured data at 1Hz at different $\alpha$. As seen in Fig.5, $C(\omega)$ approximately minishes linearly along with increasing the active carbon. When $\alpha=$ 0, 0.2, 0.4, 0.6, 0.8, 1, the discharge curve of composite electrodes at 3mA constant current can be seen in Fig.6. In terms of the calculated equation, the specific capacitances are respectively: 131F/g, 230F/g, 345F/g, 567F/g, 667F/g, 776 F/g, and when $\alpha$=0.1, 0.3, 0.5, 0.7, and 0.9 that cannot be seen in Fig.5, the specific capacitances are: 160F/g, 289F/g, 436F/g, 587F/g and 692F/g. For the variety of specific capacitance, it shows that when the content of RuO$_2$·xH$_2$O is low, the grains of RuO$_2$·xH$_2$O are almost covered by the particles of active carbon, and composite electrodes represent the nature of active carbon; When the content of RuO$_2$·xH$_2$O increase gradually, the effects of RuO$_2$·xH$_2$O strengthen. For the capacitance of RuO$_2$·xH$_2$O is decuple higher than that of active carbon, the specific capacitance of composite electrodes increase rapidly along with increasing the content of RuO$_2$·xH$_2$O.

Therefore, it can be seen that the RuO$_2$·xH$_2$O mass ratio of composite electrode $\alpha=0.6$ is perfect from the results of the simulation and experiments, that minishes the inner resistance as ensuring the high specific capacitance.

In this paper, RuO$_2$·xH$_2$O/active carbon composite electrodes for hybrid super-capacitor is studied. The relationships of the resistance and capacitance with the mass ratio $\alpha$ of RuO$_2$·xH$_2$O in the composite electrode that is made of RuO$_2$·xH$_2$O powder and active carbon, is analyzed. The simulation and experiment results show that adding active carbon into RuO$_2$·xH$_2$O can improve the impedance of composite electrodes, but reduce the specific capacitance. Considered the above aspects, when the mass ratio of ruthenium oxide is about 60%, the specific capacitance of composite electrodes is 567F/g and the inner resistance is 0.4331Ω.

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