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Short communication

Resistance distribution in electrochemical capacitors with a bipolar structure

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Abstract

The distribution of internal resistance in a 5-cell electrochemical capacitor comprising an electrode material with 80 wt.% $RuO_2{\cdot}xH_2O$ and 20 wt.% activated carbon and an electrolyte of 38 wt.% H_2SO_4 acid solution was analyzed. It was found that over 94% of the internal resistance in the capacitor was contributed to various contacts with the current collector of the conducting plastic sheet. Careful analysis of three different contact sources including the current collector to the end metal plate, the current collector to the neighboring current collector, and the current collector to the electrode, it was found that the resistance was dominated by the contact resistance between the current collector and the electrode. A composite current collector, made with conducting plastic sheet coated with metal films on both surfaces, was proposed for reducing all kinds of contact resistances. Using the composite current collector, the internal resistance can be reduced to about only 26% of that using conventional conducting plastic sheet.

Keywords: Internal resistance; Contact resistance; Bipolar structure; Electrochemical capacitors; Composite electrodes

1. Introduction

The maximum current density and power density of electrochemical (EC) capacitors are limited by the internal resistance, which comprise the electrical and ionic resistances. The ionic resistance depends on the ionic conductivity of the electrolyte, the porosity of the electrode and separator/membrane paper, the thickness of the electrode and membrane paper. During pulsed and transient performance, the concentration of ions (from the electrolyte) near the electrode surface can also be a dominating factor [1–3]. The electrical resistance is mainly due to the electrode material including the bulk resistance and the contact resistance between particles, the contact between the current collector and the electrode, the contact between the current collector to the neighboring current collector for a multi-cell capacitor, and the contact between the current collector and the end metal plate. It can be seen that the electrical resistance is mostly associated with the current collector. In EC capacitors, mainly three types of current collectors are used. For EC capacitors with aqueous electrolytes including H_2SO_4 and KOH solutions, conducting plastic sheet and nickel foil, are used as current collectors. [4,5] For EC capacitors with non-aqueous electrolytes, aluminum foil is used as the current collector [6,7].

In this paper, we will provide a detailed analysis of the distribution of resistance inside a capacitor made of powder electrode materials and aqueous electrolytes. It was found that the contact between the electrode and the current collector, the current collector and the end metal plate, and one current collector and the neighboring current collector are important sources of internal electrical resistance in EC capacitors. Contact resistances using different current collectors will be reported.

2. Resistance in EC Capacitors

A 5-cell EC capacitor was made with a bipolar structure using a $RuO_2{\cdot}xH_2O$/activated carbon (80/20 wt.%) composite electrode [8] and 38 wt.% H_2SO_4 electrolyte. The current collector and separator paper were conducting plastic sheet and Celgard 3500, respectively. The top and bottom end plate was made with stainless steel. Fig. 1 shows the schematic diagrams of a bipolar EC capacitor and a single-cell inside

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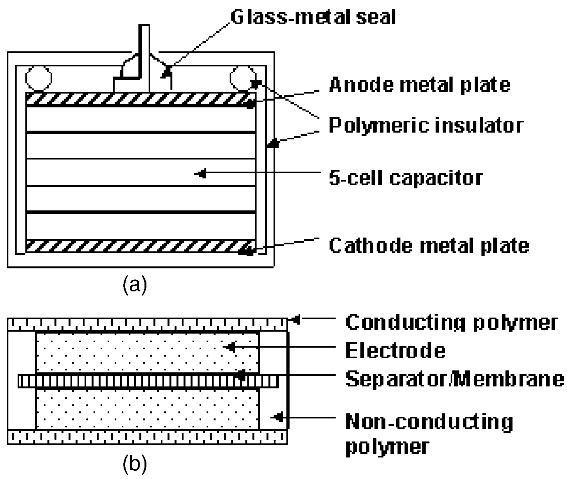

Fig. 1. A schematic structure of: (a) a 5-cell EC capacitor and; (b) a single-cell EC capacitor.

the capacitor. The size of the current collector is 5.0 cm in diameter. The size of the electrode is 3.9 cm in diameter. The thickness of each electrode, current collector, and separator paper are about 50, 50, and 25 μm, respectively. The AC impedance of the capacitor was measured by a Solartron electrochemical unit (model 1280B) with frequency ranging from 10 to 20 kHz. During the AC impedance measurement, a sinusoidal source with amplitude of 10 mV was supplied to the capacitor; all measurements were conducted at room temperature. The Nyquist plot (as shown in Fig. 2) shows a typical capacitor behavior under different applied pressures. From Fig. 3 it can be seen that the resistance and capacitance are dependent on the applied pressure. It can be seen that at applied pressure less than 4 kg/cm^2, the resistance decreased and capacitance increased with increasing applied pressure; however, at an applied pressure greater than 4 kg/cm^2, the resistance and capacitance were insensitive to the applied pressure, and the resistance decreased with increasing applied pressure at a much slower rate. An internal resistance

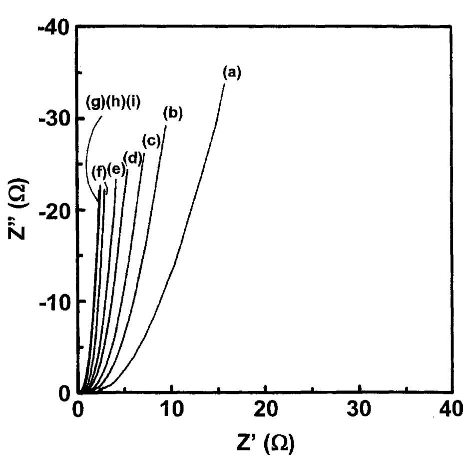

Fig. 2. The Nyquist plot measured from a 5-cell capacitor under different applied pressures of: (a) 0.29; (b) 0.60; (c) 0.81; (d) 0.98; (e) 1.27; (f) 1.89; (g) 4.07; (h) 6.95 and; (i) 8.93 kg/cm^2.

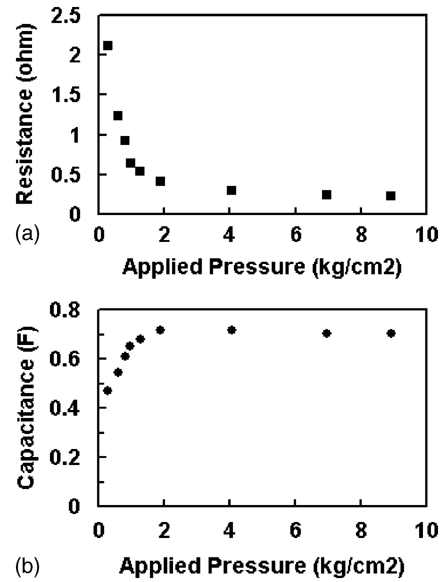

Fig. 3. The resistance and capacitance as a function applied pressure. The resistance and capacitance were measured at 1 and 10 mHz, respectively.

of about 0.24 Ω (0.573 Ω cm^2/cell) was obtained at applied pressure of 5 kg/cm^2.

In order to understand the details of the resistance distribution inside the capacitor, resistances due to electrode, separator paper, and current collector were measured separately. For the electrode, $RuO_2 \cdot xH_2O$/carbon (80/20 wt.%) powder was filled into a stainless steel die with a diameter of 1.17 cm. A Teflon sleeve was placed inside the die in order to electrically insulate the electrode material from the die. Two copper rods polished on plane surfaces, which contacted with electrode material, were introduced at the bottom and top, and the pressure was applied through the copper rods. The resistance between the two copper rods was measured using a four-probe method at different applied pressures. The thickness of electrode material as a function of applied pressure was also measured in order to calculate the resistivity of the electrode material. Fig. 4 shows resistivity of the electrode material as a function of applied pressure. It can

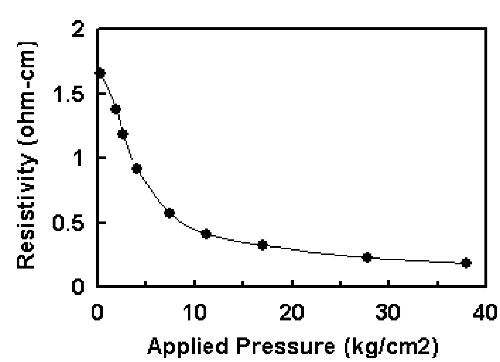

Fig. 4. The electrical resistivity measured from $RuO_2 \cdot xH_2O$/carbon composite electrode under different applied pressures. The loading of electrode material is 0.675 g.

be seen that the resistivity decreased with increasing applied pressure, and in general it is less than 1 Ω cm. At applied pressure of about 5 kg/cm^2, the resistivity of the electrode was about 0.75 Ω cm, which corresponds to a resistance of 0.0038 Ω cm^2 for a 50 μm thick electrode. Therefore, in the 5-cell capacitor, the electrical resistance contributed by electrodes should be about 0.0031 Ω and is much less than the total resistance of the capacitor. For the current collector, the resistivity was calculated based on a standard resistivity measurement using a four-probe method and is about 1 Ω cm. The resistance contributed of the current collectors is about 0.004 Ω and is also much less that the total resistance of the capacitor. For the separator paper, it was impregnated with 38 wt.% H_2SO_4 solution using the vacuum and backfill method, then the separator was sandwiched between two cylindrical stainless steel electrodes with polished surface. The ionic impedance was measured by an AC impedance meter with frequency ranging 1 to 1 MHz. It was found that the resistance and resistivity of separator/electrolyte are about 0.019 Ω cm^2 (25 μm thick) and 7.6 Ω cm at frequency of 20 kHz, respectively. The resistivity is about eight times greater than the resistivity of the electrolyte itself due to the porosity of the separator paper. The resistance contributed from separator/electrolyte is less than 0.008 Ω.

3. Contact resistance

From the above measurements, the combined resistance of the electrode, separator paper, and current collector is less than 0.014 Ω and is only about 6% of the total resistance of the capacitor. Therefore, the major resistance of the EC capacitor with bipolar structure is contributed by the electrical contact resistance. The three major sources of electrical contact resistance are due to the contact of the current collector to the end metal plate, the current collector to the current collector of neighboring cell, and the current collector to the electrode. The total resistance of the capacitor was about 0.24 Ω at the applied pressure of 5 kg/cm^2; this corresponds to 2.87 Ω cm^2 and 0.57 Ω cm^2/cell.

The large contact resistance can be explained as follows: the current collector is composed of 20–30% conducting carbon fibers with non-conducting plastic. The actual electrically conducting path in the current collector is the carbon fibers and their network. Only a few particles at the interface of the electrode side are directly in contact with carbon fibers at the current collector side; therefore, the interface is a bottleneck for the current flow, and causes a high electrical resistance for the capacitor. For the same reason, high electrical resistance will also result from the contact between the current collector and neighboring current collector for a multi-cell capacitor. The dependence of the contact resistance on the applied pressure is illustrated in Fig. 5. When pressure is applied, the plastic sheet will be deformed, and more particles from the electrode will directly contact the carbon fibers in the current collector. In order to ensure the necessary high pressure, rigid packaging material must be used, resulting in a heavy and bulky device and a reduction in the energy density of the EC capacitor.

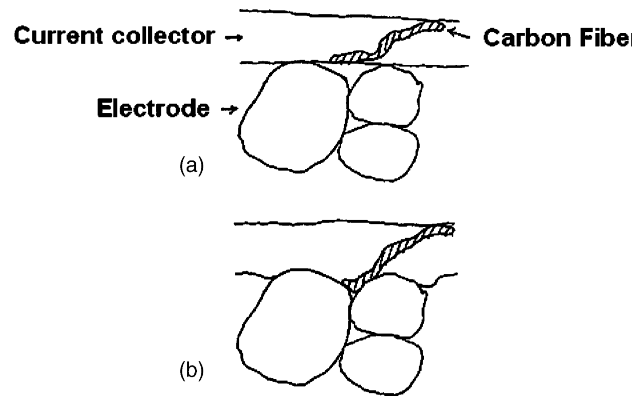

Fig. 5. One example of the interfacial contact between the powder electrode and the conducting plastic sheet: (a) without and; (b) with high mechanical pressure.

A metallic sheet can be used as the current collector for reducing the contact resistance, but most metals are not chemically stable in strong acid solutions. Titanium sheets have been used as the current collector for EC capacitors made with ruthenium oxide film electrodes; [9] however, operating at temperatures above 50 °C must be avoided. Besides the chemical stability, another reason for avoiding metallic current collectors in EC capacitors made with powder electrodes is that the power performance decays with time. Because during the charge and discharge processes, evolution of oxygen and/or hydrogen gases will occur. The gases will stay inside the electrode for while, and will eventually permeate out from the capacitor. During the process of gas evolution, accumulation, and permeation, the contact between collect collector and electrode material will not be as tight as that of a ‘just-built’ capacitor, and the resistance will increase with time. A capacitor made with conducting plastic current collectors is relatively stable because of the elastic nature of those materials, which are able to maintain the tightness between the current collector and the electrode.

4. Composite current collector

In this study, a new composite current collector that combines both advantages from the elastic and chemically stable properties of conducting plastic sheets, and highly electrically conductive properties of metallic sheets was made and tested. The composite electrode was made with a conducting plastic sheet coated with a layer of nickel film on both surfaces. In order to study the feasibility of using the composite current collector for reducing the electrical contact resistance of EC capacitors and distribution of contact resistances, the following three experiments were conducted.

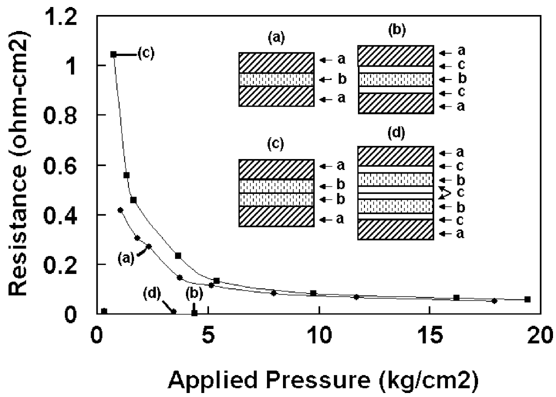

Fig. 6. The resistance for two end metal plates sandwiched a conducting plastic sheet: (a) without and; (b) with metallic coatings. Two end metal plates sandwiched two conducting plastic sheets: (c) without and; (d) with metallic coatings, where a, b, c are copper blocks, conducting plastic sheet, and nickel coatings, respectively.

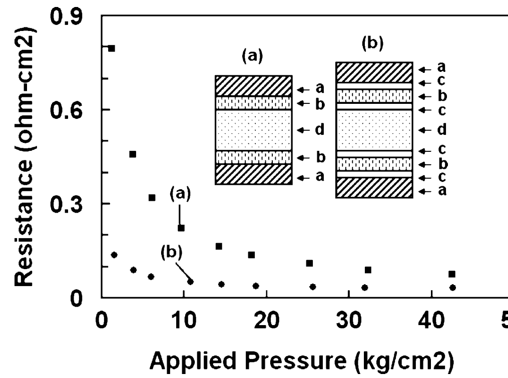

Fig. 7. The contact resistance between the electrode and the conducting plastic sheets: (a) without and; (b) with metallic coatings, where a, b, c, d are copper blocks, conducting plastic sheet, nickel coatings, ruthenium oxide/carbon composite electrode materials, respectively. The loading of electrode material is 0.065 g.

4.1. Contact resistance of the current collector to the end plate

The experimental arrangement was a current collector sandwiched by two end metal plates shown as insert (a) and (b) in Fig. 6. Two different current collectors, a conducting plastic sheet with and without nickel coating, were used. The thickness of the conducting plastic sheet and the nickel film are 50 μm and about 1.5 μm, respectively. The area of the current collector is 3.56 cm^2. Two copper blocks were used as end plates. A mechanical force was applied in the vertical direction to the copper block, and was measured by a force gauge. Fig. 6(a) and (b) show the resistance as a function of applied pressure for both current collectors. The strong dependence of resistance to the applied pressure was observed from the conventional conducting plastic sheet, and indicated that the resistance was dominated by the electrical contact of the current collector to the end plate. It could also be seen that a minimum pressure of 5 kg/cm^2 was required in order to obtain a low contact resistance at about 0.1 $\Omega\,cm^2$. In contrast, the contact resistance of the composite current collector to the end plate was insensitive to the applied pressure, and was less than 10 $m\Omega\,cm^2$ even under applied pressure as low as 0.3 kg/cm^2.

4.2. Contact resistance of the current collector to the neighboring current collector

This contact resistance was measured with two identical current collectors one on the top of another, and then was sandwiched by two end plates shown as insert (c) and (d) in Fig. 6. The resistance difference measured from two current collectors (c) and (d) and single current collector (a) and (b) should be the contact resistance between two current collectors. From Fig. 6 it could be seen that for a conventional current collector, this contact resistance was relatively high and decreased with increasing applied pressure. At applied pressure of 5 kg/cm^2, the contact resistance between neighboring current collectors was about 0.04 $\Omega\,cm^2$. However, for the composite current collector, the contact resistance was low and independent of the pressure.

4.3. Contact resistance of the electrode to the current collector

The experimental arrangement is shown in Fig. 7. The electrode material was placed between two identical current collectors, and was the composite electrode material of $RuO_2{\cdot}H_2O$/carbon (80/20 wt.%). No electrolyte and separator were involved. Fig. 7 shows the resistance as a function of applied pressure. It was clearly demonstrated that the resistance measured from composite current collector was an order of magnitude lower than that from a conventionally conducting plastic sheet. At an applied pressure of 5 kg/cm^2, the resistance was about 0.35 and 0.08 $\Omega\,cm^2$ when using conducting plastic sheet and composite current collector, respectively.

4.4. Distribution of contact resistance

The resistance values shown in Fig. 6(a) and (b) are two contact resistances of the current collector to the end metal plate. The resistance values shown in Fig. 6(c) and (d) are the sum of two contact resistances of the current collector to the end metal plate, and one contact resistance of the current collector to the neighboring current collector. The resistance values appeared in Fig. 7 are the sum of two contact resistances of the current collector to the end metal plate, and two contact resistances of the current collector to the electrode. With simple mathematical calculation, different contact resistances can be determined and are summarized in Table 1. It can be seen that among of contact resistances, the resistance due to the contact between the current collector and the electrode dominates all other types of contact resistance. The total contact resistance for a 5-cell capacitor in

Table 1
Summary of contact resistances in EC capacitors at applied pressure of 5 kg/cm^2

Type of current collector	Collect collector/ end metal plate	Current collector/ current collector	Current collector/ electrode material	Total contact resistance for a 5-cell capacitor
Conducting plastic sheet	0.05 Ω cm^2	0.04 Ω cm^2	0.125 Ω cm^2	1.51 Ω cm^2
Composite	0.002 Ω cm^2	0.005 Ω cm^2	0.038 Ω cm^2	0.40 Ω cm^2

Table 1 was estimated based on 10 contact resistances of the current collector and the electrode, four contact resistances of the current collector to the neighboring current collector, and two contact resistances of the current collector to the end metal plate.

Based on the contact resistance values listed in Table 1 and resistances measured from electrode material, current collector, and separator, at applied pressure of 5 kg/cm^2, a projected resistance for a 5-cell capacitor should be about 0.15 Ω (or 0.358 Ω cm^2/cell), which is less than that measured from an actual capacitor. In order to understand the reason for causing the resistances difference, the actual mass density of the electrode material in the capacitor was estimated based on the capacitance value as follows:

The capacitance of a 5-cell capacitor was measured with an AC impedance measurement at 10 mHz, and was at about 0.73 F as shown in Fig. 3(b). Typically, the capacitance measured using DC charge and discharge cycle was about 20–30% greater than that measured using the AC impedance method. It can be easily calculated that the average capacitance of each electrode in a 5-cell (total 10 electrodes) arrangement is about 8.8–9.5 F. The specific capacitance of a composite electrode (80/20 $RuO_2 \cdot xH_2O$/carbon) is about 634 F/g. [10] The mass of each electrode can be obtained and is 13.9–15.0 mg. With the size of 3.9 cm in diameter and 50 μm in thickness for each electrode, the mass density of electrode is 0.23–0.25 g/cm^3. This value is much less than that obtained from the composite electrode without electrolyte at an applied pressure about 5 kg/cm^2. A possible explanation for this difference is that in an actual capacitor, the electrolyte inside the electrode reduces the effective contact area between the current collector and the electrode and particles inside the electrode; therefore, the actual contact resistances in an EC capacitor including the contact between the particles inside the electrode material and contact between the electrode to current collector are greater than that measured without electrolyte. The reason for having excessive electrolyte in the EC capacitor is due to one of shortcomings of the current technique used for assembling EC capacitors with aqueous electrolytes. Because the electrode material and separator are pre-wetted by electrolyte before being sealed into a cell, the quantity of the electrolyte is very difficult to control. From this analysis, we suggest that in order to effectively reduce the resistance due to the excess electrolyte, the EC capacitor should be assembled with a dry electrode, and a method of filling the electrolyte in each cell under the designed applied pressure must be developed.

5. Conclusion

After carefully analyzing the resistance distribution in a 5-cell capacitor using the conducting plastic sheet as the current collector, it was found that the contact between the conducting plastic sheet and the electrode is a predominant resistance source. It was demonstrated that a low contact resistance could be achieved with a composite current collector, which is made with conducting plastic sheet coated with metallic films on both surfaces, and with low mechanical pressures. These experiments also open the possibility that low resistance and high-performance EC capacitors can be made with a light packaging structure such as a prismatic and button cell structure.

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