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Matching ratio between positive and negative electrodes for double-layer capacitors

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Abstract

For double-layer capacitors in alkaline electrolyte, the specific capacitance of the positive electrode is not equal to that of the negative one. Thus, capacitor performance cannot be optimal with a positive/negative electrode matching ratio of 1. In this study nanoporous glassy carbons (NPGCs) were employed as the electrodes of capacitors, and the influence of matching ratio between positive and negative electrode on capacitor performance was systematically investigated. In aqueous KOH, the specific capacitance of the positive electrode is lower than that of the negative electrode. The matching ratio at which a maximum capacitance is obtained is dependent on the values of the positive and negative electrode capacitance. At low current rate, the highest specific capacitance is achieved at a matching ratio slightly higher than 1. At high current rate, a capacitor has the highest specific capacitance with the lowest resistance at a matching ratio of 1.5. This indicates that an optimum matching relationship between positive and negative electrodes is attained.

1. Introduction

Electrochemical capacitors (ECCs) are a new type of energy storage device, which can store much more energy than conventional capacitors and offer much higher power density than batteries. ECCs fill the gap between high-powered traditional capacitors and high-energy batteries. In addition, ECCs have other advantages such as longer cycle life (>100,000), quick recharge, excellent performance at cold temperature (−70 °C), simple device design, high reliability, high cycle efficiency and environmentally comparability. They are regarded as promising energy storage devices for civil and military applications [1–4]. At present, according to the charge storage mechanism, ECCs can be divided into carbon-based double-layer capacitors (DLCs), pseudo-capacitors with electrode materials such as noble-metal oxides or conducting polymers and hybrid capacitors [5–7]. In DLCs, charge is stored in the electrochemical double-layer formed at the electrode/electrolyte interface. In pseudo-capacitors the charge is stored via faradaic redox reactions in the bulk of the electrode material. A hybrid capacitor is based on two different kinds of electrode material. Although pseudo-capacitors and hybrid capacitors are enjoying growing interest, DLCs have been commonly developed and commercialized over the last few decades.

As the most important component of DLCs, carbon materials have been extensively developed with very promising results [8]. However, capacitor performance depends not only on the electrode materials used but also the design. Now, the mass of the positive carbon electrode equals that of the negative carbon electrode in a double-layer capacitor. Although the positive and negative electrodes are chemically inert carbon materials, the mass of the positive and negative electrodes should not be equal due to the different electrochemical behavior of the positive and negative electrodes in alkaline solutions, which leads to large differences in their contributions to the DLC. Thus, how to obtain the matching ratio between the positive electrode and the negative one that optimizes the performance of DLCs becomes the target of this research. Liu et al. [9] measured charge/discharge curves of the capacitor composed of two activated carbon electrodes in a three-electrode cell. The results obtained indicated that the capacitance of the positive electrode is lower than that of the negative electrode, but further explanations were not given. The anodic and cathodic capacitance in various organic R_4PBF_4/PC solutions was determined by Morimoto et al. [10]. The cathodic and anodic capacitance was dependent on the size of cations and anions in the electrolyte. Up to now, there are no reports about the matching ratio between positive and negative carbon electrodes for double-layer capacitors in an inorganic alkaline solution.

In the present study, nanoporous glassy carbons (NPGCs) prepared in our lab [10] served as the electrodes. Under preconditions wherein the apparent area of the positive electrode is the same as that of the negative electrode, and the total mass of both positive and negative electrodes is kept constant, the influences of matching ratio between positive and negative carbon electrodes on the performance of the DLCs are investigated. Meanwhile, the matching ratio between positive and negative carbon electrodes is optimized.

2. Experimental

2.1. *Sample preparation*

The starting material for the electrodes was a Novolac resin (melting point lower than 85 °C, dissociative phenol less than 7%). It was mixed with a certain amount of hexamethylene tetramine by ball milling. The mixture was heated in air to be cured. The cured resin was ground into fine particles and compacted into a disc under a stress of 380 MPa. Then, the compacted resin disc was carbonized at around 600 °C for 30 min in N_2, followed by CO_2-activation at 900 °C for 25 min to form NPGCs with an area of $2\ \mathrm{cm}^2$ and different thickness. The typical pore size distribution (PSD) and pore structure parameters for the NPGCs are shown in Figure 1. It can be seen that the sizes of pores in the NPGC are in the narrow mesopore and wide-micropore range of less than 2 nm, having a relatively large surface area and pore volume.

2.2. *Cell construction and electrochemical measurements*

All the electrochemical measurements were performed with two-electrode capacitors composed of the phenolic resin-derived NPGCs in an aqueous solution of $7\ \mathrm{mol\ l^{-1}}$ KOH. The total mass of positive and negative electrodes was kept constant (0.18 g), while the positive electrode mass was varied in order to build a series of capacitors of matching ratios ranging from 1/3 to 3. The matching ratio calculation is defined as the weight ratio of positive to negative carbon electrodes. Electrochemical characterizations were performed by galvanostatic charge–discharge using a LX PCBT-128D-D mutlichannel test equipment (Wuhan, China). Cyclic voltammetry for five cycles with a scan rate of $2\ \mathrm{mV\ s^{-1}}$ and electrochemical impedance spectroscopy (EIS) in the frequency range 20 kHz to 0.1 Hz were carried out using Solartron1280Z test system (England), a constant DC bias of 1.0 V and AC perturbation of 5 mV were applied to the cells. The Equivalent series resistance (ESR) of capacitors was measured at 1 kHz and at 1 bias.

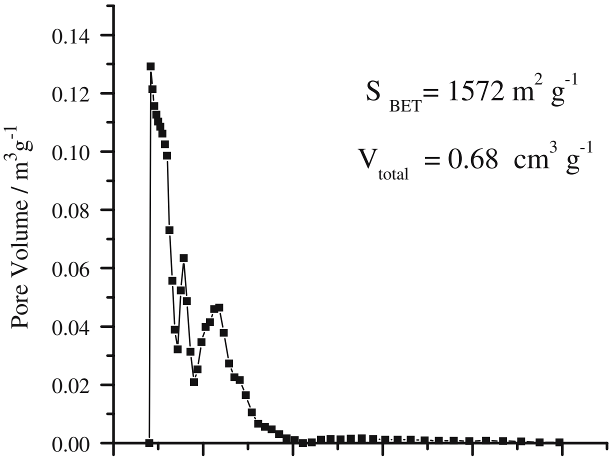

Fig. 1. Typical pore size distribution and parameters for NPGCs.

The galvanostatic charge–discharge measurements were performed on a three-electrode configuration (cell 3E). Cell 3E for electrochemical experiments involves two NPGC electrodes and a Hg/HgO reference electrode (as shown in Figure 2). All these elements are placed in glass vessels. The two NPGC electrodes constitute the model supercapacitor where there is a very large excess of electrolyte in comparison with the charge storage possibilities of the DLC. The whole cell is open to air due to no effects of air on the performance of capacitors employing inorganic aqueous solutions as electrolytes. Potentials of the positive and negative electrodes during charge–discharge cycles are expressed versus the Hg/HgO electrode, which is connected to the negative electrode through a salt bridge full of $7\ \mathrm{mol\ l^{-1}}$ KOH electrolytic solution. So, the reference electrode is situated far away from the EDLC electrodes so that it is not subject to any significant variation of ionic concentration to the electric field. This guarantees that the reference electrode does not influence the charge–discharge measurement of the model capacitor.

3. Results and discussion

When the charge–discharge cycles are stable, the capacitance is calculated as follows: $C = (I \times t)/(\Delta V m)$, where I is the discharge current, t is the discharge time, ΔV is the potential change on discharge and m is the total mass of two carbon electrodes. The dependence of the

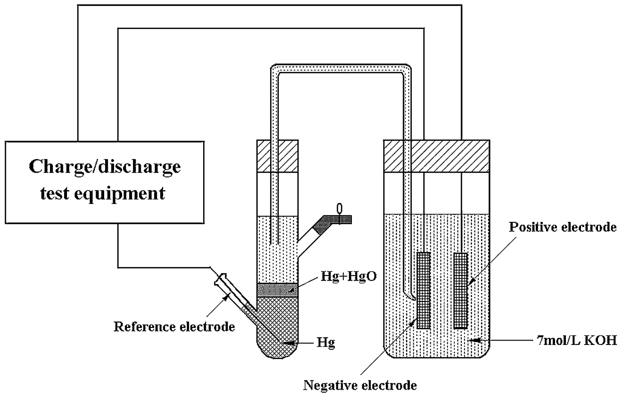

Fig. 2. Schematic drawing of the three-electrode cell used for galvanostatic charge–discharge measurements with two NPGC electrodes of 1.6 cm diam. and a Hg/HgO reference electrode.

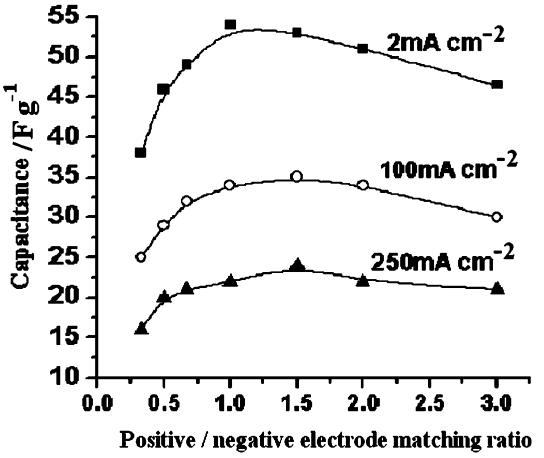

Fig. 3. The specific capacitance of capacitors vs. matching ratio of positive/negative electrode at different current rates.

capacitance of capacitors on the matching ratio and charge–discharge current density is shown in Figure 3. At a low current rate (2 mA cm^{-2}), the highest capacitance is achieved for a matching ratio slightly higher than 1, followed by a slow decrease as the matching ratio is further raised. With increasing current density, the matching ratio at which the maximum capacitance is obtained shifts to 1.5. This suggests that improvement in the capacitor performance is facilitated when the mass of the positive electrode exceeds that of the negative to some extent, especially at a high current rate.

Figure 4 shows voltammograms of the DLCs with different matching ratio in two-electrode cells recorded during the initial 5 cycles in the potential range 0–1 V. Apart from the first cycle, only a slight variation is observed among the remaining voltammograms. This indicates that there are irreversible electrochemical processes taking place during the first potential scan, which is more obvious for the DLC with the lower matching ratio. After the cycle becomes stable, it does not exhibit the symmetrical rectangular shape expected for an ideal capacitor. The larger the matching ratio, the more rectangular are the voltammograms. Otherwise, the voltammograms are inclined and distorted showing a decrease in capacitance of the positive electrode. As a result, the capacitance of the DLC is the highest at a matching ratio of 1, which is basically consistent with the galvanostatic charge–discharge results at low current rate.

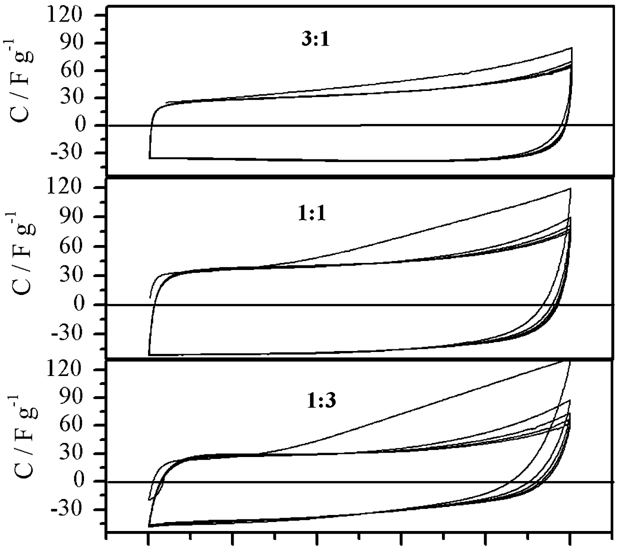

Fig. 4. Cyclic voltammograms of model capacitors traced at different matching ratios of positive/negative electrode, as indicated from 0 to 1 V. Scan rate: 2 mV s^{-1}.

The internal resistance of capacitors composed of NPGC electrodes with different matching ratios was measured by the Nyquist plots as shown in Figure 5. It can be seen that loops corresponding to the electrochemical polarization almost disappear at high frequency, starting with a 45° impedance line that is explained as arising from the diffusion of ions in porous electrodes and approaching an almost vertical slope at low frequency. At a matching ratio lower than 1, the impedance increases gradually with decreasing matching ratio. At a matching ratio higher than 1, the impedance tends to decrease initially and then increase, suggesting that too high a matching ratio may lead to an increase in impedance. As a result, the lowest impedance is achieved at a matching ratio of 1.5.

According to the formula:

$$P_{\max} = V^2/4R, \tag{1}$$

in which V is the voltage and R is the internal resistance of capacitors, it is clear that the maximum power density is dominated by the magnitude of the internal resistance. Figure 6 shows the variation of the internal resistance with matching ratio. It is found that the lowest resistance is achieved for a matching ratio of 1.5. As the matching ratio is raised to 2, the internal resistance increases slightly. However, when the matching ratio is higher than 2 or lower than 1.5, the internal resistance increases significantly. This suggests that capacitors can deliver the highest power density at a matching ratio of 1.5.

In order to investigate the reason for the dependence of capacitor performance on matching ratio, charge/discharge curves of a cell with different matching ratio and that of negative electrode were recorded during galvanostatic charge/discharge cycles at current density of 2 mA cm^{-2} in cell 3E, respectively. The charge/discharge curves of the positive electrode were obtained by subtracting the potential of the negative electrode from the cell voltage. The results are shown in Figure 7. With increasing matching ratio, the highest charge potential (vs. Hg/HgO) of the positive electrode decreases. At a matching ratio of 2.4 the highest charge potential of the positive electrode is lower than 0 V. Indeed, it is demonstrated from our previous studies [11] that the influence of side reactions on the positive electrode tends to diminish with a drop in the highest charge potential (vs. Hg/HgO) of positive electrodes, improving the capacitance performance.

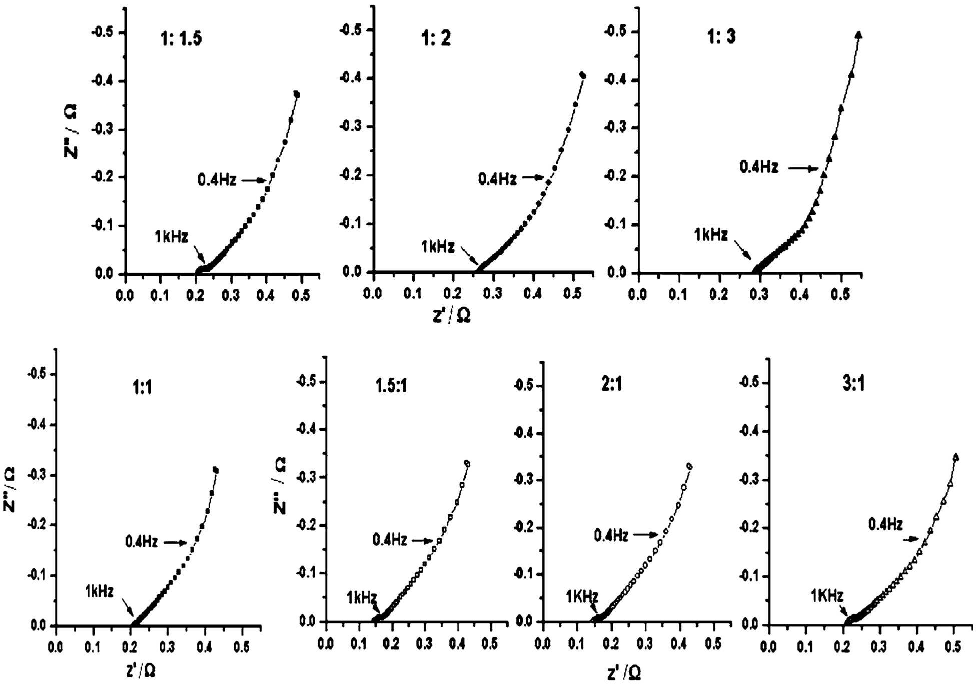

Fig. 5. Impedance plots of model capacitors at different matching ratios of positive/negative electrode, as indicated from 0.1 Hz to 20 kHz.

Some data obtained from Figure 7 are summarized in Table 1. Regardless of matching ratio the specific capacitance of the negative electrode is always higher than that of the positive electrode. With an increase in matching ratio, the specific capacitance of the positive electrode decreases while that of the negative electrode increases.

When the specific capacitance of positive and negative electrodes is unequal, the specific capacitance of capacitors can be written as:

$$C = \frac{m_1 - m_1^2}{\frac{1}{C_1} + \left(\frac{1}{C_2} - \frac{1}{C_1}\right)m_1} \tag{2}$$

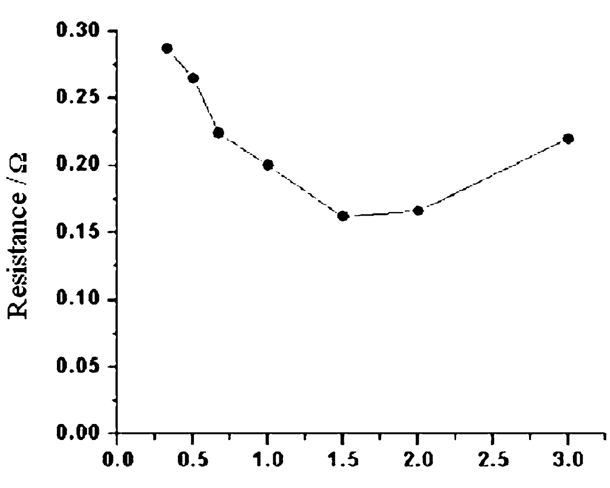

Fig. 6. Dependence of the internal resistance of two-electrode capacitors on matching ratio of positive/negative electrode.

where m_1 is the matching ratio of the negative electrode, C_1 is the specific capacitance of the negative electrode and C_2 is the specific capacitance of the positive electrode. When the total mass of two carbon electrodes (m) is constant, a maximum capacitance is shown on the C vs. matching ratio $(1-m_1)/m_1$ curve, the magnitude and position of which may vary with the value of C_1 and C_2. Thus, expressions for C_1 and C_2 were obtained by linearly fitting the negative and positive specific capacitance in Table 1 as a function of m_1 as follows:

$$C_1 = 324 + 157m_1 \tag{3}$$

$$C_2 = 58 + 163m_1 \tag{4}$$

Equation (2) was fitted by substituting C_1 and C_2 in Equation (2) with Equations (3) and (4) or with the values of capacitance obtained at a current rate of 2 mA cm^{-2} for a matching ratio of 1. The fitting curves are shown in Figure 8. The tendency of the fitting curves is very consistent with that derived from experiments, especially when the former fitting method was employed. With the current rate increasing, C_1 and C_2 are reduced. But, C_2 decreases more quickly than C_1 due to the larger size of hydrated OH$^-$ ions[12]. Thus, it is expected that the matching ratio at which a maximum capacitance is obtained will increase with the current rate rising. This explains why the matching ratio at which a maximum capacitance is obtained shifts from 1 to 1.5 with increasing current rate.

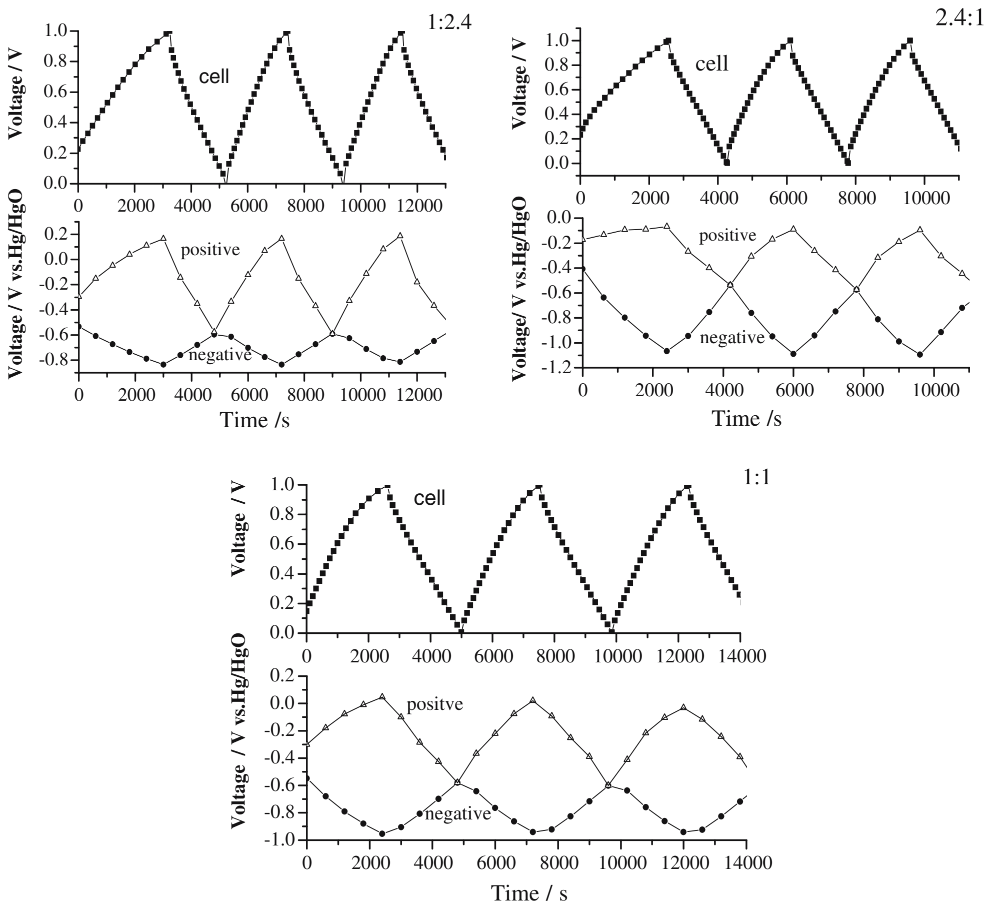

Fig. 7. Charge/discharge characteristics for the 3-electrode cell as a function of matching ratio of positive/negative electrode at 2 mA cm^{-2}.

4. Conclusion

Nanoporous glassy carbons (NPGCs) served as the electrodes in this study and the influence of the matching ratio on capacitor performance was systematically investigated. The following conclusions can be drawn.

(1) In an KOH solution, cyclic voltammograms of two-electrode cells with different matching ratios are not symmetrical and show different electrochemical behavior. The specific capacitance of the positive electrode is lower than that of the negative electrode.

(2) From the charge–discharge curves of positive and negative electrodes, it is observed that the highest charge potential of the positive electrode decreases as the matching ratio is increased, and this leads to a lower effect of side reactions on the positive electrode and an improvement in capacitance performance.

(3) Under the condition that the total mass of the two carbon electrodes is kept constant, at a matching ratio slightly higher than 1, the highest specific capacitance is obtained at a low current rate. At a high current rate, the specific capacitance of positive electrodes decreases more quickly than that of negative electrodes due to the larger size of hydrated OH^-. At a matching ratio of 1.5, the capacitors exhibit optimal capacitance performance, i.e. the highest specific capacitance with the lowest resistance.

Table 1. Positive and negative electrode discharging voltages and capacitance for different matching ratios of positive/negative electrode at a current rate of 2 mA cm^{-2}

Matching ratio	Change of positive electrode potential/*V* (vs. Hg/HgO)	Specific capacitance of positive electrode/*F* g^{-1}	Change of positive electrode potential/*V* (vs. Hg/HgO)	Specific capacitance of negative electrode/*F* g^{-1}	Specific capacitance of capacitor/*F* g^{-1}
2.4/1	$-0.107\sim-0.667$	100	$-1.107\sim-0.667$	275	40
1/1	$0.066\sim-0.557$	150	$-0.934\sim-0.557$	251	47
1/2.4	$0.12\sim-0.630$	166	$-0.880\sim-0.630$	211	36

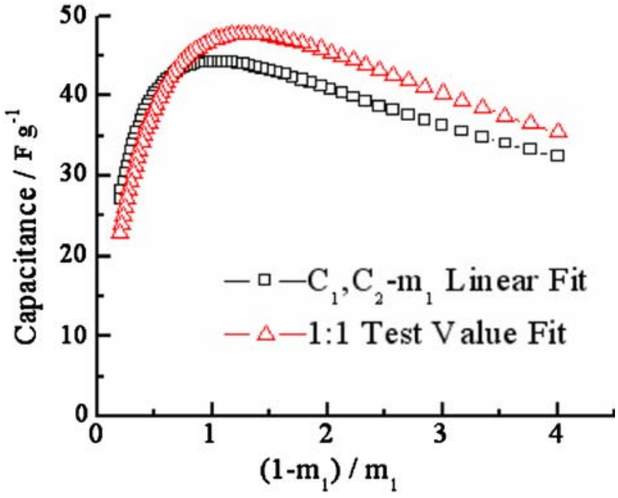

Fig. 8. The specific capacitance of capacitors vs. matching ratio of positive/negative electrode $(1-m_1)/m_1$ fitting Curves at a low current rate of 2 mA cm^{-2}.

Acknowledgement

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