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ORIGINAL PAPER

Mechanistic studies for the limitation of carbon supercapacitor voltage

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Abstract This paper investigates the discrepancy between double-layer supercapacitor voltage and the maximum electrochemical window voltage in an alkaline electrolyte. The electrochemical window is determined by the potential difference between hydrogen evolution and oxygen evolution. As the specific capacitance of a negatively polarized carbon material may be different from its positively polarized counterpart, the hydrogen evolution and oxygen evolution in the electrode may not occur at the same time. To achieve the electrochemical window voltage, the two electrodes in a double-layer supercapacitor need to be balanced and have the same capacitance to ensure that oxygen and hydrogen are generated at the same time.

Keywords Supercapacitor · Maximum voltage · Specific capacitance · Activated carbon · Electrochemical window

1 Introduction

During the past decade, the power requirements for the fast growing applications of electric vehicles and consumer electronics have exceeded the capability of conventional battery designs. These applications require an electrical power output with time-dependent pulse on-demand. These power output characteristics are different from those of conventional battery systems which are considered low power devices.

Electrical energy can be stored in two ways, firstly, the energy can be stored and released through the Faradic redox reaction as chemical energy in electrochemical active materials; secondly, it is stored as non-Faradic electrostatic charges on the two separated electrodes. Chemical energy is stored in a conventional battery system and the electrostatic charges are stored in the electrode double-layer as an electrochemical double-layer capacitor. The transition from “supercapacitor” to “battery behavior” in electrochemical energy storage was discussed by Conway [1]. A “battery like” supercapacitor was introduced based on Faradic pseudo-capacitance of redox reaction at two-dimensional electrode surfaces and three-dimensional surfaces in a microporous transition metal hydrous oxide. Since then, electrochemical supercapacitors with Faradic pseudo-capacitance have been reported using various electrode materials [2–5]. Even though capacitors made with electrodes with pseudo-capacitance or asymmetric capacitors in which one electrode is based on the Faradic interfacial reaction provide high specific energy, the symmetric double-layer supercapacitor still remains superior because of its high power, excellent low temperature performance, long cycle and calendar life [6, 7]. However, it remains a challenge to increase the energy density for double-layer supercapacitors. The amount of energy (U) stored in a capacitor and the maximum power (P_{max}) it can deliver are given by Eqs. 1 and 2, respectively:

$$E = \frac{1}{2}CV^2 \tag{1}$$

$$P_{\max} = \frac{V^2}{4R} \tag{2}$$

where C is the total capacitance, V is the voltage and R is the equivalent series resistance (ESR). The capacitance is proportional to the accessible surface area of the porous

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electrode and related to the surface functionalities of the electrode materials. Pore size distribution of the activated carbon materials was reported to play an important role for the energy and power density of the supercapacitors [8]. The activated carbons with a larger percentage of bigger pores are more suitable to high-power applications because they can deliver high energy at high rates, but they store less total energy. The specific double-layer capacitance (F m^{-2}) was found to relate to the surface properties [9]. Asymmetric double-layer capacitor was reported by using electrodes with different pore size distributions in a non-aqueous electrolyte in order to accommodate anion and cation of different sizes [10]. After investigating each individual electrode in a carbon double-layer supercapacitor in KOH electrolyte, Wen et al. [11] reported that the maximum capacitance can be achieved when the mass of the positive electrode exceeds that of the negative one, especially at a high current rate. It was proposed that the phenomenon is due to the fact that the influence of side reaction on the positive electrode tends to diminish with a drop in the highest charge potential of positive electrodes, thus more carbon in the positive electrode than that in the negative electrode is needed to limit the maximum potential of the positive electrode. According to Eq. 1, the energy stored in a capacitor is proportional to the voltage square. Therefore, a small increase in capacitor voltage can significantly increase the amount of energy stored in the capacitor. This paper reports the factors that impact an alkaline double-layer supercapacitor.

2 Experimental details

Activated carbon (M-20) material used in the experiment was obtained from SpectraCorp (USA). M-20 was chosen for the investigation, because its porosity and surface functionality were thoroughly studied and the results were reported [8, 9].

30 wt% aqueous KOH solution was used as the electrolyte in all experiments at a temperature of 298 ± 1 K. The potentials reported, unless otherwise specified as the voltage of a two electrode capacitor, are referred to the Hg/HgO reference electrode immersed in the KOH solution of the same concentration as the experimental electrolyte.

M-20 was mixed thoroughly with 10 wt% (dry material) of a Teflon suspension (DuPont T-30) as a binder. The resulting Teflonized carbon was left to air-dry before being hot-rolled to form flexible thin films. The electrodes were then punched out of the big sheet in the desired size. Two pieces of the activated carbon disk were sandwiched on a Pt current collector by the screw-fitting plug, and the electrode holder was hung in the center of a large Pt-mesh net counter electrode to ensure homogeneous current distribution. The Hg/HgO reference electrode resided close to the electrode holder. If a two-electrode system was used, the two disc electrodes were mounted face to face into the holder with a non-woven separator in between and two Pt meshes were used as current collectors. The Hg/HgO reference electrode was put close to the cell holder. The potentials of each individual carbon electrodes were recorded against the reference electrode along with the capacitor voltage during the charge and discharge processes of the supercapacitor.

An EG&G 170 potential/galvanstat controlled by the Q&R Smart Data package was used for all electrochemical measurements.

3 Results and discussion

As demonstrated in Eq. 1 and 2, both the specific energy and the power of a supercapacitor are determined by cell voltage. Theoretically, the maximum voltage is related to electrolyte stability and determined by the electrolyte decomposition potential. The maximum voltage is related to the hydrogen evolution and oxygen evolution overpotentials on the carbon electrode in alkaline solution and should be higher than 1.2 V. The electrochemical window for the M-20 activated carbon electrode in 30 wt% KOH electrode is demonstrated in a three-electrode configuration, as shown in Fig. 1. The hydrogen and oxygen evolution potentials are about −1130 mV vs. Hg/HgO and 160 mV vs. Hg/HgO, respectively. Thus, the theoretical maximum voltage for the supercapacitor should be about 1.3 V. However, the voltage of a symmetric alkaline supercapacitor made with activated carbon electrodes of the same type and the weight has always been around 1.1 V. The phenomenon where the supercapacitor made with two identical M-20 electrodes was charged to the maximum voltage before gas generation and then charged to the maximum of opposite polarization is shown in Fig. 2. The capacitor made with identical electrodes can only be charged to 1.12 V before significant gas generation.

To investigate this discrepancy, an Hg/HgO reference electrode was implanted in the device. Thus the potential of each carbon electrode in the supercapacitor can be individually monitored in real-time during polarization. Figure 3 show the potential changes for the two individual carbon electrodes vs. the same Hg/HgO reference electrode during the charge/discharge of the supercapacitor at both polarization directions. Figure 3a, b show the charge/discharge curves for the two carbon electrodes polarized at opposite directions. The arrows identify the polarization curves for the two electrodes under the same supercapacitor charge/discharge cycles. While the supercapacitor was at 0 V or Open Circuit Voltage (OCV), the potential for

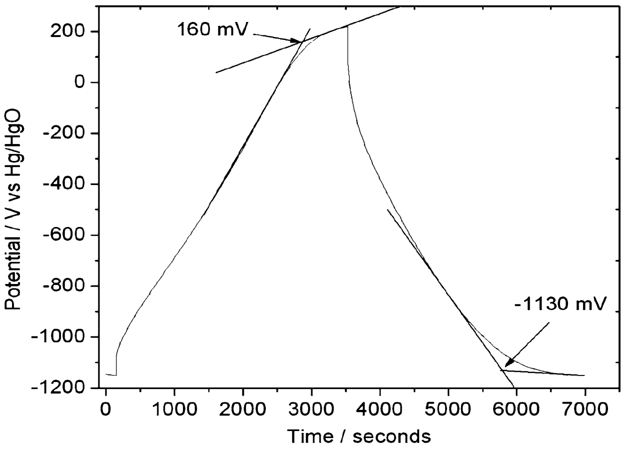

Fig. 1 Constant-current charge and discharge of an M-20 activated carbon electrode in a three-electrode configuration with incorporation of a Hg/HgO reference electrode and a Pt counter electrode

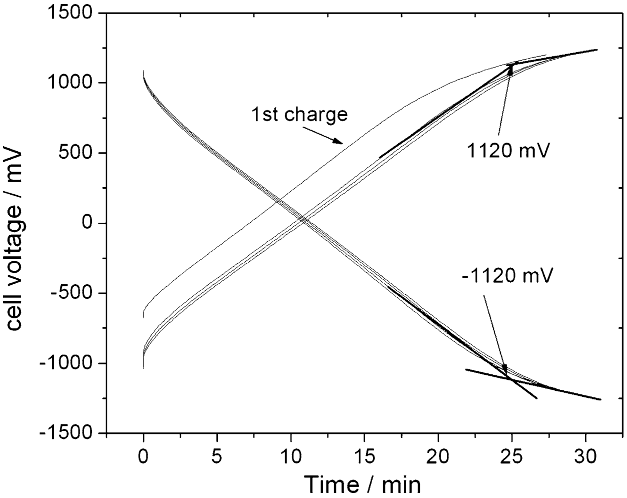

Fig. 2 Multiple constant-current charge and discharge of two-electrode supercapacitor made by M-20 activated carbon electrodes. The capacitor was charged/discharged to the maximum voltage at both polarization directions

each individual electrode was about −540 to −550 mV vs. Hg/HgO. The rest potential for a carbon electrode is believed to relate to the surface functionality [8]. The limitation for the maximum voltage is clearly demonstrated in Fig. 3. When the supercapacitor was charged, one carbon electrode was positively polarized and another electrode was negatively polarized. The ideal situation happens when hydrogen evolution on the negatively polarized electrode and oxygen evolution on positively polarized electrode occur at the same time, so that the supercapacitor can achieve the maximum theoretical voltage. However, as shown in Fig. 3, for the supercapacitor using two identical electrodes, oxygen starts to generate on the positively polarized electrode when the potential of the electrode reaches about 120 mV vs. Hg/HgO reference electrode, the potential of the negatively polarized electrode was about −1000 mV vs. Hg/HgO reference electrode, which is about 150 mV more positive than the hydrogen evolution potential. The "would-be" hydrogen evolution potential is labeled in both figures. As soon as gas starts to generate, the charge of a real supercapacitor has to be halted to prevent gas accumulation inside the capacitor case that could increase the internal pressure and cause the rupture of the vent mechanism. Obviously, in the supercapacitor made with identical M-20 electrodes, hydrogen and oxygen generation do not take place at the same time. Therefore, the energy and power capabilities of the supercapacitor are limited not only by lower than expected voltage but also by the unused electrode double-layer capacitance. This occurs because the negatively polarized electrode is not fully utilized when hydrogen starts to generate on the positively polarized electrode.

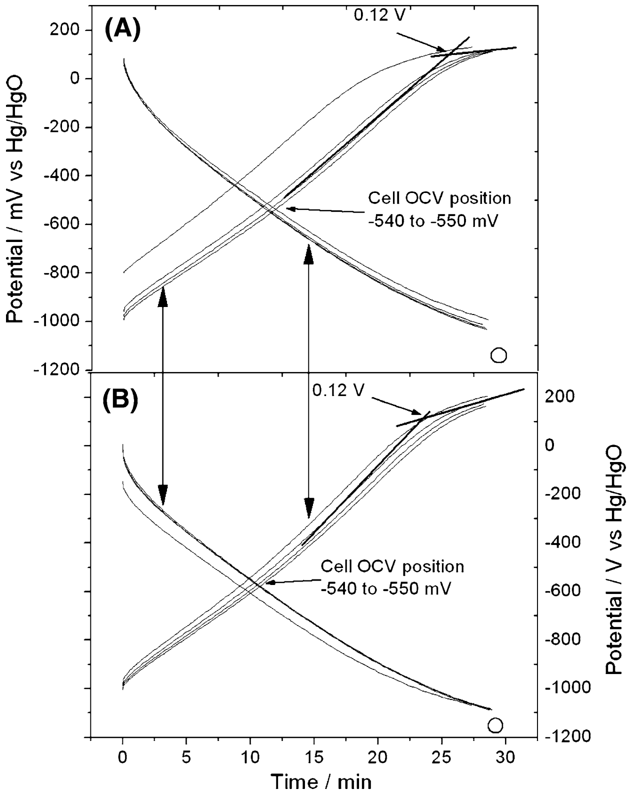

Fig. 3 Charge and discharge curves for individual electrodes **a** electrode 1 and **b** electrode 2 in the symmetric supercapacitor. The potential was measured against the Hg/HgO reference electrode. The arrows indicate the electrode couples in the same supercapacitor charge/discharge cycles. The circles indicate the hydrogen evolution potential. The weight of each electrode was 0.079 g

As well known for the Hg electrode, the positively charged electrode experiences strong anion adsorption from the electrolyte compared with weaker cation adsorption at the negatively charged electrode. The seminal case is also valid on the carbon electrode [12, 13]. Thus, the specific capacitance (F m^{-2}) of a positive electrode would be appreciably greater than a negative electrode. On the other hands, the surface of activated carbon is normally covered with functional groups of various kinds determined by the pre-cursor materials and manufacturing processes. Therefore, not only the adsorption of anion and cation, but also the surface functionalities would contribute to the specific capacitance of the carbon electrode. The impact of the surface functionalities on supercapacitors have been investigated in detail [9]. The functional groups, which are not electrochemically active within the potential range of supercapacitor operation, could either make the surface more hydrophobic or more hydrophilic. These electrochemically active functional groups, however, could also contribute to the total "apparent capacitance" of the electrode, as much as the Faradic reactions can meet the criteria of "pseudo-capacitance" [1]. It has to be emphasized that due to the complexity of the organic surface compounds, the type of electrochemical reactions taking place in the different potential ranges may be different. In addition, the surface functional groups may favor the adsorption of either anions or cations or both, due to electrostatic forces and specific chemical adsorption. Figure 4 demonstrates the phenomena occurring when the M-20 activated carbon electrode is used. When the electrode is positively polarized, anions accumulate in the solution side of the double-layer; cations displace anions in the double-layer when the electrode is negatively polarized. It is obvious that the specific capacity of the positively polarized M-20 electrode is not the same as that of the negatively polarized electrode and the transition takes place at around −500 mV vs. Hg/HgO reference electrode. The two electrodes in a supercapacitor are polarized at opposite directions. In the symmetric supercapacitor in which the two carbon electrodes are identical, the two electrodes may not reach the gas evolution potentials at the same time due to the fact that the specific capacitance of the same material in different potential ranges may not be the same. Additionally, the initial OCV of the electrode may not be right in the middle of the electrochemical window. Thus, gas may first start to generate on one electrode while charges are still being used to charge double-layers on another electrode. In the case of the symmetric supercapacitor made with M-20 activated carbon material, even though the OCV (about −500 mV) is roughly in the middle of the electrochemical window (−1.2 V to 0.1 V vs. Hg/HgO), the specific capacitance for the positively polarized electrode is lower than the negatively polarized one. Oxygen starts to generate on the positively polarized electrode while charges are used to charge the double-layer on the negatively polarized electrode, as shown in Fig. 3. It is worth to pointing out that unlike the clean Hg electrode, pseudo-capacitative component resulted from the redox reaction of surface functional groups could contribute significantly to the specific capacitance of a carbon electrode. Pseudo-capacitance may be different in different potential ranges. It appears that the pseudo-capacitance for the M-20 electrode was higher when it was negatively charged than it was positively charged.

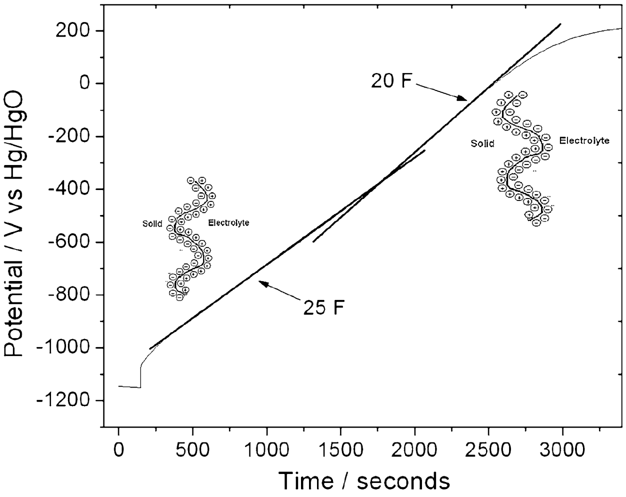

Fig. 4 The charge/discharge curve for the M-20 electrode in 3-electrode configuration. Potential was measured against the Hg/HgO reference electrode. The capacitances during positive and negative polarization are 20 F and 25 F, respectively

To approach the theoretical maximum cell voltage and fully utilize the available double-layer capacitance for maximizing the total capacitance of the supercapacitor, which is housed in a container with fixed volume, the actual capacitance of the two electrodes needs to be balanced by taking into consideration both the OCV and specific capacitance in different ranges of polarization potentials. The mass of the two electrodes needs to be adjusted relative to each other in order to balance the density of anodic and cathodic charge storage and delivery. Figure 5 show an example of such balance. Instead of using symmetric M-20 electrodes, one electrode is heavier (0.079 g) than the other (0.054 g). The charge and discharge curves within the full electrochemical window are shown in the figures and the arrows display the polarization curves of the two electrodes of the supercapacitor under the same operation. While the larger electrode is positively polarized and the smaller one is negatively polarized, the negatively polarized electrode reaches its hydrogen evolution potential around the same time as the positively polarized electrode reaches its oxygen evolution potential. Hydrogen and oxygen start to generate around the same time. Figure 6 shows that the voltage of the supercapacitor approaches the theoretical maximum value. When the polarization of the supercapacitor was reversed, the lighter electrode was positively polarized and the heavier one was negatively polarized. The maximum voltage of the supercapacitor is even lower than the symmetric configuration

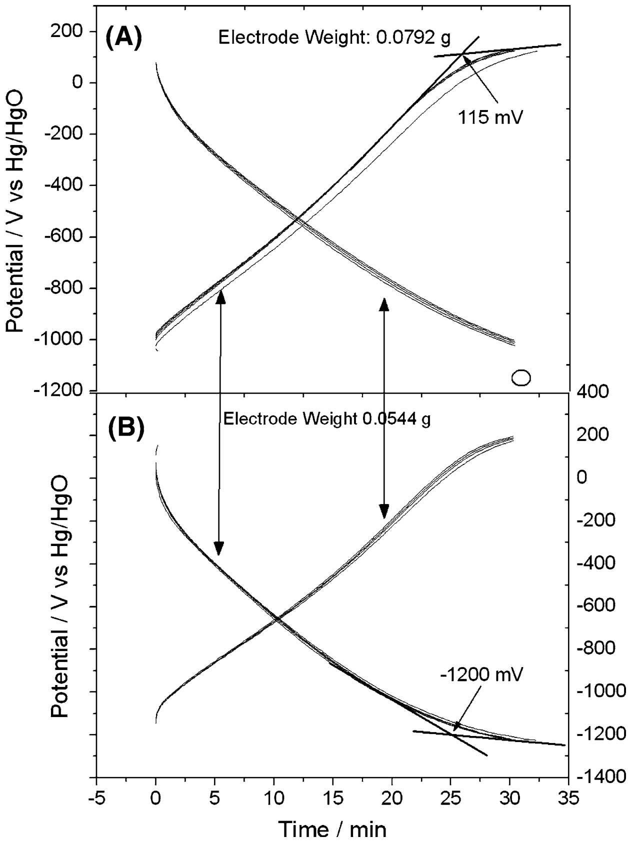

Fig. 5 Charge and discharge curves for individual electrodes in the non-symmetric supercapacitor. The two electrodes weighed 0.079 and 0.054 g, respectively. The arrows indicate the electrode couples in the same supercapacitor operation. The circle indicates the hydrogen evolution potential

as the potential of the negatively polarized electrode is further away from the hydrogen evolution potential when oxygen begins to generate on another electrode.

4 Conclusion

The investigation of the discrepancy between the double-layer supercapacitor voltage and the maximum electrochemical window potential has revealed the following:

1. The specific capacitance for the same carbon electrode may be different in different potential ranges due to the specific anion and cation adsorptions and possible pseudo capacitance of surface functional groups. Thus, both double-layer capacitance and pseudo-capacitance vary with the potential.
2. The OCV of an activated carbon electrode may not in the middle of the electrochemical window.
3. The voltage discrepancy results from the fact that hydrogen evolution and oxygen evolution may not take place at the same time.
4. To achieve the maximum voltage, the capacitance of both the electrodes has to be balanced to ensure hydrogen evolution and oxygen evolution take place simultaneously.

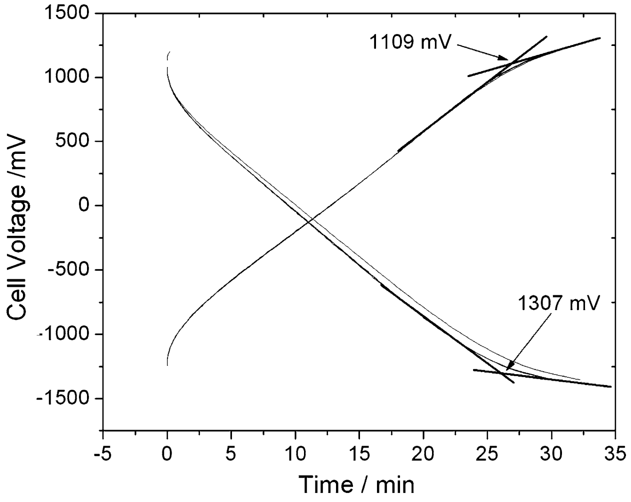

Fig. 6 Charge and discharge curves for the non-symmetric supercapacitor. The electrodes weighed 0.079 (**a**) and 0.054 g (**b**), respectively. The supercapacitor approached theoretical maximum voltage (1.3 V) when the heavier electrode was positively polarized; when the heavier electrode was negatively polarized, the cell voltage can only reach 1.1 V

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