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# From symmetric AC/AC to asymmetric AC/graphite, a progress in electrochemical capacitors

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## Abstract

Graphitic carbon instead of activated carbon has been employed as the positive electrode material in the activated carbon (AC)/carbon capacitors using organic electrolytes. The advantageous electrochemical performance of the AC/graphite capacitors has been investigated as compared with the AC/AC capacitors. The charge storage mechanism of anions on the graphite positive electrodes in the AC/graphite capacitors has been studied by in situ XRD measurements.
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## 1. Introduction

Recently, supercapacitors have drawn extensive attention because of their potential applications as electric storage devices in many fields. In the conventional electric double-layer capacitors (EDLCs), the storage of charge on electrodes is through the non-faradaic adsorption at the interfaces between the electrodes and electrolyte. Generally, both the positive and negative electrodes in EDLCs are identical activated carbon (AC) electrodes. This type of symmetrical capacitors inevitably restricts their functional ranges such as specific capacitance, working voltage, energy density, etc. [1,2], although they possess the merits of long cycle life and high power density. Moreover, during the course of industrial production, the precursor of activated carbon is mixed with a big amount of activating agents like KOH and heated at a certain high temperature (e.g., $1000\,^{\circ}C$) in the inert atmosphere. Considerable portions of carbon are "rotted" off to construct the porous structure and wasted. These complex processes make the cost of activated carbon not economic for large-scale production of EDLCs.

An alternative choice is the hybrid supercapacitor of an asymmetrical configuration in which battery electrode replaces one activated carbon electrode [3–6]. The battery electrodes accumulate charge through faradaic electrochemical process (redox reaction), which cannot only increases the specific capacitance of the capacitor, but also extends the working voltage. As a result, the energy density of capacitor is enlarged considerably. Generally, there are three categories of redox-reaction materials are used in the hybrid supercapacitors nowadays, metal oxides, conductive polymers and intercalation compounds.

We realized that the properties of the interface between the electrodes and the electrolyte limit the performance of the whole capacitor. Many limitations of the EDLC nowadays actually can be ascribed to this point. In fact, most solvated ions instead of "bare" ions are adsorbed on the surface of activated carbon electrodes. Of course, the coordinating solvent molecules of ions may occupy the space adsorbing ions. Since the solvent molecules are electric neutral and contribute no electric charge, the "dilution" of the ions on the activated carbon electrode surface by the solvent molecules may decrease the capacitance of the capacitor. On the other hand, these coordinating solvent molecules of ions are very near the adsorption sites on the surface of activated carbon and easy to be catalyzed to decomposition under the ultrahigh strength of electric field. (We have witnessed the burst of the AC/AC capacitors when we charged the capacitors to high voltages, say, 3.5 V.) An ideal case is that "bare" ions are closely adsorbed on the accessible surface of carbon electrode. Then we expected that the interlayer space in graphitic carbon selectively accommodates ions and sieves out the parasite coordinating solvent molecules. In previous studies, a concept of

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"dual carbon" battery has been proposed, in which both positive and negative electrodes are based on the intercalation compound of graphitic carbon [7–9]. Of course, the ions may be intercalated into the interlayer spaces deeply to form the intercalation compounds in the batteries. Nevertheless, "dual-carbon" battery cannot meet the needs of high rate performance (high power) for capacitors because ion diffusion in the interlayer space is generally a slow process. Moreover, $Li^+$-containing electrolytes are often used in this kind of batteries. But the intercalation of $Li^+$ at negative electrode in fact involves solvent co-intercalation and de-solvation processes, which cost high activation energy [10]. Because the potential of Li-graphite intercation compound is very near to that of Li metal, Li metal plating probably happens at negative graphite electrode at high current densities (high power). So graphitic carbon is not suitable as a negative electrode in capacitors using $Li^+$-electrolytes. On the contrary, the anion intercalation into graphite needs not so high activation energy because the co-intercalation of solvent molecules into the interlayer spaces of graphite hardly occurs [10]. Therefore, the shallow insertion of anions from the edge-plane surface into interlayer space may be applicable for capacitor. Actually, the electrochemical intercalation of anions from organic electrolytes into graphitic carbon electrodes has been investigated towards battery utilization from 1970s to 1980s [11–13]. Based on the above consideration, we attempted a new type of capacitor comprising two asymmetric carbon electrodes [14,15]. A graphitic carbon was chosen as the positive electrode to store anions, while an activated carbon was employed as the negative electrode to accommodate cations. Organic electrolytes were used to ensure the high working voltage as high as 3.5 V. The superiority of the asymmetric activated carbon/graphite capacitor over conventional EDLCs can be clearly seen in the practical applications, it possesses high capacitance, high voltage, high energy density, low cost, etc. This kind of capacitor is a very promising electric storage device in the near future. In this study, we investigated the electrochemical behavior of AC/graphite capacitors by the means of galvanostatic charge–discharge and in situ XRD measurements, etc. Some factors influence the performance of the capacitors will be addressed.

## 2. Experimental

Artificial graphite (KS6, Timcal) was selected as the positive electrode material, whereas activated carbon (PW15M13130 from Kureha, specific surface area, $1050 \, m^2 \, g^{-1}$, activated by steam) was applied as the negative electrode material in this study. The electrode materials were mixed with conductive binder TAB (teflonized acetylene black) and pressed on a stainless steel mesh as a current collector. The electrolyte used in this study were 1.5 M $TEMAPF_6$ or 1.5 M $TEMABF_4$ dissolved in PC solvent (Tomiyama) (TEMA stands for triethylmethyl ammonium). Coin cells were fabricated for galvanostatic (constant current) charge–discharge tests. In a coin cell, glass fiber filters soaked with the electrolyte were sandwiched by the positive and negative electrodes (geometric area, $2 \, cm^2$). Coin cell assembling was performed in a glove box filled with Ar atmosphere (dew point, lower than $-80 \, °C$). Gavanostatic

charge–discharge tests were carried out to test the electrochemical behavior of the asymmetric capacitors. Generally, the constant current density was controlled at $0.5 \, mA \, cm^{-2}$. The voltage range was from 0 to 3.5 V for AC/graphite capacitors. To trace the positive and negative electrode potentials independently, three-electrode cells were also constructed. Graphite positive electrode, AC negative electrode and the reference electrode (Li metal chip or AC electrode with much higher weight than the negative AC electrode), were dipped into the electrolyte contained in a glass beaker. During the course of galvanostatic charge–discharge between the positive and negative electrodes, the potentials of either positive or negative electrodes with respect to the reference electrode were measured by an auxiliary potentiometer. Generally, the electrode potentials were reported against Li metal. The potential of heavy AC electrode versus Li is about 3 V. The total voltage of the capacitor actually equals to the difference between the potentials of positive and negative electrodes.

From the linear portions in the potential profiles, we calculated, respectively, the specific capacitance values of the total capacitor, positive and negative AC electrodes according to the following formulas:

$$C_{total} = it/(w_+ + w_-) \, \Delta V_{total};$$
$$C_+ = it/w_+ \, \Delta V_+;$$
$$C_- = it/w_- \, \Delta V_-.$$

$C_{total}$, $C_+$, $C_-$ stand for the specific capacitance values of the total capacitor, positive and negative electrodes, respectively. $w_+$ and $w_-$ designate the weight of the active materials in the positive and negative electrodes, respectively. $\Delta V_{total}$, $\Delta V_+$ and $\Delta V_-$ represent, respectively, the changes of the total capacitor voltage, positive electrode and negative electrode potentials. $t$ is the charge (or discharge) time (s) and $i$ is the constant current value during galvanostatic charge–discharge.

By contrast, charge storage ability of the capacitors is also expressed as capacity ($Q$, $mAh \, g^{-1}$). It is calculated by the following formula: $Q = it/w_+$, where $i$ (mA) stands for current passing through the capacitor during galvanostatic charge–discharge, $t$ (h) means the time for charge (or discharge) between the cutoff voltage range and $w_+$ (g) denotes the weight of positive electrode.

Powder X-ray diffraction (XRD, Rint-1100, Rigaku, Japan) measurement using Cu Kα radiation was employed for in situ XRD study of graphite positive electrodes. The in situ XRD cells used in this study is diagrammed in Fig. 1. It consists of two electrodes separated by glass fiber filters soaked with electrolytes. Thin Al film was applied as the current collecter for graphite positive electrode as well as X-ray window. The slurry containing KS6, acetylene black powders together with PVDF/NMP solution was coated onto an Al foil by a doctor blade to prepare the positive graphite electrode for in situ XRD measurement.

## 3. Results and discussion

Fig. 2 shows the potential profiles of a conventional EDLC (AC/AC) during galvanostatic charge–discharge cycles (the
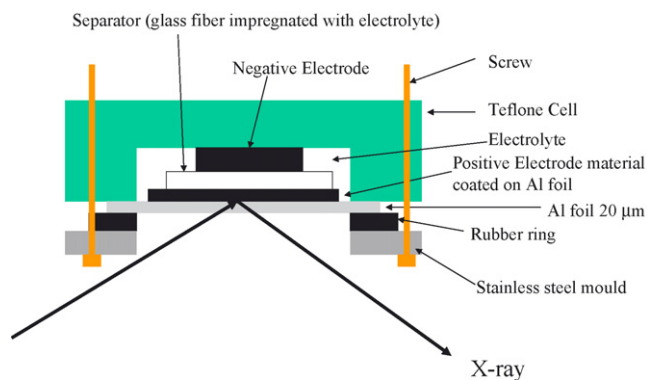
Fig. 1. Schematic view of in situ XRD cell.



Fig. 3. SEM image of activated carbon (AC) negative electrode material.

positive and negative electrodes have the same weights of active material). The potential profiles of both the positive and negative AC electrodes are almost linear as well as the cell voltage curve. At the point of charge cutoff in each cycle (capacitor voltage 2.7 V), the potential of the positive electrode can reach as high as about 4 V against Li metal (ceiling potential), while that of the negative electrode drops down to 1.3 V against Li metal (bottom potential). On the other hand, when the capacitor voltage becomes 0 V, both the positive and negative electrodes have the same potential of about 2.5 V against Li metal. Therefore, the interface between positive electrode and electrolyte is burdened with about 1.5 V (4 − 2.5 V) from the total working voltage of 2.7 V. On the other hand, that corresponding to the negative side shares 1.2 V (2.5 − 1.3 V) from the total working voltage of 2.7 V. So the faradaic solvent electrolysis at the positive electrode may be very mild because PC solvent decomposition starts at about 4.3 V versus $Li/Li^+$ [2]. At the negative side, the electrolyte decomposition might happen somehow since the onset of faradaic reactions was detected at potentials lower than 1.5 V versus $Li/Li^+$ [2]. But the decomposition product may form some passivating films in initial cycles at electrode surface and protect them from further electrolyte decompositions. As calculated from the potential profiles, the initial specific capacitance values of total AC/AC capacitor, AC positive and negative electrodes are 23.2, 87 and 102 F g$^{-1}$, respectively. It is of interest that $C_-$ is larger than

$C_+$ by about 16%. Even in the "ideal" symmetric configuration (the positive and negative elctrodes are the same), the charge storage ability on both electrodes is actually not equal. From the viewpoint of ionic radius (TEMA$^+$, 0.327 nm; PF$_6^-$, 0.254 nm), $C_+$ ought to be larger than $C_-$ [16]. To explain this deviation, we tentatively ascribe it to the solvated PF$_6^-$ anions adsorbed at the positive electrode. Probably PF$_6^-$ are more liable to solvent molecules than TEMA$^+$. The AC applied in this study was activated by a steam, the pore size on the surface is too big to screen out the heavily solvated ions. The SEM image of AC is shown in Fig. 3. Macropores can be clearly found on the surface of each AC particle. Therefore, in the conventional EDLC (AC/AC capacitor), the restriction of energy density might be attributed mainly to the positive electrode side. Not only the potential, but also the capacitance at the interface between the positive electrode and the electrolyte is heavily shackled.

We considered the disadvantages of the AC positive electrode as mentioned above and attempted to use the graphite positive electrode instead of AC. Fig. 4 shows the potential profiles of the AC/graphite capacitor during galvanostatic charge–discharge processes (the positive and negative electrodes have the same weights of active material). The potential profile of graphite positive electrode in the AC/graphite capacitor is quite different
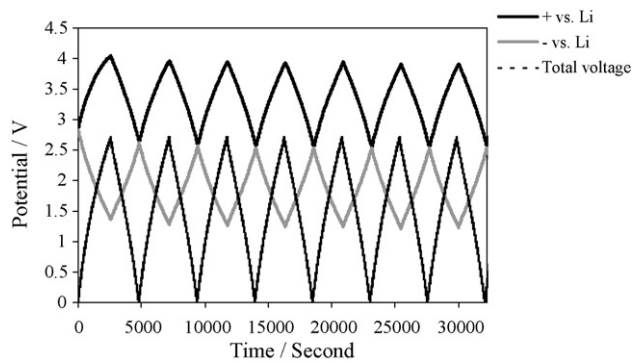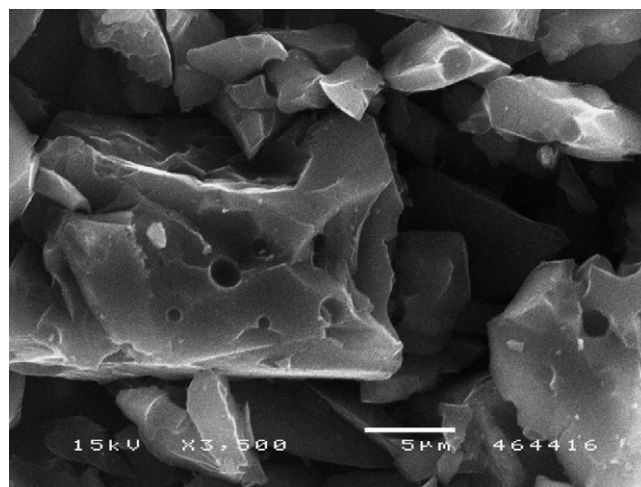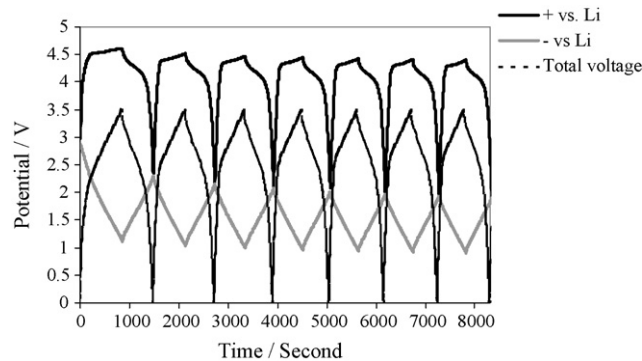


Fig. 2. Potential profiles of a conventional EDLC (AC/AC) during galvanostatic charge–discharge cycles (the positive and negative electrodes have the same weights of active material (9.3 mg), electrolyte: 1.5 M TEMAPF$_6$-PC).



Fig. 4. Potential profiles of the AC/graphite capacitor during galvanostatic charge–discharge processes (the positive and negative electrodes have the same weights of active material (5.5 mg), electrolyte: 1.5 M TEMAPF$_6$-PC).

from that of the AC positive electrode in conventional EDLC. In the initial charge process of the AC/graphite capacitor, the potential of graphite positive electrode jumps up suddenly to about 4 V against Li metal at first, and then rises up slowly until about 4.5 V against Li metal. On the other hand, the potential of AC negative electrode drops down almost linearly in the charge process of capacitor, it can reach the lowest potential of about 1.2 V against Li metal. Accordingly, the total voltage curves of the graphite/AC are bent lines, roughly comprise two linear portions with different slopes. In the AC/graphite capacitor, the graphite positive electrode works principally at rather high potential ranges, the linear portion from 4.5 to 4 V against Li metal occupies a big part of the capacity delivered by the positive electrode. Although some electrolyte decomposition at the graphite positive electrode is inevitable at high potentials, it is not so drastic since the surface area of graphite is not so high as activated carbon. During the charge process of the AC/graphite capacitor, the anion-PC species are gathered at the interface between graphite positive electrode and the electrolyte at first. Because the surface area of the graphite positive electrode is not so big to accommodate many adsorbed anion-PC species (highly polarizable electrode), the potentials of the graphite positive electrode rises up quickly until it arrives at certain high value, say, 4 V against Li metal. The anions start to insert into the interlayer spaces of graphitic carbon and the potential profile bend and rise up pace slowly (a nearly non-polarizable electrode). Since the size of anion is rather big ($PF_6^-$, 0.254 nm; graphite interlayer distance, $d_{002} = 0.335$ nm), it seems that the anions enter into the interlayer spaces of graphitic carbon without PC molecules solvated. At the edge-plane surface, most PC solvent will be stripped off the anions and screened out, only the anions can penetrate into the interlayer spaces of graphitic carbon. The generally used anions like $PF_6^-$ and $BF_4^-$ have higher anodic stability than the PC solvent [17]. So the graphite positive electrode can be used in the high potential range safely. Since the potential profile of the positive electrode and the total voltage curve of AC/graphite capacitor are not purely straight lines, it is difficult to calculate the specific capacitance values precisely. As an approximation, we picked up the linear parts at higher voltage ranges (positive electrode, 4–4.5 V; total voltage, 2–3.5 V) and count the corresponding capacitance from the potential curves. The initial specific capacitance values of total AC/graphite capacitor, the graphite positive and the negative AC electrodes are 34.3, 202 and 109 F g$^{-1}$, respectively. It is of interest to note that the specific capacitance of the AC negative electrode ($C_-$) in the AC/graphite capacitor is very near to the $C_-$ in AC/AC capacitor. On the other hand, the specific capacitance value of graphite positive electrode is over twice the

value of AC positive electrode. Thus, the specific capacitance of total AC/graphite capacitor is greatly enlarged as compared with AC/AC capacitor.

From the above comparison between AC/graphite and AC/AC capacitors, it is clear that the new type capacitor (AC/graphite) has advantages in the terms of high capacitance, high working voltage and high energy density. However, its potential shortcomings must be taken into account before practical applications. Since the storage mechanism of anions at graphite positive electrode involves the insertion of anions into interlayer spaces between graphene layers, deep intercalation might deteriorate the rate performance and cycle-ability of AC/graphite capacitors, especially at high weight ratios of AC to graphite [15]. We performed in situ XRD measurements on the graphite positive electrode in the graphite/AC capacitor to test whether deep intercalation really occurs in the positive graphite electrode. Fig. 5 shows the in situ XRD patterns of the graphite (KS6) positive electrode during the initial charge process of AC/graphite capacitor with different weight ratios of AC to graphite. At the low weight ratio of 1, the (0 0 2) diffraction peak of KS6 positive electrode remains its shape and position in the XRD patterns in the whole working voltage range. This means that deep intercalation does not takes place because the crystal lattice of the host (KS6) does not change apparently. In our previous study [15], we show that peak splitting and shift happens for the (0 0 2) peak in the case of another artificial graphite (MAG D-20 from Hitachi Kasei Ltd. Co.) under similar conditions (AC/graphite weight ratio, 1; electrolyte, 1.5 M TEMAPF$_6$-PC). What is the main difference between KS6 and MAG D-20? Comparing the XRD patterns of these graphite samples in the powder form, we found that MAG D-20 is more crystalline than KS6 because the (0 0 2) peak of MAG D-20 is sharper than that of KS6. Presumably, turbostratic disorder in graphitic carbon help depress the intercalation of anions into interlayer spaces. The above assumption is similar to the case of lithium cation intercalation into graphitic carbon [18]. On the other hand, the (0 0 2) peak of KS6 splits and shifts to low diffraction angles at high AC/graphite weight ratios (2 and 4). The above fact implies that as the weight ratio of AC to graphite rises, the anions insert more deeply into graphite lattice. This conclusion accords with the result in our previous study, that is, with the rise in weight ratio of AC to graphite, the cycle performance of AC/graphite capacitor becomes worse. It is likely that bigger volume changes of graphite matrix due to anion intercalation destroy more severely the crystal structure of graphite electrode.

The fact that the cycle-ability becomes worse with the weight ratio of AC to graphite can be explained from another viewpoint.

Table 1
Electrode potential values of AC/KS6 capacitor in the initial galvanostatic charge–discharge process (electrolyte, 1.5 M TEMABF$_4$-PC)

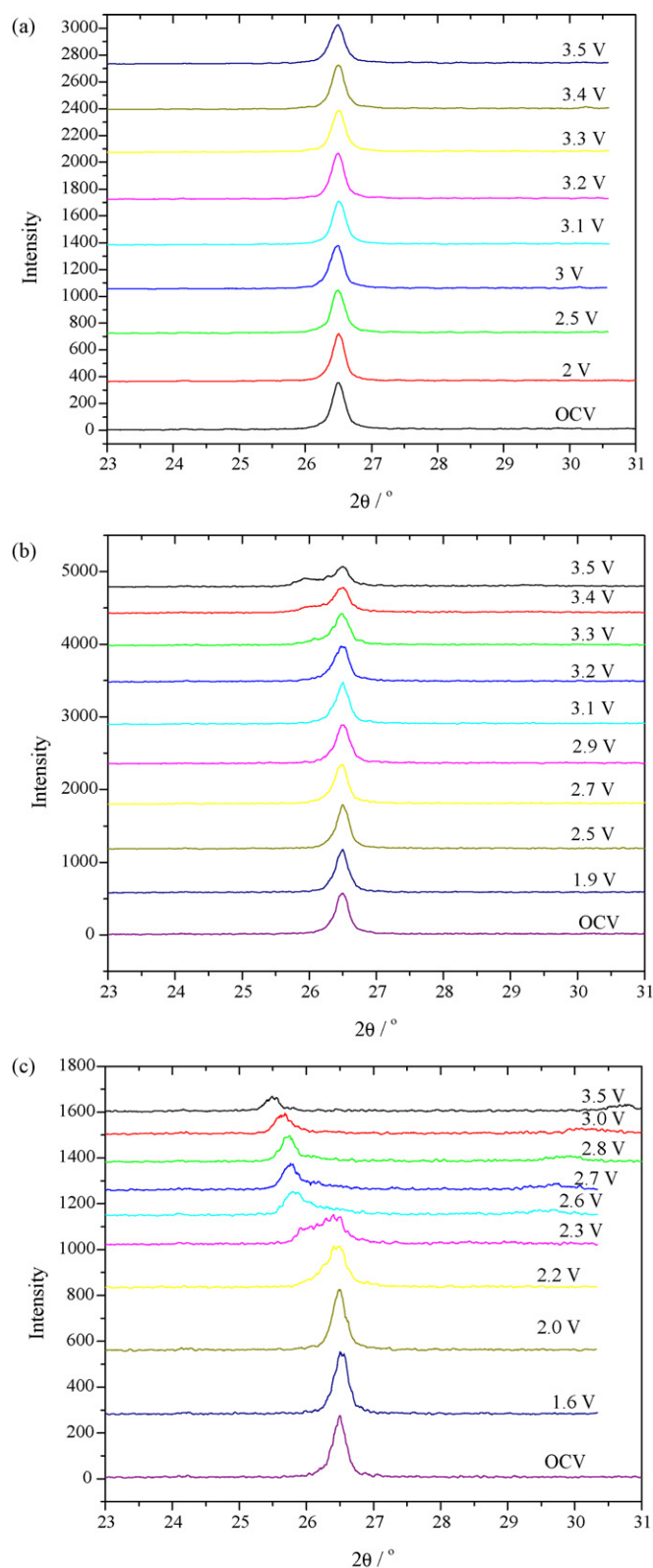| Weight ratio of AC to graphite | Ceiling potential of graphite positive electrode (V vs. Li) | Bottom potential of AC negative electrode (V vs. Li) |
|---|---|---|
| 1:1 | 3.83 | 1.34 |
| 1:2 | 5.04 | 1.55 |
| 1:4 | 4.99 | 1.50 |

Fig. 5. In situ XRD patterns of the graphite (KS6) positive electrode during the initial charge process of AC/graphite capacitor with different weight ratios of AC to graphite, electrolyte: 1.5 M TEMABF₄-PC: (a) graphite:AC = 1:1, (b) graphite:AC = 1:2 and (c) graphite:AC = 1:4.
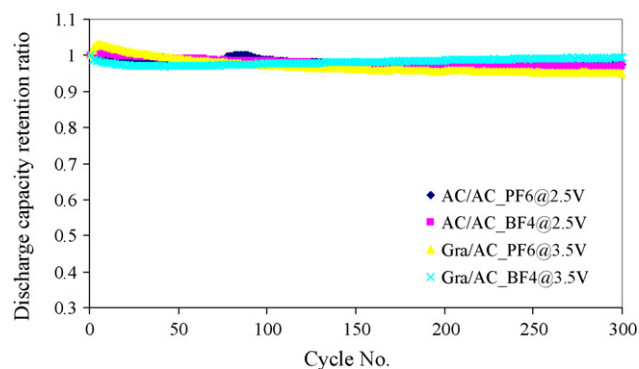


Fig. 6. Cycle performance of AC/graphite and AC/AC capacitors (AC/graphite capacitors were cycled between 0 and 3.5 V; AC/AC capacitors were cycled between 0 and 2.5 V; weights of the active electrode materials: in AC/graphite capacitor, 11.6 mg/11.6 mg for both the electrolytes; in AC/AC capacitors, 8.0 mg/8.0 mg for the electrolyte of 1.5 M TEMABF₄-PC, 8.2 mg/8.2 mg for the electrolyte of 1.5 M TEMAPF₆-PC).

As measured from the three-electrode cells, the potential of graphite positive electrode against the reference electrode likely experiences higher voltage load at higher graphite/AC weight ratio. Table 1 lists the potentials of graphite and AC electrodes in the capacitor (versus Li metal) with different weight ratios of AC to graphite when the capacitor was charged to 3.5 V. Generally, both the ceiling potential of graphite positive electrode and the bottom potential of AC negative electrode rise with the increase in the weight ratio of AC to graphite. As the AC/graphite weight ratio becomes bigger than 2, the potential of graphite positive electrode is higher than 5 V versus Li while the potential of AC negative electrode climbs up to over 1.5 V versus Li. Thus, the irreversible decomposition at AC negative electrodes will becomes milder, whereas the irreversible decomposition at graphite positive electrodes will gets more severe. The heavy voltage burden on the graphite positive electrode destroys the cycle performance of graphite/AC capacitors.

If the weights of graphite and AC are controlled to be equal, the cycle performance of the AC/graphite capacitor is quite satisfactory. Fig. 6 compares the cycle performance of AC/graphite and AC/AC capacitors (the weights of positive and negative electrode materials are equal). The cycling voltage ranges were arranged to 0–3.5 V for AC/graphite capacitors and 0–2.5 V for AC/AC capacitors. Here, we adopted a parameter of discharge capacity retention ratio to evaluate the cycle-ability of the capacitors. This parameter equals to the ratio of $n$th-cycle discharge capacity to the initial discharge capacity. After 300 cycles, the retention ratios of AC/graphite capacitors in both the electrolytes of 1.5 M TEMABF₄ or TEMAPF₆ dissolved in PC is very near to those of AC/AC capacitors.

## 4. Conclusion

As compared with the conventional EDLCs (symmetric AC/AC type), the asymmetric AC/graphite capacitors have the advantages of high capacitance in the high voltage range, high energy density, etc. The weight ratio of negative electrode material (AC) to the positive electrode material (graphite)

has great effects on the electrochemical performance of the AC/graphite capacitors. In situ XRD measurements prove that at high AC/graphite weight ratios, anions intercalates into the interlayer spaces deeply during the charge process of the capacitor. Moreover, high AC/graphite weight ratios cause the graphite positive electrode to be burdened with more heavy voltage load. These factors lead to the deterioration of the cycle-ability of the AC/graphite capacitors.

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