Short communication

Performance of AC/graphite capacitors at high weight ratios of AC/graphite

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Abstract

The effect of negative to positive electrode materials' weight ratio on the electrochemical performance of both activated carbon (AC)/AC and AC/graphite capacitors has been investigated, especially in the terms of capacity and cycle-ability. The limited capacity charge mode has been proposed to improve the cycle performance of AC/graphite capacitors at high weight ratios of AC/graphite.
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Keywords: Capacitors; Graphite; Activated carbon; Organic electrolytes; Intercalation

1. Introduction

Recently, we have explored the capacitor of activated carbon (AC)/graphite using organic electrolyte [1–3]. This kind of capacitors have remarkable advantages over the traditional electric double-layer capacitors (EDLCs) of symmetric AC/AC configuration in the terms of higher working voltage, higher energy density, and low cost, etc. We noticed that the weight ratio of AC negative to graphite positive electrode materials plays an important role in the performance of AC/graphite capacitors. As AC/graphite weight ratio is lower than 1, the charge storage mechanism at the positive graphite electrode is principally concerned with some of specific anion adsorption and the intercalation of anions into the graphite positive electrode can be suppressed. In the case of some KS series graphite samples from Timical Co. Ltd., the shift of (0 0 2) diffraction peak for graphite could be hardly observed in the *in situ* XRD measurements [4]. This charge storage mechanism in the AC/graphite capacitor is somehow similar to that of the EDLCs. As the AC/graphite weight ratio rises to over 1, the capacity of the graphite positive electrode increases and anions start to intercalate into the crystal lattice of graphite accordingly. Then the potential of graphite positive electrode shifts to higher values and the cycle-ability of the AC/graphite capacitor becomes deteriorated. So AC/graphite capacitors at high AC/graphite weight ratios actually belong to electrochemical capacitors. For the practical applications, the weigh ratio of AC/graphite is generally kept at around 1. With the progress of this study, some new phenomena have been discovered. These phenomena provide deep insights into the practical application of AC/graphite capacitors. In this paper, we would like to present these new insights in detail.

2. Experimental

Most experimental details, including the graphite and AC electrode materials, electrode fabrications, glove box operations, instrumentation, cells, etc. were similar to those described in the previous studies, unless otherwise specified [3]. 1.5 M TEMAPF$_6$ (TEMA stands for triethylmethyl ammonium) dissolved in PC was employed as the electrolyte in this study.

Charge storage ability of the capacitors was generally expressed as capacity (Q, mAh g^{-1}). It is calculated by the following formula: $Q = IT/w_+$, where I (mA) stands for the current passing through the capacitor during galvano-static charge–discharge, T (h) means the time for charge (or discharge) between the cutoff voltage range and w_+ denotes the weight of positive electrode material.

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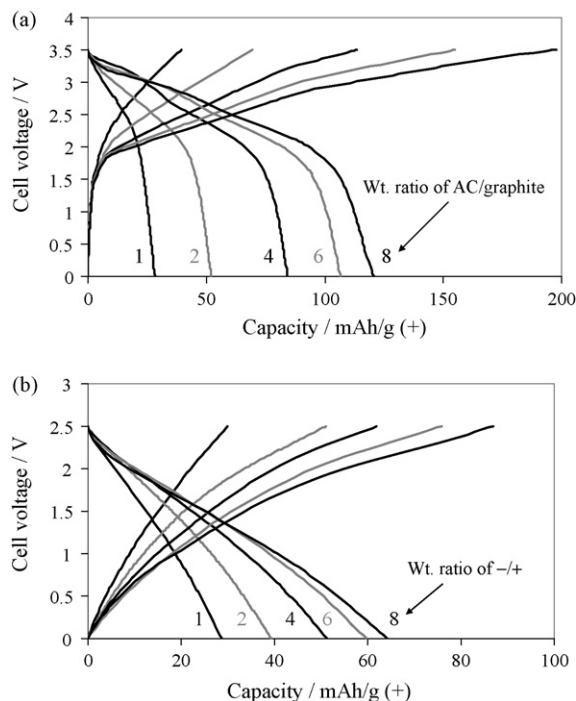yoshio@cc.saga-u.ac.jp (M. Yoshio).

Fig. 1. Initial charge–discharge curves of AC/graphite (a) and AC/AC capacitors at different weight ratios of negative/positive electrode materials.

3. Results and discussion

Fig. 1 shows the initial galvano-static charge–discharge curves of AC/AC and AC/graphite capacitors at different weight ratios of negative/positive electrode materials. The shapes of the charge–discharge curves of both capacitor systems are different. AC/graphite capacitors have bent curves, but AC/AC capacitors possess straight lines, especially in the cases of discharge processes. Fig. 2 compares the different trends of initial discharge capacity versus weight ratio of negative/positive electrode materials in AC/AC and AC/graphite, respectively. Both curves demonstrate that the discharge capacity rises with the increase in the weight ratio of negative/positive electrode materials. However, the climb-up pace of discharge capacity in the AC/graphite capacitor is remarkably bigger than that in the AC/AC capacitor. At the weight ratio of 1, the capacity of AC/AC capacitor is a little higher than that of AC/graphite capacitor. At
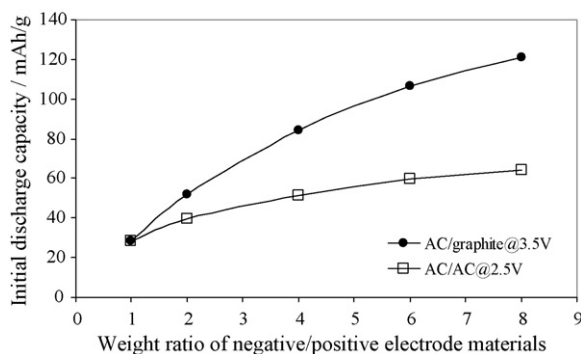

Fig. 2. Relationship between the initial discharge capacity and the weight ratio of negative to positive electrode materials in AC/AC and AC/graphite capacitors.

very large weight ratios of negative/positive electrode materials, the rise-up trend of discharge capacity in the AC/AC capacitor actually becomes sluggish. It appears that the discharge capacity in AC/AC capacitors approaches some saturation value once the weight ratio of negative/positive electrode materials becomes large enough. From the following derivations, the saturation value of discharge capacity in AC/AC capacitors can be predicted.

In a capacitor, the following relationship holds for:

$$\frac{1}{(w_+ C_+)} + \frac{1}{(w_- C_-)} = \frac{1}{C_{cell}}$$

w_+ and w_- denote the weights of the positive and negative electrode material, respectively. C_+ and C_- are the specific capacitance values (given in the unit of $F\,g^{-1}$) for positive and negative electrode materials, respectively. C_{cell} means the capacitance (given in the unit of farads) of the whole capacitor (cell).

If w_- becomes extremely large compared with w_+ ($w_-/w_+ \to \infty$), then $1/(w_- C_-) = 0$.

Thus it turns out:

$$\frac{1}{(w_+ C_+)} = \frac{1}{C_{cell}}$$

or

$$w_+ C_+ = C_{cell}$$

Since $C_{cell} = it/\Delta V$

(ΔV, the changes of the total capacitor voltage; i, the current passing through the capacitor during galvano-static charge–discharge; t (s), the time for charge (or discharge) between the cutoff voltage range)

$w_+ C_+ = it/\Delta V$ (in this case, i is given the unit of amperes)

Then, $it/w_+ = C_+ \Delta V$,

or $IT/w_+ = C_+ \Delta V/3.6$ (e.g., $Q = C_+ \Delta V/3.6$, ΔV equals to 2.5 V in AC/AC capacitors). Here I and T are expressed in the units of mA and h, respectively.

If the specific capacitance of the positive AC electrode (C_+) is a limited value, the saturation value of discharge capacity can be got.

To obtain the specific capacitance values of the positive and negative electrodes in the capacitors, we must trace the individual potential responses of positive and negative electrodes during charge–discharge cycles in a 3-electrode cell consisting both a positive and a negative electrode, together with a reference electrode (AC electrode). From the potential profiles of the positive and negative electrodes against the reference electrode, we could calculate the specific capacitance values of the separate positive or negative electrodes as described in the previous study [3]. Fig. 3 compares the specific capacitance values of the positive and negative electrodes in both the AC/AC and AC/graphite capacitors versus the weight ratio of negative to positive electrode materials. For the AC/AC capacitors, the specific capacitance value corresponding to the AC positive electrode climbs up somehow as the −/+ weight ratio rises. For example, at low −/+ weight ratios such as 1 or 2, the specific capacitance values of AC positive electrode are around $82\,F\,g^{-1}$. When the −/+ weight ratio increases to larger values like 6 or 8, the specific
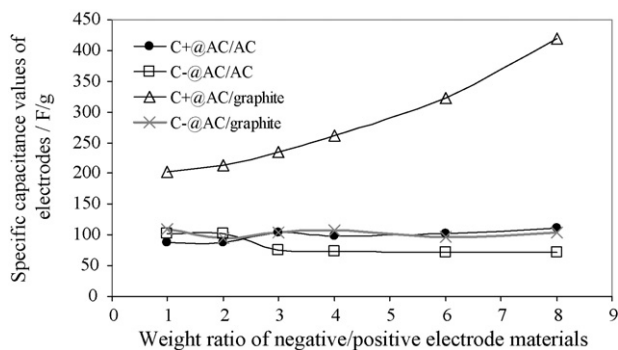
Fig. 3. Relationships between the specific capacitance values of the positive and negative electrodes and the weight ratio of negative to positive electrode materials in AC/AC and AC/graphite capacitors.

capacitance of AC positive electrode becomes near $110\,\mathrm{F\,g^{-1}}$. We believe the above trend can be ascribed to the following fact. At higher $-/+$ weight ratios, the potential of the positive electrode actually shift to higher voltages against the reference electrode. It is well known that the AC/AC capacitor over-charged at high voltage shows increased capacitance values. These two cases are in fact very similar. If we use $C_+ = 110\,\mathrm{F\,g^{-1}}$ to calculate the saturation capacity of AC/AC capacitor, then we obtained that $Q = C_+ \Delta V/3600 = 110\,\mathrm{F\,g^{-1}} \times 2.5\,\mathrm{V}/3.6$, which equals to $76.4\,\mathrm{mAh\,g^{-1}}$. On the other hand, the specific capacitance values corresponding to the AC negative electrode in AC/AC capacitors gets smaller to some extent with the rise in the $-/+$ weight ratio (from 102 to $72\,\mathrm{F\,g^{-1}}$ corresponding to $-/+$ weight ratios from 1 to 8). This trend is still an open question now.

In big contrast to the AC/AC capacitors, the specific capacitance value of the graphite positive electrode in the AC/graphite capacitors jumps up remarkably with the rise in the $-/+$ weight ratio. This is mainly due to the intercalation of PF_6^- anion into graphite. Here the great charge storage ability of graphite positive electrode can be clearly observed as compared with that of AC positive electrode. On the contrary, in AC/graphite capacitors, the specific capacitance value of the AC negative electrode fluctuates smoothly around $100\,\mathrm{F\,g^{-1}}$. This specific capacitance value ($C_- \cong 100\,\mathrm{F\,g^{-1}}$) is close to the C_- values in the AC/AC capacitors at low $-/+$ weight ratios.

Fig. 4 compares the cycle performances of AC/AC and AC/graphite capacitors at different weight ratios of negative to positive electrode materials. For both the AC/AC and AC/graphite capacitors, the cycle-ability gets worse with the rise in the $-/+$ weight ratio. However, in the case of AC/AC capacitors, the capacity fading (for either charge or discharge) is not so big, as compared with the corresponding series of AC/graphite capacitors. There are two possible reasons for the deterioration in cycle performance of AC/graphite capacitors at high $-/+$ weight ratios, the high potential of positive electrode (severe oxidizing environment) and the big volume expansion/contraction in crystal lattice of graphite, as mentioned in the previous study [2,3]. By contrast, the deterioration in the cycle performance of AC/AC capacitors at high $-/+$ weight ratios can be solely attributed to the high potential of positive AC electrode (caustic oxidation).
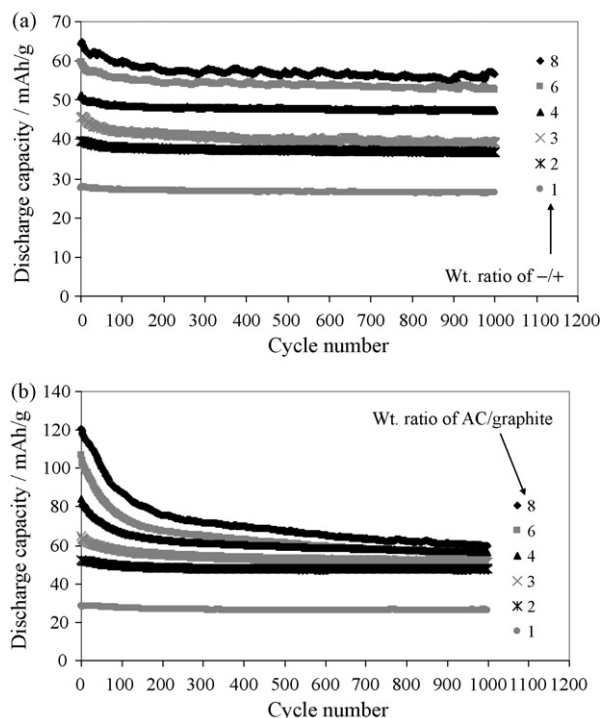

Fig. 4. Comparison of the cycle performances of AC/AC (a) and AC/graphite (b) capacitors at different weight ratios of negative to positive electrode materials.

The big volume change in the crystal lattice of AC can hardly happen because AC is highly disordered in crystal structure and the "turbostratic" disorder helps to suppress the ion intercalation into crystal lattice of carbon. On the other hand, in the cases of AC/graphite capacitors, the higher $-/+$ weight ratio is, the more prominent the capacity fading along with the cycle numbers becomes. Considerable parts of the capacity fading in the AC/graphite capacitors can be ascribed to the drastic volume change during anion intercalation into graphite positive electrode, especially at higher $-/+$ weight ratios since the ceiling potential of graphite positive electrode almost keeps near 5 V vs. Li metal when the $-/+$ weight ratio is over 2 [3].

Fig. 5 shows the *in situ* XRD patterns of graphite positive electrode in the AC/graphite capacitor (wt. ratio of AC/graphite is 3). From 2.9 V, the (0 0 2) diffraction peak of graphite at 26.5°
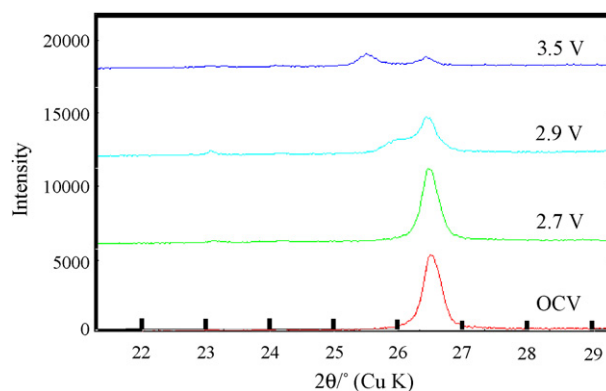

Fig. 5. *In situ* XRD patterns of the graphite positive electrode in the AC/graphite capacitor (weight ratio of AC/graphite is 3; electrolyte: 1.5 M TEMAPF$_6$-PC).
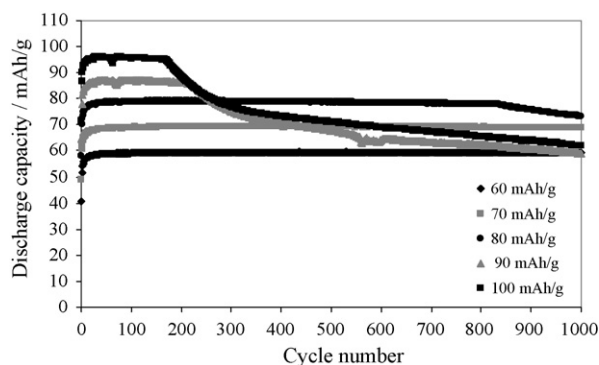
Fig. 6. Comparison of the cycle performance of the AC/graphite capacitor under different degrees of limited charge capacity (the AC/graphite weight ratio equals 8).

starts to split. With the rise in the cell voltage, a new peak appears at a diffraction angle lower than $26.5°$. As the cell voltage reaches 3.5 V (the cutoff voltage of the capacitor), the new peak shifts to about $25.6°$, while the $(0\,0\,2)$ peak still persists at $26.5°$ although the peak intensity becomes weaker. Seel and Dahn have studied the intercalation of $PF_6{}^-$ into graphite in the Li^+-based electrolytes and they ascribed a peak at $25.2°$ to stage 7 [5]. They got a small $PF_6{}^-$ intercalated gallery height (near $4.5\,\text{Å}$), as compared with the much bigger value of about $7.8\,\text{Å}$ adopted by other groups [6,7]. Actually, the ascription of stage number needs good care. Generally speaking, the acceptor-type graphite intercalation compounds always show the strongest peaks of $(0\,0\,n+1)$ or $(0\,0\,n+2)$ instead of $(0\,0\,n)$ (n stands for the stage number) in XRD patterns [8]. In the present study, we did not find other peaks (besides the two peaks at $25.6°$ and $26.5°$) within the limited scan range of diffraction angle from $20°$ to $30°$. However, from the diffraction peak at $25.6°$ in 2θ and the Bragg equation, we can calculate the value of d as $3.48\,\text{Å}$. When we adopt the interlayer spacing of $C/PF_6{}^-/C$ as $7.8\,\text{Å}$ and $(0\,0\,n+1)$ as a strongest peak, the stage number can be evaluated to be 6. In more detail, we should calculate the structure factors for the GIC, and therefore, further experiments are necessary.

In fact, we could set a "valve" charge capacity value during the galvano-static charge–discharge tests. That is, the capacitor was charged at the constant current of 1 mA, once the cell voltage reaches the cutoff voltage of 3.5 V or the charge capacity approaches the certain set values, the charge process stops. The discharge process was the simple galvano-static mode with the constant current of 1 mA and the cutoff voltage of 0 V. In this way, we deliberately limited the degree of the anion intercalation under certain charge capacity values. Fig. 6 compares the cycle performance of AC/graphite capacitors ($-/+$ weight ratio is 8) under different levels of "valve" charge capacity. At the limited charge capacity values of 60, 70 and 80 mAh g^{-1}, the cycle performance of the capacitors is satisfactory. By contrast, at higher values of limited charge capacity such as 90 and 100 mAh g^{-1}, capacity fading can be clearly observed after long cycles. This phenomenon implies that the AC/graphite capacitor can demonstrate stable cycle-ability even at high $-/+$ weight ratios if the charge capacity of the AC/graphite capacitor is suppressed under 70 mAh g^{-1}.

4. Conclusion

So far, we have addressed the relationship between the weight ratio of negative to positive electrode materials and the electrochemical performances for both AC/AC and AC/graphite capacitors. Generally speaking, for both capacitor systems, with the rise in the $-/+$ weight ratio, the capacity increases but the cycle performance becomes worse. However, the deterioration in the cycle-ability of AC/graphite capacitors can be partly attributed to the big volume change in the crystal lattice of graphite positive electrode if the charge capacity is not limited to low levels of anion intercalation (less than 70 mAh g^{-1} based on the graphite weight).

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