Short communication

Effect of water contamination in the organic electrolyte on the performance of activated carbon/graphite capacitors

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ABSTRACT

The effect of water contamination in the electrolyte on the performance of AC/graphite capacitor has been investigated by electrochemical tests and *in situ* XRD measurements. The deterioration mechanisms for the charge storage ability of the electrodes in the capacitors using polluted electrolytes have also been addressed.

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1. Introduction

Recently, we have explored the activated carbon (AC)/graphite capacitors using organic electrolytes [1–5]. This kind of capacitors possess the virtues of high working voltage, high capacitance and thus high energy density. However, the performance of the AC/graphite capacitors is very sensitive towards the composition of electrolyte solution [6–8]. In the high-voltage electric energy storage systems like lithium-ion batteries and electrochemical capacitors, the dipolar aprotic solvents have always been applied because of their broad electrochemical windows. However, a trace amount of water contamination seems inevitable during the preparation process of the electrolyte solutions, which can be detrimental to the performance of the electrochemical devices. For instance, more than 300 ppm water in the organic solvent can significantly restrict its oxidation potential to lower values [9]. Ue et al. have used rotating disk technique to investigate the impurities from the hydrolysis of solvent and solute [10]. Recently, Asakawa et al. have carried out a detailed study on the degradation process between AC electrodes and organic electrolytes [11].

Because of its high working voltage, it is expected that the water contamination may be more destructive to the performance of

AC/graphite capacitor than that of tradition EDLC (AC/AC capacitor). In this study, we have deliberately added different amount of water into a dry electrolyte solution and test the electrochemical performance of AC/graphite capacitors using these "polluted" electrolytes. Thus the deterioration mechanism of AC/graphite capacitors in the water-contaminated electrolytes can be somehow clarified.

2. Experimental

In the AC/graphite capacitors, KS6 (graphite from Timcal Co. Ltd.) and RP-20 (activated carbon from Kuraray Co. Ltd.) were employed as the positive and negative electrode materials, respectively. Some physical properties of these electrode materials have been described in the past reports [2,3]. The weight ratio of negative to positive electrode materials was kept at 1, unless otherwise specified. The virgin "dry" electrolyte applied in this study was 1.5 M TEMAPF$_6$ dissolved in PC (TEMA stands for triethylmethylammonium) with water content less than 20 ppm. Different amounts of distilled water were deliberately added into the dry electrolyte solution and the polluted electrolytes were stored for 1 week in a glove box before cell fabrication.

The coin cell fabrication, *in situ* XRD measurement and glove box conditions were the same as those described in the past reports [2–4]. The galvanostatic charge–discharge tests of the coin cell were performed at the constant current density of 0.4 mA cm^{-2}. The cut-off voltages were set as 0 and 3.5 V for AC/graphite capacitors, whereas 0 and 2.5 V for AC/AC capacitors. Charge storage ability of the total capacitor (coin cell) was expressed in the terms of capacity (mAh g^{-1}). The capacity values were calculated according to the

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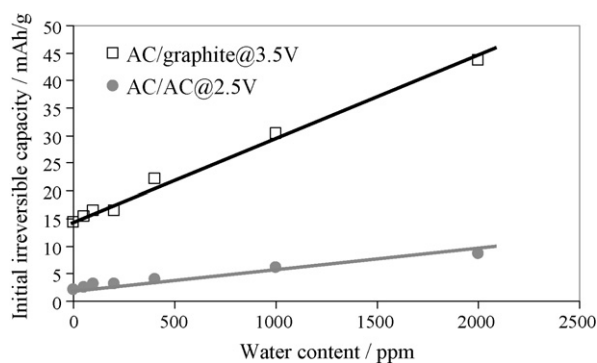
Fig. 1. Relationship between the initial irreversible capacities of the AC/graphite and AC/AC capacitors and the water content in the electrolytes.

following formula: $Q = IT/w_+$ (I, constant current (mA); T, the time for charge or discharge between cut-off voltages (h); w_+, the weight of positive electrode (g)).

Three-electrode beaker cells have also been used to evaluate the performance of the electrode materials in different electrolytes. As described before [3], this kind of cell contains three electrodes, a positive electrode, a negative electrode and a reference AC electrode.

3. Results and discussion

The detrimental influence of the water on the electrolyte is mainly reflected in two aspects: (1) the big irreversible capacity due to the decomposition of electrolyte and (2) the poor cycle-ability of the capacitors. Fig. 1 compares the initial irreversible capacity (the difference between charge and discharge capacities in the first cycle) of the AC/graphite and AC/AC capacitors using the electrolytes containing different amounts of contaminated water. Generally speaking, for both kinds of capacitors, there is an almost linear relationship between the initial irreversible capacity and water content. Moreover, the curve stand for the AC/graphite capacitor have much sharper slope than that corresponding to the AC/AC capacitor.

Then what is the reason for this fact? From the three-electrode cell tests, we obtained *some* parameters as listed in Table 1, which includes the ceiling potentials of the positive electrodes (C.P. (+)) and bottom potentials of the negative electrodes (B.P. (−)) in the AC/graphite and AC/AC capacitors using the dry and water-contaminated (2000 ppm) electrolytes. The definitions of C.P. (+) and B.P. (−) can be found in our previous study [4]. It can be clearly observed that 2000 ppm contaminated water shifts both the C.P (+) and B.P. (−) values to lower voltages by about 0.13–0.16 V in both AC/KS6 and AC/AC capacitors. Thus the cathodic electrolyte decomposition at negative AC electrodes become more drastic in the polluted electrolyte as compared with the dry electrolyte, but the anodic electrolyte decomposition at the positive electrodes is likely to be milder in the water-containing electrolyte from a viewpoint of the working potential range. Moreover, given the same electrolyte, the B.P. (−) value of AC negative electrode in the AC/KS6 capacitor is lower than the corresponding B.P. (−) value in the AC/AC capacitor, so the cathodic decompositions of the electrolyte in AC/graphite

Table 1
Some parameters obtained from the three-electrode cell tests.

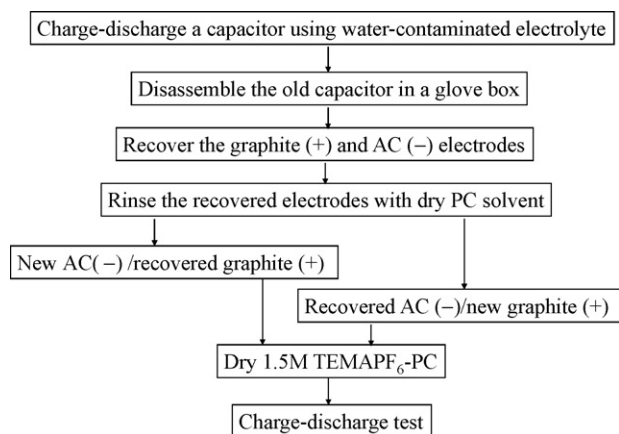| Capacitor type	AC/graphite		AC/AC	
Cutoff voltage of the capacitor (V)	0–3.5		0–2.5	
Water content in electrolyte (ppm)	2000	0	2000	0
C.P. (+) (V vs. AC Ref.)	1.72	1.85	0.96	1.12
B.P. (−) (V vs. AC Ref.)	−1.77	−1.64	−1.53	−1.37
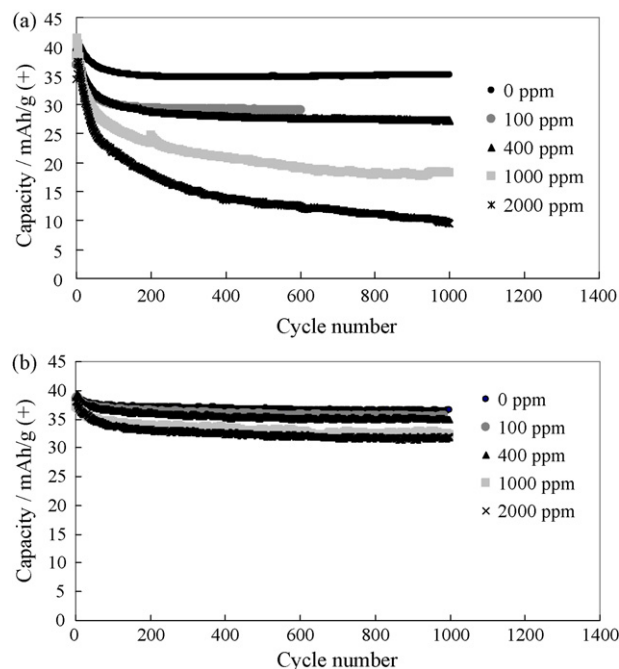
Fig. 2. Cycle performance of the AC/graphite (upside) and AC/AC (downside) capacitors using electrolytes containing different amounts of water.

capacitors may be more apparent than that in the AC/AC capacitor.

We have witnessed the bulge in the coin cells of AC/graphite capacitors using the heavily water-polluted electrolytes after long cycles of charge–discharge. This means that the big decomposition of the water-contaminated electrolyte in the AC/graphite capacitors may liberate large amount of gases, which have a severe safety risk. Fig. 2 compares the cycle performance of the AC/graphite and AC/AC capacitors using electrolytes containing different amounts of water. In the AC/graphite capacitors, the fading tendency in the discharge (reversible) capacity along with cycles gets more significant as the water content rises up. By big contrast, the water content appears little influential on the cycle-ability of AC/AC capacitors. This fact somehow coincides with the comparison of the irreversible capacities between AC/graphite and AC/AC capacitors.

We have also performed a "recycled" test. The details are described in Fig. 3. After certain long cycles using the water-contaminated electrolyte, the coin cell was disassembled in the glove box filled with dry Ar atmosphere. Then both the positive

Fig. 3. Procedures of the recycle test on the AC/graphite capacitor.
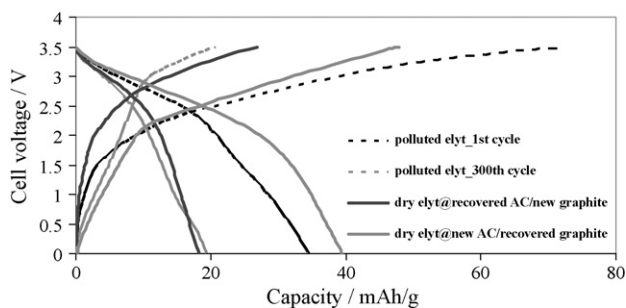
Fig. 4. Initial charge–discharge curves of both the old and new cells in the recycle test.

graphite and negative AC electrodes were recovered and washed with dry PC solvent. These two recovered electrodes were suited to new fresh partner electrodes, respectively and new coin cells were fabricated. Dry electrolyte of 1.5 M TEMAPF$_6$–PC was used in the new cells. Then these two new cells were subject to the charge–discharge tests. Fig. 4 compares initial charge–discharge curves of both the old and new cells. The cell using the recovered positive graphite electrode shows satisfactory performance. On the contrary, the cell using the recovered negative AC electrode demonstrates bad behavior. Thus the poor cycle-ability of the AC/graphite capacitor using water-contaminated electrolyte can be probably ascribed to the deterioration of AC negative electrode. This conclusion can be correlated with the low B.P. (−) value of the AC negative electrode in the capacitor using the electrolyte-containing water impurity. In fact, after disassembling the coin cell using the water-polluted electrolyte, we have witnessed some viscous gel-like liquid attached on the AC negative electrode surface. We believe that this kind of liquid may block the pores of AC negative electrode from cation adsorption. Naoi and coworkers have found similar cathodic decomposition products of water-contaminated organic electrolyte on the surface of AC negative electrode [11]. They ascribed this to be aryl-alcohol (the dehydration product of 1,2-propanediol). Further studies of the charge–discharge tests show that the past history in the polluted electrolyte has also some negative impressions on the performance of recovered graphite positive electrode in the new cell. Fig. 5 mainly shows the cycle performance of the AC/graphite capacitors using recovered electrodes in the dry electrolyte. The capacitor of new AC/recovered graphite delivers high discharge capacities in the initial several cycles, then the discharge capacity declines quickly with cycles.

To clarify the above phenomenon of the recovered graphite electrode, we have performed *in situ* XRD measurements on the graphite positive electrodes in AC/graphite capacitors using the dry and water-contaminated electrolytes, respectively. As compared in Fig. 6, the intercalation of anions into graphite positive electrode
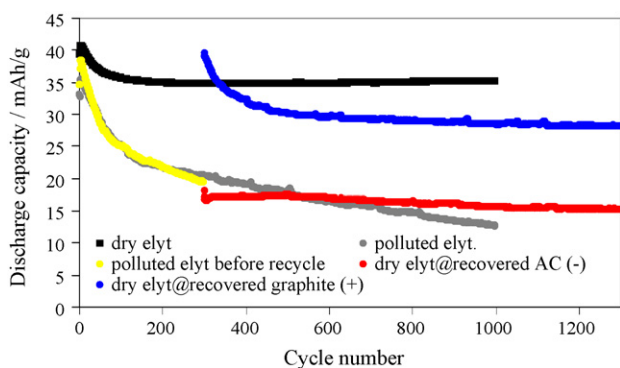

Fig. 5. Cycle performance of the AC/graphite capacitors using recovered electrodes in the dry electrolyte.
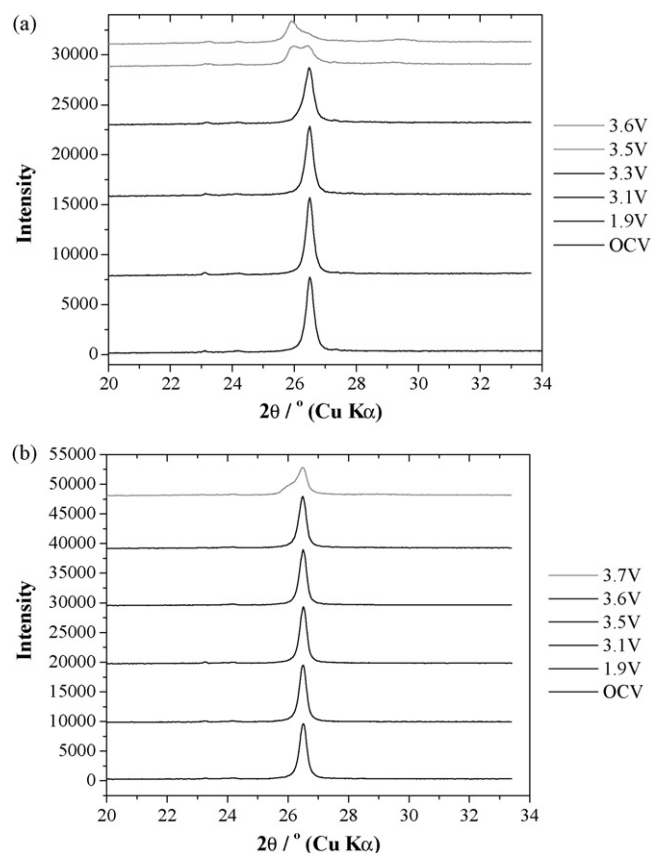

Fig. 6. *In situ* XRD patterns of the graphite positive electrodes in AC/graphite capacitors using the dry (downside) and water-contaminated (upside) electrolytes, respectively.

becomes easier in the case of polluted electrolyte, as evidenced by the peak split at 3.3 V. By contrast, there is no peak splitting or shift in the capacitor using the dry electrolyte until 3.6 V. From the three-electrode test results listed in Table 1, the graphite positive electrode potential moves to a lower value with the water contamination in the electrolyte. However, the intercalation of anion is unlikely to happen at lower potentials of the graphite positive electrode. Then how to explain this contradiction? It has been proved that the intercalation of anions into graphite positive electrode will deteriorate the cycle performance of the graphite positive electrode since the big volume change in the crystal lattice of the electrode material can lead to cracking of the graphite particles. One may expect that the hydrolysis product of PF$_6^-$ anion is likely to generate some ionic species (say, PF$_4$O$^-$) with smaller size than PF$_6^-$ in the polluted electrolyte. These smaller anions can intercalate into graphite positive electrode more smoothly than PF$_6^-$. However, the size difference between these anions like PF$_6^-$ and PF$_4$O$^-$ can hardly lead to the significant contrast of anions intercalation energies as reflected by the cell voltages of peak splitting (3.6 and 3.3 V, respectively). A more liable reason may be provided as follows. It is well known that the pollution of water in the organic electrolyte actually can increase the conductivity of electrolyte drastically, which causes the over-potential (polarization) of the graphite positive electrode becomes apparently smaller. Thus the intercalation of anions into graphite happens earlier (at lower voltages).

4. Conclusion

In conclusion, the water contamination in the electrolyte has a detrimental effect on the performance of AC/graphite capacitors. It leads to large irreversible capacity due to the big decomposition

of the electrolyte and poor cycle-ability. For the capacitor after long charge–discharge cycles in water-contaminated electrolyte, both the graphite positive and AC negative electrodes have experienced some damages in their charge storage ability. Especially, the deterioration in the ion adsorption behavior of AC negative electrode cannot be recovered if recycled in the capacitor using dry electrolyte.

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