



Short communication

Utilization of (oxalato)borate-based organic electrolytes in activated carbon/graphite capacitors

Yongxun Wang^a, Cheng Zheng^{a,b}, Li Qi^a, Masaki Yoshio^{c,1}, Kazuharu Yoshizuka^d, Hongyu Wang^{a,*}^a State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China^b Graduate University of Chinese Academy of Sciences, Beijing 100039, China^c Advanced Research Center, Saga University, 1341 Yoga-machi, Saga 840-0047, Japan^d Department of Chemical Engineering, Faculty of Environmental Engineering, The University of Kitakyushu, Japan

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ABSTRACT

The electrolyte salts composed of tetramethylammonium (TMA⁺) cation and difluoro(oxalato)borate (DFOB⁻) or bis(oxalato)borate (BOB⁻) anions have been proposed for the application in activated carbon (AC)/graphite capacitors. The electrochemical performance of AC/graphite capacitors has been studied using these electrolyte salts dissolved in propylene carbonate (PC). The intercalation behaviors of anions (BF₄⁻, DFOB⁻, and BOB⁻) at the graphite positive electrodes have been investigated by *in situ* XRD measurements. The bigger the anion is, the higher the cell voltage is where the intercalation happens. Accordingly, the bigger the anion is, the smaller discharge capacity delivered by an AC/graphite capacitor. The charge mechanism of TMA⁺ at the AC negative side has also been addressed. Compared with other bigger quaternary alkyl ammonium cations, the specific capacitance of the AC negative electrode towards TMA⁺ adsorption is somehow smaller as estimated.

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1. Introduction

In the past decade, more and more attention has been paid to exploring electrochemical capacitors with high energy densities. There are two strategies for this purpose. One is to employ electrode materials capable of high contents of ion accommodation (high specific capacitance) [1–6]. The other is to elevate the working voltages of electrochemical capacitors by applying organic electrolytes containing quaternary alkyl ammonium salts [7–10]. Tetraethylammonium tetrafluoroborate (TEABF₄) dissolved in propylene carbonate (PC) is a typical electrolyte solution with broad electrochemical window [11,12].

Recently, we have developed the asymmetric activated carbon (AC)/graphite capacitors using organic electrolytes. Concentrated (1.5 M) Triethylmethylammonium hexafluorophosphate (TEMAPF₆) or TEMABF₄ dissolved in PC were generally used as the electrolyte solutions for this kind of capacitors, which satisfy the high energy density [13–19]. Since the specific capacitance of graphite positive electrode is much higher than that of the AC negative electrode, the total capacitance of the AC/graphite capacitor actually is principally determined by the adsorption of

quaternary alkyl ammonium cations at the AC electrode. Then it is expected that the smallest quaternary ammonium cation, tetramethylammonium (TMA⁺) would lead to a remarkable increase in the energy density of AC/graphite capacitors. However, the low solubility of TMAPF₆ and TMABF₄ salts in the organic solvent of PC may significantly depress the specific capacitance values of AC negative electrode [12,20]. To enlarge the ionic dissociation degree of TMA⁺-based salts, bigger counter anions containing (oxalato)borate moiety like bis(oxalato)borate (BOB⁻), difluoro(oxalato)borate (DFOB⁻) have been adopted in the electric double-layer capacitors [21–23]. Nevertheless, the application of TMABOB and TMADFOB in AC/graphite capacitors might be an interesting exploration in the research field of electrochemical capacitors. On one hand, the storage mechanism of BOB⁻ and DFOB⁻ at the graphite positive electrode is an open question. On the other hand, the adsorption ability of TMA⁺ cations in AC electrode can be further evaluated.

Bearing the above speculation in mind, we investigated the electrochemical performance of AC/graphite capacitors using the TMABOB or TMADFOB-based electrolytes in this study. The charge storage mechanisms at both the graphite positive and the AC negative electrodes have also been addressed.

2. Experimental

KS6 (graphite from Timcal Co. Ltd.) and PW15M13130 (AC from Kureha Co. Ltd.) were used as the positive and negative electrode

* Corresponding author. Tel.: +86 431 85262287; fax: +86 431 85262287.

E-mail addresses: yoshio@cc.saga-u.ac.jp (M. Yoshio), hongyuwang@ciac.jl.cn (H. Wang).¹ Tel.: +81 952 20 4729; fax: +81 952 20 4729.

materials for capacitors, respectively. Most experimental details, including electrode fabrications, glove box operations, instrumentation, cells, etc., were similar to those described in the previous studies, unless otherwise specified [14,15]. The electrolytes applied in this study were 1 M TEMABF₄, 0.9 M TMABOB and 0.9 M TMADFOB dissolved in PC (propylene carbonate), respectively.

Galvanostatic charge–discharge tests were performed on coin cells to evaluate the charge storage ability of the total AC/graphite capacitors. Generally, the constant current density was 0.4 mA cm⁻² and the cutoff voltages were set as 0 and 3.5 V. Charge storage ability of a total capacitor (coin cell) was expressed in the terms of capacity (mAh g⁻¹). The capacity values were calculated according to the 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 constructed for assessing the specific capacitance value of a single electrode (graphite positive electrode or AC negative electrode). The details of 3-electrode configuration, calculation method of specific capacitance value can be found in the previous studies [14,15,18]. In a three-electrode cell, a heavy AC electrode was employed as the reference electrode. During the course of galvanostatic charge–discharge between the graphite positive and the AC negative electrodes, the potentials of the graphite positive or the AC negative electrodes with respect to the AC reference electrode were measured by an auxiliary potentiometer. The potential of an AC reference electrode versus Li metal is about 3 V [24].

Most of the details of *in situ* XRD measurements on the graphite electrodes in AC/graphite capacitors can be found in the reference [14]. Thin Al foil was used as both the current collector and the X-ray window of a graphite electrode.

3. Results and discussion

In electrochemical capacitors, charge storage mechanisms at the interface between electrolytes and electrodes will always involve the compatibility between the guest charge carriers (cations or anions) and the host (electrode material) structure. In AC/graphite capacitors, the charge storage mechanism at the AC negative electrode side is comparatively simple, just the adsorption of cations into the pores with wider openings. Conversely, the charge storage mechanism at the graphite positive electrode side is rather complex. In the cases of electrolyte solutions containing ABF₄ or APF₆ (here A stands for quaternary alkyl ammonium), whether BF₄⁻ or PF₆⁻ intercalate into graphite positive electrodes in AC/graphite capacitors depends on many factors, as judged by the *in situ* XRD patterns of graphite positive electrodes in the capacitors. For instance, the highly crystalline graphite, say, natural graphite is liable to be intercalated, whereas KS6 with some disorders and defects in crystal lattice appears more immune to anion intercalations [14]. Solvents and weight ratio of electrode materials also have profound influences on the intercalation behavior of anions into graphite [14,16,19]. Of course, shallow insertion of anions into graphite electrode is beneficial for the performance of AC/graphite capacitors in some respects [14]. To control the intercalation extent of anions into a graphite positive electrode, tailoring the size of anion may be a simple and effective way. Table 1 compares the van der Waals volume of some ions. Most of the volume values are cited from the published paper [25]. It can be clearly observed that the van der Waals volume values of anions are in the order of BF₄⁻ < DFOB⁻ < BOB⁻. So it is expected that DFOB⁻ and BOB⁻ are more difficult to insert into graphite than BF₄⁻.

Fig. 1 compares the initial galvanostatic charge–discharge curves of AC/graphite capacitors using different electrolyte solutions. For all these electrolytes, the AC/graphite capacitors

Table 1
van der Waals volume values of some ions.

Abbreviation for ion	Full name of ion	van der Waals volume/Å ³
BF ₄ ⁻	Tetrafluoroborate	49
DFOB ⁻	Difluoro(oxalato)borate	77
BOB ⁻	Bis(oxalato)borate	110
TMA ⁺	Tetramethyl ammonium	93
DEDMA ⁺	Diethyl dimethyl ammonium	126
TEMA ⁺	Triethyl methyl ammonium	143
TEA ⁺	Tetramethyl ammonium	159
TPA ⁺	Tetrapropyl ammonium	226
TBA ⁺	Tetrabutyl ammonium	293

demonstrate bent charge–discharge curves, similar to the results in our previous studies [14–19]. The discharge capacity values delivered by the capacitors rank in the following order with respect to the anions: BF₄⁻ > DFOB⁻ > BOB⁻, just opposite to the order of their sizes. Thus it is deduced that the electrochemical performance of an AC/graphite capacitor is considerably affected by the storage behavior of the anion on the graphite positive electrode.

In situ XRD measurement is a very powerful tool to investigate the charge storage mechanism of anions as shown in our previous studies [14,16]. Fig. 2 compares the *in situ* XRD patterns of the graphite electrodes in AC/graphite capacitors using the electrolytes of 1 M TEMABF₄, 0.9 M TMADFOB, and 0.9 M TMABOB, respectively, dissolved in PC. In the capacitor using 1 M TEMABF₄-PC, the splitting of (0 0 2) diffraction peak of graphite starts from the cell voltage of 3.7 V, which phenomenon indicates the apparent BF₄⁻ intercalation into the interlayer spaces between graphene layers of graphite electrode. By big contrast, the splitting of (0 0 2) peak occurs at the cell voltage near 4.7 V when the electrolyte of 0.9 M TMABOB-PC is applied in the AC/graphite capacitor. In the case of 0.9 M TMADFOB, the splitting of (0 0 2) peak takes place at the cell voltage of about 3.9 V. The above facts imply that the anions with bigger size are more sluggish to insert into the graphite positive electrode than smaller ones and the corresponding intercalation takes place at higher cell voltages. This trend coincides with the relationship between the discharge capacity values of AC/graphite and the anion size.

Because of the low discharge capacity delivered, TMABOB is not a satisfactory electrolyte salt for AC/graphite capacitors in practice. As a compromise, TMADFOB may be a hopeful choice. The AC/graphite capacitor using TMADFOB shows comparably

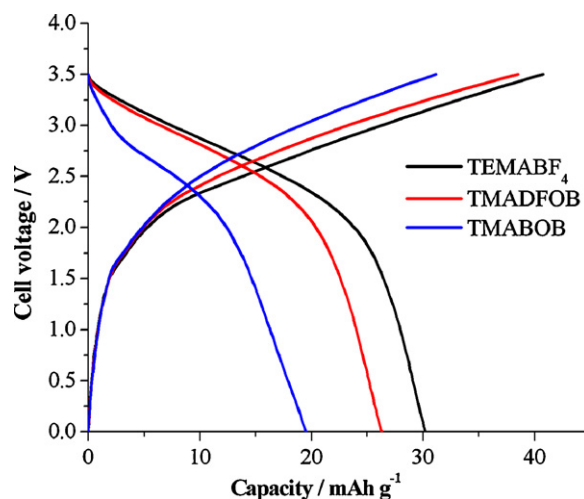


Fig. 1. Initial galvanostatic charge–discharge curves of AC/graphite capacitors using the electrolyte solutions of 1 M TEMABF₄, 0.9 M TMADFOB, and 0.9 M TMABOB dissolved in PC.

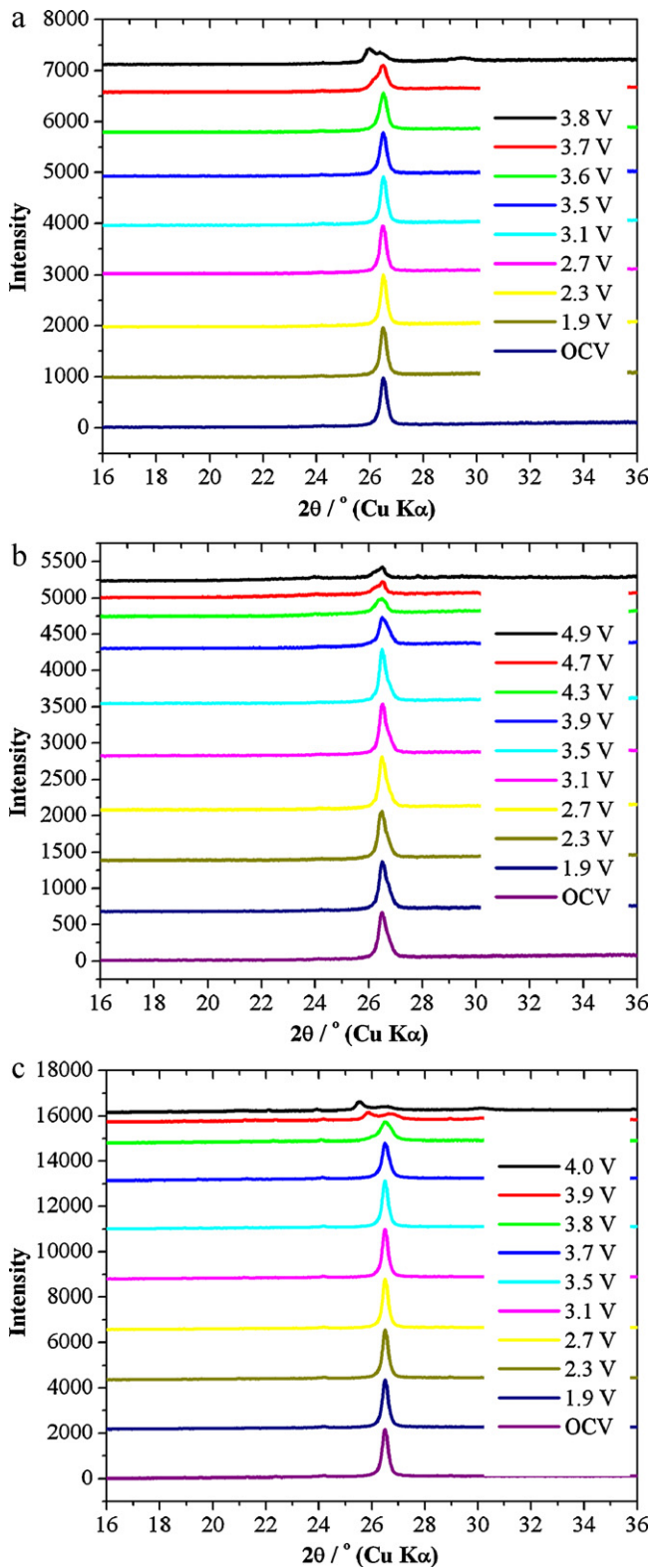


Fig. 2. *In situ* XRD patterns of the graphite electrodes in the AC/graphite using the electrolytes of 1 M TEMABF₄ (a), 0.9 M TMABOB (b), and 0.9 M TMADFOB (c), respectively, dissolved in PC.

reasonable discharge capacity and considerable durability towards anion intercalation. Fig. 3 shows the potential profiles of an AC/graphite capacitor using the electrolyte of 0.9 M TMADFOB-PC. The potential profiles of the graphite positive electrode versus the reference electrode are bent curves, whereas the potential profiles

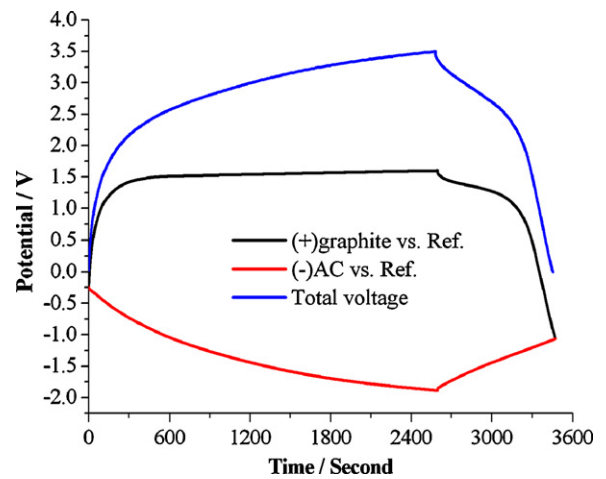


Fig. 3. Potential profiles of an AC/graphite capacitor using the electrolyte of 0.9 M TMADFOB-PC. Heavy AC electrode was used as the reference electrode.

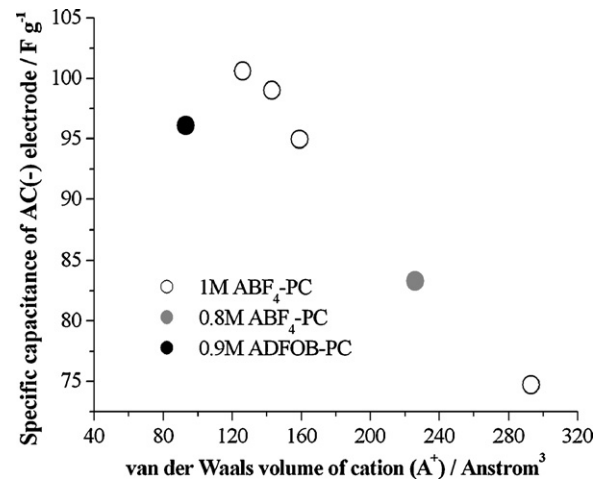


Fig. 4. Relationship between the specific capacitance of AC negative electrode (PW15M13130) and van der Waals volume of quaternary alkyl ammonium cation.

of the AC negative electrode versus the reference electrode are composed of rather straight lines. From the slope of the potential profile for the AC negative electrode during the initial discharge process, the specific capacitance value of AC negative electrode (corresponding to the adsorption of TMA⁺ cation) can be calculated as 96.1 F g⁻¹. This value is slightly higher than that for the same AC negative electrode (PW15M13130) towards TEA⁺ cation adsorption (about 95 F g⁻¹) under similar experimental conditions [15,18]. To make a clear comparison, we plot the relationship between the specific capacitance of AC negative electrode (PW15M13130) and the van der Waals volume of quaternary alkyl ammonium cation as shown in Fig. 4. The rough trend is that as the van der Waals volume of cation rises, the specific capacitance of AC negative electrode decreases. However, the accommodation capability of TMA⁺ into the pores of AC is not as high as expected. A plausible explanation for this deviation is the solvation of TMA⁺ by PC solvent, which enlarges the real volume TMA⁺ cation as compared with that of naked TMA⁺ as deduced from theoretical calculations.

4. Conclusion

So far, the electrochemical performance of AC/graphite capacitors using TMABOB and TMADFOB-based electrolytes has been studied in terms of galvanostatic charge–discharge tests and *in situ*

XRD measurements, etc. Because of their bigger sizes, the anions of BOB⁻, DFOB⁻ are more difficult to be intercalated into the interlayer spaces of graphite positive electrodes. Thus the shallow insertion of the bigger anions into graphite within the limited cutoff voltage range has a two-faced consequence, on one hand, the decrease in the discharge (reversible) capacity of AC/graphite capacitors, on the other hand, the improved cycle life of graphite positive electrode due to depressed expansion of crystal lattice. At the present stage, a compromising electrolyte system based on TMADFOB may be a potential alternative for future applications. However, the smallest quaternary alkyl ammonium cation TMA⁺ in the electrolyte solution cannot guarantee a reasonably high specific capacitance value of AC negative electrode.

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