



Short communication

## KPF<sub>6</sub> dissolved in propylene carbonate as an electrolyte for activated carbon/graphite capacitors

Hongyu Wang<sup>a,\*</sup>, Masaki Yoshio<sup>b,1</sup><sup>a</sup> State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China<sup>b</sup> Advanced Research Center, Saga University, 1341 Yoga-machi, Saga 840-0047, Japan

## ARTICLE INFO

## Article history:

Received 30 July 2009

Received in revised form 27 August 2009

Accepted 27 August 2009

Available online 2 September 2009

## Keywords:

Activated carbon

Graphite

Electrochemical capacitors

Potassium hexafluorophosphate

Propylene carbonate

## ABSTRACT

KPF<sub>6</sub> dissolved in propylene carbonate (PC) has been proposed as an electrolyte for activated carbon (AC)/graphite capacitors. The electrochemical performance of AC/graphite capacitor has been tested in XPF<sub>6</sub>-PC or XBF<sub>4</sub>-PC electrolytes (X stands for alkali or quaternary alkyl ammonium cations). The AC/graphite capacitor using KPF<sub>6</sub>-PC electrolyte shows an excellent cycle-ability compared with other electrolytes containing alkali ions. The big decomposition of the PC solvent at the AC negative electrode is considerably suppressed in the case of KPF<sub>6</sub>-PC, which fact has been correlated with the mild solvation of K<sup>+</sup> by PC solvent. The relationship between the ionic radius of cation and the corresponding specific capacitance of AC negative electrode also proves that PC-solvated K<sup>+</sup> ions are adsorbed on AC electrode instead of naked K<sup>+</sup> ions.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

In recent years, electrochemical capacitors have drawn much attention as electric storage devices. The most common AC (activated carbon)/AC capacitors use the interface between the activated carbon electrode and the electrolyte (electric-double layer) to accumulate ions. Due to the limitations of the electric-double layers, the energy density of AC/AC capacitors is not high [1,2]. To solve this problem, we have replaced the AC positive electrodes by graphite electrodes in the capacitors. The energy density of an AC/graphite capacitor is over twice that of an AC/AC capacitor [3,4]. There are some factors that may influence the performance of AC/graphite capacitor, like the weight ratio of AC/graphite, the type of graphite, electrolyte, etc. [4–8]. The effect of electrolyte is very significant on the performance of AC/graphite capacitor.

In the previous study [7], we have found that Li<sup>+</sup>-based organic electrolytes are not suitable for the AC/graphite capacitors. This is mainly because the adsorption of PC-solvated Li<sup>+</sup> cation on AC negative electrode. The PC solvent adsorbed into the pores of AC electrodes is liable to decomposition at certain low potentials (about 1.2 V vs Li). The decomposition products may accumulate during long cycles and cover the surface of AC electrodes, thus

leads to the increase in IR drop. Instead, in the cases of quaternary ammonium-based electrolytes, the cations are not so heavily bonded with the organic solvent molecules, and nearly “naked” cations are adsorbed on the AC negative electrode, which are more inert to decomposition at low potentials.

From the view point of practical application, both the Li and quaternary ammonium-based salts are not so economic. The choices of some other alkali salts such as NaPF<sub>6</sub> and KPF<sub>6</sub> can considerably save the cost in the electrolyte solution. Moreover, in the series of alkali cations, the solvation with PC becomes weaker as the ionic radius grows up. So we expect that the solvation of K<sup>+</sup> cation by the organic solvent may be comparatively mild. Thus the problem with the drastic IR drop in the AC/graphite using Li<sup>+</sup>-based electrolytes may be alleviated to a big extent if we use K<sup>+</sup>-based electrolyte instead in the AC/graphite capacitors.

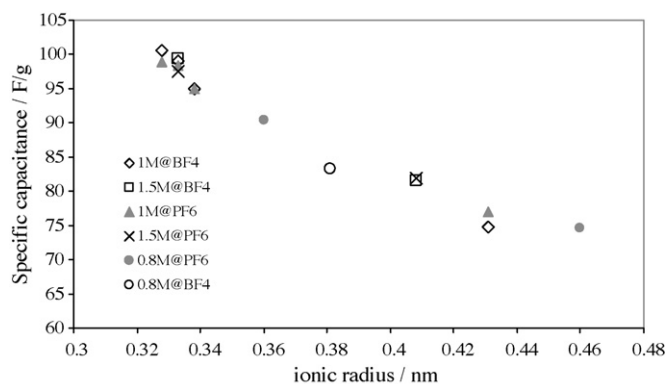
In this study, we mainly investigate the electrochemical behavior of AC/graphite capacitors in both the electrolytes of KPF<sub>6</sub>-PC and NaPF<sub>6</sub>-PC. The performance of the capacitors in different electrolytes has been correlated with the chemical structures of cations in the PC organic solvent.

### 2. Experimental

KS6 (graphite from Timcal Co. Ltd.) and PW15M13130 (AC from Kureha Co. Ltd.) were employed as the positive and negative electrode materials for capacitors, respectively. Some physical properties of KS6 and PW15M13130 have been described in the past reports [3–7]. Most of the pores of PW15M13130 have the

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

E-mail addresses: [wanghongyu@hotmail.com](mailto:wanghongyu@hotmail.com), [hongyuwang@ciac.jl.cn](mailto:hongyuwang@ciac.jl.cn) (H. Wang), [yoshio@cc.saga-u.ac.jp](mailto:yoshio@cc.saga-u.ac.jp) (M. Yoshio).<sup>1</sup> Tel.: +81 952 20 4729; fax: +81 952 20 4729.



**Fig. 1.** Relationship between the specific capacitance value of the AC negative electrode and the ionic radius of cations in the PC solutions.

size near 1 nm. The weight ratio of AC/graphite was kept at 1. The electrolytes applied in this study were generally denoted as XPF<sub>6</sub> or XBF<sub>4</sub> dissolved in PC (X stands for the cation type). X includes the alkali cations (Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>) and quaternary alkyl ammonium cations (DEDMA<sup>+</sup>, TEMA<sup>+</sup>, TEA<sup>+</sup>, TPA<sup>+</sup> and TBA<sup>+</sup>). DEDMA, TEMA, TEA, TPA and TBA are the abbreviations of diethyldimethyl ammonium, triethylmethyl ammonium, tetraethyl ammonium, tetrapropyl ammonium and tetrabutyl ammonium, respectively. The cell fabrication and glove box conditions were the same as those described in the past reports [3–7]. A coin cell comprised mainly of two electrodes (AC negative and graphite positive) and the electrolyte. The galvanostatic charge–discharge tests of the coin cell were generally performed at the constant current density of 0.4 mA cm<sup>-2</sup>. The cut-off voltages were set as 0 and 3.5 V. Charge storage ability of the total capacitor (coin cell) was expressed in the terms of capacity (mAh g<sup>-1</sup>). 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 (hour);  $w_+$ , the weight of graphite positive electrode (gram)).

3-Electrode beaker cells have also been applied to evaluate the performance of the electrode materials in different electrolytes. As described before [4,5], this kind of cell contained 3 electrodes, a graphite positive electrode, an AC negative electrode and an AC reference electrode. The potential against AC electrode is almost 3 V lower than the potential value against Li metal. The potential profiles of the individual positive and negative electrodes with respect to the reference electrode, respectively during the galvanostatic charge–discharge tests can provide us very important information.

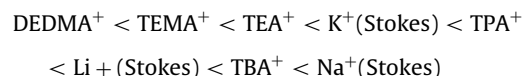
### 3. Results and discussion

From the 3-electrode cell tests, we could estimate the specific capacitance of the AC negative electrode in different electrolytes as introduced in the previous study [5]. Fig. 1 plots the specific capacitance of AC negative electrode with respect to the corresponding ionic radius of cation in the PC-based electrolytes. With the increase in ionic radius of cation, the specific capacitance of AC negative electrode becomes smaller. The rough trend appears a curved line. The linear relationship estimated in the previous study comes from the lack of cation types [7]. Not all the pores are accessible for all the

**Table 1**  
Some physical values for the alkali cations in PC solvent.

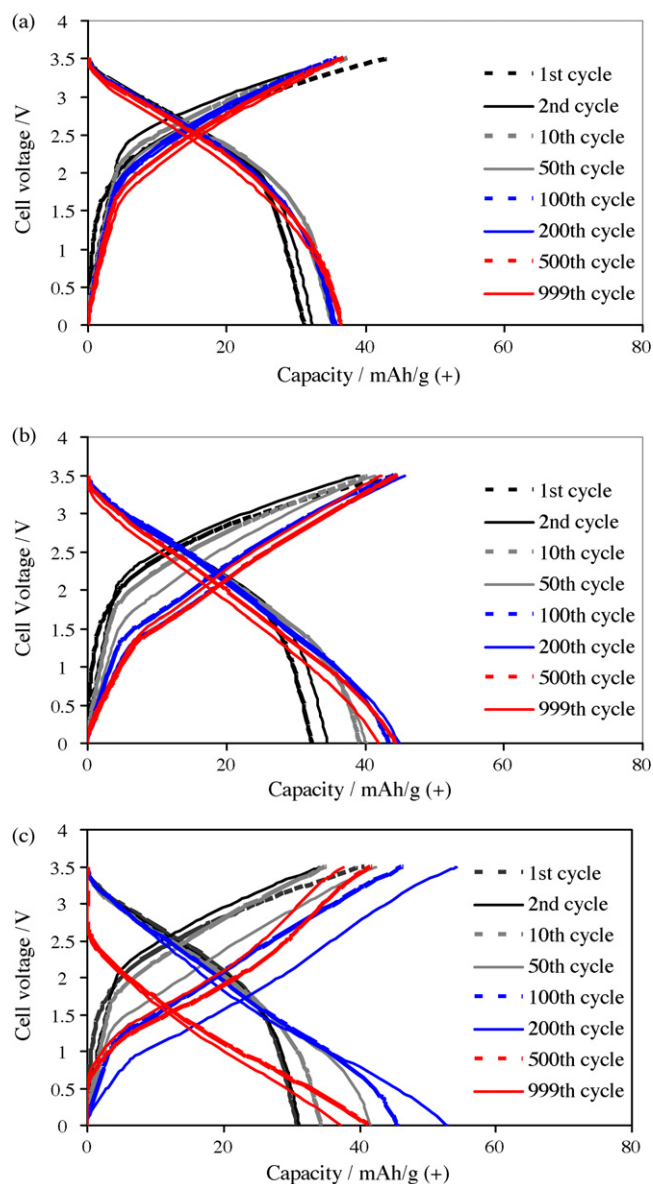
Alkali metal	Stokes radius in PC (nm)	Solvation no.	Reference cited
Li	0.408	~3	[10]
Na	0.46	2.8	[11]
K	0.36	1.3	[11]

cations. Bigger cations can hardly penetrate into smaller pores. As the ionic radius gets smaller, the rise-up tendency of the specific capacitance becomes sharper. On the other hand, as the ionic radius increases to certain values over 0.4 nm, the drop-down tendency of the specific capacitance becomes slower and levels off. The order of ionic radii for these cations is as follows.



For all the quaternary alkyl ammonium cations, the ionic radius values are cited from Reference [9]. These values actually correspond to the naked cations. By big contrast, for all the alkali cations, the Stokes ionic radii are used in Fig. 1 instead of the crystallographic ones. This is a proof for the alkali cation-PC solvation. The above fact means that instead of the naked ions, PC-solvated alkali cations are adsorbed on the AC negative electrode.

Table 1 lists some exact physical values for the alkali cations in PC solvent. These values were picked up from References [10,11].



**Fig. 2.** Charge–discharge curves of the AC/graphite capacitors in 0.8 mol l<sup>-1</sup> XPF<sub>6</sub>-PC electrolyte solutions (X stands for alkali metal cations: K<sup>+</sup> (a), Na<sup>+</sup> (b) and Li<sup>+</sup> (c)).

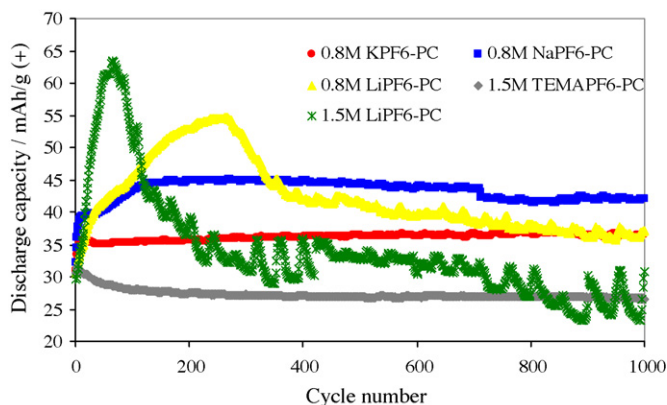


Fig. 3. Cycle performance of the AC/graphite capacitors in different electrolytes.

Both  $K^+$  and  $Na^+$  cations are not heavily solvated with PC molecules like  $Li^+$ . The above fact implies that not so many PC molecules approach to the surface very tightly together with the adsorbed cations of  $K^+$  or  $Na^+$ . Thus it is expected that the decomposition extent of the solvent PC becomes milder at low potential of the negative AC electrode in the electrolytes of  $KPF_6$ -PC or  $NaPF_6$ -PC.

Fig. 2 shows the charge–discharge curves of the AC/graphite capacitors (two-electrode coin cells) in 0.8M  $XPF_6$ -PC electrolyte solutions (here X stands for alkali metal cations as  $Li^+$ ,  $Na^+$  and  $K^+$ , respectively). For all these three electrolyte solutions, the discharge curves shift to lower voltage (IR drop rises up) along with the cycles, and generally the discharge capacity becomes larger. We ascribe the IR drop increase with the cycles to the accumulative decomposition of the PC solvent at the negative AC electrode. The decomposition product may form some SEI (Solid Electrolyte Interface) film, which permits naked alkali cations to pass through, but prohibits the entrance of the solvent molecules. Along with the cycles, the SEI film becomes denser to cover the “outer” surface of AC negative electrode, and more and more naked alkali cations are stripped from the PC solvent molecules before passing through the SEI film and enter into the micropore. Instead of PC-solvated alkali cations, some naked alkali cations are adsorbed at the negative AC electrodes after certain long cycles, which fact contributes to a higher capacity. Especially for  $Li^+$ , this trend is the

most apparent. However, if the SEI film is too thick, it will also block the entrance of  $Li^+$  into the pores of AC negative electrode. In the case of  $K^+$ , the decomposition of PC solvent at the negative AC electrode is rather soft. The cycle-ability of the AC/graphite capacitors in different electrolyte solutions is compared in Fig. 3. The effect of  $KPF_6$  is much better than that  $LiPF_6$  in the PC; even more satisfactory than  $TEMAPF_6$ -PC, the commonly used electrolyte solution. But  $KPF_6$  has one disadvantage, the low solubility in PC solvent of ca. 0.8 M. By contrast,  $NaPF_6$  dissolved in PC also appears a good candidate for the electrolyte in AC/graphite capacitors in the terms of high capacity and relatively stable cycle-ability as demonstrated in Figs. 2 and 3. However, the comparatively big IR drop of the capacitor using this electrolyte after certain long charge–discharge cycles may shift the working voltage apparently to lower values, and thus decrease the energy density. If taking most of the key issues into account, like IR drop, cycle-ability, capacity, and low cost,  $KPF_6$  is still the best choice among all the alkali-based electrolytes.

#### 4. Conclusion

In the AC/graphite capacitors using the alkali-PC organic electrolytes, the alkali cations solvated by PC molecules are adsorbed on the AC negative electrodes. PC molecules thus approaching to the pores of AC negative electrodes lead to the big decomposition of the electrolyte in the charge process of capacitors.  $K^+$  is not so heavily by PC molecules, and contributes little deterioration of the performance of AC/graphite capacitors.

#### References

- [1] O. Barbieri, M. Hahn, A. Herzog, R. Kötz, Carbon 43 (2005) 1303.
- [2] M. Hahn, A. Würsig, R. Gallay, P. Novák, R. Kötz, Electrochem. Commun. 7 (2005) 925.
- [3] M. Yoshio, H. Nakamura, H. Wang, Electrochem. Solid-State Lett. 9 (2006) A561.
- [4] H. Wang, M. Yoshio, Electrochem. Commun. 8 (2006) 1481.
- [5] H. Wang, M. Yoshio, A.K. Thapa, H. Nakamura, J. Power Sources 169 (2007) 375.
- [6] H. Wang, M. Yoshio, J. Power Sources 177 (2008) 681.
- [7] H. Wang, M. Yoshio, Electrochem. Commun. 10 (2008) 382.
- [8] H. Wang, M. Yoshio, J. Power Sources 195 (2010) 389.
- [9] K. Naoi, A. Nishino, T. Morimoto (Eds.), Electrochemical Capacitors Compact Dictionary, NTS, 2004, p. P89.
- [10] M. Ue, J. Electrochem. Soc. 141 (1994) 3336.
- [11] Y. Matsuda, H. Nakashima, M. Morita, Y. Takasu, J. Electrochem. Soc. 128 (1981) 2552.