Short communication

Feasibility of quaternary alkyl ammonium-intercalated graphite as negative electrode materials in electrochemical capacitors

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ABSTRACT

The electrochemical capacitor of graphite/activated carbon (AC) using quaternary alkyl ammonium-based organic electrolytes has been proposed. The charge storage mechanisms involve the adsorption of anions into pores of the AC positive electrode and the intercalation of ammonium cations into crystal lattice of the graphite negative electrode, respectively. The intercalation processes of ammonium cations have been investigated by *in situ* XRD measurements on graphite negative electrodes and the effect of cation size has been intensively addressed. Among the four quaternary alkyl ammonium cations, the intercalation of the biggest cation tetrabutyl ammonium demonstrates the largest degree of crystal lattice expansion of graphite, but the best cycle-ability. By contrast, the insertion of second big cation tetraethyl ammonium into graphite gives the smallest expansion degree of graphite crystal lattice, but poor cycle performance of capacitor. A mechanism has been proposed to explain the above phenomenon.

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1. Introduction

In the big family of electric energy storage systems, electrochemical capacitors are becoming more and more attractive in many application fields. Traditional electric double-layer capacitors (EDLCs) still prevail in most of the application scope. However, to meet the needs of both high power and high energy densities, hybrid capacitors with an asymmetric configuration have been drawing more and more research attention in recent years. We have developed activated carbon (AC)/graphite capacitors (AC negative electrode, graphite positive electrode) using organic electrolytes, say, $TEMAPF_6$ (TEMA, triethylmethyl ammonium) dissolved in propylene carbonate (PC) [1–5]. This kind of asymmetrical capacitors demonstrate more promise for high energy density utility as compared with the symmetrical AC/AC capacitors (common EDLCs). If we look at the asymmetric capacitors from another viewpoint, we can get a new kind of capacitors. That is a capacitor consisting of a graphite negative electrode and an AC positive electrode. Consequently, the charge storage mechanism at the graphite negative electrode involves the insertion of quaternary alkyl ammonium (like $TEMA^+$) cation into graphite, while that at the AC positive electrode relates to the adsorption of PF_6^- anion. The question whether graphite/AC capacitors using quaternary alkyl

ammonium-based organic electrolytes can be used in practical applications aroused our research interest.

Of course, the attempt of graphitic carbon/AC capacitors using Li^+-based electrolytes proved promising [6]. Here the charge storage mechanism at the graphitic carbon negative electrode involves the Li^+ intercalation while at the AC positive electrode relates to anion adsorption. This capacitor system has the operating voltage over 4 V. Moreover, the graphite negative electrode delivers a high capacity of charge storage. However, there are two big problems with this capacitor system using Li^+-based electrolytes. On one hand, the risk of Li metal deposition on the negative carbon electrode cannot be avoided, which can cause the explosion of capacitor. On the other hand, the incompatibility between the graphitic carbon and the Li^+–PC electrolytes is also a severe problem [7,8].

Quaternary alkyl ammonium-based electrolytes obviously exclude these two shortcomings of Li^+-based electrolytes. At first, no metal deposition can take place during charge process because the electrolytes are free of metal ions in the capacitors. Moreover, since the quaternary alkyl ammonium cations are not so tightly bonded with solvent molecules in the electrolytes as Li^+ [5], the co-intercalation of solvent molecules (like PC) together with the cations into graphite is unlikely to happen. Therefore the drastic decomposition of the solvent molecules in the interlayer space between the graphene layers and the great exfoliation of graphite can hardly occur at low potentials of graphite electrode.

In fact, some previous investigations have been performed on the electrochemical intercalation of quaternary alkyl ammonium

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cations into graphite [9–15]. The consensus appeared that since quaternary alkyl ammonium is large enough to expand the interlayer spaces between graphene layers significantly, the drastic volume expansion may cause big stress in graphite particles and thus deteriorate the cycle performance of graphite electrode. We believe this anticipation lacks the systematic investigations on the effect of quaternary alkyl ammonium cations. In this paper, the feasibility of graphite/AC capacitors has been investigated by typical electrochemical methods in connection with the *in situ* XRD measurements. The influence of quaternary alkyl ammonium-based electrolytes has been addressed in detail.

2. Experimental

PW15M13130 (AC from Kureha Co. Ltd.) and KS6 (graphite from Timcal Co. Ltd.) were chosen as the positive and negative electrode materials for capacitors, respectively. Some physical properties of PW15M13130 and KS6 have been described in the past reports [2,3]. The weight ratio of graphite to AC was generally kept at 1. From the pore size distribution result of the AC (PW15M13130), most of the pores have the size near 1 nm. The electrolytes employed in this study were denoted as 1 M or 1.5 M X-BF$_4$ dissolved in PC (X stands for the cation type). The cell fabrication, glove box conditions and *in situ* XRD procedures were the same as those described in the past reports [2–5]. The galvanostatic charge–discharge tests of the coin cell were generally performed at the constant current density of 0.4 mA cm^{-2}. 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^{-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 AC positive electrode (g)).

Computational calculation with the Gaussian09 program package was performed to evaluate the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy values of these quaternary alkyl ammonium cations. The geometries of quaternary alkyl ammonium cations were fully optimized without symmetry constraints by the density functional theory (DFT) method, with hybrid Beck's three-parameter functional and Lee–Yang–Parr functional (B3LYP). The 6-311G (d,p) basis set was used for all the atoms.

3. Results and discussion

The cycle performance of the graphite/AC and AC/graphite capacitors using the electrolyte of 1 M TEMABF$_4$–PC is shown in Fig. 1. The discharge capacity delivered by graphite/AC capacitor drops down more remarkably with cycles as compared with that of AC/graphite capacitor. The poor cycle-ability seems to prove that the graphite/AC capacitor is not applicable in practical industry. This shortcoming probably comes from the deterioration of graphite electrode as suggested in the previous study [15]. As a matter of fact, the ionic size of TEMA$^+$ is bigger than that of BF$_4^-$. So it is expected that the intercalation of TEMA$^+$ into the of graphite electrode cause more severe volume expansion in crystal lattice than that of BF$_4^-$.

In situ XRD measurement is a powerful technique to investigate the charge storage mechanism of ions in the graphite electrode. Fig. 2 shows the *in situ* XRD patterns of the graphite negative electrode in the graphite/AC capacitor using the electrolyte of 1 M TBABF$_4$–PC (TBA stands for tetrabutyl ammonium). There is almost no change in the (0 0 2) peak of graphite (26.5°) until 2.7 V during the charge process. As the cell voltage rises up to 2.9 V, a small peak appears at a lower diffraction angle. With the increase in cell voltage, this peak grows up in the intensity and shifts to lower
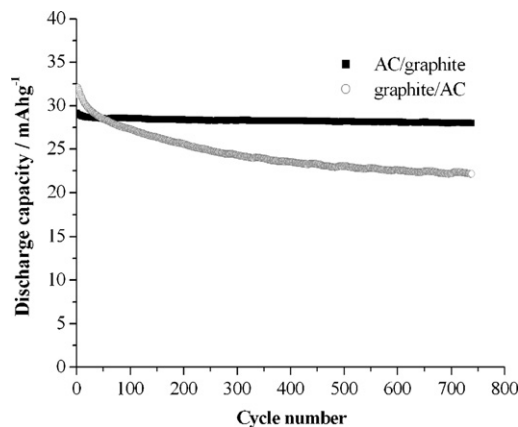

Fig. 1. Cycle performance of the graphite/AC and AC/graphite capacitors using the electrolyte of 1 M TEMABF$_4$–PC.

diffraction angles. At the same time, the intensity of (0 0 2) peak of graphite becomes weaker and two new diffraction peaks appear at higher diffraction angles. One is close to the (0 0 2) peak of graphite. Another weak peak locates at diffraction angles higher than 30°. These new diffraction peaks provide a profound evidence of the stage formation of the cation-graphite intercalation compound during charge process. The electrolytes of 1 M DEDMABF$_4$ and TEMABF$_4$–PC give series of *in situ* XRD patterns of graphite negative electrode similar to Fig. 2. Here DEDMA represents <u>d</u>i<u>e</u>thyl<u>d</u>imethyl ammonium.

By contrast, the *in situ* XRD result of graphite negative electrode using the electrolyte of 1 M TEABF$_4$–PC has big difference
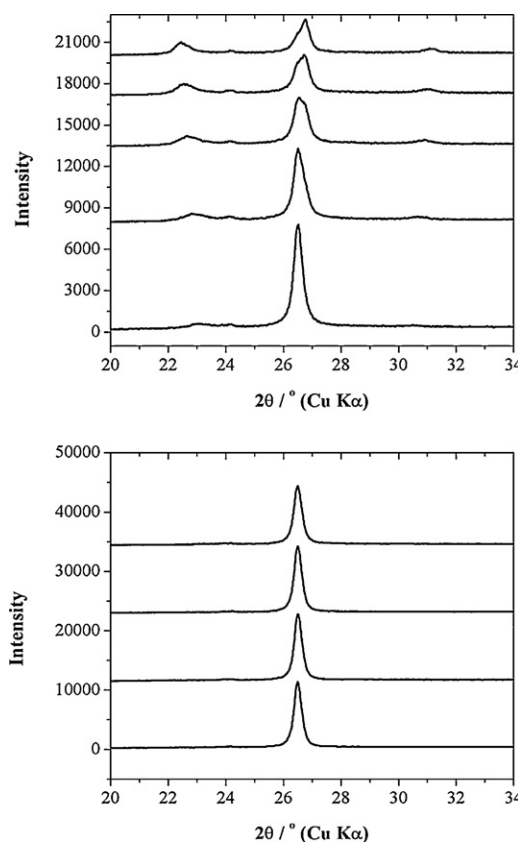

Fig. 2. *In situ* XRD patterns of the graphite negative electrode in the initial charge process of a graphite/AC capacitor using the electrolytes of 1 M TBABF$_4$–PC. The capacitor voltages rise in the following order: OCV (open circuit-voltage), 1.9 V, 2.3 V, 2.7 V, 2.9 V, 3.1 V, 3.3 V, 3.4 V, 3.5 V.
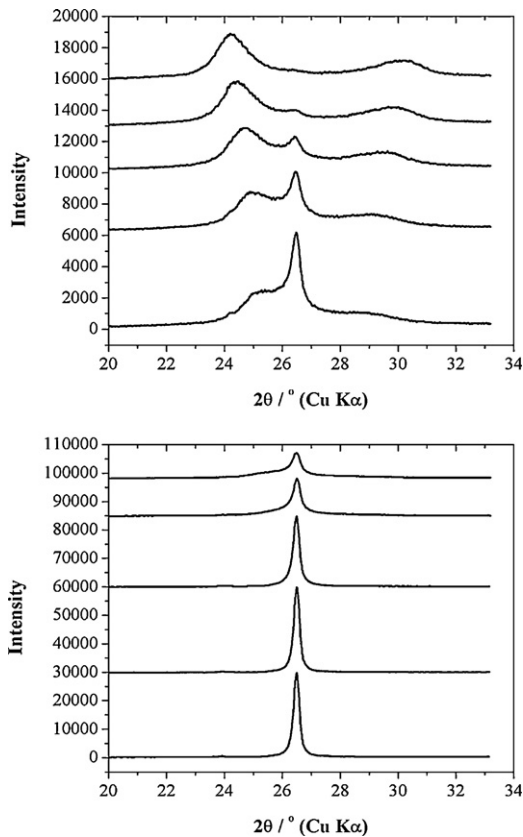
Fig. 3. *In situ* XRD patterns of the graphite negative electrode in the initial charge process of a graphite/AC capacitor using the electrolytes of 1 M TEABF$_4$–PC. The capacitor voltages rise in the following order: OCV, 1.9 V, 2.3 V, 2.7 V, 2.9 V, 3.1 V, 3.3 V, 3.5 V, 3.7 V, 3.9 V.

with those corresponding to other quaternary alkyl ammonium–PC electrolytes. Here TEA is the abbreviation of tetraethyl ammonium. Fig. 3 shows the *in situ* XRD patterns of the graphite negative electrode in the graphite/AC capacitor using the electrolyte of 1 M TEABF$_4$–PC. During the initial charge process of the capacitor, the change in the XRD patterns at first is reflected by the significant decrease in the intensity of graphite (0 0 2) peak when the cell voltage rises up to over 2.7 V. This trend is the same as that reported in the previous study [15]. As the cell voltage gets higher than 3.1 V, two broad diffraction peaks appear at both sides of the (0 0 2) peak of graphite, which phenomenon has not been found before [15]. These two peaks deviate apart from the (0 0 2) peak of graphite respectively and the intensities of these two new peaks become a little stronger along with the rise in cell voltage. At the same time, the (0 0 2) peak of graphite becomes weaker. The presence of new diffraction peaks besides (0 0 2) peak of graphite in the *in situ* XRD patterns is somehow different from the result in the previous study. We deliberately charged the capacitor to high cell voltages until 3.9 V to make sure of the new diffraction peaks. At 3.9 V, the (0 0 2)

peak of graphite at 26.5° does not exist in the XRD pattern. Instead, two broad peaks can be clearly observed at about 24.2 and 30.4°, respectively.

In the case of 1.5 M LiBF$_4$–PC electrolyte, the appearance of new peaks can be hardly seen during the charge process although we have raised the cell voltage to 4.1 V, only the irreversible decrease in the intensity of graphite (0 0 2) peak takes place in the *in situ* XRD measurements.

Table 1 summarizes the *in situ* XRD results of the graphite negative electrode in the graphite/AC capacitor using these electrolytes. To correlate with the cation effect, the ionic radius values picked up from previous reports have also be included in this table [16,17]. Here, we have coined a term of "stage initiation voltage" to stand for the cell voltage at which the new diffraction peaks other than graphite (0 0 2) peak begin to appear (stage formation of cation-graphite intercalation compound). The stage initiation voltages corresponding to the cations rank in the following order: DEDMA$^+$ ∼ TEMA$^+$ < TBA$^+$ < TEA$^+$ < Li$^+$–PC. Generally speaking, the bigger cation gets more difficult to intercalate into graphite, thus the stage initiation voltage becomes higher. However, the sluggish stage initiation voltage for TEA$^+$–graphite is very unique as compared with other quaternary alkyl ammonium–graphite intercalation compounds. The absence of new diffraction peaks in the case of Li$^+$–PC electrolyte can be easily understood in the terms of the co-intercalation of PC molecules with Li$^+$ into graphite. PC inserted into graphite crystal lattice may be decomposed before the stage formation of intercalation compounds and the resulting gas may destroy the crystal structure of graphite. It should be noted that the Stocks ionic radius value of 0.408 nm is chosen to stand for PC solvated Li$^+$ instead of the crystallographic value of 0.076 nm (naked Li$^+$).

We also listed in Table 1 the diffraction peaks of graphite negative electrode at the cell voltage of 3.5 V of the graphite/AC capacitor using these electrolytes. The peak at lower diffraction angles (<26.5°) in each XRD pattern is the most important parameter to evaluate the intercalation behavior of cations into graphite since it correlates with the expansion extent in the interlayer distance between graphene layers. We name this peak as "α" peak. The bigger the dimension expansion happens in the interlayer distance (intercalation of bigger cation), the lower diffraction angle the α peak locates. The order of α peak positions corresponding to the quaternary alkyl ammonium cations is: TBA$^+$ < TEMA$^+$ < DEDMA$^+$ < TEA$^+$. As we can expect, the intercalation of the biggest cation (TBA$^+$) leads to the largest volume expansion in crystal lattice of graphite. However, instead of smaller cations like DEDMA$^+$ or TEMA$^+$, the intercalation of TEA$^+$ into graphite causes the least volume expansion in the crystal lattice of graphite.

It is commonly believed that the big volume change in the crystal lattice during ions intercalation/de-intercalation is the main reason for the cracking in electrode material. This fact is directly responsible for the failure in charge storage of the electrode material after long cycles of charge/discharge. Thus from the α peak position in the *in situ* XRD results of the graphite negative electrode, we can predict the cycle performance of graphite/AC capacitor using the

Table 1
In situ XRD results of the graphite negative electrode in the graphite/AC capacitor using different electrolytes.

Electrolyte: X-BF$_4$ dissolved in PC	1 M DEDMA	1 M TEMA	1 M TEA	1 M TBA	1.5 M Li
Ionic radius of cation X [nm]	0.313	0.327	0.343	0.415	0.408
Stage initiation voltage [V]	2.3	2.3	3.1	2.9	
Diffraction peaks at 3.5 V [°]	23.01 (α)	22.68 (α)	24.73 (α)	22.45	<u>26.5</u>
	26.56	26.61	<u>26.5</u>	26.76	(Graphite (0 0 2))
	27.62	27.55	(Graphite (0 0 2))	31.3	
			29.64		

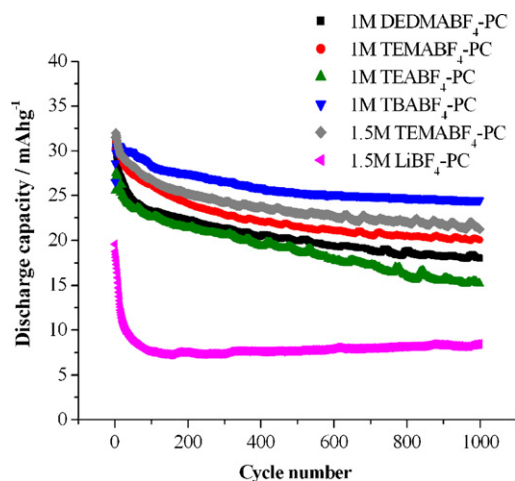Underline value is residual (0 0 2) peak of the graphite phase.

Fig. 4. Comparison of the cycle performance of (−) graphite/AC (+) capacitor in the electrolytes of X-BF$_4$ dissolved in PC (X stands for Li$^+$, DEDMA$^+$, TEMA$^+$, TEA$^+$, and TBA$^+$).

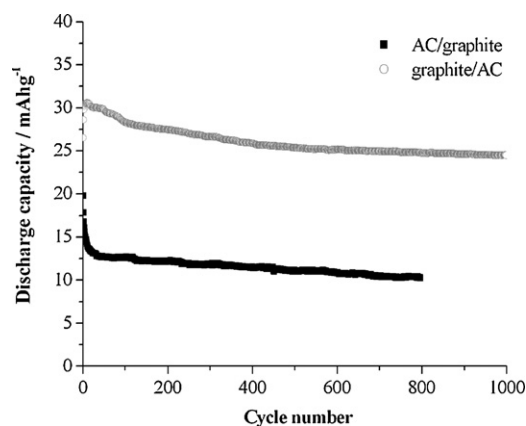**Fig. 5.** Comparison of cycle performance of the AC/graphite and graphite/AC capacitors using the electrolyte of 1 M TBABF$_4$–PC.

quaternary alkyl ammonium-based electrolytes ranks in the order of TBA$^+$ < TEMA$^+$ < DEDMA$^+$ < TEA$^+$.

Fig. 4 compares the cycle performance of graphite/AC capacitor in the electrolytes of X-BF$_4$ dissolved in PC (X stands for the cations of Li$^+$, DEDMA$^+$, TEMA$^+$, TEA$^+$, and TBA$^+$). For all these electrolytes, the discharge capacity of the capacitor generally becomes smaller as the cycle number increases. However, the fading tendencies in discharge capacity using these electrolytes are quite different. The cycle-ability (retention extent in the discharge capacity with cycles) of the capacitor ranks in the following order of cations: TBA$^+$ > TEMA$^+$ > DEDMA$^+$ > TEA$^+$ > Li$^+$. The worst cycle performance demonstrated in the case of LiBF$_4$–PC can be well understood since PC-solvated Li$^+$ intercalates into the graphite negative electrode and decompose to break the crystal lattice of graphite in the charge process. This can be verified by the irreversible decrease in the (0 0 2) peak density of graphite during the *in situ* XRD measurement. To our surprise, the order in the cycle-ability of the capacitor using the quaternary alkyl ammonium-based electrolytes is just contrary to the prediction from the α peak positions in the *in situ* XRD results. The biggest cation (TBA$^+$), which can expand the interlayer distance most significant during intercalation into graphite, contributes to the most satisfactory cycle performance of the capacitor. On the other hand, TEA$^+$, which can expand the interlayer distance to the lowest extent, provides the inferior cycle performance among all the quaternary alkyl ammonium cations.

Besides the expansion degree of crystal lattice during a cation intercalation into a graphite negative electrode, there are other factors may also influence the cycle-ability of the graphite electrode. One of them is likely to be the tolerance of quaternary alkyl ammonium cation towards cathodic reduction. The work of Ue et al. has shown that TBA$^+$ is more cathodically stable than other smaller cations (Table IV in Ref. [18]). This conclusion coincides with our computational calculation results as listed in Table 2. The LUMO energy values of these quaternary alkyl ammonium cations rank in the following order: TBA$^+$ > TEA$^+$ > TEMA$^+$ > DEDMA$^+$, in accordance with their abilities against cathodic reduction. It may

Table 2
HOMO and LUMO energy values of some quaternary alkyl ammonium cations.

	DEDMA$^+$	TEMA$^+$	TEA$^+$	TBA$^+$
LUMO [eV]	−3.528	−3.377	−3.145	−2.742
HOMO [eV]	−14.096	−13.823	−13.643	−12.170

be a strong proof for the extraordinarily stable cycle life of the graphite/AC capacitor using the TBA$^+$-based electrolyte. We believe that the delicate compromise between different factors including the volume change of graphite crystal lattice and the cathodic stability of a cation, etc., determines the cycle performance of a graphite/AC capacitor at last. However, the rather poor cycle performance of the graphite/AC capacitor using TEA$^+$-based electrolyte is an open question. TEA$^+$ is not inferior to DEDMA$^+$ and TEMA$^+$ in terms of tolerance towards cathodic reductions. Moreover, the stage formation of intercalation compound for TEA$^+$–graphite is not fluent as shown the *in situ* XRD results.

From the viewpoint of cycle performance, the electrolyte of TBABF$_4$–PC appears the most valuable for the practical application of the graphite/AC capacitor systems among the electrolytes used in this study. Actually, the electrolyte of TBABF$_4$–PC is not suitable for the AC/graphite capacitor at all. As shown in Fig. 5, given the same electrolyte of 1 M TBABF$_4$–PC, the cycle performance of AC/graphite capacitor is much poorer than that of graphite/AC capacitor. As to the reason for the poor cycle-ability of the AC/graphite capacitor using the electrolyte of TBABF$_4$–PC, we ascribe it to the irreversible TBA$^+$ "cation trapping" in the micro-pores of AC. Since the size of TBA$^+$ (roughly estimated to be 0.431 × 2 = 0.862 nm) is very close to the average pore size of AC (near 1 nm), it is likely that some TBA$^+$ cations entering inside the smaller pores of AC cannot be driven out during the de-sorption process (corresponding to the discharge of AC/graphite capacitor), similar to the case in a previous report [19].

4. Conclusion

In conclusion, the graphite/AC capacitors using quaternary alkyl ammonium–PC electrolytes show some promise as an electric energy storage device. The charge storage mechanism of quaternary alkyl ammonium cations at the graphite negative electrode involves the intercalation of these cations into graphite crystal lattice, which can be observed from the *in situ* XRD patterns of the graphite negative electrode during charge process. The size of the quaternary alkyl ammonium cations plays a very important role in the electrochemical performance of the capacitor. Within the four quaternary alkyl ammonium cations (DEDMA$^+$, TEMA$^+$, TEA$^+$, and TBA$^+$), the biggest cation of TBA$^+$ appears most suitable for the application in the capacitor because of the good cycle performance of the capacitor using the electrolyte of TBABF$_4$–PC, although the intercalation of TBA$^+$ into graphite expands the interlayer distance between graphene layers to the biggest extent among these four cations.

Acknowledgements

References

[1] M. Yoshio, H. Nakamura, H. Wang, Electrochem. Solid-State Lett. 9 (2006) A561.
[2] H. Wang, M. Yoshio, Electrochem. Commun. 8 (2006) 1481.
[3] H. Wang, M. Yoshio, A.K. Thapa, H. Nakamura, J. Power Sources 169 (2007) 375.
[4] H. Wang, M. Yoshio, J. Power Sources 177 (2008) 681.
[5] H. Wang, M. Yoshio, Electrochem. Commun. 10 (2008) 382.
[6] H. Tanizaki, K. Matsui, S. Tasaki, N. Ando, Y. Hato, H. Shibuya, The 47th Battery Symposium in Japan, 3C-04 (2006) p288.
[7] R. Fong, U. von Sacken, J.R. Dahn, J. Electrochem. Soc. 137 (1990) 2009.
[8] J.O. Besenhard, M. Winter, J. Yang, W. Biberacher, J. Power Sources 54 (1995) 228.
[9] J.O. Besenhard, H.P. Fritz, J. Electroanal. Chem. 53 (1974) 329.
[10] R. Santhanam, M. Noel, J. Power Sources 66 (1997) 47.
[11] M. Hahn, O. Barbieri, F.P. Campana, R. Kötz, R. Gallay, Appl. Phys. A 82 (2006) 633.
[12] M. Hahn, O. Barbieri, R. Gallay, R. Kötz, Carbon 44 (2006) 2523.
[13] F.P. Campana, M. Hahn, A. Foelske, P. Ruch, R. Kötz, H. Siegenthaler, Electrochem. Commun. 8 (2006) 1363.
[14] L.J. Hardwick, M. Hahn, P. Ruch, M. Holzapfel, W. Scheifele, H. Buqa, F. Krumeich, P. Novak, R. Kötz, Electrochim. Acta 52 (2006) 675.
[15] P.W. Ruch, M. Hahn, F. Rosciano, M. Holzapfel, H. Kaiser, W. Scheifele, B. Schmitt, P. Novak, R. Kötz, A. Wokaun, Electrochim. Acta 53 (2007) 1074.
[16] M. Ue, J. Electrochem. Soc. 141 (1994) 3336.
[17] K. Naoi, A. Nishino, T. Morimoto (Eds.), Electrochemical Capacitors Compact Dictionary, NTS, 2004, p. 89.
[18] M. Ue, K. Ida, S. Mori, J. Electrochem. Soc. 141 (1994) 2989.
[19] D. Aurbach, M.D. Levi, G. Salitra, N. Levy, E. Pollak, J. Muthu, J. Electrochem. Soc. 155 (2008) A745.