Short communication

Intercalation of PF$_6$$^-$ anion into graphitic carbon with nano pore for dual carbon cell with high capacity

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ABSTRACT

Intercalation property of PF$_6$$^-$ into graphitic carbon was studied for a hybrid capacitor with different ratio of cathode and anode amount. Graphene sheet distance increased with increasing PF$_6$$^-$ intercalation amount and it saturated at 0.4 nm at high applied potential, which is corresponded to stage 2 structure. On the other hand, it was found that nano size pore into graphene sheet was introduced at higher applied potential with 20 times larger anode carbon and this nano porous carbon shows a large capacity for intercalation capacity of 147 mAh g^{-1}. The estimated energy density of the hybrid capacitor using carbon with nano bubble structure was ca. 400 Wh kg^{-1}.

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1. Introduction

Recently, battery is a key technology for supporting the high performance of various mobile equipments. Li ion battery has popularly used for this purpose [1]. However, due to the high reactivity of Li, Li ion battery has a disadvantage from a view-point of safety, i.e., flammable, overcharging, and also insufficient cycle stability. Electrochemical capacitor is also attracting much interest as the electric storage devices recently. However, electrochemical double layer capacitor (EDLC) has a drawback of limited capacity [2]. On the other hand, recently, ionic liquid is also attracting much interest because of its unique properties such as non-volatility, non flammability, and high ionic conductivity [3,4]. Ionic liquid is now considered for the application to the solvent in various organic reactions, the electrolyte of battery [5], and the reaction field for various catalysts. In particular, application of ionic liquid for the electrolyte of battery [6–8] or capacitor [9–11] is expecting and studied extensively. However, these advantages of ionic liquid are not fully used up to now. In this study, we apply the ionic liquid of n-buthyl pyridinium PF$_6$ for electrolyte of dual carbon type battery. Recently, Wang et al. reported the capacitor using graphitic carbon for anode and tetraethyl ammonium PF$_6$ for electrolyte as a new capacitor with large capacity [12,13], however, the capacity is still small (less than 40 mAh g^{-1}). It is reported that PF$_6$$^-$ intercalation between graphene sheet can be applied for battery [14], however, application of PF$_6$$^-$ intercalation for so-called hybrid capacitor is still not studied in detail. In this study, the hybrid capacitor, which is intermediate between battery and capacitor, i.e. electrochemical intercalation of PF$_6$$^-$ and adsorption of organic cation, was studied by using the graphitic and the activated carbon for cathode and anode, respectively and also n-buthyl pyridinium PF$_6$ (n-BPPF$_6$) ionic liquid in propion carbonate–methyl ethyl carbonate (PC–MEC = 1:2) for the electrolyte. Effects of graphitic and activated carbon ratio on the intercalation capacity of PF$_6$$^-$ were mainly studied.

2. Experimental

The commercial graphitic carbon with (0 0 2) distance of 0.336 nm (KS-6 from Thimcal Co. Ltd.) was always used for the cathode after ball milling treatment in air (200 rpm, 1 h, planetary ball mill mixer by using Fritsch type p-7). BET surface area of the used graphite is 15 m^2 g^{-1} after ball milling treatment. It is also noted that BET surface area of the used carbon black binder and that for cathode were 69.6 and ca. 24 m^2 g^{-1}, respectively. Electrochemical intercalation of PF$_6$$^-$ was measured by mixing the graphitic carbon with acetylene black and polytetrafluoroethylene (PTFE) as a binder at the weight ratio of 60:30:10. Then the mixture was pressed onto the stainless steel current collector (SUS 316, 100 mesh) at 81 MPa which is determined from reasonable

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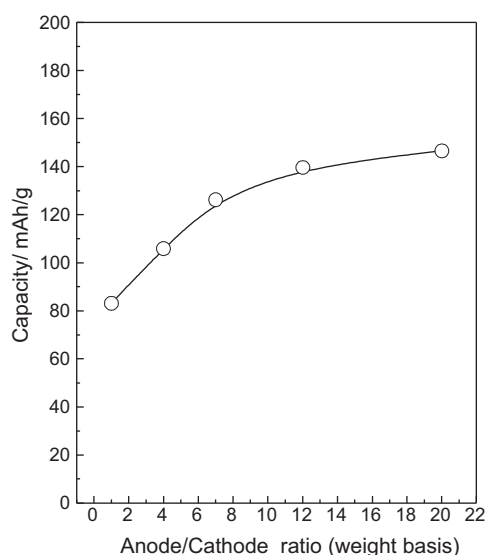*E-mail address:* ishihara@cstf.kyushu-u.ac.jp (T. Ishihara).

Fig. 1. Capacity of the PF_6^- intercalation as a function of the amount of active carbon anode. Electrolyte: 1 M n-BPPF$_6$ in PC–MEC (2:1), cathode: graphitic carbon, 10 mg.

mechanical strength for handing and low contact resistance. The estimated capacity of the cathode for PF_6^- adsorption is smaller than 3 mAh g^{-1}. The electrolyte used was 1 M n-butyl pyridinium PF$_6$ (n-BPPF$_6$) ionic liquid compound in PC:MEC (1:2 vol%) (UBE Kosan Co. Ltd.). The active carbon was also used for anode, of which BET surface area is 1500 m^2 g^{-1}. Unless otherwise noted, the charge and discharge property of the graphitic carbon was measured in the potential range from 0 to 3.5 V vs. counter electrode by applying a constant current (mainly 0.4 mA cm^{-2}) with the computer controlled dc source (Hokuto Denko Co. Ltd.). The used cell was a typical Swageloc type cell of which details were described in our previous paper [15]. TEM observation was performed using JEOL, type JEM 2010 CM with 200 kV acceleration voltage. The sample was taken away from the experimental set-up at the desired potential under humidity controlled globe box and the graphite sample was once dispersed into propylenecarbonate (PC) and scooped on Cu grid mesh. In situ XRD was also measured with the commercial cell using Al window and details of the measured cell were reported in our previous report [16].

3. Results and discussions

Fig. 1 shows the capacity as a function of the amount of activated carbon anode for hybrid capacitor. Capacity was strongly related with the amount of anodic carbon and obviously, it increases with increasing the amount of the used carbon for anode. As shown in Fig. 1, the largest capacity was exhibited on the cell using the carbon of which amount is 20 times larger than that of cathode graphitic carbon. Under this condition, the capacity of the cell is achieved to a value of 150 mAh g^{-1}, which is larger than that of EDLC by an order of magnitude and even larger than that of the current Li ion rechargeable battery, LiCoO$_2$ (140 mAh g^{-1}). It is also noted that the usage of the active carbon anode with the larger BET surface area is effective for the larger capacity. These data suggest that the capacity of anode is smaller than that of cathode and limited the total capacity.

Fig. 2 shows the charge and discharge curves of the cell using 20 times larger activated carbon. In contrast to the typical charge–discharge curves of EDLC, the potential increased significantly up to 1.8 V and then gradually increased and finally almost independent of capacity. We studied electrochemical intercalation of PF_6^- into graphitic carbon with cyclic voltamograph and three
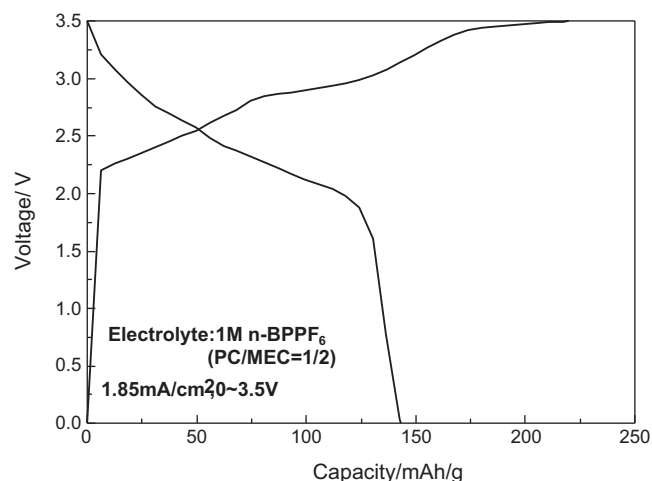

Fig. 2. Typical charge–discharge curves of the proposed new hybrid capacitor. Cathode: graphitic carbon, anode: activated carbon.

peaks were observed at 5, 4.5 and 4 V Li/Li$^+$ [15]. Therefore, three different stage structures are suggested for the cathode reaction of this new capacitor. It is also noted that large irreversible capacity was observed at initial cycles. In any way, the capacity in the potential range smaller than 1 V is negligibly small, but that higher than 2 V is much larger and occupied the main part of the total capacity for PF_6^- intercalation. This property is suitable as the electric source, since the small potential cannot be used for the large part of the electrics. On the other hand, capacity of the cell is stable over 100 times charge and discharge cycles and after 100 times repetitions, the capacity of 150 mAh g^{-1} is still exhibited. Therefore, the proposed capacitor is quite suitable as the electric storage devises like battery.

Fig. 3 shows the charge and discharge capacity of the proposed hybrid battery as a function of charge–discharge cycles. It is seen that the discharge capacity of the cell is stable over 100 times charge–discharge cycles and after 100 times repetitions, the capacity of 150 mAh g^{-1} is still exhibited. However, at initial 50 cycles, irreversible capacity is slightly large, which seems to be assigned to the decomposition of electrolyte and intercalated PF_6^-, or trap of intercalated PF_6^- into graphitic carbon. Irreversible capacity
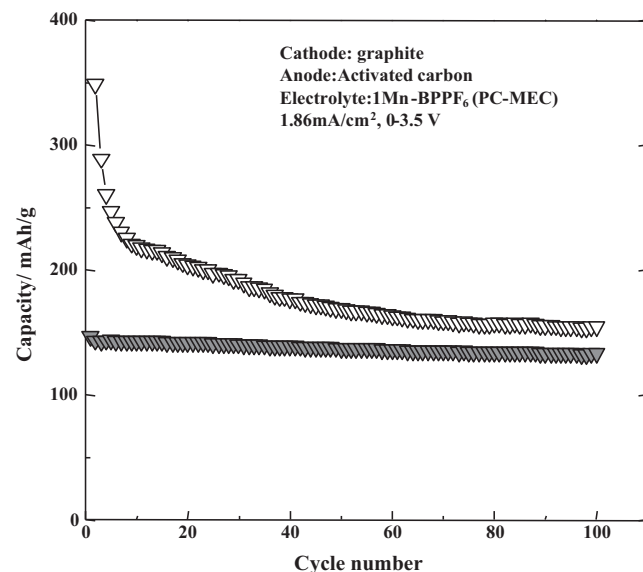

Fig. 3. Cycle stability of charge–discharge capacity of the proposed new hybrid capacitor. Cathode: graphitic carbon, anode: activated carbon.
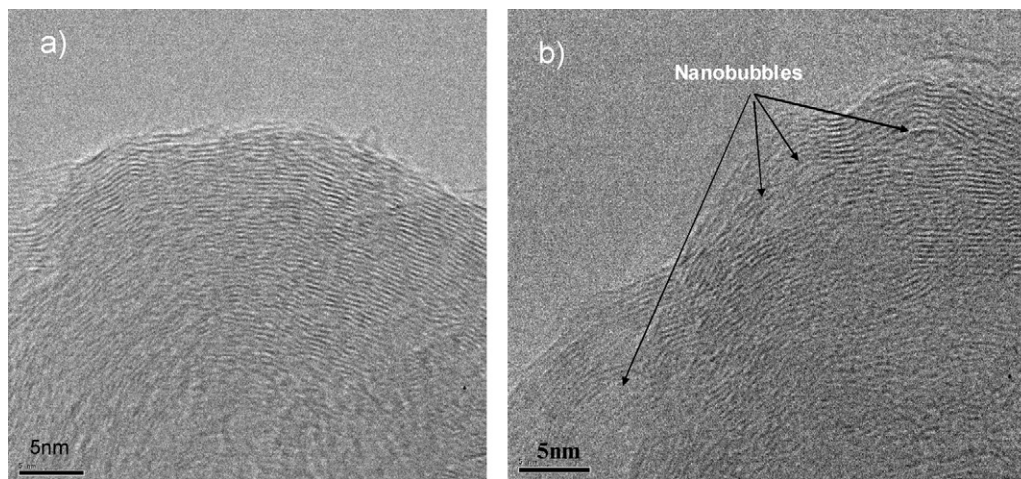
Fig. 4. TEM image of (0 0 2) plane of the graphitic carbon before (a) after application of 3.1 V (b).

gradually decreased with cycle number. In any case, it can be said that the stability of discharge capacity is high over 100 cycles.

In order to identify the high capacity in this new hybrid capacitor, in situ XRD measurement and TEM observation was performed. TEM observation was performed for analysis of intercalated PF_6^- between graphene sheet (Fig. 4). TEM image of the (0 0 2) plane distance of the sample was expanded with increasing the applied potential.

On the other hand, in situ XRD patterns of cathode graphite carbon were also shown in Fig. 5. The diffraction peaks around 26°, which is corresponded to (0 0 2) plane, was shifted to higher angle at the applied potential higher than 1.5 V and drastically changed at potential higher than 2.5 V. This suggests that stage structure was only observed by XRD measurement.

Fig. 6 shows the distance of graphene sheet estimated by TEM and in situ XRD measurement. It is seen that the estimated (0 0 2) distance by XRD and TEM is well agreed. Apparently, the graphene sheet distance begins to expand at the potential higher than 1.6 V and it is once independent of applied potential followed by increase after ca. 3 V. The distance of (0 0 2) plane was estimated to be 0.405 nm at 3.5 V. Dhan et al. reported that 0.45 nm of PF_6^- in graphene sheet, and considering the plane distance of graphite, stage 2 structure is suggested from plane distance. If stage 2 structure and 0.45 nm of PF_6^- ion size is assumed, then the estimated (0 0 2) plane distance is 0.392 nm, which is well agreed with the
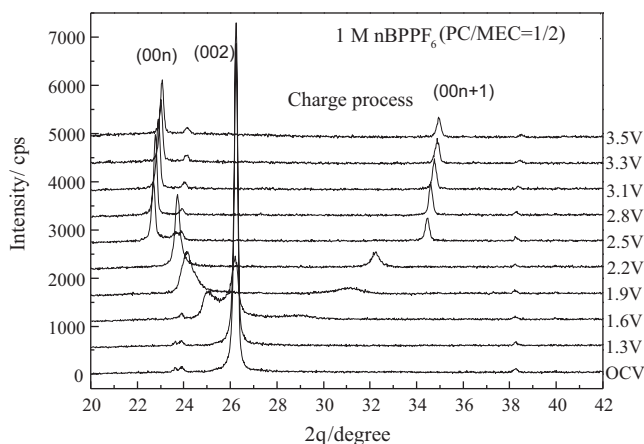
observed value. This dependency of the graphene sheet distance on the applied potential reflects so-called "stage structure" [14]. However, detail analysis of the (0 0 2) plane structure at high potential in TEM image in Fig. 4 suggests that the each plane has almost the same distance. With increasing the potential, unusual intercalation of PF_6^- is occurred and nano bubble structure were formed, i.e., the extremely expanded nano porous structure of graphene sheet, which is pointed out by arrow in Fig. 4, were observed. Considering the small expansion of (0 0 2) layer comparing with the ionic size of PF_6^- and slightly decreased layer distance at higher potential, intercalation of PF_6^- at higher potential is not simply expressed by so-called "stage" structure but the nano bubbles in graphene sheet forms near the surface area, which may be formed around defects in graphene sheet. Since no regular structure for nano bubbles were recognized, nano bubble structure is not detected by XRD (Fig. 5) and it seems to be the origin of the high capacity of the present cell. It is apparent that such nano bubble formation at the electrical potential higher than 1.5 V is the origin of the small expansion of graphene sheet, resulting in enlarged intercalation capacity.

On the other hand, in situ XRD of the anode active carbon was also studied, and apparently, there is no change in XRD patterns as well as TEM image of active carbon cathode at the potential up
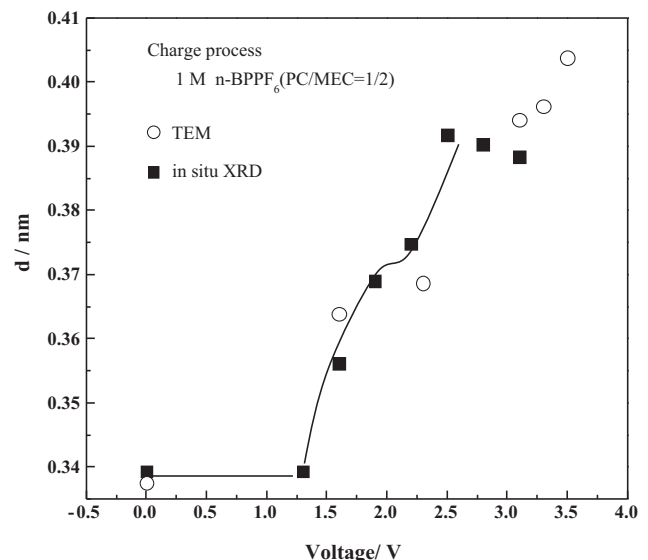

Fig. 5. In situ XRD patterns of cathode graphite under potential applied condition. Electrolyte: 1 M n-BPPF$_6$ in PC–MEC (2:1), cathode: graphitic carbon, anode activated carbon.

Fig. 6. Distance of (0 0 2) plane in graphene sheet estimated by TEM and in situ XRD measurement.

to 3.5 V. Therefore, for the case of active carbon anode, there is no electrochemical reaction occurred and so, in the developed capacitor, n-butyl pyridinium cation simply adsorbs like that in capacitor, which enable the superior rate property. Since PF_6^- anion is not solvated in organic electrolyte, intercalation of PF_6^- is faster than that of Li because it is well known that desolvation of Li is slow step and required a large activation energy [17]. Therefore, it is considered that PF_6^- intercalation is faster than that of Li because of small activation energy for intercalation. As a result, the energy density of the proposed cell is similar to that of Li ion battery and much higher than that of EDLC. On the other hand, the power density is similar to that of EDLC and higher than that of the present Li ion battery, and so the proposed cell is suitable for mobile applications. By using physical adsorption for anode, it is also noted that the rate property is much better than that of the cell using electrochemical intercalation for both electrodes, so-called "dual carbon" cell [14]. Consequently, this study reveals that new type of electric storage devices is achieved based on PF_6^- intercalation and n-butyl pyridinium cation adsorption.

4. Conclusion

Effects of the amount of activated anode carbon on the PF_6^- intercalation were studied and it was found that intercalated state of PF_6^- at high potential (>2.2 V) is not simply expressed a so-called "stage structure" but nano bubble structure. The estimated (0 0 2) layer distance was saturated around 0.40 nm because of the formation of nano bubble structure at the applied potential of ca. 3.0 V and the layer distance at this stage is corresponded to "stage 2" assuming 0.45 nm of molecular size of PF_6^-. The observed capacity for PF_6^- intercalation was achieved a value of 147 mAh g^{-1}, which

is reasonably high capacity for cathodic reaction of rechargeable battery. The large capacity can be explained by the formation of nano bubble structure. Therefore, this study shows the intercalation of PF_6^- is highly useful for cathode reaction of new type hybrid capacitor.

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