



Hexafluorophosphate intercalation into graphite electrode from gamma-butyrolactone solutions in activated carbon/graphite capacitors



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H I G H L I G H T S

- GBL suppresses PF_6^- insertion into graphite.
- This retardant effect of GBL is weaker than EC.
- Transport of EC-solvated PF_6^- inside graphite is sluggish.
- Intercalation of PF_6^- from GBL shares a similar pattern with that of BF_4^- from EC.

A R T I C L E I N F O

Article history:

Received 28 April 2015

Received in revised form

9 June 2015

Accepted 24 June 2015

Available online 6 August 2015

Keywords:

Hexafluorophosphate

Gamma-butyrolactone

Ethylene carbonate

Graphite intercalation compounds

In situ Raman spectroscopy

Electrochemical capacitors

A B S T R A C T

In our recent work, the solvent of ethylene carbonate (EC) has been found to retard the intercalation of anions into graphite electrodes. Here we demonstrate that gamma-butyrolactone (GBL) also exhibits suppressive effect on the intercalation of PF_6^- into the interlayer space between the graphene planes. The intercalation process of PF_6^- into graphite electrode from GBL has been investigated by *in situ* XRD, *in situ* Raman and EQCM. Furthermore, the effect of GBL has been compared with those of EC and propylene carbonate (PC).

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1. Introduction

Recently, the anion-intercalated graphite compounds become revived as positive electrode materials in the community of energy storage and transformation [1–6]. They can deliver reversible capacity more than 110 mAh g^{-1} at high working potentials (4.5–5.5 V vs. Li/Li^+) [7,8]. Graphite resource is abundant, economic, and environmentally benign. Moreover, in electric energy storage devices using this kind of positive electrodes, the choice of negative electrode materials is flexible [9–11]. A wide range of

cation-storage materials may be taken into account. Although these advantages are evident, this kind of positive electrode materials are far away from practical applications unless enough knowledge on the fundamental aspects such as their crystal structure evolution, compatibility with electrolyte solutions and the ambient influences, has been acquired. During the course of exploring activated carbon (AC)/graphite capacitors in the last decade, we were aware of the essential role of organic solvents in determining the performance of capacitors. Specially, the suppression effect of EC on anions intercalation into graphite has been discovered [12–14]. This fact is mainly ascribed to the strong solvation of some anions by EC. In addition, the intercalation modes of EC-solvated anions also depend on the anion species.

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These findings encourage us to search for other organic solvents with considerable binding strength with anions. Thus we can collect more clues on the solvation states of anions inside the interlayer galleries of graphite electrode in AC/graphite capacitors. Here we picked up GBL as the solvent to probe PF_6^- intercalation. The selection of PF_6^- -GBL combination is based on the following considerations. At first, PF_6^- may be the most popular anion utilized in high-voltage electric energy storage devices. Secondly, PC, EC and GBL are the most commonly used organic solvents with high anodic stability, high permittivity and low toxicity. Furthermore, the anion-solvent combinations of PF_6^- -EC and PF_6^- -PC have been studied previously [12], in which cases very contrastive intercalation behaviors of the anion can be observed although these two solvent molecules only differ by one methyl group. So the PF_6^- -GBL combination is likely to incur another fashion of intercalation into graphite, which will be a good example for fairly accessing a system of standard techniques to address these issues.

In this study, the electrolyte solutions of 1.5M SBPPF₆ (SBP: spiro-(1,1′)-bipyrrrolidinium) dissolved EC, PC and GBL are used in AC/graphite capacitors. The performance of these capacitors was tested by conventional electrochemical methods. A series of *in situ* techniques are employed to trace the electrochemical processes in the graphite electrodes. The electrochemical patterns of graphite electrodes are correlated with the performance of corresponding capacitors.

2. Experimental

2.1. Preparation of SBPPF₆

SBPPF₆ (SBP: spiro-(1,1′)-bipyrrrolidinium) was used as the PF_6^- -based electrolyte salt. Its synthesis method was described in the reference [15]. The purity was confirmed by ITMS (ion trap mass spectroscopy) as shown in Fig. 1.

2.2. Electrochemical measurement

The positive and negative electrode materials were graphite (natural graphite flakes purified by Kansai Coke and Chemicals Co. Ltd.) and AC (PW15M from Kureha Co. Ltd.), respectively. Their physical properties, such as specific surface area, pore size distribution, morphology, have been described in our previous work

[13,16].

Unless otherwise specified, 10 mg active material (graphite or AC) was homogeneously mixed with 5 mg conductive binder (TAB, teflonized acetylene black) and this mixture was pressed on a piece of aluminum mesh (current collector) to fabricate an electrode. Organic solvents including EC, PC and GBL were dried by molecular sieves until the water contamination contents were lower than 20 ppm prior to the preparation of electrolyte solutions. Beaker and coin cells were assembled in a glove box filled with Ar atmosphere. A beaker cell comprised three electrodes soaking in an electrolyte solution. These electrodes include an AC and a graphite electrode with the same mass, and a quasi-reference electrode (QRE) made from excess amount of AC [17]. Within a coin cell there were two electrodes (graphite and AC) sandwiched by glass fiber filter (separator) which was soaked with about 0.3 ml electrolyte solution. The mass of graphite equaled to that of AC. Galvanostatic charge–discharge tests of cells were performed at the constant current density of about 0.1A/g. The charge–discharge voltage ranges were 0–3.5 V for AC/graphite capacitors. *in situ* XRD and EQCM measurements were employed for *in situ* study of graphite electrodes, and the detail was described in the reference [9,14], *in situ* Raman measurements were conducted with a LabRam HR800 spectrometer (Horiba Jobin Yvon), using a two-electrode cell whose schematic diagram was shown in Ref. [18]. A HeNe laser with a wavelength of 632.8 nm was employed as the excitation source. Raman shift wavenumber was calibrated against Si wafer (520.8 cm^{-1}).

3. Results and discussion

As introduced in our previous studies, the effect of solvent on anion intercalation into graphite could be preliminarily reflected from the discharge capacity values of AC/graphite capacitors [12–14]. Fig. 2 compares the capacity values of AC/graphite capacitors using not only the neat-solvent, but also binary-solvent electrolyte solutions. The respective impacts of these three solvents (EC, GBL and PC) could be clearly distinguished here. The AC/graphite capacitors using solutions rich in PC deliver higher capacity values, whereas EC in AC/graphite capacitors decreases their capacity values drastically. Regarding the influence on the capacity values, GBL appears an intermediate level between EC and PC. As

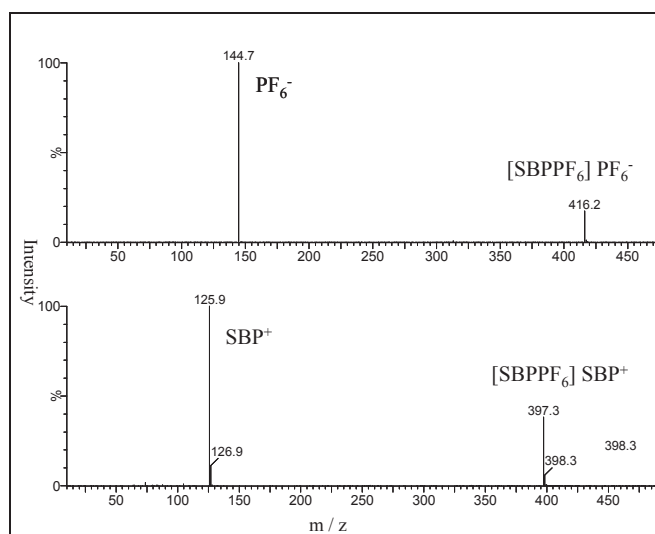


Fig. 1. The MS of synthesized SBPPF₆.

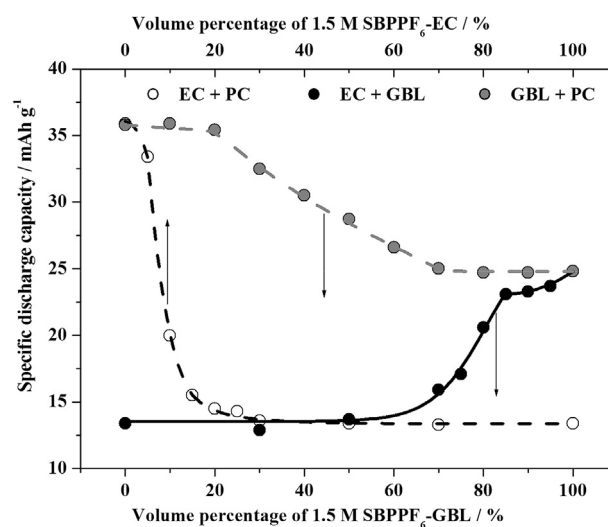


Fig. 2. Relationship between the discharge capacity of AC/graphite capacitors in the 1st galvanostatic charge–discharge cycle and the volume percentage of 1.5 M SBPPF₆-GBL (or -EC) in the binary mixed electrolyte solutions.

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