



Intercalation manners of perchlorate anion into graphite electrode from organic solutions



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ARTICLE INFO

Article history:

Received 1 April 2015

Received in revised form 28 May 2015

Accepted 24 June 2015

Available online 6 July 2015

Keywords:

Perchlorate anion

Solvents

Graphite intercalation compounds

in situ Raman spectroscopy

Electrochemical capacitors

ABSTRACT

Anion graphite intercalation compounds are an excellent candidate for high-potential positive electrode materials. Solvents play an important role during the intercalation processes of anions into graphite. In this contribution, the intercalation behaviors of perchlorate (ClO_4^-) from propylene carbonate (PC), γ -butyrolactone (GBL) and ethylene carbonate (EC) were studied with activated carbon (AC)/graphite capacitors. Both *in situ* Raman spectroscopy and *ex situ* X-ray diffraction were employed to detect the structure change of graphite electrodes caused by the electrochemical intercalation of ClO_4^- . Influence of solvents on the insertion of ClO_4^- was discussed. Besides, temperature effect was also explored.

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1. Introduction

Graphite is called a redox-amphoteric material, because it can be reduced as well as oxidized electrochemically and chemically, accompanying intercalation of various cations or anions, and leading to so-called donor-type or acceptor-type graphite intercalation compounds (GICs) [1]. Among numerous GICs, lithium-graphite intercalation compound (Li-GIC) has been the most attractive in the past few decades. The discovery of highly efficient intercalation of lithium ion into graphite in suitable solvent-supporting electrolyte systems, lays a foundation for lithium ion batteries (LIBs). Compared with Li-GIC, anion-intercalated graphite compounds have drawn less attention. However, situation is changing as people begin to be aware of their outstanding merits as follows. First, many anions can intercalate into graphite reversibly [2–6], even though their sizes are much larger than Li^+ ; Second, a relatively high specific capacity of more than 110 mAh g^{-1} can be delivered [4,7,8]; Third, the potential for the intercalation process ranges from 4.5 to 5.5 V vs. Li/Li^+ , which is still a heavy task for most lithium-storage positive electrode materials at present [9–11]. Apart from the above, the beneficial properties also include low cost, high electronic conductivity, abundant sources et al. In short,

anion-intercalated graphite compounds are qualified to pave a way for some new types of electric storage devices.

Due to the high working potentials of anion-GICs, the stability of electrolyte solutions against oxidation becomes very crucial. Recently, much attention has been focused on ionic liquids which allow reliable operation in highly oxidizing circumstance [1,2,5,8–10,12–16]. However, the drawbacks such as relatively poor compatibility with graphitic electrodes and high viscosity at room temperature may become problems in practical applications [10]. The alternative choice is organic solvent-based electrolytes. In fact, studies on the intercalation of anions into graphite electrode from organic solvents started much earlier [17,18]. Nevertheless, many results were not satisfactory, which might be disturbed by the low anodic stability and co-intercalation of some solvents [19]. Afterwards, only sporadic investigations have been made on anion intercalations into graphite from organic solvent-based electrolytes [7,20–23]. Given the prosperity of electric storage devices in the past decades, our understanding about the intercalation of anions into graphite from organic solvent-based electrolytes is quite limited. Thanks to the commercialization of LIBs and electric double-layer capacitors (EDLCs), organic solvent-based electrolytes, including organic solvents, electrolyte salts, and additives, have been greatly developed. On the other hand, many powerful analytical techniques, *ex situ* and *in situ*, have successfully been employed to probe these electric storage devices. So it is the time to ruminant and update the knowledge about the role of organic solvents in anion-GICs.

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In our previous work on activated carbon (AC)/graphite capacitors, we have found that ethylene carbonate (EC) can suppress the intercalation of some anions like BF_4^- , PF_6^- and difluoro(oxalato) borate (DFOB^-) [20,24,25], which fact was ascribed to the strong solvation of anions by EC molecules. Moreover, combination of *in situ* XRD and electrochemical quartz crystal microbalance (EQCM) measurements unambiguously proved the co-intercalation of the solvents with BF_4^- into graphite. In contrast, *in situ* XRD technique can't definitely judge the co-entrance of PF_6^- or DFOB^- into graphite with EC [20,25]. In fact, not only solvent, but also anion can profoundly affect the intercalation patterns. In order to systematically address the special effect of EC, ClO_4^- was picked up in this study. Compared with PF_6^- and DFOB^- , ClO_4^- has much in common with BF_4^- : with the same geometric structure (tetrahedron), similar ionic radius (0.217 nm vs. 0.209 nm) [26] and the ability of reversible intercalation into graphite. It also can be considered as an interpolation point between BF_4^- and PF_6^- , which makes the evaluation of this issue get more accurate, delicate and coherent. Here the intercalation of ClO_4^- into graphite from PC, GBL and EC-solutions was investigated by electrochemical tests in conjunction with *ex situ* XRD and *in situ* Raman measurements. Moreover, the temperature effect on the intercalation of ClO_4^- and BF_4^- from EC-solutions was also studied.

2. Experimental

2.1. Materials

The negative and positive electrode materials were activated carbon (PW15M13130 from Kureha Co. Ltd) and graphite (nature graphite flakes purified by Kansai Coke and Chemicals Co. Ltd), respectively. Their physical properties have been described in our previous work [25,27]. Solvents were purchased from Tokyo Kasei Kogyo Co. Ltd.. The electrolyte salt was mainly SBPClO_4 , which was synthesized according to the method described in Reference [28]. Its purity was confirmed by ITMS (ion trap mass spectroscopy), which was shown in Fig. 1.

2.2. Electrochemical measurements

The homogenous mixture of 10 mg active materials (AC or graphite) and 5 mg TAB (teflonized acetylene black) was pressed on a piece of aluminum mesh and used as an electrode. All the cells were assembled in a glove box full of Ar gas with the content of water and oxygen lower than 0.5 ppm. The weight ratio of AC to graphite was 1. The electrolyte solutions were 1.5 M SBPClO_4 dissolved in the organic solvents of EC, GBL, PC or their mixtures.

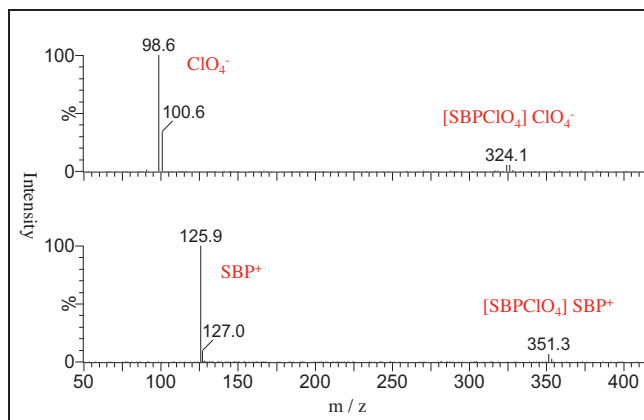


Fig. 1. The MS of synthesized SBPClO_4 .

Galvanostatic charge-discharge tests of AC/graphite capacitors were generally performed at the constant current density of 0.1 A g^{-1} between the cutoff voltages of 0 and 3.5 V. In the cases of tracing separate potential profiles of each electrode in an AC/graphite capacitor, a three-electrode cell was employed, in which a heavy activated carbon electrode was added as the quasi-reference electrode (QRE) [29].

2.3. *ex situ* XRD and *in situ* Raman measurements

XRD measurements were carried out using Rigaku MiniFlex 600 X-ray diffractometer equipped with a $\text{Cu-K}\alpha$ (1.542 Å) radiation. The scanning range was from $2\theta = 10^\circ$ to 40° with a speed of 10° per minute at an accelerating voltage of 40 kV and a current flow of 15 mA. *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 reference [30]. 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}).

Unless otherwise specified, all the measurements were performed at the room temperature (ca. 22°C).

3. Results and Discussion

Fig. 2 depicts the potential profiles of graphite positive electrodes and AC negative electrodes versus an AC-QRE during the 1st galvanostatic charge-discharge cycle of AC/graphite capacitors using different electrolyte solutions. The potential gap between each pair of AC and graphite electrodes is equal to the total voltage of corresponding AC/graphite capacitor. Great difference was revealed between capacitors using the EC- solution and those using the PC- or GBL- solutions: smaller specific charge/discharge capacity, lower efficiency and larger IR drop. A close observation tells that all the potential profiles of AC electrodes were almost overlapped, while the potential plateau of graphite electrode in the EC- solution was obviously higher than that in the PC- or GBL- solution. Then, two conclusions can be made according to the results: first, AC/graphite capacitors are an appropriate platform to investigate the intercalation of ClO_4^- into graphite. This is because the adsorption of SBP^+ into pores of AC electrodes demonstrates little discrimination towards these solvents, and consequently, the behavior of ClO_4^- at graphite electrodes is decisive to the performance of the resultant AC/graphite capacitors. Second, EC suppressed the insertion of ClO_4^- into graphite, which was attributed to its stronger interaction with ClO_4^- .

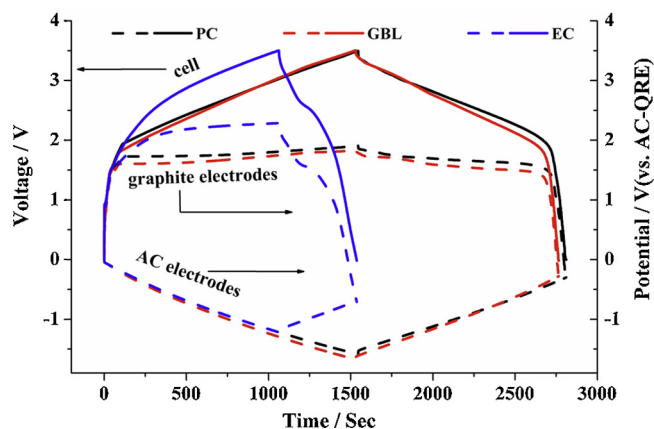


Fig. 2. Potential profiles of graphite positive electrodes and AC negative electrodes vs. AC-QRE in the AC/graphite capacitors using the electrolytes of 1.5 M SBPClO_4 -PC, -GBL and -EC, respectively, during the 1st galvanostatic charge-discharge cycle.

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