

Difluoro(oxalato)borate anion intercalation into graphite electrode from ethylene carbonate



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ABSTRACT

Anion-graphite intercalation compounds are a promising candidate for high-potential positive electrode materials. However, electrochemical anion intercalation into graphite always suffered from the interference of organic solvent in practice. Ethylene carbonate (EC) could suppress the intercalation of some symmetrical anions into graphite like BF_4^- , ClO_4^- and PF_6^- . Herein, the electrochemical intercalation behavior of an anisotropic anion, difluoro(oxalato)borate (DFOB^-) into graphite from pure EC solvent has been studied in activated carbon (AC)/graphite capacitors. Some fundamental electrochemical techniques in conjunction with *in situ* Raman spectroscopy and *ex situ* XRD have been applied to probe the charge storage of EC-solvated anion within graphite electrode. The influence of ambient temperature has been addressed as well. From the comparative studies on the intercalation and de-intercalation processes of EC-solvated DFOB^- and BF_4^- into and from graphite electrodes, the extraction of EC-solvated DFOB^- anion from graphite electrode has been confirmed to be a crucial step dependent on the ambient temperature.

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1. Introduction

The development of human society calls for new electric storage devices. Recently, anion-graphite intercalation compounds (GICs) have been becoming promising candidates for high-potential (5V vs. Li/Li^+) positive electrode materials in some new electric storage devices [1–3]. Accordingly, the electrochemical intercalation behavior of anions from various electrolyte solutions into graphite electrode has drawn much more attention than before in the community of electric energy storage. For instance, the research group at University of Münster has systematically investigated the intercalation of bis(trifluoromethanesulfonyl)imide (TFSI^-) anion into graphite electrodes from ionic liquids [4–6]. In such a case, the electrolyte was free of the organic solvents, and the intercalation pattern of anion appears rather simple in the absence of solvation interference. In contrast, we have encountered at least three types of intercalation modes for solvated BF_4^- [7]. In the subsequent studies on intercalation of PF_6^- and ClO_4^- from different organic solvents, we found that both anion and solvent can profoundly affect the intercalation posture of a solvated anion into graphite electrode [8,9]. Unfortunately, we have grasped little knowledge on anion-solvent interactions within confined space such as the interlayer galleries between graphene layers. It is still a long and winding road to clarify the nature of anion's solvation. At the first sight, complex anions consisting of multiple atoms have a big difference

in chemical structure with the single-atom cations like Li^+ , Na^+ , Mg^{2+} , Zn^{2+} and Al^{3+} . Then the previous understanding on the solvation of these metallic cations doesn't fit with these anions. At the present stage, we can only envisage that some atoms of an anion may be more apt for interacting with solvent molecules. Therefore, many delicate aspects of an anion such as configuration, size and geometry, may play important roles. To shed more lights on this subject, it is necessary to tailor the chemical structure of anions and investigate physical or chemical traits of the corresponding solvated anions.

Until now, we have applied series of *in situ* electrochemical techniques in probing the intercalation processes of BF_4^- , ClO_4^- and PF_6^- from the solvents of ethylene carbonate (EC), gamma-butyrolactone (GBL), and propylene carbonate (PC) [7–9]. All these anions belong to highly symmetrical tetrahedrons or octahedrons composed of only two elements. Moreover, their van der Waals volume values are near (49 \AA^3 for BF_4^- , 54 \AA^3 for ClO_4^- and 69 \AA^3 for PF_6^-). Under such a circumstance, the solvation shell around each anion in the electrolyte solutions can be considered as symmetrically orientated in the three-dimensional space. In contrast, the interlayer spaces between graphene layers of graphite electrode can be rather treated as a nearly two-dimensional environment. Therefore, the transport of these solvated anions from the electrolyte solutions into graphite electrodes must involve some rearrangements of solvent molecules around each anion. Although we have gained some rudimental acquaintance of solvated anions and the corresponding intercalation manners, our understanding on the charge transfer process related to the solvated anions across the solution/electrode interface is still very limited. To further expand the knowledge

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territory of solvated anion-graphite intercalation compounds, less symmetrical anions also need to be taken into account. So we turned to a special anion, difluoro(oxalato)borate (DFOB^-) [10,11], which possesses an anisotropic geometry and a larger van der Waals volume. It also can be considered as a chemical hybrid of BF_4^- and bis(oxalato)borate (BOB^-). Due to its anisotropic configuration, the solvent shell around DFOB^- anion must be asymmetric in the electrolyte solution. Then its solvation features can be effectively modified at least in the solution phase. The consequent responses from its intercalation process into graphite electrode will provide some valuable information on the solvation effect.

In a recent study, we have preliminarily addressed the intercalation processes of DFOB^- into graphite from the mixtures of EC and PC [11]. Similar to the cases of symmetrical anions [7–9,12], the addition of EC also decreases the storage capacity of DFOB^- in graphite electrode. This was ascribed to the solvation of anions by EC. More intriguingly, we have also witnessed that the small capacity can significantly increase at elevated temperatures. At that time, we roughly attributed this fact to the thermal disturbance on the bondage between DFOB^- and EC. In contrast, a more recent study on BF_4^- and ClO_4^- intercalation into graphite electrode from pure EC also demonstrated this activation tendency coming from temperature elevation. The comparison of intercalated gallery height values of charged graphite electrodes strongly supported that EC enters together with BF_4^- or ClO_4^- anions into graphite at the elevated temperature. So the probability of EC co-intercalation with DFOB^- into graphite looks very high. In this study, we applied activated carbon (AC)/graphite capacitors as a reliable platform to investigate this issue in detail. An electrolyte solution based on neat EC solvent was deliberately employed to prevent from doubtful infections of co-solvents. EC-based solutions are likely to take solid state due to its high melting point. Fortunately, the electrolyte salt chosen here, TMADFOB (TMA: tetramethyl ammonium), has such a high solubility in EC that the concentrated electrolyte solutions (say, 1.5M) are in liquid state at room temperature.

We have manifested the combination of *in situ* Raman and *ex situ* XRD a very powerful tool to characterize anion-graphite intercalating compounds, especially in the presence of solvent [7–9]. In connection with more conventional electrochemical methods, they can provide comprehensive clues and improve the understandings deeply. This study attempts to organize different *in situ* and *ex situ* electrochemical techniques in the context of EC- DFOB^- storage within graphite electrode. The interplay of them will stage a kaleidoscopic view on solvated anion-graphite intercalation compounds, promising a family of electric-energy storage materials from now on.

2. Experimental

Electrochemical measurements were generally performed on AC/graphite capacitors. Natural graphite and AC were appointed as the positive and negative electrode materials, respectively. The electrolyte salt of TMADFOB was synthesized as before [11]. EC solutions dissolving 1.5M TMADFOB and 1.5M TEMABF_4 (TEMA: triethylmethyl ammonium) were applied as electrolyte solutions. The details of electrode materials, the fabrication of electrodes and the assembly of capacitors were described in the previous studies [7,11]. Galvano-static charge-discharge tests on AC/graphite capacitors were conducted with CR2032 coin cells. The cutoff voltages were set to 0 and 3.5 V.

Three-electrode cells were also assembled to access the inherent electrochemical traits of single electrodes. Here a quasi-reference electrode (QRE) with an excess amount of AC was introduced. Its validity has been testified in the previous studies [7,13,14].

The measurement procedures of *ex situ* XRD, *in situ* Raman for graphite electrodes were similar to those in the previous reports [7–9]. Unless otherwise specified, all the measurements were carried out at the room temperature near 22 °C.

3. Results and discussion

For many times, AC/graphite capacitors have been successfully applied as a suitable device evaluating electrochemical anion intercalation processes into graphite electrodes. There are at least three advantages for this device. At first, the absence of chemically active metals like lithium or sodium ensures the safety inside the device. Second, main components of the device, including carbon-based electrode materials, Al current collectors, stainless casing, etc., are environmentally benign, and then can be readily disposed and recycled. Third, as pointed out in our recent report [9], the voltage slope of the device is very convenient for accurate electrochemical control on graphite electrodes in the course of *in situ* measurements. This is a quite charming aspect here.

However, a series of total cell voltage values for a capacitor is too concise to comprehensively and directly reflect the respective potential changes at both electrodes. To answer this call, a simple “translation” experiment was performed by introducing an AC-QRE inside the capacitor. Respective potential values of single electrodes (graphite or AC) were separately monitored against the AC-QRE when galvano-static charge-discharge proceeded for the total capacitor. Thus, the series of total cell voltage values could be smoothly translated into two series of respective potential values of electrodes, and then these three series of values were plotted together *versus* time. This technique was first adopted by Morimoto in the research on electric double-layer capacitors [15]. Here we call it as the “galvano-static cell voltage-separate electrode potential (GSCV-SEP) translation”. Fig. 1 mainly compares the GSCV-SEP translation plots of an AC/graphite capacitor using 1.5M TMADFOB-EC at the room and elevated temperatures. The plot for 1.5M TEMABF_4 -EC at room temperature is also included here for better assessment. Similar to that using TMADFOB-EC/PC in the previous study [11], the capacitor using TMADFOB-EC delivers low charge-discharge capacities at 22 °C (discharge capacity is less than 20 mAh g^{-1} for graphite), whereas the capacities significantly increase at 45 °C (discharge capacity reaches about 30 mAh g^{-1} for graphite). Moreover, the potential profiles of the graphite positive electrode in the capacitor using TMADFOB-EC at 22 °C exhibit a drastic gap between the charge and discharge branches. This easily reminds of those analogous potential profiles of graphite electrodes in the cases of ClO_4^- or PF_6^- EC at room temperature [8,9], which is characteristic of the failure in smooth intercalation of anions into graphite's crystal lattice. With the rise in temperature, the charge-discharge potential plateaus of graphite electrodes in TMADFOB-EC approach each other and thus the polarization shrinks remarkably. Especially, the potential plateau in the discharge branch perches an apparently higher level, even on the top of the discharge potential plateau of graphite electrode in TEMABF_4 -EC. This fact means that the movement of DFOB^- anion inside graphite

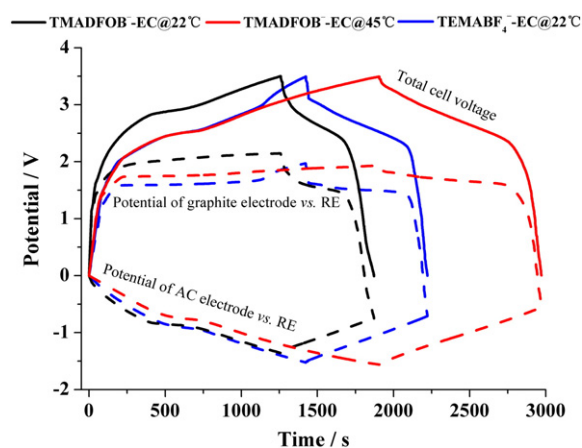


Fig. 1. GSCV-SEP translation plots of the AC/graphite capacitors using the EC solutions at 22 and 45 °C.

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