Enhanced performance of natural graphite in Li-ion battery by oxalatoborate coating

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Abstract

We report an effect of surface modification on the performance of natural graphite in Li-ion battery. A graphite electrode was treated with a mixed solution of H_3BO_3 and $H_2C_2O_4$ (2:3 molar ratio) in methanol, followed by condensation at 100–110 °C under vacuum. The above treatments result in formation of oxalatoborate coating on the graphite surface. It is shown that the resulting coating can effectively increase reversibility of the initial forming cycle of Li/graphite half-cell. More interestingly, such a coating significantly suppresses self-delithiation of the lithiated graphite, which hence increases the storage performance of Li-ion battery, especially at elevated temperatures. With progressive cycling, the coated graphite shows excellent capacity retention while the control one starts fast capacity fading from around 70th cycle.
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1. Introduction

Graphite has been chosen as a standard anode material of Li-ion batteries due to high capacity (339 mAh/g) and low potential (0.1–0.3 V versus Li^+/Li) of its lithium intercalation compound (Li_xC_6, $x = 1$). Reversible intercalation and deintercalation of Li^+ ions with graphite are attributed to successful formation of a stable and protecting solid electrolyte interphase (SEI) on graphite surface, which is known to complete in initial few cycles [1,2]. Previous studies have shown that initial reversibility of graphite is greatly affected by electrolyte composition, morphology and chemistry of graphite surface [3,4]. Therefore, a number of papers previously focused on improving initial reversibility of graphite either by modifying the surface of natural graphite [5–7] or by introducing functional additive into electrolyte solution [8–12]. Surface modification is a process that coats a protecting layer onto the graphite surface [5–7]. It is believed that the resulting coating either incorporates to form a more stable SEI or deactivates catalytic effects of the fresh graphite surface on the electrochemical reduction of electrolyte solvents. Functional additives are a variety of electrochemically active compounds, such as SO_2 [8],

ethylene sulfite [9], vinylene carbonate (VC) [10,11], and acrylonitrile [12], which are usually reduced at slightly higher potential than the major electrolyte solvent and the resulting products assist forming a more stable SEI.

Some of electrochemically inert boron compounds, such as B_2O_3 [13] and organic borates [14,15], have been studied as an electrolyte additive to improve formation of the SEI. It is speculated that such compounds can be incorporated to form a more stable SEI. It has proven that addition of boron-based compounds into the electrolyte could significantly improve cycling stability of Li-ion batteries while with little impact on the initial reversibility [13–15]. Meanwhile, different sources [16–18] have shown that the cycling stability of Li-ion batteries can be greatly improved when a boron-based anion receptor is a co-solvent of the electrolyte. On the other hand, we have found that lithium bis (oxalato) borate (LiBOB), a boron-based lithium salt, not only enables natural graphite to be cycled reversibly in pure propylene carbonate [19] but also significantly enhances cycling stability of Li-ion battery at elevated temperature [20]. X-ray photoelectron spectroscopy (XPS) analysis showed that the resulting SEI comprises a variety of oxalatoborate moieties, which are originated from a single-electron reduction of LiBOB [21]. We believe that enhanced stability of the SEI is associated with chemistry of the oxalatoborate moieties and that the presence of oxalatoborate-like compounds facilitates forming a more stable SEI. Therefore, in

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this work we report the use of the oxaltoborate-like compound to treat the graphite surface, instead of adding it to the electrolyte solution.

2. Experimental

The electrolyte used was a 1.0 m $LiBF_4$ solution in a 1:1:3 (wt.) mixture of propylene carbonate (PC), ethylene carbonate (EC) and ethyl methyl carbonate (EMC). The water content of the electrolyte was determined to be 10–15 ppm by Karl–Fisher titration. Natural graphite (99%, 300 mesh, Alfa Aesar) was coated onto a copper foil by using 5 wt.% of poly(acrylonitrile–methyl methacrylate) (AMMA, AN/MMA = 94 : 6) as binder and N-methyl pyrrolidinone as solvent [22]. The loading of the electrodes was about 1.2 mAh/cm^2. The graphite electrode was treated with a mixed solution of 0.02 M H_3BO_3 and 0.03 M $H_2C_2O_4$ in methanol as follows. The electrode was dipped into the solution and immediately taken out of the solution. After drying at room temperature in air, the electrode was calendared between two rollers to make good contact for the graphite particles. For comparison, an electrode without H_3BO_3–$H_2C_2O_4$ treatment also was calendared under the same conditions. Both electrodes with and without treatment

A Tenney Environmental Oven Series 942 was used to provide a constant temperature environment for cell storage tests. A Maccor Series 4000 tester was used to cycle the cells. Unless otherwise specified, the cells were cycled between 1.0 and 0.002 V at 0.5 mA/cm^2 with discharge being tapered to 0.1 mA/cm^2 at 0.002 V.

3. Results and discussion

3.1. Preparation of the oxalatoborate coating

In previous work [19,21], we have found that LiBOB can be easily synthesized with high yield (∼95%) by heating a stoichiometric mixture of H_3BO_3, $H_2C_2O_4$, and $LiHC_2O_4$ at ∼100 °C under vacuum for a few hours. We consider that the drying conditions described in the experimental section are enough to make intermolecular condensation (dehydration) between H_3BO_3 and $H_2C_2O_4$. Due to the multifunctional groups of reactants, the resulting products of the condensation are complicated. The most likely products are these two compounds with structure (I) and (II), in which compound (II) is a crosslinked polymer with low molecular weight. Upon extended heating under vacuum, oxalatoborate may randomly lose CO and CO_2 to form –B–O–B– bonds, typically those compounds, such as (III) and (IV).

(I)

(II)

(III)

(IV)
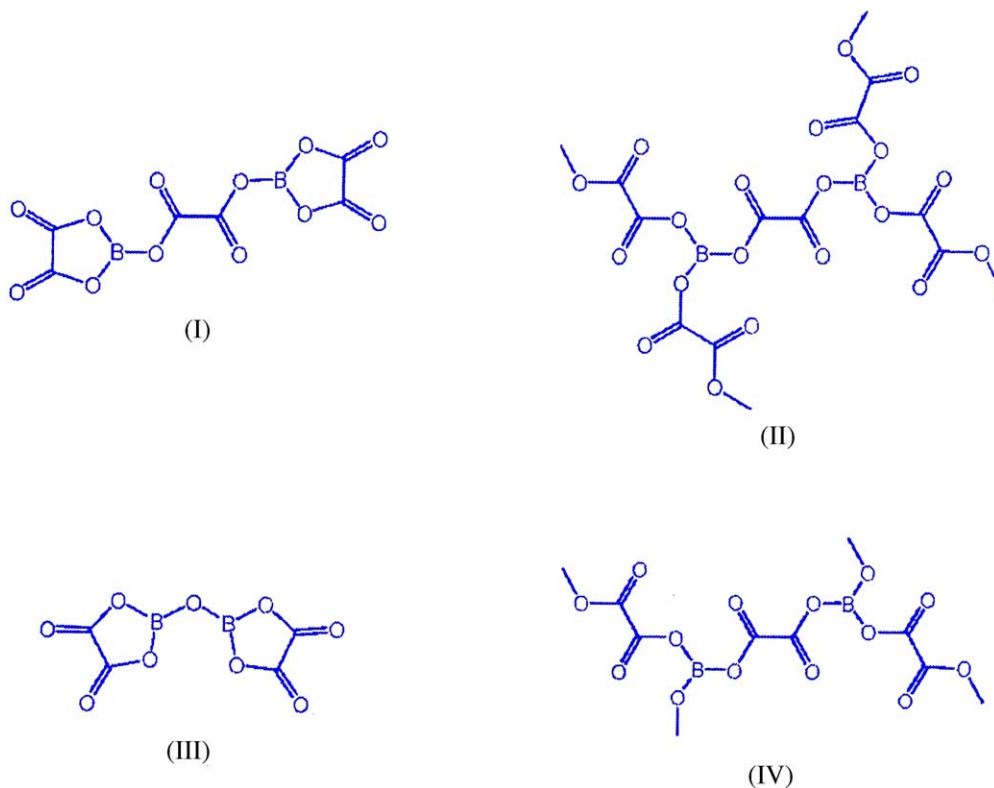
were punched into small discs with an area of 1.27 cm^2 and dried at 100–110 °C under vacuum for 16 h. Li/graphite button cells were assembled using Celgard separator and filled with 150 μl electrolyte in an argon-filled glove-box.

All the above compounds are rarely soluble in organic solvents and remain as a protecting layer, called an oxalatoborate coating hereafter, on the graphite surface while being in contact with liquid electrolyte. It has been reported [23] that the morphology and chemistry of the graphite surface
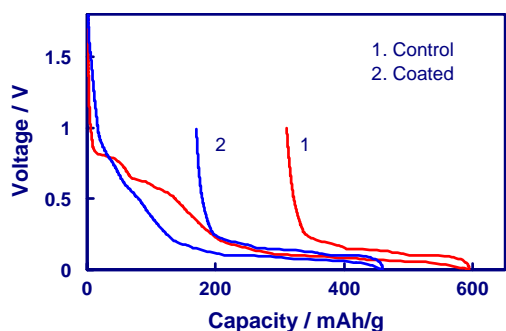
Fig. 1. Voltage-capacity plot of graphite in the first cycle, which was recorded at 0.1 mA/cm^2.

are inhomogeneous, and that active areas such as catalytic sites and edge planes are most responsible for reduction of the electrolyte solvents during the initial interaction of Li$^+$ ions with the graphite. In general, active areas have relatively higher affinity for the adsorbate molecules. Therefore, we consider that the oxalatoborate coating is predominantly formed on these active sites of the graphite surface.

3.2. Formation of the SEI

Fig. 1 compares cycling performance of graphite in the first cycle. It is shown that the irreversibility above 0.3 V, which reflects solvent reduction and its related SEI formation, is greatly reduced by oxalatoborate coating. Cycling efficiency of graphite with and without oxalatoborate coating is estimated to be 63 and 48%, respectively. To observe the voltage regions of various electrochemical steps, we plot differential capacity versus voltage of the Li/graphite half-cell in Fig. 2. It is shown that oxalatoborate coating effectively reduces differential capacities around 0.6 and 0.8 V (Fig. 2a) while it has little impact on those below 0.30 V (Fig. 2b). This observation indicates that solvent reduction above 0.3 V has been effectively suppressed by the oxalatoborate coating. According to our previous study [2], most of the products of solvent reduction above 0.3 V are either soluble in organic electrolyte or form a loose and highly resistive SEI. Such a SEI cannot withstand high temperatures and is unable to protect the solvent from electrochemical reduction. However, its presence affects stability of the compact and protecting SEI, which is subsequently formed below 0.3 V where intercalation of Li$^+$ ion into graphite is undergone. Therefore, we consider that the SEI formed in the presence of oxalatoborate coating is more stable. It should be mentioned that even for the oxalatoborate-coated graphite, its initial efficiency is only 63%, which is too low to be feasible in practical Li-ion batteries. To evaluate the effectiveness of oxalatoborate in reducing initial irreversibility, we examined the effect of 2 wt.% vinylene carbonate (VC), which is known to be one of the most effective electrolyte additives in Li-ion batteries [10,11], on the same electrolyte and graphite. We found that the initial efficiency of the graphite improved by VC additive and oxalatoborate coating, respectively, was
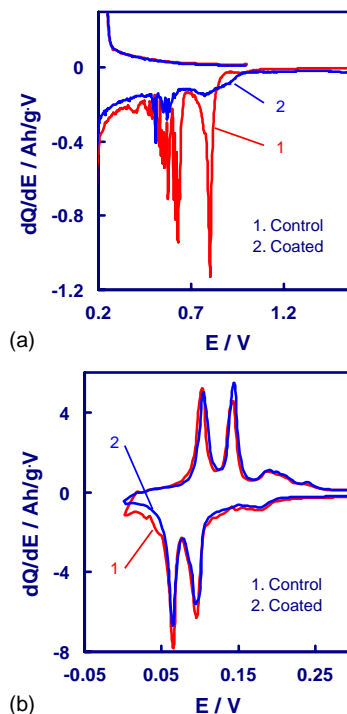

Fig. 2. Plot of differential capacity vs. voltage of Li/graphite half-cell, which was recorded at 0.1 mA/cm^2 in the first cycle: (a) from OCV to 0.2 V; (b) from 0.3 to 0.002 V.

very similar. This means that improving efficiency of the electrolyte additive and surface coating greatly depends on properties of graphite and electrolyte. Improving efficiency can be achieved only when applied to an appropriate combination of graphite and electrolyte.

3.3. Enhancement of storage performance by oxalatoborate coating

Fig. 3 shows self-delithiation of the fully lithiated graphite at 45 °C. After a 48-day storage, the open-circuit voltage (OCV) of the graphite without coating was increased to 0.64 V through three major stages characterized by the voltage regions of ~0.09, 0.12–0.13, and >0.13 V, while OCV of the oxalatoborate-coated one remained at 0.12 V (at begin-
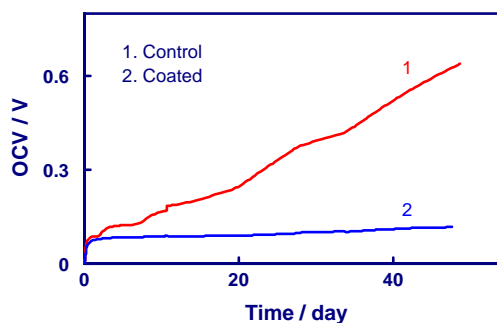

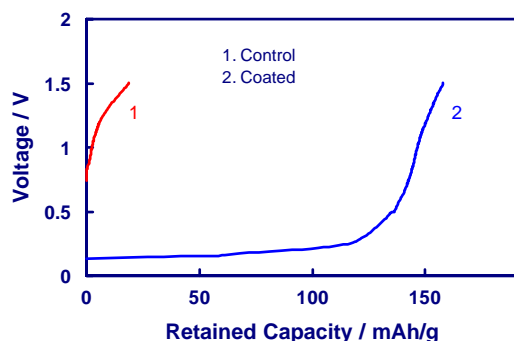Fig. 3. Self-delithiation of fully lithiated graphite with and without oxalatoborate coating at 45 °C.

Fig. 4. Retained capacity of Li/graphite cells with and without oxalatoborate coating after 48-day storage at 45 °C.

ning of the second stage). There is a good corresponding correlation of the voltage plateaus between the self-delithiation and a normal delithiation, as indicated by the peaks of differential capacities in Fig. 2b. Therefore, the observed increase in the OCV can be described by this reaction:

$$\text{Li}_x\text{C}_6 \rightarrow \text{Li}_{x-\delta}\text{C}_6 + \delta\text{Li}^+ + \delta e^- \qquad (1)$$

Immediately after storage test, we measured capacity retention of the Li/graphite half-cells by delithiating (charging) them to 1.5 V. Fig. 4 compares the retained capacity of the cells after 48-day storage at 45 °C. We see that the oxalatoborate-coated graphite retained 158 mAh/g capacity (corresponding to 68% of the original capacity), while the control cell only 19 mAh/g (~8%). Subsequent cycling showed that most of the capacity loss suffered during the storage is recoverable. We have found that the recoverable capacity loss mainly relates to a local reduction–oxidization process of the graphite electrode, and self-delithiation greatly depends on the SEI [24]. Results in Figs. 3 and 4 clearly show that the SEI formed with oxalatoborate can better protect the lithiated graphite from self-delithiation.

There are two possibilities, which are associated with enhanced stability of the SEI by the oxalatoborate coating. The one is that it participates in the chemistry of the SEI, and the other possibility is that it improves the morphology of the SEI. In our early work [19], we have found that natural graphite can be cycled very well in pure propylene carbonate when LiBOB is used as an electrolyte salt. This merit is ascribed to LiBOB incorporation to form a more stable SEI. XPS analysis indicates that the chemistry of such a SEI mainly is a variety of oxalatoborate moieties, predominantly those with a structure of (I) and (II) [21]. In a similar manner, we speculate that the pre-existing oxalatoborate on the graphite surface can participate in the chemistry of the SEI, which enhances the stability of the SEI. On the other hand, it has been reported that instability of the SEI formed in LiBF$_4$-based electrolytes is related to the presence of many isolated LiF crystals since LiF does not form an SEI [25]. We believe that the strong electron-receiving feature of the five-member-ring oxalatoborate, as shown in structures (I) and (III), makes it possible to reduce or eliminate the LiF

crystals. That is, it reacts with LiF to form a new salt by this reaction:

$$(2)$$
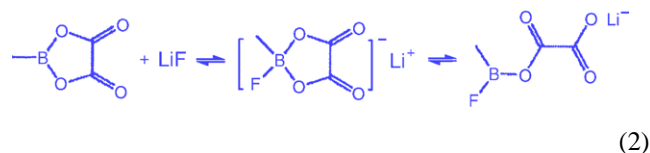
The resulting salt can participate in the formation of the SEI due to its similar structure with the pre-existing oxalatoborate. The above explanation can be supported by previous literature [16–18], which reported that boron-based anion receptors could enhance thermal stability and cyclability of Li-ion batteries due to their ability of dissolving LiF when they were used as a co-solvent of the electrolyte.

3.4. Effect of oxalatoborate coating on cycling performance

After 45 °C-storage test, the cells were cycled at room temperature. Fig. 5 plots dilithiation capacities as a function of the cycle number. Initially, these two cells had similar capacities (260–280 mAh/g). With progressive cycling, the oxalatoborate-coated one showed excellent capacity retention while the control one started a rapid capacity fading around 70th cycle. Because all conditions are identical in these two cells, the phenomena observed above can be entirely ascribed to the difference in stability of the SEI, which can be explained in terms of its chemistry. As discussed above, the chemistry of the SEI formed on the coated graphite surface is dominated by oxalatoborate-like compounds, while that formed in a EC-based electrolyte is mainly composed of semicarbonates, such as (CH$_2$CH$_2$OCO$_2$Li)$_2$ and (CH$_2$OCO$_2$Li)$_2$ [23,25]. Semicarbonates are known to be metastable, and may be transformed more stable Li$_2$CO$_3$ during storage or cycling by consuming Li$^+$ ions, for example:

$$(\text{CH}_2\text{OCO}_2\text{Li})_2 + 2\text{Li}^+ + 2e^- \rightarrow 2\text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4 \qquad (3)$$
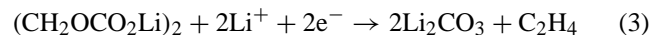
In order to compensate the transformation from semicarbonates to less protecting Li$_2$CO$_3$, additional formation of the
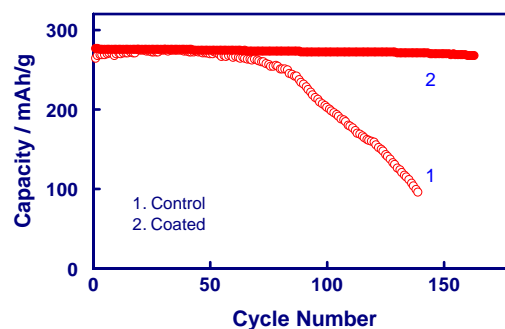

Fig. 5. Cycling performance of Li/graphite cells with and without oxalatoborate coating after 48-day storage at 45 °C.

SEI is needed, which not only consumes Li^+ ions but also increases the resistance of the SEI. All these factors accelerate capacity fading of the cell.

4. Conclusions

Oxalatoborate can be easily coated onto the graphite surface by wetting electrodes with a mixed solution of H_3BO_3 and $H_2C_2O_4$ (in 2:3 molar ratio) in methanol and then condensing (dehydrating) at $\sim$100 °C under vacuum. The resulting oxalatoborate coating can effectively increase reversibility in the formation of SEI. It is speculated that the pre-existing oxalatoborate incorporates to form a more stable SEI. Due to insolubility and excellent stability of the oxalatoborate-based SEI, the treated graphite exhibits lower self-delithiation in storage and excellent capacity retention in progressive cycling.

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