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Effect of covalently bonded polysiloxane multilayers on the electrochemical behavior of graphite electrode in lithium ion batteries

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Abstract

Polysiloxane multilayers were covalently bonded to the surface of natural graphite particles *via* diazonium chemistry and silylation reaction. The as-prepared graphite exhibited excellent discharge–charge behavior as negative electrode materials in lithium ion batteries. The improvement in the electrochemical performance of the graphite electrodes was attributed to the formation of a stable and flexible passive film on their surfaces. It was also revealed that the chemical compositions of the multilayers exerted influence on the electrochemical behavior of the graphite electrodes. The result of this study presents a new strategy to the formation of elastic and strong passive film on the graphite electrode *via* molecular design. Owing to the diversity of polysilxoane multilayers, this method also enables researchers to control the surface chemistries of carbonaceous materials with flexibility.

Keywords: Polysiloxane multilayers; Covalently bonded; Diazonium chemistry; Silylation reaction; Negative electrode; Lithium ion batteries

1. Introduction

It is well-known that surface modification of natural graphite is an effective strategy to improve their electrochemical performance in lithium ion batteries [1]. In particular, the irreversible capacity losses associated with the formation of the solid electrolyte interface (SEI) film on graphite electrodes can be considerably reduced after such treatment. However, the cycling life of a natural graphite electrode is still limited by the volume change of graphite particles during lithium intercalation–deintercalation process [2]. The mechanism responsible for this phenomenon is that the SEI film formed on graphite surface is usually inhomogeneous and fragile, which cannot accommodate the expansion and contraction of graphite particles during discharge–charge cycling [3,4]. It is concluded that, therefore, a flexible SEI film that strongly bonded to graphite particle is necessary for the good performance of graphite electrode. Much effort had been devoted to achieve this goal, and some examples of these attempts included surface modification of natural graphite [5,6] and introduction of additives to electrolytes [7].

Recently, modifying carbon surface with silanes was found to reduce the irreversible capacity losses of carbon electrode to some extent [8,9], which made this method a valuable tool in lithium ion batteries [10,11]. However, an effective silylation of carbon surface needs anchoring sites such as carboxyl and hydroxyl groups for silanes. Therefore this method becomes little practical use in the case of nature graphite because the amount of functionalities on their surface is very limited.

In our previous work [12], aromatic multilayers of 4-benzoic acid had been covalently attached to the surface of natural graphite particles *via* the reduction of corresponding diazonium salt, and the resulting graphite electrodes showed improved electrochemical properties. Inspired by these results, we report here to modify the surface of graphite particles with polysiloxane multilayers. The rationale of this method involves the initial formation of 4-benzoic acid multilayers that bonded to the graphite surface by means of diazonium chemistry [13], and followed reaction with siloxane to form polysiloxane layer (Scheme 1).

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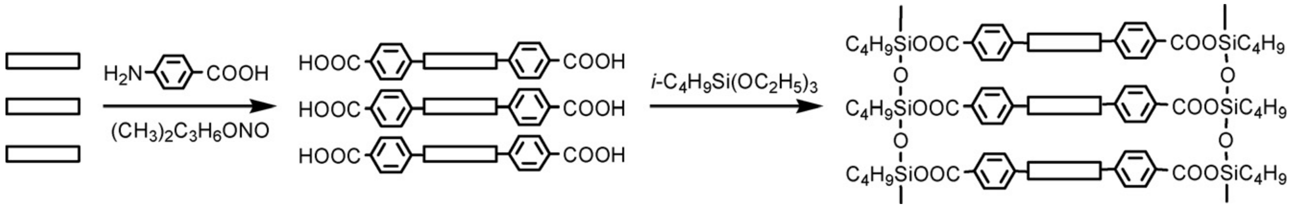

Scheme 1. Schematic illustration for the formation of polysiloxane multilayers on graphite surface.

The tethered polysiloxane multilayers cannot only change the electroactivity of graphite surface but also contribute to the formation of a robust SEI film on graphite electrode. As the initial trial, isobutyltriethoxysilane (C4TES) is chosen to coat the surface of natural graphite particles in consideration of the protective characteristics of the alkyl-terminated group. We demonstrate here that the polysiloxane-coated natural graphite possess excellent electrochemical performance, which shows not only high reversible capacity but also good capacity retention.

2. Experimental

The natural graphite powder used in this study was obtained from Nanshu Graphite Co. (Shandong province, PR China). The mean particle size and Brunauer–Emmett–Teller (BET) surface area of the natural graphite are 11.1 μm and $17.5\,\mathrm{m^2\,g^{-1}}$, respectively. Before use, the natural graphite powder was washed with 1.0 M HCl at 50 °C for 2 h, then filtered and rinsed with water, and dried under vacuum at 100 °C.

X-ray photoelectron spectroscopy (XPS, ESCALAB2020IXL) measurements were performed in an ultrahigh vacuum (UHV, 2.5×10^{-10} Torr base pressure) with the use of a monochromatic Al Kα source (1486.6 eV). Scanning probe microscope (SPM, Solver P47, NT-DMT) was used to investigate the surface of the graphite samples.

4-Aminobenzoic acid (99.5%, Shangpu Chemical Company Ltd., Shanghai, China), isoamyl nitrite ($\geq$90%, Qianjin Chemical Company, Shanghai, China) and isobutyltriethoxysilane (95%, Wuhan Droer Chemical Industry Co. Ltd., Wuhan, China) were used as-received.

In a typical experiment, 1 g of natural graphite powder was added to 5 ml of anhydrous CH_3CN solution contained 4-aminobenzoic acid (0.5 g) in a nitrogen-filled flask. Later, 1 ml of isoamyl nitrite was added dropwise with a syringe under vigorous stirring. The mixture was kept stirring at room temperature for 12 h. After reaction, the mixture was filtered and washed with ethanol by sonication until the filtration became colorless, and the solid was dried under vacuum at 100 °C.

After chemical grafting, the graphite powder was added into a 50 mM acetone solution of isobutyltriethoxysilane [$C_4H_9Si(OC_2H_5)_3$, C4TES] at room temperature for 4 h under a dry atmosphere. Once filtrated with acetone, the solid was treated with 10 mM H_2O solution in acetone for 10 min at room temperature and then rinsed in CH_3CN for a few minutes to form polymer film. Finally, the coated graphite was filtered and dried under vacuum.

Graphite electrodes were prepared using polyvinylidene fluoride (PVDF) as binder and *N*-methyl pyrolidinone (NMP) as solvent. A mixture of graphite powder, PVDF (9:1 w/w) and NMP was mixed by stirring for 30 min. The slurry was coated onto a copper foil to a thickness of 200 μm. The solvent was removed by baking at 90 °C under vacuum.

The rolled electrodes film was cut into $1\,\mathrm{cm^2}$ circle plates as the negative electrodes. The cathode was lithium metal foil. The electrolyte solution was 1.0 M $LiPF_6$ (99.5%, Bike Battery Company, Shenzhen, China) dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 v/v). The water content in the electrolyte was lower than 2 ppm. Coin cells were assembled in a glove-box under argon atmosphere. The electrochemical performances of cells were evaluated by galvanostatic discharge/charge measurement using a computer-controlled battery tester (Neware, Shenzhen, China), corresponding to a rate of C/10 ($1\,\mathrm{C} = 372\,\mathrm{mA\,g^{-1}}$) between 0.010 and 1.5 V. Cyclic voltammograms (CV) and electrochemical impedance spectrum (EIS) measurements were carried out using a CHI604 potentiostat. Impedance spectra were potentiostatically measured by applying an ac voltage of 5 mV amplitude over the frequency range 10 kHz to 10 mHz after the electrode had attained equilibrium at each potential. All the potentials indicated here were refereed to the Li/Li^+ electrode potential.

3. Results and discussion

3.1. Characterization of polysiloxane multilayers

The presence of benzoic acid and polysiloxane groups on the graphite surfaces is first verified by XPS analysis, as illustrated in Fig. 1. After initial diazonium reaction, there are two peaks center at 286.3 and 289.6 eV in the C1s spectrum (Fig. 1b), which can be assigned to the carbon atoms of aromatic ring and carboxylic group, respectively. The spectrum of O1s also shows two peaks (Fig. 1c). The peak at 532.2 eV is related to the oxygen of C=O in a carboxylic group and that at 533.3 eV is associated with the oxygen of OH of a carboxylic group. This result indicates the presence of benzoic acid groups on the graphite surface.

After silylation reaction, the XPS spectra in Fig. 1d display two new peaks at 103.5 and 154.1 eV. The first peak located at 103.5 eV is attributed to the Si 2p signal of Si–O–Si and that at 154.7 eV is related to the Si 1s peak of Si–O–Si (Fig. 1e). Meanwhile, the O 1s spectrum in Fig. 1f shows a peak at 531.6 eV, indicating the presence of the oxygen of Si–O–Si group. The observation above confirms that a layer of polysiloxane is coated

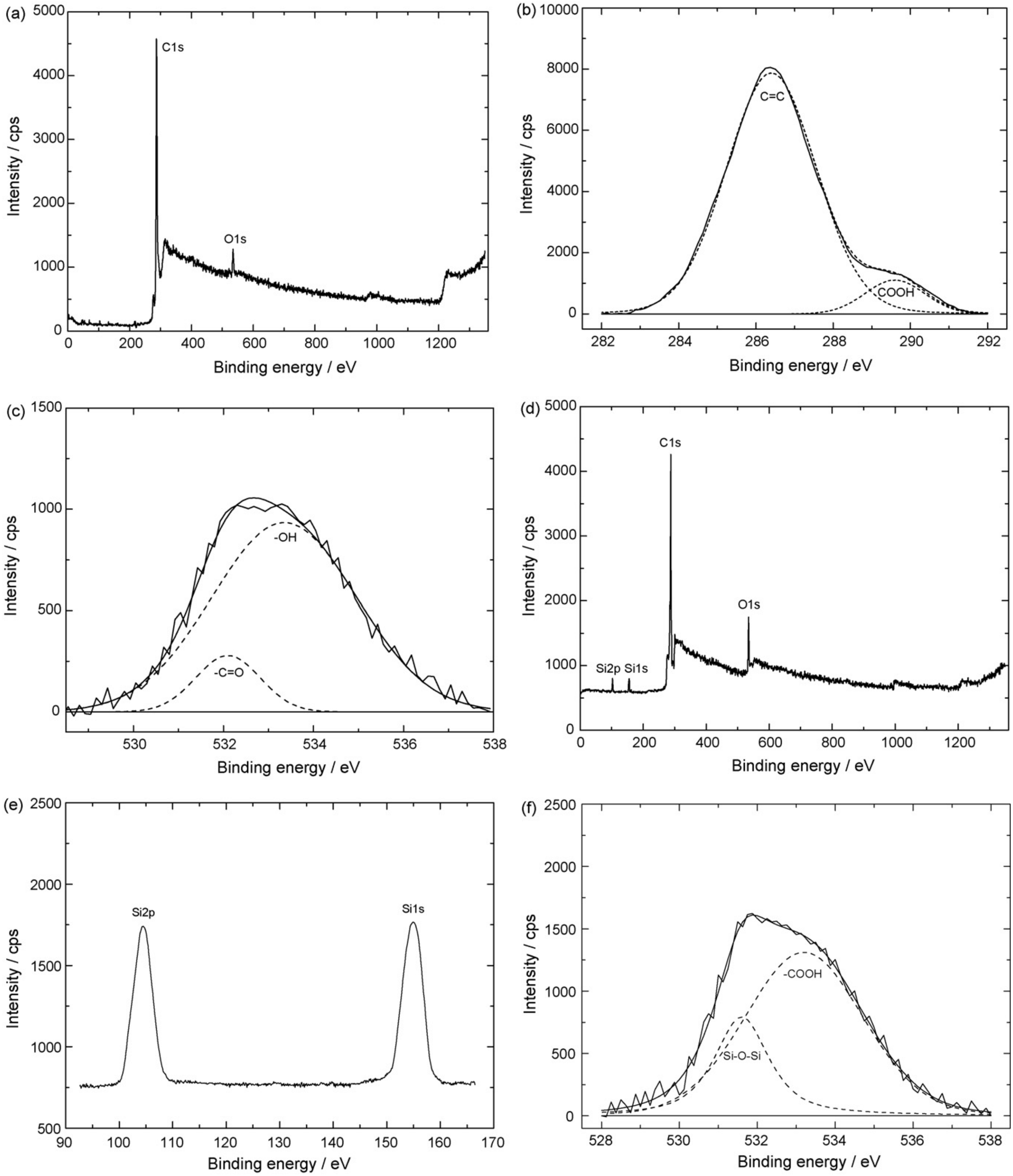

Fig. 1. XPS spectra of the benzoic acid (a, b, c) and polysiloxane (d, e, f) modified graphite samples. Wide scan (a, d). High resolution scans in the carbon region (b), the oxygen region (c, f), and the silicon region (e).

on the graphite surface *via* initial diazonium and subsequent silylation reactions. The fitting result of O1s spectrum also implies that only part of carboxylic groups react with isobutyltriethoxysilane to form polysiloxane, as evidenced by the strong O 1s peak at 533.2 eV in Fig. 1f.

Direct observation of the benzoic acid and polysiloxane layers on the graphite surface is demonstrated by scanning probe microscope (SPM), as shown in Fig. 2. After the graphite reacted with 4-benzoic acid, the SPM images show that their surfaces have changed. Bright spots appear on the images and these spots

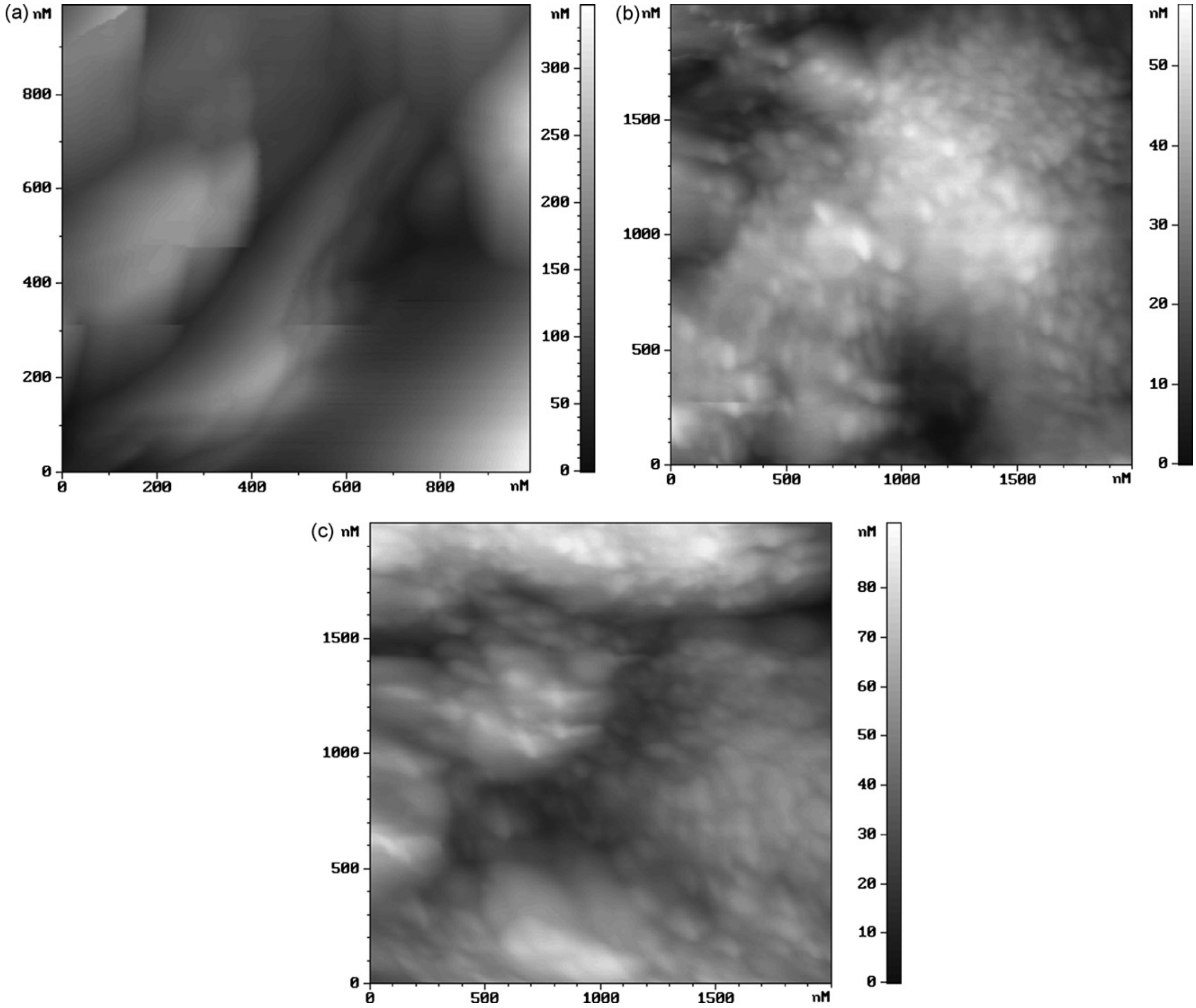

Fig. 2. Scanning probe microscopy images of the pristine (a), benzoic acid (b) and polysiloxane (c) modified graphite samples.

coalesce into a compact and continuous film, which correspond to the deposition of an organic layer with thickness about 10 nm. Meanwhile, the edges of the graphene planes become blurry. After further treatment with isobutyltriethoxysilane, an increase in the surface roughness and the diameter of the spots is observed in Fig. 2c, indicating that a thicker film forms on the graphite surface. The thicker film is considered to arise from the reaction between benzoic acid and isobutyltriethoxysilane. On the contrary, the SPM image of the pristine graphite displays flat platelets with distinct edges.

Based on the above results, the nanoparticles on the graphite surface after diazonium and silylation reactions can be ascribed to the existence of benzoic acid and polysiloxane moieties, and the diameters of the particles indicate that the organic films are thicker than a monolayer. The films can resist vigorous ultrasonic rinsing; which leads us to conclude that the multilayers are strongly attached to the graphite surface *via* covalent bonds under these conditions. As illustrated by SPM images, the bright spots distribute across the graphite surface, implying that the attachment of organic moieties has taken place almost everywhere, albeit with different thickness.

The formation mechanism of benzoic acid multilayers on the graphite surface involves the attachment of initial aromatic layer and subsequent growth process. At first, the atomic scale defects such as atomic vacancies, sp^2 hybridized carbon atoms and unoccupied sp^2 sites pre-exist on the plane are responsible for the formation of a covalent bond with the aryldiazonium [14,15], leading to the attachment of initial aromatic layer [16]. Another possibility resulted in film formation is azo coupling of diazonium cation with surface functionalities such as phenolic, carboxyl and carbonyl groups. The phenolic groups may undergo a coupling reaction with diazonium cations to form the initial layer of azo derivatives on graphite [17,18]. After an initial aromatic layer formed, then, the subsequently generated radical will attack an attached phenyl ring to form multilayers [19,20].

3.2. Electrochemical properties of the polysiloxane-coated graphite

Preliminary electrochemical evaluations of the polysiloxane-coated graphite in lithium ion batteries were carried out by galvanostatic discharge–charge measurement and cyclic voltam-

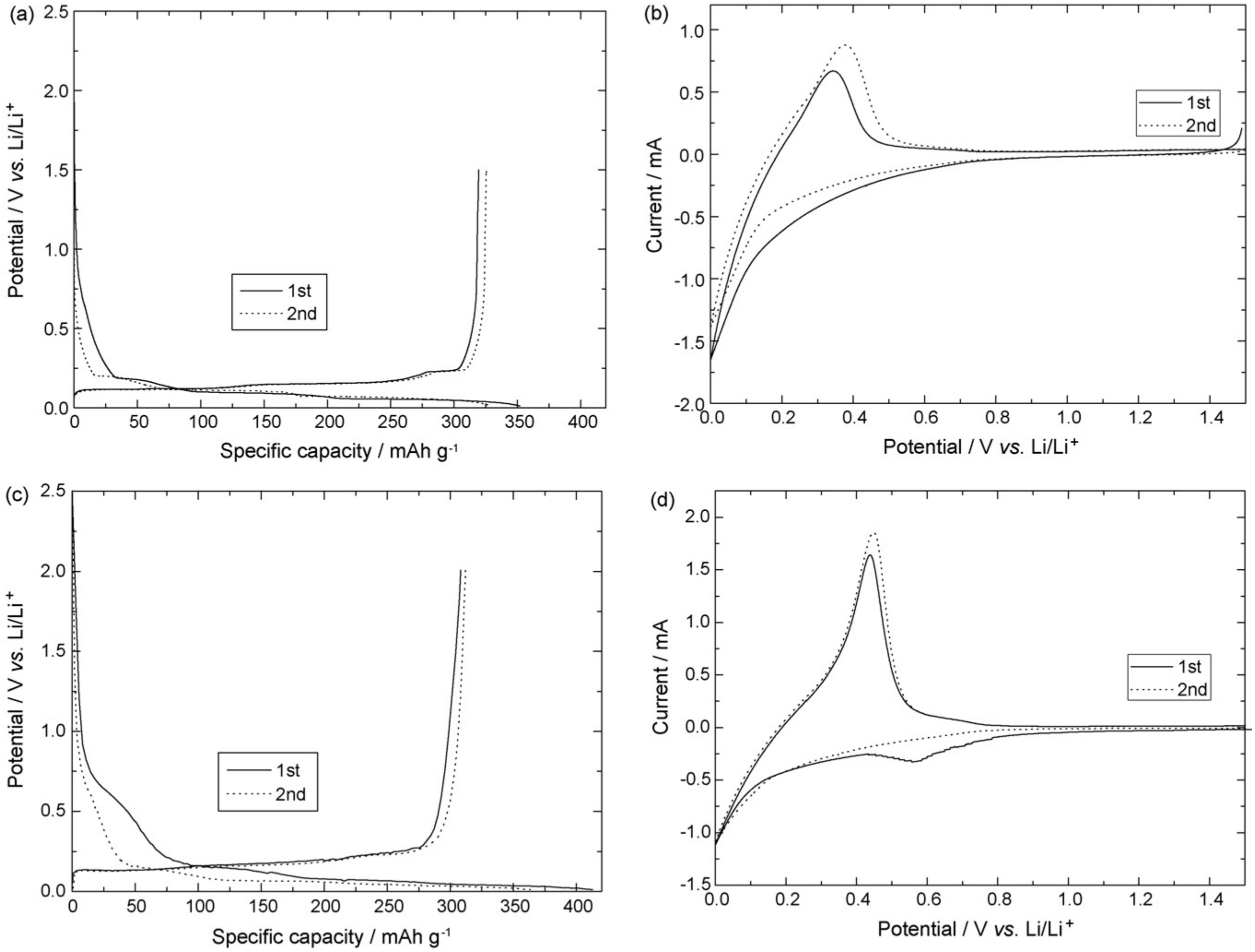

Fig. 3. Initial two discharge-charge plots and cyclic voltammograms of the pristine (a, b) and polysiloxane modified (c, d) graphite electrodes in 1.0 M $LiPF_6$ in EC/DMC (1: 1 by volume). Scan rate: 0.5 mV s^{-1}. Current density: 0.10 mA cm^{-2}.

metry, as shown in Fig. 3. For the purpose of comparison, the same electrochemical tests were also conducted on the pristine graphite. It can be seem in Fig. 3a that the initial intercalation capacity for the modified graphite electrodes is larger than 350 mAh g^{-1}, while their deintercalation capacity is about 308 mAh g^{-1}. The initial coulombic efficiency of the electrodes is estimated to exceed 90.5%. On the contrary, the deintercalation capacity and initial efficiency for the pristine graphite are about 308 mAh g^{-1} and 74.6%, respectively (Fig. 3c). More interestingly, the cyclic voltammograms (CVs) in Fig. 3b do not show any cathodic peak attributed to the electrolyte decomposition and subsequent SEI formation at the first sweep, which forms a contrast to the CVs of the pristine graphite (Fig. 3d). However, the sharp anodic and cathodic waves of the modified graphite imply that the polysiloxane multilayers have no adverse impact on the intercalation and deintercalation process of lithium ion in the graphite.

The improved initial coulombic efficiency of the modified graphite is due to the introduction of the polysiloxane multilayers that chemically bonded to the graphite surface. At first, the acidic functional groups such as –COOH, –OH as well as detrimental water impurities on the pristine graphite surface can be consumed by the reaction with isobutyltriethoxysilane. The polysiloxane multilayers also effectively reduce the exposed edges surface to the electrolytes and thus suppressing the decomposition of electrolyte components during the initial lithium intercalation process. Consequently, the irreversible capacity related to the formation of the SEI film reduces significantly. It should be noted that the reversible capacity increases after surface modification of the graphite. The higher reversible capacity of the modified graphite is considered to be due to a thinner SEI film forms on the graphite surface, as evidenced by the lower irreversible capacity loss during the first cycle. The thinner SEI film indicates a lower resistance between graphite particles and an increased utilization of active materials.

The modified graphite also displays good cycling performance and the capacity as a function of cycling numbers is shown in Fig. 4. It is evident that the modified graphite electrode shows better cyclability and higher reversible capacity than those of the pristine graphite. The electrode is able to keep a stable capacity of 324 mAh g^{-1} after 20th cycle. These results indicate that the polysiloxane modified graphite electrode is a promising candidate as negative electrode in lithium ion batteries. To understand the origin for this improvement in cyclability of the

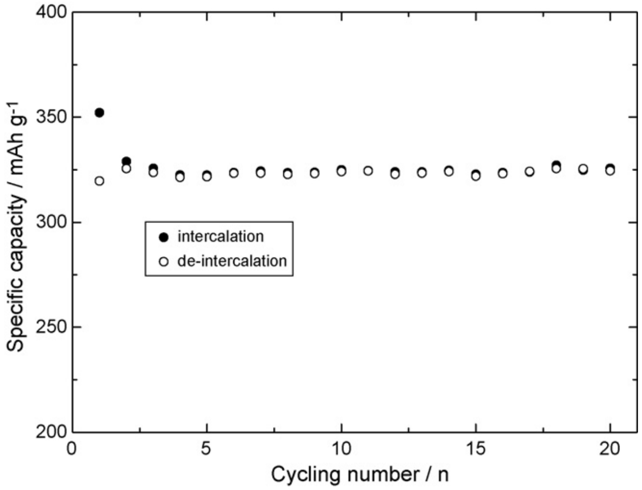

Fig. 4. Capacity as a function of cycling number of the polysiloxane multilayers coated graphite electrode in 1 M $LiPF_6$ in EC/DMC (1: 1). Current density: 0.10 mA cm^{-2}.

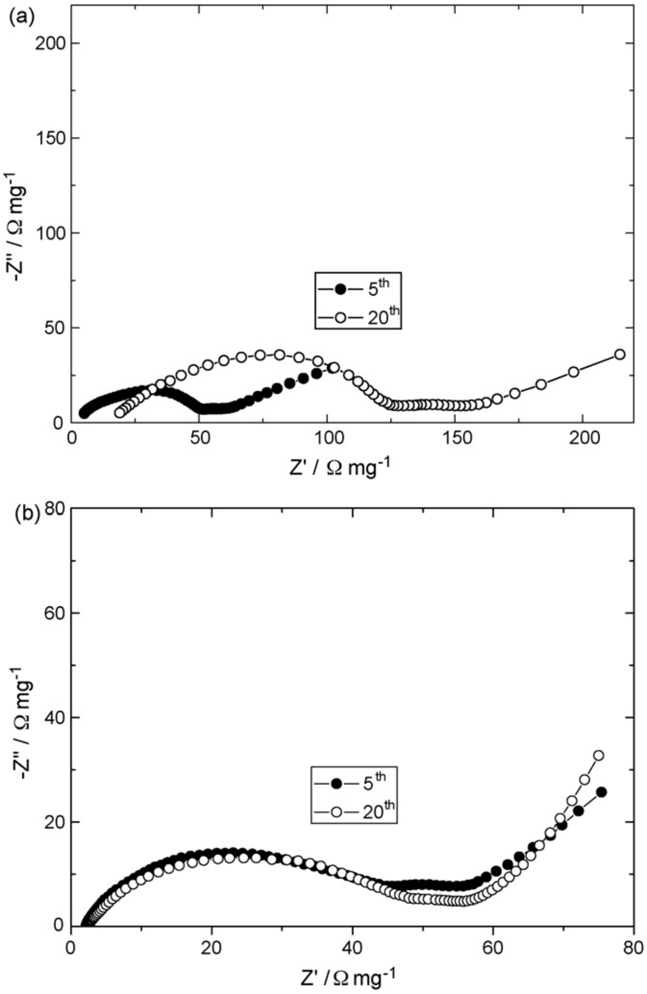

Fig. 5. Impedance spectra of the pristine (a) and polysiloxane modified (b) graphite electrodes after 5th and 20th discharge-charge cycle.

modified graphite, we measured the electrochemical impedance spectra of the pristine and modified graphite electrodes at 5th and 20th cycles, and the Nysquist diagrams are shown in Fig. 5. Typically, the EIS consists of two overlapped semicircles at high and medium frequency regions, and a slopping straight line at low frequency regions. It is observed in Fig. 5 that the semicircles of the modified graphite electrode almost remain unchanged upon cycling, while those of the pristine graphite enlarge greatly. According to previous studies, the high-frequency semicircle corresponds to the migration of Li ions through the SEI film, and the second semicircle at lower frequency is attributed to the charge transfer kinetics [21]. In order to analyze the measured impedance spectra in detail, an equivalent circuit depicted in Fig. 6 is used to fit the obtained data, and the results are summarized in Table 1. Here, R_{SEI} and C_{SEI} are the resistance and capacitance of the SEI film on the graphite electrode. R_e is bulk resistance of the cell, while R_{ct} and C_{dl} are charge-transfer resistance and its relative double-layer capacitance. W is the Warburg impedance related to a combined effect of the diffusion of lithium ions on the electrode–electrolyte interfaces [22]. As shown in Table 1, the modified graphite shows more stable R_{ct}, and R_{SEI} values compared to pristine graphite. On the contrary, the R_{ct} and R_{SEI} values of the pristine graphite electrode increase dramatically after discharge–charge for 20 cycles. These results indicate that the SEI film formed on the modified graphite keeps stable physical properties such as electrical conductivity, thickness; and the charge transfer kinetics at the graphite/electrolyte interface remains unchanged during repeated cycling.

Table 1
Fitting results for the EIS of pristine and polysiloxane modified graphite electrodes

	Pristine graphite	Polysiloxane graphite
5th cycle		
R_{ct} ($\Omega\,mg^{-1}$)	14.27	10.58
R_{SEI} ($\Omega\,mg^{-1}$)	44.82	42.99
20th cycle		
R_{ct} ($\Omega\,mg^{-1}$)	33.27	10.65
R_{SEI} ($\Omega\,mg^{-1}$)	107.09	45.55

It is well accepted that poor cyclability of graphite electrode is mainly due to the continuous thickening of the SEI film during discharge–charge process [23,24]. Exfoliation of graphite flakes caused by cointercalation of solvent molecules, as well as volume change of graphite particles is responsible for this film thickening. Though the multilayers of polysiloxane formed on the graphite surface are predominantly organic film that can be penetrated by electrolytes, however, their presence may protect the graphite from the cointercalation of solvent molecules by the shielding effect. Moreover, the silylation reaction changes the

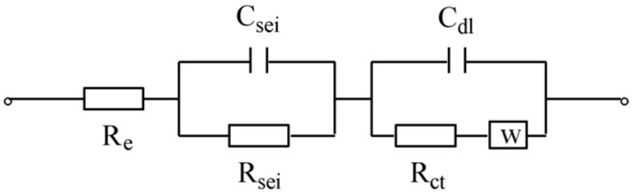

Fig. 6. Equivalent circuit used to analyze the electrochemical impedance spectrum of Li/graphite cells.

Table 2
Summary for the electrochemical performance of three kinds of graphite electrodes

	Pristine graphite	COOLi–graphite	Polysiloxane–graphite
1st discharge capacity (mAh g^{-1})	413.1	377.0	352.1
1st charge capacity (mAh g^{-1})	308.3	345	319.5
Initial efficiency (%)	74.6	91.5	90.5
Reversible capacity (mAh g^{-1})	310	345	320
20th capacity retention (%)	88.5	98.5	99.6

surface chemistry of graphite by introducing flexible −Si–O− bonding that can rotate in unconstrained fashion [25], which contributes to the formation of a more elastic SEI film on the graphite electrode. This flexible SEI film is able to accommodate the volume change of graphite particles during lithiation and delithiation process. As a result, the broken of the SEI film and subsequent reduction of the electrolyte components (i.e. at the crack of the SEI film) during cycling process can be avoided for the modified graphite electrode, which favors the SEI film to keep constant resistance and thickness.

3.3. *Effect of multilayers composition on the electrochemical performance of graphite electrodes*

In our previous study, we reported the graphite electrodes modified with the multilayers of lithium benzoate for lithium ion batteries through the similar procedure. In order to investigate the multilayers composition on the electrochemical performance of the graphite electrodes, the electrochemical results of the lithium benzoate and polysiloxane modified graphite electrodes are summarized in Table 2. It is clear that the reversible capacity and initial efficiency of the lithium benzoate modified graphite are about 345 mAh g^{-1} and 91.5%, respectively [12]. In contrast, the polysiloxane-coated graphite exhibits lower reversible capacity and initial efficiency. This difference is caused by the fact that the polysiloxane multilayers coated on the graphite surface are thicker than those of lithium benzoate films, which may increase the resistance of the graphite electrode and thus exerting adverse effect on charge transfer kinetics at the graphite/multilayers interface [10].

Moreover, an increase in the hydrophobicitiy of the graphite surface should be regarded as well [8]. It is evident that the polysiloxane multilayers coated on the graphite surface are highly hydrophobic. While the surface of the lithium benzoate modified graphite is hydrophilic. Therefore, a difference in the multilayers composition will affect the electrochemical wettability of the graphite electrodes. Certainly, a hydrophilic layer of lithium benzoate favors the penetration of the electrolyte components through the graphite/multilayers interface, which will reduce the interfacial resistance of graphite electrode and thus increasing the utilization of active materials. On the contrary, the hydrophobic films of polysiloxane will influence the free transportation of the hydrophilic components such as $LiPF_6$ in electrolytes.

It is interesting to observe that the polysiloxane modified graphite electrode exhibits better cyclability than that of the lithium benzoate-coated counterpart (Table 2). The reason responsible for this discrepancy is the presence of polysiloxane multilayers, which will increase the flexibility of the SEI film formed on graphite surface as discussed above.

On the basis of above results, we can conclude that the chemical composition of multilayers has impact on the electrochemical performance of the modified graphite electrodes. This is because that the chemistry of multilayers will change the electrochemical wettability of the electrodes, which may affect the interfacial resistance of graphite electrodes and thereafter the utilization of active materials. A hydrophilic layer is desirable for a modified graphite electrode with good electrochemical performance because the electrochemical reactions between the active material and electrolytes, such as electronic kinetics and the transportation of lithium ions, can be more readily achieved.

4. Conclusion

Multilayers of polysiloxane were covalently bonded on the surface of natural graphite particles *via* initial diazonium and subsequent silylation reactions, and the resulting graphite electrode exhibited good electrochemical performance in lithium ion batteries. We also confirmed that the chemical composition of multilayers exerted impact on the electrochemical behavior of the modified graphite electrodes. The advantage of this method lies in that a robust and flexible SEI film is expected to form on graphite particles, which provides a solution to the instability, fragility and un-uniformity of the SEI film associated with graphitic electrodes. Owing to the diversity of polysiloxane multilayers, this method enables researchers to design the surface chemistries of carbonaceous materials with flexibility.

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