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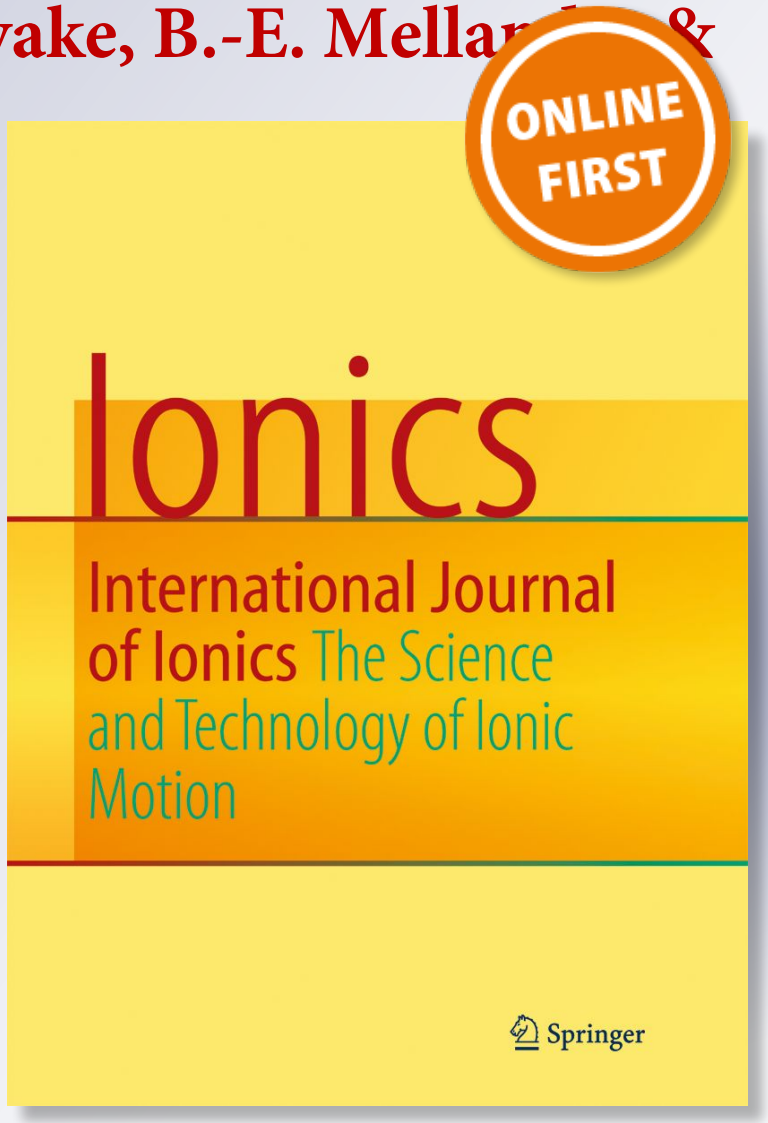

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ORIGINAL PAPER

Surface modification of natural vein graphite for the anode application in Li-ion rechargeable batteries

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Abstract
Natural vein graphite with high purity and crystallinity is seldom used as anode material in lithium-ion rechargeable batteries (LIB) due to impurities and inherent surface structure. This study focuses on improving the surface properties of purified natural vein graphite surface by employing mild chemical oxidation. Needle-platy graphite sample with initial average carbon percentage of 99.83% was improved to 99.98% after treatment with 5 vol.% HCl. Surface modification of purified graphite was done by chemical oxidation with $(NH_4)_2S_2O_8$ and HNO_3. Fourier-transform infrared spectra of graphite after chemical indicating surface oxidation of graphite surface. X-ray diffraction and scanning electron microscopic studies show the improvement of graphite structure without modification of crystalline structure. Electrochemical performance of lithium-ion cell assembled with developed anode material shows noticeable improvement of the reversible capacity and coulombic efficiency in the first cycle and cycling behavior after surface modification.

Keywords Vein graphite · Surface modification · Lithium-ion battery

Introduction

Expensive electrode materials used in LIB lead to higher unit costs that hinder the development of LIB as a low-cost portable power source. Still, expensive porous carbon materials and synthetic graphite are the most commonly used anode materials in commercial LIB [1, 2]. Vein graphite is renowned for its high purity and crystallinity [3]. However, it is rarely used in electrochemical systems. Four structurally distinct vein graphite varieties, namely, shiny-slippery-fibrous graphite (SSF), needle-platy graphite (NPG), coarse striated-flaky graphite (CSF), and coarse flakes of radial graphite (CFR) have been identified [2]. Each structural type consists of 95–99% of carbon. Impurity content in each structural type varies depending on the mode of occurrence and nature of the graphite vein [3, 4]. Those impurities are either mechanically attached to the graphite surface or intercalated between adjacent graphene layers.

The purity level in natural graphite normally required for electrochemical applications is in the range of < 0.1% ash with the accepted level of heavy metals < 10 ppm [1, 5]. Various thermal and chemical purification methods have been investigated to remove the mechanically attached and intercalated impurities in natural graphite with more than 98% of carbon [6–8]. Our previous study suggested a cost effective method for removing the impurities in vein graphite and upgrading the carbon content to 99.99% [9]. Chemical oxidation has been used to synthesize graphene oxide and anode materials for LIB from vein graphite [10–14]. The surface structure of graphite is a crucial factor for the formation of the solid electrolyte interface (SEI) layer and consequently its electrochemical performance in LIB [15–25]. Mild oxidation by thermal and chemical treatments has been identified as a successful method for surface modification [15–24]. Acid digestion technique that uses a combination of HF, HNO_3, and H_2SO_4 acids has been used to purify vein graphite for the anode application

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of lithium-ion battery [13]. However, those methods, which used corrosive and expensive chemicals for the purification and modification, are unfavorable for practical applications. Therefore, this present work focuses on investigating the possibility of developing vein graphite as anode material in LIB by surface modification via chemical oxidation using low concentrated mineral acid and chemical oxidant in economically viable and eco-friendly approach.

Experimental

Purification

Needle-platy graphite (NPG) from Sri Lanka, with particle size < 53 μm and carbon content 99.83%, was used for this study. Small chips of graphite were crushed in a vibratory disk mill for 3 to 4 min to form a powder. Particle size fraction < 53 μm separated by mechanical sieving was used for the experiment. The raw graphite powders (3.75 g) were leached in aqueous solutions containing 5 vol.% HCl (25 ml) separately and heated to 60 °C for 75 min [9]. The acid-leached materials were washed to neutral. The material was dried under vacuum to remove moisture. The treated graphite was further leached by leached in aqueous solutions containing 5 vol.% HCl (25 ml) separately and heated to 60 °C for 75 min. The acid-leached materials were washed to neutral. The material was dried under vacuum to remove moisture.

Surface modification

The modification of the purified graphite surface was carried out by chemical oxidation. Two strong oxidizing agents, hot concentrated HNO_3 (NO method) and 1 M $(NH_4)_2S_2O_8$ in 1 M H_2SO_4 (NS method) were used for the chemical oxidation [16]. For the NO method, graphite powder (3 g) was reacted with 69% HNO_3 solution (100 ml) at 60 °C for 24 h, followed by washing with distilled water until all the acid was removed. Then, the treated sample was dried under vacuum. The modification of graphite powder by the NS method was carried out by treating graphite powder (3 g) with 1 M $(NH_4)_2S_2O_8$ in 1 M H_2SO_4 (100 ml) at 60 °C for 24 h. After oxidation, the carbon powder was washed with distilled water until all sulfates were removed, which was determined by titrating the filtered solution with $BaCl_2$. Finally, the sample was dried under vacuum.

Material characterization

Carbon percentages of the treated and untreated graphite samples were determined by heat treating at 950 °C for 3 h in a muffle furnace, according to ASTM–C 561. X-ray diffraction was used to identify the crystalline structure, impurity phases, and the effect of surface modification (XRD, Siemens D5000). Effects of purification and surface modification morphology of the graphite was observed using Scanning Electron Microscopy (SEM, FEI Quanta 200 FEG-ESEM). Thermogravimetric measurements of raw and treated graphite were taken between 25 and 800 °C under nitrogen atmosphere (Perkin-Elmer TGS-2 Thermogravimetric System). Nicolet 6700 Fourier-transform infrared spectroscopy (FT-IR) was used to analyze the surface structure of purified and surface-modified graphite in the 400–4000-cm^{-1} region for absorption mode. The d.c. four probe electrical conductivity measurements were performed on the uniaxially pressed dense pellets between room temperature (25 °C) and 200 °C.

Electrochemical analysis

Coin Cells (CR 2032) were assembled in an argon-filled glovebox (Lab Start 50). In order to study the electrochemical properties of the prepared graphite electrode materials, lithium foil (Sigma-Aldrich) was used as a standard counter and reference electrode for all test cells. Electrode was prepared by casting a mixture of 90% of active material (developed vein graphite) and 15% of PvDF (KynarFlex 2801) binder together with acetone (Sigma-Aldrich) solvent on a copper current collector. Circular disks of 12-mm diameter and approximately 100 μm thickness, punched from the fabricated electrodes, were used as working electrodes. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) (1:1:1 wt.%) (LP71, BASF, USA). Microporous membranes, Celgard 2400, were used as the separator. Finally, the charge-discharge study of the assembled cells was carried out at C/5 rate with a cutoff voltage of 0.002–1.5 V at room temperature using a Metrohm Auto Lab (PGSTAT302N) controlled by Nova 1.1 program.

Results and discussion

Purification and surface modification of vein graphite

NPG sample with initial average carbon percentage of 99.83% was improved to 99.98% after treatment with 5 vol.% HCl. Figure 1 shows the X-ray diffractograms obtained on NPG powders before and after acid leaching purification and after surface modification with $(NH_4)_2S_2O_8$ and HNO_3. The diffraction pattern of the powdered sample exhibits well-developed peaks, indicating the high crystallinity of graphite powder. It can be clearly seen that the diffraction peaks corresponding to the impurity phases were eliminated after the purification process. XRD diffractograms of raw NPG show a small diffraction peak related to pyrite. This peak is absent in purified NPG. Furthermore, the diffractograms clearly indicate that the purification and mild chemical oxidation of the graphite power do not affect the crystallographic structure of

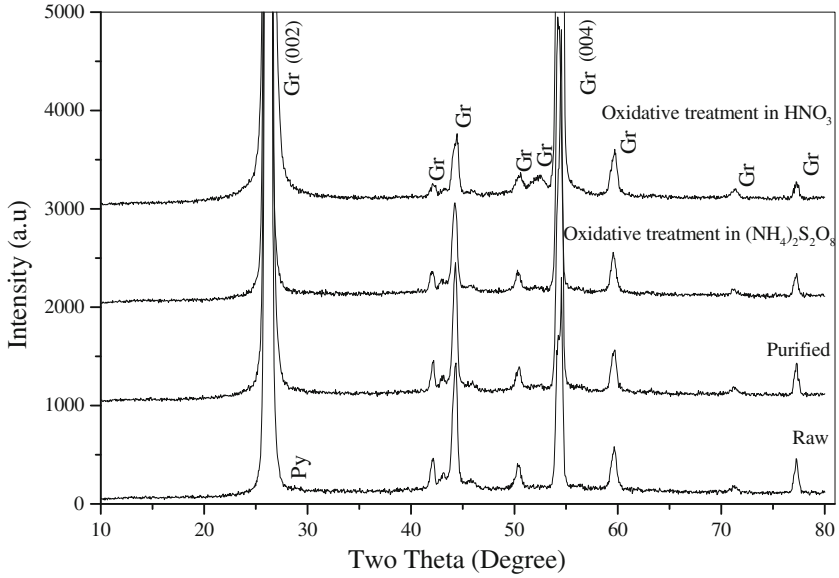

Fig. 1 The X-ray diffractograms obtained on NPG before and after the acid leaching purification and after surface modification with $(NH_4)_2S_2O_8$ and HNO_3

NPG powder and do not involve the formation of an intermediary graphite intercalation compound or other secondary phases [12–14].

Thermogravimetric analysis was also used to investigate the effect of mild oxidation of purified NPG. Figure 2 shows the TGA of the purified NPG before and after the mild oxidation in air and the chemical oxidation. TGA results suggest that the temperature at which combustion began to increase after the chemical oxidation compared to the purified NPG. The more reactive component in the carbon mixture will oxidize at lower ignition temperature [23, 24]. Therefore, mild chemical oxidation leads to a stabilization of the graphite structure due to elimination of some reactive structural imperfections at the graphite surface [16, 19]. Consequently, the temperature of combustion started to shift to high temperatures after mild oxidation treatments as evident by TGA data. The modified NPG samples exhibit decreased values of weight loss of about 0.5 to 1.7 wt.% compared to the purified NPG (4.75 wt.%). The decreased values suggest a lower concentration of functional groups on the graphite surface [19]. Relating to the previous results, it seems that a decreased amount of surface "defects" and possible removal of surface impurities by mild oxidation treatment leads to a thermally more stable graphite surface structure [19]. The oxidation ability of chemical oxidants governs the formation of oxidizing species on the graphite surface [25]. Combustion began at a higher temperature, 659 °C, for mild oxidized NPG chemically oxidized with $(NH_4)_2S_2O_8$ compared to that oxidized by HNO_3 (611 °C).

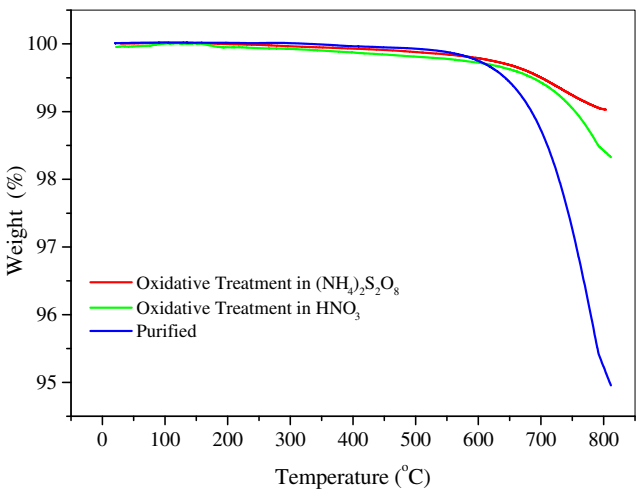

Fig. 2 Thermogravimetric (TG) curve for NPG before and after the acid leaching purification and after surface modification with $(NH_4)_2S_2O_8$ and HNO_3

Figure 3 shows the SEM images of raw, purified, and mildly oxidized NPG (purified) by chemical oxidation. These SEM images indicate some improvement of surface morphology of the mild oxidized graphite samples compared to raw and purified NPG sample. Generally, this surface inhomogeneity is reduced due to attacks on structural imperfection such as edge atoms and carbon chain by the oxidation process. The FT-IR technique is used widely to identify the formation of acidic groups or an oxide layer on the graphite surface [13, 15, 18]. FT-IR spectra of the purified NPG and mild oxidized NPG by chemical oxidation using NO and NS methods are shown in Fig. 4. In the FT-IR spectra, the broad band between 3500 and 3100 cm^{-1} is attributed to the bending mode of the molecular water. The band at 2330 cm^{-1} can be assigned to CO_2 in the gas phase physically adsorbed on the material surface. The purified NPG (prior to oxidation) spectrum shows no significant features apart from the weak absorption band owing to $\nu_{C=C}$ stretching at 1645 cm^{-1} and a doublet

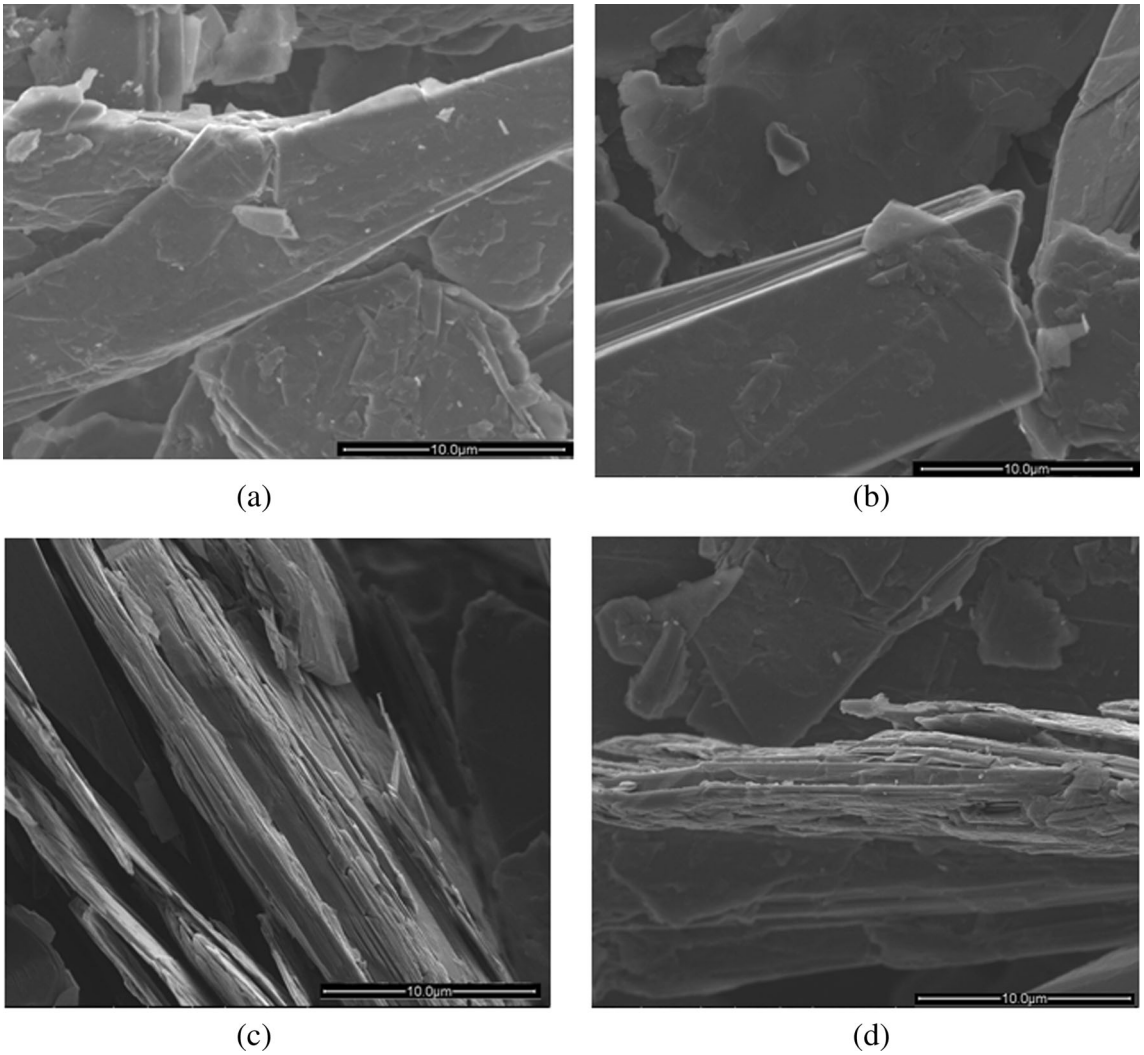

Fig. 3 SEM image of the of NPG (**a**) before purification and (**b**) after acid leaching purification (**c**) after chemical oxidation in $(NH_4)_2S_2O_8$, (**d**) after chemical oxidation in HNO_3

band at 2921 and 2850 cm^{-1} corresponding to the presence of aliphatic C–H bonds. However, mild oxidized NPG by chemical oxidation using NO and NS methods shows evidence of formation of carboxylic acid groups on the surface of graphite [13]. Vibrational bands corresponding to $\nu_{C=O}$ stretching at 1720–1680 cm^{-1}, ν_{O-H} stretching at 1360 cm^{-1} and ν_{C-O} stretching at 1260–1100 cm^{-1} imply the formation of carbonyl groups, alcoholic phenolic groups, and single C–O groups respectively. Further, a wide, weak band corresponding to $\nu_{(C-O-C)}$ appears around 1000 cm^{-1}. Therefore, the FT-IR spectrum clearly shows the formation of acidic groups or an oxide layer on the surface of the graphite surface after the mild oxidation.

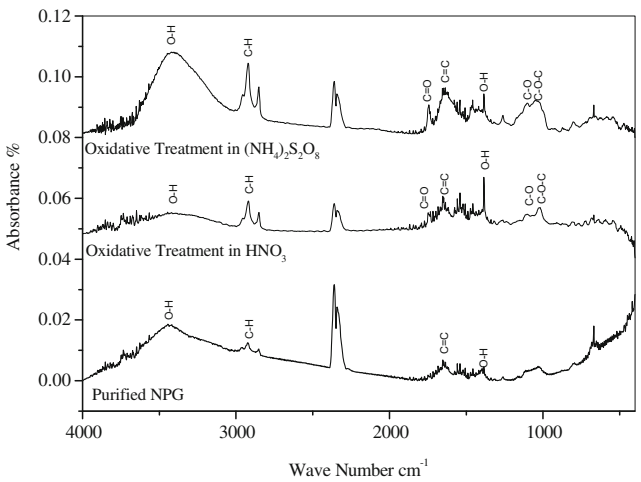

Fig. 4 FT-IR spectra of the purified and surface modified NPG

Electrical conductivity of graphite and graphite electrodes

The electrical conductivity of dense pellets and sheet conductivity of graphite electrodes prepared by graphite powder are given in Table 1. D.C. electrical conductivity measurements of

Table 1 D.C. electrical conductivity of dense pellets and sheet conductivity of graphite electrodes prepared using graphite powder

Treatment	Electrical conductivity (Scm^{-1})	
	Dense pellet	Electrode
NPG	5.59	0.97
Purified NPG	8.23	1.21
Purified NPG after chemical oxidation with $(NH_4)_2S_2O_8$	4.59	1.45
Purified NPG after chemical oxidation with NHO_3	4.25	0.98

the graphite powders show the semiconducting behavior. They are suggestive that a sufficient electrical conductivity value could be obtained for the anode application. Furthermore, they show that the mild oxidation has not caused any adverse effect on the electronic properties of graphite. The sheet conductivity of graphite electrodes is lower than the D.C. conductivity of the graphite pellets due to the effect of the binder used for the preparation of electrodes.

Electrochemical performance

Thermogravimetric analysis, studies of surface morphology by scanning electron micrographs and surface analysis by FT-IR measurements, imply that the chemical oxidation with strong oxidizing agents effectively modifies the graphite surface structure. Therefore, the electrochemical performance of raw NPG, purified NPG, and chemically oxidized NPG by NS and NO methods was studied. Table 2 summarizes the results of the charge-discharge study conducted using the NPG at a 0.2 C rate between 0.002 and 1.5 V.

The initial discharge capacity of raw NPG was 317 mAh g^{-1} with an irreversible capacity of 49 mAh g^{-1} and coulombic efficiency of 84%. For the cells where the graphite had been purified by acid leaching, the discharge capacity of NPG increased slightly to 327 mAh g^{-1} with an irreversible capacity of 39 mAh g^{-1} and coulombic efficiency of 87%. For cells with purified NPG by chemical oxidation, the discharge capacity increased to 341 mAh g^{-1} (NO) and 345 mAh g^{-1} (NS), the irreversible capacity decreased from 39 to 27 mAh g^{-1} (NO) and 19 mAh g^{-1} (NS). The coulombic efficiency in the first cycle increased from 87 to 91% (NO) and 94% (NS), respectively. As indicated in TG and SEM analyses, some reactive structural imperfections were eliminated effectively during the chemical oxidation. In addition, the surface of NPG was covered with a fresh and dense layer of oxides mainly hydroxyl/phenol, ether, and ester as indicated by the FT-IR data of chemically oxidized graphite. This layer acted as a part of SEI when lithium intercalated and blocked the co-intercalation of solvated Li^+ [15–25]. As a result, the coulombic efficiency increased after the chemical oxidation.

The first cycle charge-discharge curves of the raw NPG, purified NPG, and chemically oxidized NPG by NS and NO methods are illustrated in Fig. 5. Raw NPG shows a plateau near 0.80–0.90 V vs. Li/Li^+ which is a characteristic of a formation of an SEI film on the graphite surface and solvent decomposition [11–13]. Hence, impurities in raw NPG, surface imperfections, and defects as evident by XRD, SEM, and TG data may result in solvent decomposition that lead to the above plateau. The extent of the plateau near 0.80–0.90 V vs. Li/Li^+ gets reduced or disappears after the chemical purification and chemical oxidations (point B in Fig. 5). It maybe due to removing impurities and surface imperfections as evident by TG, SEM, and chemical analysis which lead to solvent decomposition. Moreover, dance oxide layer on the graphite surface as evident by FT-IR data may lead to formation of effective SEI layer during the first cycle [13, 16, 19]. The plateau between about 0.4 and 0.20 V vs. Li/Li^+ is related to the exfoliation of graphite due to co-insertion of solvent molecules, with lithium migration between graphene layers [11–13]. It can be clearly seen that the exfoliation have reduced after the purification and surface modification. After that, the voltage gradually decreases with the lithium intercalation. Three stages for the lithium intercalation of graphite

Table 2 Results of first cycle charge-discharge study conducted using the NPG at a 0.2 C rate between 0.002 and 1.5 V

	Discharge capacity (mAh g^{-1})	Charge capacity (mAh g^{-1})	Efficiency (%)	Irreversible capacity (mAh g^{-1})
NPG	317.6	267.8	84.3	49.8
Purified NPG	327.6	287.5	87.8	39.7
NPG NS	345.4	326.1	94.4	19.2
NPG NO	341.4	313.5	91.8	27.9

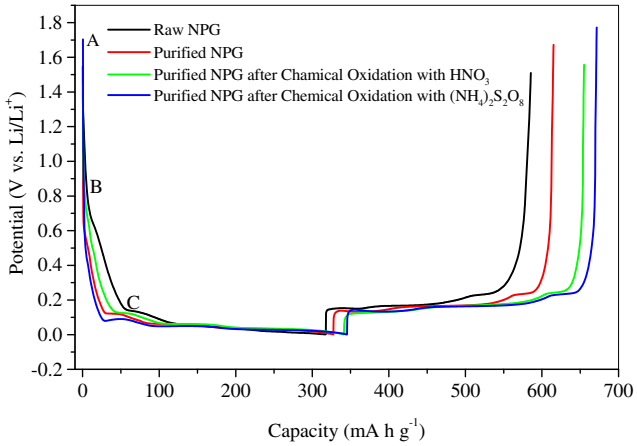

Fig. 5 Discharge and charge profiles in the first cycle of the natural vein graphite of NPG type before and after treatment at C/5 current rate between 0.002 and 1.5 V

electrode can be identified below 0.20 V vs. Li/Li^+ that corresponds to different stages of Li intercalation.

Cycling behavior of raw NPG, purified NPG, and chemically oxidized NPG by NS and NO methods are illustrated in Fig. 6. In the case of natural graphite, the discharge capacity faded rapidly from 317 to 199 mAh g^{-1}. After the purification with the acid leaching process, the discharge capacity of NPG faded from 327 to 227 mAh g^{-1}. It can be clearly seen that the rate of capacity fading reduces after the 7th cycle compared to the raw NPG. The discharge capacity of purified NPG oxidized with HNO_3 decreases from 341 to 247 mAh g^{-1} over the 10 cycles. The best cycling behavior was found for the chemically oxidized NPG with the strong oxidative agent, $(NH_4)_2S_2O_8$ where the discharge capacity faded from 345 to 309 mAh g^{-1} over 10 cycles. It is interesting to note that the coulombic efficiency of the 10th cycles was 99.9 and 99.6%, respectively, for the purified NPG oxidized with the NS ad NO methods.

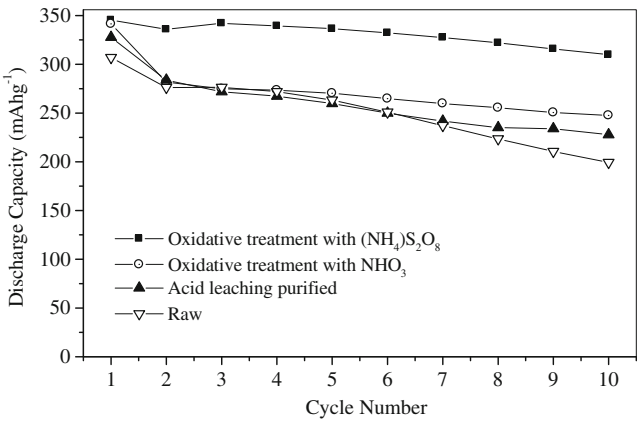

Fig. 6 Cycling behavior of NPG before and after treatment at C/5 current rate between 0.002 and 1.5 V

Conclusion

The treatment of purified vein graphite with oxidative solutions of $(NH_4)_2S_2O_8$ and HNO_3 resulted in a marked improvement of the electrochemical performance as anode materials for LIB. The increased stability of the graphite surface by elimination of imperfections with high activities towards lithium and the formation of dense layers of oxides on the graphite surface is responsible for such improvements. As a result the reactivity of the surface decreases, the decomposition of electrolyte molecules is blocked, and matrices for lithium storage and inlets and outlets for lithium intercalation and deintercalation increases. Therefore, the reversible capacity of raw NPG increases from 317 to 354 mAh g^{-1}; the coulombic efficiency in the first cycle increases from 84 to 94% with improved cycling performance after purification and mild surface oxidation with $(NH_4)_2S_2O_8$.

The present study confirms that the tested purification method together with surface modification can be successfully used to enhance the electrochemical properties of vein graphite making it suitable for the anode of LIB. All processes take place in the liquid-solid interface, and hence, the uniformity of the product can be easily controlled. Therefore, vein graphite can be successfully used as an anode active material due to its unique morphology, low cost, and high purity.

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