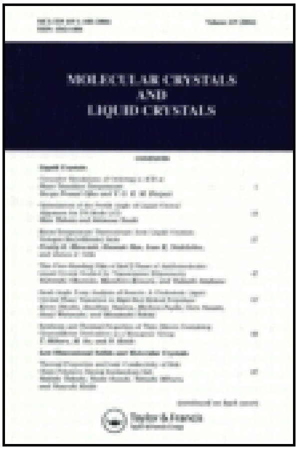

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

IR Study of Ozone Modified Graphite Matrix

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IR Study of Ozone Modified Graphite Matrix

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The oxidation of graphite powder was reported to enhance the capacity of graphite anodes in Li-ion batteries. Here we present IR-spectroscopic study of the graphite powder modified via oxidation by ozone with the subsequent LiOH or butyl-Li treatment compared to the results obtained by "wet" acid oxidation. Ozone treatment leads to the formation of ozonides, C-O-O-C, carboxylic and epoxy groups on graphite surface. Subsequent treatment of ozone modified graphite with LiOH eliminates the majority of C-O containing groups and yields only a few COOLi surface groups. Treatment of ozonated graphite with butyllithium appears to be more efficient.

Keywords: ozone; oxidation; graphite; surface; IR-spectroscopy; solid electrolyte interface; lithium ion batteries

INTRODUCTION

Secondary lithium batteries or their derivatives (lithium-ion batteries) are being intensively studied owing to the considerable challenge they present for applications - high electromotive force, high energy density (two-three times greater than that of any conventional secondary batteries like Ni-metalhydride, Ni-Cd), long cycle life, excellent high-temperature performance and safety, since no metallic Li is used. In the search for electrode materials for use in rechargeable lithium batteries, the well known ability of different forms of carbon to intercalate lithium metal is very useful. Improving of electrode characteristics requires maximizing reversible capacity (Q_R) at minimum irreversible capacity (Q_{IR}) loss due to the formation of Solid Electrolyte Interface (SEI). Mild burn-off was reported to improve performance in Li/Li$_x$C cells[1]: Q_R was increased by 10-30%, Q_{IR} was generally decreased and Li$_x$C$_6$ degradation was much lower. Chemical oxidation of graphite powder by the strong oxidizing agents ammonium peroxysulfate and hot concentrated nitric acid increases the reversible capacity during cycling from 370 to 430 mAh/g, whereas Q_{IR} is reduced[2]. The oxidation of the graphite results in the formation of a wide variety of surface functional groups. These groups contain carbon-oxygen bonds which are covalently attached to the graphite surface. These groups can be used to form the so-called CB SEI (chemically bonded SEI). During the first intercalation process, these acid groups are converted into surface Li-carboxylic salt and surface O-Li groups. These groups in presence of EC-, DEC-, DMC-, or PC-based electrolytes are converted into Li_2CO_3-based SEI. It is believed that this SEI is chemically bonded to the surface with -COOLi and -OLi groups[1].

The enhanced capacity observed may be attributed not only to the formation of CB SEI, but also to the accommodation of extra lithium in cavities or nanovoids produced during "wet" chemical oxidation[2]. To avoid the formation of these we proposed to use ozone as an oxidizer since it was shown to be a mild oxidizing agent (2-6% of ozone in O_3/O_2 mixture, room temperature) when used for the modification of activated carbons[3].

Here we report a comparative spectroscopic study of oxidized graphite powder by ozone and "wet" chemical oxidation. The modifications in graphite matrix during the oxidation and subsequent treatment with LiOH or butyl-Li are examined by IR spectroscopy.

EXPERIMENTAL

The oxidation of graphite powder (Alfa, 325 mesh) was carried out by four different methods according to the following procedures:

- HNO_3 treatment - 200 mg of graphite was treated with 2.6 ml of 16N nitric acid at 120°C for 3 h followed by washing with distilled water to pH 7 of the filtered solution and dried in 10^{-2} Torr vacuum for 40 min at 50-60°C;
- H_2SO_4/HNO_3 method - a charge of 200 mg of graphite was oxidized in the mixture of 1 ml of 96% H_2SO_4 and 0.13 ml of 16N HNO_3 at room temperature. After 40 min the mixture was diluted by distilled water;
- $H_2SO_4/KMnO_4$ method - 200 mg of graphite powder was added to 1 ml of 96% H_2SO_4; 30 mg of powdered $KMnO_4$ was then added to the mixture in small portions while the mixture was continuously stirred. The reaction was quenched after 30 min by pouring the mixture into distilled water. The suspension was then treated with 3% H_2O_2 solution to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate, washed and dried.
- Ozone oxidation was carried out in gas-flow reactor with O_3/O_2 gas mixture (2 - 6% of ozone) passing through the fluidized bed of graphite powder at room temperature. The details of this technique can be found elsewhere[5].

Oxidized samples were treated with 100°C Li hydroxide (3M LiOH aq. solution, 2 hours[2]) or with butyl-Li solution in cyclohexane (room temperature, 20 hours).

IR spectra of pristine, oxidized and oxidized/lithiated samples were measured using a Specord-M-82 spectrophotometer (Karl Zeiss) in 400-4000 cm^{-1} region. All samples were weighted, milled in nujol to make a suspension and placed into the hermetic transparent cell. The concentration of oxygen containing groups was calculated from Lambert's and Beer's laws from experimentally observed extinction. For the extinction coefficient the value of specific extinction of di-n-oxy-phenolic ether of terephthalic acid was used.

RESULTS AND DISCUSSION

Figure 1 presents IR spectra obtained from graphite powder treated by $H_2SO_4/KMnO_4$ (Fig. 1^b) and powder which was subsequently treated with a LiOH solution (Fig. 1^c). An IR spectrum obtained from untreated graphite powder is presented for comparison (Fig. 1^a). Spectrum 1^b shows mainly two bands that may be attributed to carbonyl bonds vibrations. The most intensive band at 1650 cm^{-1} may be attributed to C=O groups conjugated with the electronic system of graphite; the second one - at 1715 cm^{-1} denotes C=O bonds not conjugated with any π-electron system. Subsequent LiOH treatment (Fig 1^c) eliminates these COOH groups (1650 cm^{-1} and 1715 cm^{-1} bands disappear) and new bands at 1515 cm^{-1} and 1540 cm^{-1} may be attributed to COO ions. The results obtained for hot nitric acid and H_2SO_4/HNO_3 treatment showed qualitatively similar results.

IR spectra of the graphite powder treated with ozone (4.7% in O_3/O_2 mixture) are presented in Figure 2^b. Wide bands observed in the region 1250-1100 cm^{-1}, are commonly attributed to vibrational modes of single C-O bonds in ozonides, ethers, esters and other compounds containing single C-O bonds and the bands in 1720^{-1}-1620 cm^{-1} region are due to C=O bonds vibrations. The variation of ozone concentration in O_3/O_2 flow does not change the shape of IR spectra and affects only the overall intensity of the bands. For all samples treated with ozone, the relative intensity of the bands in 1250-1100 cm^{-1} region is substantially higher than the intensity of the bands in a longer wave region. Accordingly, the calculated concentration of the groups containing single C-O bonds is nearly twice as large as that of groups with double C=O bonds. This suggests that along with COO groups (which have equal amount of single and double C-O bonds), ozone modified sample contains some other oxygen containing groups with single C-O bonds. These may be ozonides, C-O-O-C or epoxy groups[4]. The wide multi-component band in 1250-1040 cm^{-1} region represents these kind of functional groups.

LiOH treatment (Fig. 2^c) almost completely eliminates the bands in 1250-1100 cm^{-1} region, whereas the band at 1720 cm^{-1} (C=O) becomes even more intensive. At the same time we do not observe any bands in 1500-1600 cm^{-1} region, typical for C=O bonds in carboxylic ions. This suggests that LiOH treatment of ozonated graphite is rather inefficient for the formation of chemically bonded COOLi or -OLi surface groups and leads to the destruction of C-O groups yielding no (or a few) COO$^-$ ions.

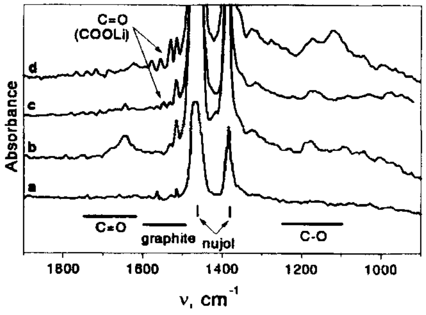

Figure 1. IR spectra for $H_2SO_4/KMnO_4$ modification. (a) untreated graphite; (b) oxidized; (c) oxidized and LiOH treated; (d) oxidized and treated with butyl-lithium

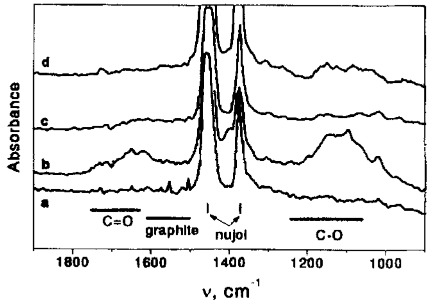

Figure 2. IR spectra for ozone (4.7% O_3/O_2) modification. (a) untreated graphite; (b) oxidized; (c) oxidized and LiOH treated; (d) oxidized and treated with butyl-lithium

Butyl-lithium, being a stronger nucleophilic agent than LiOH should more efficiently convert various single C-O bonds into -OLi groups. The ozonated graphite powder treated with n-butyl-lithium preserved in IR spectrum wide and intensive bands in 1100-1250 cm^{-1} region (C-O), but having a substantially different character compared to untreated ozonated graphite. Since C=O bonds in COOLi groups readily react with butyl-lithium excess yielding -COLi groups, almost no bands are observed in 1500-1600 cm^{-1} region.

Several well defined peaks, observed in the spectra of butyl-Li modified graphite in 580-670 cm^{-1} region (not shown in figure) may be attributed to covalent O-Li (or/and C-Li) bonding.

There is another advantage of butyl-Li treatment worth to be mentioned - the reaction is carried out in non-aqueous media, thus enabling to avoid any hydrolysis and water adsorption by carbonaceous anode material.

CONCLUSION

The mild oxidation of graphite powder for lithium-ion batteries anodes application was carried out with ozone in O_3/O_2 flow at room temperature. The oxidation leads to the formation of the variety of oxygen-containing groups on graphite surface. These are ozonides, C-O-O-C, carboxylic and epoxy groups. Subsequent treatment of thus modified graphite with LiOH (in order to form CB SEI) eliminates the majority of C-O containing groups and yields only a few COOLi surface groups. Treatment of ozonated graphite with butyl-lithium leads to the formation of mainly -COLi groups, whereas a "wet" chemical oxidation with subsequent treatment with LiOH produces mainly -COOLi groups on graphite surface. Electrochemical investigations of ozone/butyl-lithium modified electrodes in Li/Li_xC_6 cells are underway.

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