

OZONE OXIDATION OF GRAPHITE POWDER FOR ELECTROCHEMICAL APPLICATIONS: INFRARED SPECTROSCOPY CHARACTERIZATION

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Introduction

Development of high capacity carbon host lattices for lithium rechargeable batteries anodes was the goal of many research groups during the last years. The main focus of attention in improving of electrode characteristics is on maximizing reversible capacity and minimizing irreversible capacity loss due to the formation of Solid Electrolyte Interface (SEI). One of possible routes to improve the stability of carbonaceous anodes was reported by Peled [1] - mild oxidation (burning) of graphites and later - the chemical oxidation of graphite powder by the strong oxidative agents ammonium peroxysulfate and hot, concentrated nitric acid with subsequent LiOH treatment - by Ein-Eli [2]. The oxidation route was reported to increase by 10-30% reversible capacity with irreversible one decreased due to the formation of *in situ* chemically bonded solid electrolyte interface (CB SEI) and production of cavities or voids on the surface of graphite. Ozone is known to be a mild oxidizing agent used for the modification of various carbonaceous materials. Ozone treatment was reported to form mainly carbonyl and carboxyl groups on the surface of activated carbon [3].

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

Experimental

The graphite powder (Alfa, 325 mesh) was oxidized with H₂SO₄/KMnO₄ mixture as follows:- graphite powder was placed in concentrated H₂SO₄ and KMnO₄ was added to this mixture (30 mg KMnO₄ / 1 ml H₂SO₄ (96%), room temperature). The reaction was stopped in 30 min by dilution with distilled water. Suspension was treated with 3% H₂O₂ solution to reduce the residual permanganate and manganese dioxide to soluble state, washed and dried.

After oxidation the samples were treated with a hot Li hydroxide (3M LiOH aq. solution, 2 h at 100°C, followed by washing with distilled water [2]) or with butyl-Li solution in cyclohexane (room temperature, 20 hours).

Ozone modification was carried out in gas-flow reactor in O₃/O₂ gas mixture (2 - 6% of ozone) at room temperature. The kinetics of the reaction was monitored via spectrophotometric measurements of ozone concentration in the gas flow at the reactor exit.

Our IR spectra registrations were carried out using a Specord-M-82 spectrophotometer (Karl Zeiss) in 400-4000 cm⁻¹ region. The sample was milled in nujol to make a suspension and placed into the hermetic transparent cell. For the extinction coefficient for quantitative evaluation of oxygen containing groups the value determined for di-n-oxy-phenolic ether of terephthalic acid was applied.

Results and discussion

Figure 1 presents IR spectra obtained from graphite powder treated by H₂SO₄/KMnO₄ (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.

IR spectra of the graphite powder treated with ozone (4.7% in O₃/O₂ mixture) are presented in Figure 2^b. Wide bands observed in the region 1250⁻¹-1100 cm⁻¹, are commonly attributed to vibrational modes of single C-O bonds in ozonides, ethers, esters and other compounds containing 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 affect the nature of the groups containing oxygen formed in modified graphite but only changes their concentration thus affecting only the overall intensity of the bands in IR spectra. For all samples the intensity of the bands in $1250-1100\text{ cm}^{-1}$ region is substantially higher comparing to the bands in a long wave region. The quantitative evaluation of C-O and C=O groups concentration showed the number of C-O groups to be nearly twice as large as that of C=O, thus suggesting that along with COO^- groups ozone modified sample contains some other oxygen containing groups with single C-O bonds like ozonides, C-O-O-C or epoxy groups. The wide multi-component band in $1250-1040\text{ cm}^{-1}$ region represents these kind of functional groups.

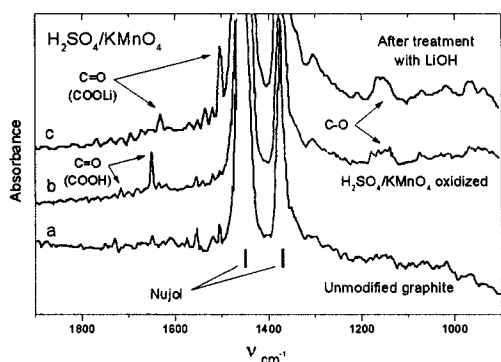


Figure 1. IR spectra for $H_2SO_4/KMnO_4$ modification

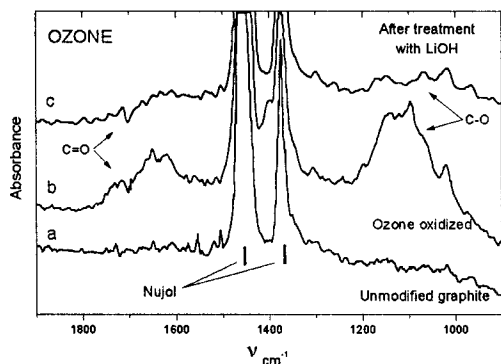


Figure 2. IR spectra for ozone ($4.7\% O_3/O_2$) modification

LiOH treatment (Fig. 2^c) almost completely eliminates the bands in $1250-1100\text{ cm}^{-1}$ 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 $1500-1600\text{ cm}^{-1}$ 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 destruc-

tion of C-O groups and yields no (or a few) COO^- ions.

The type of C-O bonds we propose to be present in O_3 modified sample should efficiently react with some strong (comparing to LiOH) nucleophilic agent. Indeed, the ozonated graphite powder treated with n-butyl lithium retained in IR spectrum several intensive bands at $1500-1600\text{ cm}^{-1}$, corresponding to $\nu_{C=O}$ in carboxylic ions and 1720 cm^{-1} peak due to $\nu_{C=O}$ in $COOR$. Wide and intensive bands preserved in $1100-1250\text{ cm}^{-1}$ region (C-O) have substantially different character comparing to starting ozonated graphite. Moreover, the spectra of Bu-Li modified graphite showed several well defined peaks in $580-670\text{ cm}^{-1}$ region, which we attribute to covalent O-Li (or/and C-Li) bonds, thus evidencing the formation of various O-Li groups chemically bonded to the graphite surface. Another advantage of treating with Bu-Li is that the reaction is carried out in non-aqueous solution, thus enabling to avoid the hydrolysis and water sorption by carbonaceous anode material.

Conclusion

The mild oxidation of graphite powder for lithium-ion batteries anodes application was carried out with ozone in $O_3(2-6\%)/O_2$ flow at room temperature. The oxidation in these conditions leads to the formation of variety of oxygen-containing groups on graphite surface - carboxylic groups, ozonides, C-O-O-C 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 oxidized graphite with butyl-lithium appears to be more efficient. Further investigations are needed to clear out the nature of the surface groups thus formed. Electrochemical investigations are underway.

References

1. Peled E, Menachem C, Bar-Tow D, Melman A. Improved graphite anode for Lithium-ion Batteries, Chemically bonded solid electrolyte interface and nanochannel formation. *J. Electrochem. Soc.* 1996; 143(1): L4-L7.
2. Ein-Eli Y, Koch V.R. Chemical oxidation: a route to enhanced capacity in Li-ion graphite anodes. *J. Electrochem. Soc.* 1997; 144(9): 2968-2973.
3. Atiaksheva LF, Yemelianova GI. The influence of temperature-time factors on the process of oxidation of carbon materials by ozone. *Vestnik Moskovskogo Universiteta, Ser 2, Khimia* 1983; 24(5): 462-466. (in Russian)

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