

Preparation of Anode Material for Lithium Ion Battery by Chemical Oxidation

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Abstract: Anode material for lithium ion battery is prepared by chemical oxidation of natural graphite. After oxidation, the properties of natural graphite are modified, such as surface structure, the content of graphite phases, the number of micropores and its stability, thus the modified natural graphite can be used as anode material for commercial lithium ion battery. The reversible capacity is increased from 100 mAh/g to above 300 mAh/g, and its cycling property is also satisfactory.

Keywords: Anode Material, preparation, chemical oxidation, lithium ion battery.

Since the oil crisis in the 60's and 70's, it has been realized that the natural resources are very important and the research of lithium secondary battery was then begun. Recently, the urgent demand of microelectronics for secondary battery with high energy density and light weight has greatly stimulated the development of lithium secondary battery. Only in the early 90's, did this kind of battery become commercial when it was found that graphite can substitute lithium or lithium alloys and solve the problems of safety and cycle life. However, the synthesis condition for graphite is critical to the industry, which needs high temperature (~2800°C). Recently, disordered carbons prepared at low temperature (<1000°C) were also studied. Though their reversible capacity is high, there is voltage hysteresis and their cycling properties are not good enough¹⁻⁴. As to natural graphite, its electrochemical property as anode of lithium ion battery is not satisfactory either, its reversible capacity is small, generally below 200 mA/g. Here, we found an economic method to prepare anode material for lithium ion secondary battery through modification of natural graphite by chemical oxidation.

Purified natural graphite with carbon content greater than 99% was dipped in a saturated solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 4mol/L H_2SO_4 for some time under stirring at room temperature. After this oxidation treatment, it was washed with water, dried and mixed with 5wt.% binder PVDF and pressed into pellets. After further drying under vacuum at 120°C, the pellets were put into an argon box free of water and oxygen to built into model cells and their electrochemical properties as anode of lithium ion battery were measured as reported³.

After this oxidation treatment, the content of oxygen is increased from 0.275 to 0.485% (atomic ratio of O/C). The results of X-ray photoelectron spectra of C_{1s} and O_{1s} and FT-IR spectra show that the surface structure of the natural graphite has changed, the oxygen atoms are mainly situated at the surface of the graphite, and they exist as groups such as carbonyl, ester, lactone and ether. Thermal gravity and differential thermal analyses under air show that the exothermal peak is increased from 742 to 788°C, which

indicates that the stability of the oxidized natural graphite has been improved. It is well known that the natural graphite is usually rich in imperfect structures such as tetrahedral carbon atoms, edge carbon atoms and carbon chains, while these kinds of carbon structure will hinder the intercalation of lithium. Consequently, electrochemical properties of natural graphite can not be satisfactory. In addition, the formed passivating film during the discharge process is not dense enough to prevent electrolyte molecules such as ethylene carbonate and diethyl carbonate from co-intercalating, which will lead to the exploitation of graphene layer and result in the destruction of graphite structure. After oxidation, these imperfect structures are eliminated and a new layer of oxides is formed. Lithium can react with the surface groups of the formed layer and produce dense passivating film, which is chemically bonded with the carbon structure and can inhibit the co-intercalation of electrolyte molecules and ensure the stability of the graphite structure.

Measurements of scanning electron microscopy and specific surface area show that the number of micropores in the modified natural graphite has increased. According to the mechanism of lithium storage^{5,6}, micropores can act as "reservoirs" for lithium storage. The larger the number of micropores, the higher the reversible capacity will be.

X-ray powder diffraction patterns show that there are no obvious changes of the interlayer distances d_{002} and d_{004} and the size of crystallites L_c . However, the ratio between intensities of two peaks around 43.32 and 44.44 degrees is increased from 0.373 to 0.520. While these two peaks are from the characteristic diffraction of 101 planes of two kinds of graphite phases, *i.e.* rhombohedral (3R) phase and hexagonal (2H) phase, it suggests that the content of 3R phase has increased. It illustrates that the above stated surface groups such as ester and ether are situated not just in a single graphene molecule, it can bond with two graphene molecules. Since 3R phase is more turbostratic than the 2H one, lithium intercalation will be favored.

From the above results, the oxidation process can effectively modify the carbon surface, introduce micropores into the graphite structure, eliminate imperfect structure and increase the content of 3R phase, it will favor the improvement of electrochemical properties as anode of lithium ion secondary battery. Results from measurement of capacity show that reversible capacity of the modified natural graphite is increased from 100 mAh/g to above 300 mAh/g after modification. Its cycling properties are also satisfactory. After 10 cycles, the reversible capacity can be up to 275 mAh/g. These show that this method is economic and practicable.

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