Preparation of Graphite Interlayer Compounds on the Carbon Fiber Surface by Electrochemical Method

Yingyi Liu, Dongxing Zhang
Materials Science and Engineer, Harbin Institute of Technology, Haerbin 150000, China
*Corresponding author: liuyingyi_hit@163.com

ABSTRACT: Because of its excellent performance, graphite interlayer compounds (GICs) get the attention of scholars and researchers recently. Electrochemical method was used in this paper to insert alkali metal lithium into the face of highly graphitized carbon fiber (T300) to improve the electrical conductivity. And the structure and all of its inter-layer particle binding ways were characterized by using X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy, at the same time through tensile test and conductive adhesive method the mechanical and electrical properties were characterized. Finally, a kind of carbon fiber composites with high strength and high conductivity can be prepared. The surface of this composite is the alkali metal-graphite interlayer compounds (Li-GICs), and the core is carbon fiber. In addition, there is no substantial decline in mechanical properties as well as the improvement in electrical conductivity.

1 INTRODUCTION

Carbon fiber is a kind of new carbon material because of its high specific modulus, heat conductivity, conductive and a series of excellent performance. It has become very important in the field of aerospace structure materials. In addition, graphite intercalation compounds (GICs) have certainly attracted the attention of theoretical physicists, chemists, and industrialists for its excellent performance. As early as 1841, H2SO4-based GICs were reported by Schafaut from Germany [1]. Table 1 indicates the continuous efforts, successes and developments in this area during the past years [2]-[6]. GICs is a kind of crystalline compound which use physical or chemical methods to make non-carbon reactants such as alkali metals, metal chlorides or acid into the graphite layer, the reagent not only comb with the hexagonal network plane but also maintain the layered structure of graphite. The characteristics of the compound on the crystal structure is foreign reactants to form independent insert layer and a superlattice in the C-axis direction of the graphite. Therefore, CIGs is a kind of nanocomposite in scale structure [7]. Among various kinds of methods to prepare GICs, the electrochemical method is the preferred method for industrialized production of GICs. For its electrolyte can be used without concentrated acid making the operation more safe. And the electrolyte not only can be recycled, saving drugs and extend the service life of equipment, but also can reduce pollution. The basement of electrochemical method is the structure of graphite. Graphite materials generally contain polyaromatic rings with sp2 carbon atoms. These aromatic planar rings are stacked together by π–π interaction of the electronic network. In order to improve the conductivity of carbon fiber, alkali metal lithium can be inserted in the surface of highly graphitized carbon fiber to get the graphite interlayer compounds [8]. Carbon fiber structure is disorderly layer graphite, which has the same characteristics can be inserted as graphite, it also has the mechanical advantages of high modulus and high strength. Therefore after insert alkali metal lithium in the surface of carbon fiber, we can get the conductive carbon fiber/Li-GICs composites with high strength.

<table>
<thead>
<tr>
<th>year</th>
<th>Topics</th>
<th>author</th>
</tr>
</thead>
<tbody>
<tr>
<td>1841</td>
<td>H2SO4-GIC</td>
<td>Schafhaut</td>
</tr>
<tr>
<td>1926</td>
<td>K-GIC</td>
<td>Fredendagen</td>
</tr>
<tr>
<td>1930</td>
<td>Graphite fluorides</td>
<td>Ruff, Keim</td>
</tr>
<tr>
<td>1932</td>
<td>FeCl3-GIC</td>
<td>H.Thiele</td>
</tr>
<tr>
<td>1940</td>
<td>Br-GICs(C8Br)</td>
<td>W.Rudorff</td>
</tr>
<tr>
<td>1964</td>
<td>K-H-GIC</td>
<td>Saeher</td>
</tr>
<tr>
<td>1974</td>
<td>Li/(CF)n primary battery</td>
<td>Ubbelohde</td>
</tr>
</tbody>
</table>
2 EXPERIMENTAL PROCEDURE

T300 (3k) carbon fiber used in experiment, belongs to the polyacrylonitrile (PAN) carbon fiber the tensile strength of 3530MPa, the elongation modulus of 230 GPa. carbon fiber need remove surface glue before used. Put carbon fiber into the tube furnace, heat to 3000℃ and last 1 hour with ventilating argon gas as protective gas to born out the glue on the surfer, take out after natural cooling. Dissolve the intercalator (LiCl) in solvent (ethylene carbonate) as the electrolyte. The melting point of ethylene carbonate is 35 to 37 ℃, so it is crystalline solid at room temperature. With the method of the water bath heat the ethylene carbonate crystal in the reagent bottle, after ethylene carbonate become colorless transparent liquid, mix it with alcohol as mole ratio of 1:3. Mixture liquid can be used as a solvent to dissolve intercalator (LiCl) to make different concentration of the electrolyte. Experimental apparatus as shown in figure 1. Cut the carbon fiber into 10 cm long, clamp 6 to 7 bundles of fiber in the copper sheet fixed on the edge of the container with electrode holder; cut the graphite paper into 2 cm wide, 5-6 cm long rectangular plate, clamp it in the copper sheet fixed on another edge as well. Keep the most part of fiber and graphite paper into the solution. The blue line as the negative pole of dc regulated power supply linked Carbon fiber, while the red line as the positive pole linked graphite paper. Carbon fiber settle off reduction reaction as the cathode of electrolytic cell, while graphite paper stetted off oxidation reaction as the anode. The experimental variables are voltage and electrolyte concentration, so there are two contrast groups. Group 1: variable keep constant(3V); As a variable electrolyte concentration is 1%, 2%, 3%, 4%, 5%, 6%, 7%, 9%, 11%, respectively. Group 2: electrolyte concentration keep constant(5%); As a variable voltage is 1V, 2V, 3V, 4V, 5V, 6V, 7V, 9V, 11V, respectively. Assemble the device and choose the variable as follow, electrolytic time is about 40 minutes. Then take the carbon fiber from the holder and put it inside drying oven to dry with test sample bag for 4-5 hours. Take out the sample after drying, fix the carbon fiber monofilament on paper frame (20mm×30mm) with conductive adhesive. The diameter of monofilament (D) and the length between conductive adhesive (L) are measured with a microscope. measure the resistance by using dc resistance bridge method. further calculate the electrical resistivity according to the formula 1 as follow.

\[ \rho = \frac{RS}{L} \]  

where \( \rho \) is the resistivity, \( R \) is the resistance, \( S \) is the cross-sectional area, and \( L \) is the length.

### Table 2. Materials and equipment used in experiment.

<table>
<thead>
<tr>
<th>Material</th>
<th>Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon fiber:T300(3k)</td>
<td>Container: plastic case (20cm×15cm×15cm)</td>
</tr>
<tr>
<td>Auxiliary electrode: graphite paper</td>
<td>Power source: DC stabilized</td>
</tr>
<tr>
<td>Solvent: ethylene carbonate</td>
<td>Clamping piece: copper sheet</td>
</tr>
<tr>
<td>Intercalator: LiCl</td>
<td></td>
</tr>
</tbody>
</table>

3 RESULTS AND DISCUSSION

3.1 Electrical resistivity

The electrical resistivity of every samples are shown in figure 2. It is obvious that the electrical resistivity is declined with the increase of voltage or electrolyte. The graphite structure in carbon fiber occurs charge exchange and transfers with intercalating agent, with functional particles carrier come into being intercalation reactions make GICs having lots of defect which form functional space. The presence of the functional particles and space make the ability of conduction current in GICs increases greatly, thus it improve the conductivity and formed a high conductor and superconductors.[9]

3.2 Proof of existence of Li-GICs

3.2.1 SEM and TEM

Among all the samples, two samples (S5V-9% and S9V-5%) resistivity decrease the most. Therefore, SEM and TEM are taken to observe these two samples. The photo is shown in figure 3, 4 and 5. SEM studies of carbon fiber show that it possesses a layered structure through the entire cross section. From figure 3(a), it can be seen that before intercalated carbon fiber surface is smooth, no bumps or ridges on it. However, figure 3(b), (c) and (d) show the surface morphology changed a lot for inserting: the carbon fiber surface become rough and appear obviously along the row of the ridges. The particles were observed by TEM and the selected area electron diffraction patterns (SAEDP) of the two samples were shown. Figure 4 and 5 are the TEM observation of the sample 9V-5% and 5V-9%: SAEDP shows fiber microcrystalline produce
diffraction rings, as the two bright spots are the (002) peak diffraction. The graphite crystallite six-party symmetrical arrangement of diffraction spots can't be seen, show that graphite crystallite quantity in the fiber used to be inserted is still very little [10]. High resolution transmission electron microscopy (HRTEM) of the surface of carbon fiber show there are light gray blankets covering on the surface clearly. Interlayer spacing of the cover can be gotten by measuring on the photo, it is 0.365nm and 0.392nm wider than 0.3435 nm, the Interlayer spacing of graphite. This suggests that intercalator (Li) have inserted into the graphite layers.

3.2.2 Raman spectroscopy
Raman spectroscopy was used to check the crystalline quality of the carbon fiber by monitoring the relative intensity of the D peak (defect-related) and the G peak (doubly degenerate zone center E2g mode). On the basis of peak profile and peak position analysis as well as optical contrast spectroscopy of the carbon fibers, we can conclude that both D peak and G peak increase for insertion (Figure 6a,b,c). As shown in Figure 6d,e the ID/IG intensity ratio increasing indicates that more defects in carbon fiber cause disorder of structure.

3.2.3 X-ray diffraction (XRD)
The inserted carbon fiber were examined by X-ray diffraction (XRD) to assess whether the long-range periodicity and the interlayer spacing associated with the c axis in thick graphite had been modified. There are part of the mix order diffraction line on the X-ray diffraction pattern , but no more complete first-order and second-order diffraction line. Although it is difficult to analysis its layer structure changes after the intercalation through X-ray diffraction (XRD), according to the structure characteristics internal graphite crystallite is lesser and immature to analyze, the amount of Li inserting in PAN carbon fiber is much less than it in the flake graphite. In fact, after the fiber was electrochemically charged in Li+ ,it expanded considerably and the (002) reflection characteristic of the π-π stacked layers was noticeably weakened and off settled to the left.

3.3 Conclusions
The electrochemical charging method developed here can be combined with alkali metal-GICs to product of carbon fiber/Li-GICs composite materials. Raman spectra studies of the fiber show that intercalator (Li) have inserted into the graphite layers confirmed by X-ray diffraction (XRD), intercalation carbon fiber has formed GICs in its internal structure, however, it has not formed the whole of the GICs structure. The conductivity of the PAN carbon fiber intercalated by electrochemical method has great improved.
REFERENCES


