Microstructure and electrochemical properties of some synthetic carbons

Min Chul Suh, Yongju Jung, Juhyoun Kwak, Sang Chul Shim

Department of Chemistry, Korea Advanced Institute of Science and Technology 373-1 Kusung-Dong, Yusung-Gu, Taejon 305-701, South Korea

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Abstract

Four kinds of synthetic carbons were prepared by vacuum pyrolysis of black polyacene-based polymers: poly[(Z)-1-methoxy-4-phenyl-1-buten-3-yne]-750, poly(1,4-diphenyl-1-buten-3-yne)-750, poly[5-(2-pyridyl)-2,4-pentadiyn-1-ol]-800, and poly(2,4-hexadiyn-1,6-diol)-800. The carbonization yields and electrochemical properties of carbons were dependent on precursor polymers. The relationship between the structure of synthetic carbons and electrochemical behavior was investigated by transmission electron microscopy (TEM), discharge/charge tests and cyclic voltammetry studies. Precursor polymers from enynes yielded synthetic carbons with many defect sites. Poly(DPBEY)-750, poly(PyPDO)-800, and PHDO-800 show smaller charge capacities than graphite (372 mA h/g), while a large charge capacity of 496 mA h/g is observed from poly(MPBEY)-750 in the first cycle. Poly(PyPDO)-800 displays very large capacity on cyclic voltammetry tests compared to other carbon samples indicating that the kinetics of lithium insertion/deinsertion in poly(PyPDO)-800 is faster than those of other carbons. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Metathesis; Graphite-like pyropolymer; Pyrolysis; Lithium insertion; Capacity

1. Introduction

Polyacene-based polymers or graphite-like materials have been attracting much interest from basic and applied viewpoints because of their stability and reversibility during the electrode reactions in the secondary battery [1]. The formation of precursor polymers is very important to make graphite-like structures because the structure of precursor polymers can directly affect the structure of carbonaceous materials.

Topochemical polymerization of diacetylenes proceeds through 1,4-addition reaction pathway. Metathesis polymerization, however, is carried out by 1,2-selective polymerization pathway. In this case, the active species is not a diradical, but a metal–carbene complex [2–7].

Masuda and Higashimura [8] reported a competing polymerization between phenyl acetylene and styrene suggesting that transition metal halides can catalyze coordination or cationic polymerization. Triple bonds are more reactive than the double bonds in coordination polymerization pathway while double bonds are more reactive in...
catalytic polymerization [8]. The acetylene moiety acts as a major reaction site during metathesis polymerization of enyne derivatives. The carbonization yields were lower than that of precursor polymers from diacetylene derivatives. Carbonaceous materials can also be observed from these polymers by vacuum pyrolysis.

Pyrolysis of polymers or high-temperature polycondensation reactions are simple procedures to obtain structures of extended graphite-like pyropolymers with relatively high electrical conductivity. Preparation of conducting polymers by this method consists of eliminating heteroatoms (halogens, oxygen, nitrogen, etc.) from the polymers by heating to form extended aromatic structures eventually approaching that of a graphite. The precursor polymers showed different carbonization yields according to their substituents. The pendant group has the important role of suppressing the gasification of the polymer itself. The morphology of final pyropolymers is also dependent on the substituents attached to the starting polymers [7]. For example, precursor polymers having nitrogen atoms and hydroxyl groups gave higher carbonization yields even though the pyrolysis pathway is very difficult to predict due to the incorporation of the heteroatoms into the graphene sheets. Various types of carbonaceous materials have been studied as anode materials for lithium ion batteries, including natural and synthetic graphites, carbon fibers, carbon blacks, cokes, and a variety of other materials prepared by the pyrolysis of organic precursors in an inert gas [9–15]. Lithium intercalation in graphite, in particular, has been most extensively studied [10,16–18]. It is well established that one lithium atom per six carbon atoms can be intercalated when lithium is fully intercalated into the graphite layer.

Recently, there have been numerous reports on lithium insertion into carbonaceous materials prepared from organic precursors at temperatures below 1000°C. In general, these materials show higher capacity than that of graphite (372 mA h/g) [15,19–21]. There are few reports on the investigation of microstructure of carbonaceous materials on the molecular level, even though the structure of precursor polymers is very important for the preparation of graphite-like structures with different electrochemical properties. We have studied polyacene-based polymers or graphite-like pyropolymers from various precursor polymers to investigate their microstructure and applicability as anode materials of lithium batteries. Investigation of the microstructure of each graphene sheet as well as the macrostructure of the pyropolymers can be helpful to clarify the Li insertion mechanism into the graphite-like materials [2].

In this article, we report the electrochemical behavior of these synthetic carbons having different properties and different structures by utilizing TEM, discharge/charge tests and cyclic voltammetry.

2. Experimental

2.1. Instruments

Elemental analyses (EA) were performed on the elemental analyzer of Foss Heraeus Analysentechnik instru-

Table 1
Polymerization of some acetylene derivatives

<table>
<thead>
<tr>
<th>Materials</th>
<th>Catalyst</th>
<th>[M] (M)</th>
<th>[Cat.] (mM)</th>
<th>[Cocat.] (mM)</th>
<th>Polymer Yield (%)</th>
<th>M&lt;sub&gt;c&lt;/sub&gt;</th>
<th>Pf&lt;sub&gt;r&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(MPBEY)</td>
<td>NbCl&lt;sub&gt;5&lt;/sub&gt;·(n-Bu)&lt;sub&gt;4&lt;/sub&gt;Sn</td>
<td>0.5</td>
<td>10</td>
<td>10</td>
<td>55</td>
<td>2483</td>
<td>1.45</td>
</tr>
<tr>
<td>poly(DPBEY)</td>
<td>TaCl&lt;sub&gt;5&lt;/sub&gt;·(n-Bu)&lt;sub&gt;4&lt;/sub&gt;Sn</td>
<td>0.5</td>
<td>16.7</td>
<td>16.7</td>
<td>80</td>
<td>1467</td>
<td>1.77</td>
</tr>
<tr>
<td>poly(PyPDO)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>TaCl&lt;sub&gt;5&lt;/sub&gt;·(n-Bu)&lt;sub&gt;4&lt;/sub&gt;Sn</td>
<td>0.5</td>
<td>16.7</td>
<td>16.7</td>
<td>97</td>
<td>insol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>–</td>
</tr>
<tr>
<td>PHDO</td>
<td>TaCl&lt;sub&gt;5&lt;/sub&gt;·(n-Bu)&lt;sub&gt;4&lt;/sub&gt;Sn</td>
<td>0.5</td>
<td>16.7</td>
<td>16.7</td>
<td>90</td>
<td>insol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>–</td>
</tr>
</tbody>
</table>

<sup>a</sup>Polymerized in chlorobenzene at 80°C for 24 h (in Ar atmosphere). The structure of monomer: Ph–C≡C–CH=CH–OCH<sub>3</sub> (MPBEY); Ph–C≡C–CH=CH=CH–Ph (DPBEY); Py–C≡C–C≡C–CH<sub>2</sub>OH (PyPDO); HOCH<sub>2</sub>–C≡C–C≡C–CH<sub>2</sub>OH (HDO).

<sup>b</sup>The precipitated polymers in methanol were gravimetrically estimated.

<sup>c</sup>Values were obtained by GPC analysis with polystyrene standards.

<sup>d</sup>Polymerized in chlorobenzene at 115°C for 24 h.

<sup>e</sup>Insoluble in any organic solvent.
ment. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 20°C/min with Perkin-Elmer TGA7. TEM was carried out with a Carl Zeiss Model EM912 Omega operating at 120 kV.

2.2. Polymerization

All the procedures for the preparation of the catalyst system and polymerization reaction were carried out under dry argon atmosphere. A typical procedure is as follows (Table 1, first row): A suspension of NbCl₅ (171 mg, 0.63 mmol) and 0.1 M solution of (n-Bu)₅Sn in chlorobenzene (6.32 ml, 0.63 mmol) was stirred at 80°C for 15 min and chlorobenzene (58 ml) solution of MPBEY (5 g, 31.6 mmol) was added with continuous stirring at 80°C for 24 h. Methanol was added to the reaction mixture followed by suction filtration to obtain the polymer (2.75 g, 55%) and the product was dried overnight under vacuum at 50°C.

2.3. Vacuum pyrolysis of polymers

The pyrolysis of polymers under vacuum was carried out using a homemade vacuum pyrolysis reactor (Fig. 1a) or a Cole-Parmer Programmable vacuum furnace. The specimen (about 1 g) was introduced into a quartz cell (inside diameter, 35 mm; length, 400 mm) for homemade vacuum furnace. For the programmable vacuum furnace pyrolysis, the specimen (about 1 g) was introduced into a stainless steel reactor (inside diameter, 25 mm; height, 500 mm) to avoid the loss of the sample by diffusion under the vacuum. The cell was closed and put into the muffle of the vacuum furnace and evacuated to around 10⁻¹ Torr. The specimens were dried for 10 min at 50°C and the reactor was heated at a ramping rate of 10°C/min. After the reaction under vacuum, the pyroproduct was cooled to room temperature and removed from the reactor after the

Table 2
Pyrolysis of precursor polymers

<table>
<thead>
<tr>
<th>Materials</th>
<th>[H]/[C]</th>
<th>[N]/[C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(MPBEY)-750</td>
<td>0.22</td>
<td>–</td>
</tr>
<tr>
<td>poly(DPBEY)-750</td>
<td>0.19</td>
<td>–</td>
</tr>
<tr>
<td>poly(PyPDO)-800</td>
<td>0.18</td>
<td>0.06</td>
</tr>
<tr>
<td>PHDO-800</td>
<td>0.11</td>
<td>–</td>
</tr>
</tbody>
</table>

*Pyrolyzed in vacuo (~ 10⁻¹ Torr) for 30 min.
*The number after polymer denotes the heat-treatment temperature (T_p).
*The molar ratios of hydrogen to carbon and nitrogen to carbon were determined by EA.

Scheme 1. Structures of precursor polymers and synthetic carbons.
Table 3
TGA of some precursor polymers at 660°C.

<table>
<thead>
<tr>
<th>The structure of monomer</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph-C=CH=CH-Ph</td>
<td>12.8</td>
</tr>
<tr>
<td>HOCH₂-C=CH=CH-Ph</td>
<td>50.1</td>
</tr>
<tr>
<td>CH₃-C=CH=CH-OCH₃</td>
<td>55.3</td>
</tr>
<tr>
<td>Ph-C=CH=CH-CH₃</td>
<td>64.4</td>
</tr>
<tr>
<td>Ac-C=CH=CH-H</td>
<td>65.4</td>
</tr>
<tr>
<td>Py-C=C-C=CH₂OH</td>
<td>66.5</td>
</tr>
<tr>
<td>HOCH₂-C=C=C-CH₂OH</td>
<td>57.0</td>
</tr>
</tbody>
</table>

a Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 20°C/min with Perkin-Elmer TGA7.

b The precursor polymers polymerized by metathesis were analyzed by TGA method.

c Polymerized in chlorobenzene at 80°C for 24 h; [M]₀/[Cat.]/[Cocat.] = 30/1/1.

d The polymer was obtained by the pyrolysis.

release of vacuum. The reaction at the highest temperature is controlled exactly for 30 min. Low-temperature under-vacuum pyrolysis (below 300°C), especially for poly-(DPBEY), was carried out using a homemade vacuum pyrolysis reactor as shown in Fig. 1b. The specimens were pyrolyzed at a heating rate of 5°C/min. When the reaction was terminated to give a brown solid, the pyroproduct was cooled to room temperature and removed from the cell. High-temperature treatment (over 400°C) for this precursor polymer was performed in a programmable vacuum furnace. The pyropolymer are denoted by polymer-\( T_p \) (\( T_p \); pyrolysis temperature).

2.4. Charge/discharge experiments

The carbons prepared were tested for anode materials of lithium ion batteries by the techniques of discharge/charge and cyclic voltammetry. The preparation of electrodes has been described in detail elsewhere [22]. Electrochemical measurements were performed in a three-electrode cell.

Fig. 2. TEM photographs of disordered particles in (a) poly(MPBEY)-750 and (d) poly(DPBEY)-750; (b) and (c) are the electron diffraction patterns of (a) and (d), respectively.
with lithium metal as a counter electrode and a reference electrode. The organic electrolyte used was 1.0 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (2/1, vol/vol) solution (battery grade, Mitsubishi Petrochemical). The cyclic voltammetry of the carbon electrodes was carried out in the range of 0.0 to 3.0 V vs. Li/Li\(^+\) at scan rates of 1 mV/s. The discharge (inserting lithium) and charge (removing lithium) tests for the carbon electrodes were carried out between 0.0 and 2.5 V vs. Li/Li\(^+\) using a constant current of 24.8 mA/g.

3. Results and discussion

The polymers were obtained by the metathesis polymerization of enynes and diacetylenes (Table 1) and pyrolyzed to yield pyropolymers (carbonaceous materials). All the heat-treated pyropolymers were subjected to EA. The molar ratios of hydrogen to carbon and nitrogen to carbon are shown in Table 2. The degree of carbonization can be controlled by the T\(^p\) applied, since the H/C and N/C molar ratios vary with T\(^p\). We can also predict a likely structure of the pyropolymers from these results even though exact structure cannot be obtained due to the defect sites of the pyropolymers that are expected to show different [H]/[C] and [N]/[C] ratios. The possible structures of single layers of each synthetic carbon are shown in Scheme 1.

Carbonization yields at 660°C are shown in Table 3. The carbonization yield varies according to the substituents directly attached to the polymer backbone because substituents have different properties of hydrogen.

![TEM photographs](image-url)
Fig. 4. TEM photographs of ordered particles in (a) poly(MPBEY)-750, (c) poly(DPBEY)-750, and (e) poly(PyPDO)-800; (b), (d) and (f) are the electron diffraction patterns of (a), (c) and (e), respectively.
bonding, dipolar interaction, partial crosslinking, etc. from each other. For example, when the poly(1,4-diphenyl-1-buten-3-yn-5-ol) [poly(DPBEY)] is kept at 250°C, the gummy brown poly(DPBEY) is converted into dark-brown powder [poly(DPBEY)-250] which shows 20% increased carbonization yield compared to that of poly(DPBEY) in TGA experiments [7]. This is due to partial intramolecular crosslinking on annealing and depolymerization on pyrolysis is decreased. The weight loss can be attributed to the cleavage of pendant groups to give graphene sheets. Another factor is the steric hindrance of bulky substituents directly bonded to the polymer backbone. The polymers are cleaved during pyrolysis because ordering is hindered by these bulky substituents and secondary fragments are evolved through a gas outlet of the reactor (e.g., vacuum pyrolysis equipment). The polymer-$T_g$ (> 500°C), therefore, should have some defect sites during recombination processes of the remaining carbon residue in accordance with the EA results (see Table 3). The TGA results of some other precursor polymers are shown in Table 3. When the substituent was changed to the hydroxyl group, the carbonization yield of polymer [poly(1-phenyl-1-penten-3-yn-5-ol); poly(PPYO)] was increased to 50.1% at 660°C strongly suggesting that there are much more defect sites in the poly(DPBEY) than in the poly(PPYO) because the phenyl group inhibits the condensation due to their bulkiness. However, carbonization can be affected by the melting properties of the precursor polymers. The carbonization yield is high when the polymers such as poly[(Z)-1-methoxy-4-phenyl-1-buten-3-yn-5-ol]poly(MPBEY)] do not melt during the pyrolysis [6].

The selected area electron diffraction (SAD) and TEM studies were carried out to check the crystallinity of synthetic carbons. Four carbonaceous materials were selected to investigate the electrochemical properties during the Li battery tests among many precursor polymers. Poly(MPBEY) is converted into the disordered carbon at 750°C as shown in Fig. 2a and b. Poly(DPBEY) which has solely carbon and hydrogen in the molecule is also converted into the defect-site-rich (or disordered) synthetic carbon at 750°C as shown in Fig. 2c and d. Precursor polymers from enynes yielded synthetic carbons having many defect sites because the olefin pendant group cannot form honeycomb structures through aromatization unlike most precursor polymers from diacetylenes. For example, TEM images of the poly(PyPDO)-800 particles prepared with polymer from diacetylenes show features different from these synthetic carbons. Poly(PyPDO)-800 is a mixture of graphitic and carbonaceous materials (Fig. 3a) [23]. Fig. 3b evidently shows SAD pattern and photograph of the semicrystalline particle. This particle shows mixed morphology of a single crystal of graphite and disordered carbon unlike those of the particles shown in Fig. 2a–d. The particles of PHDO-800, however, shows different features from poly(PyPDO)-800. PHDO-800 have disordered morphology which does not have an ordered stack-

![Fig. 5. Discharge/charge curves of the carbon samples: (a) poly(MPBEY)-750, (b) poly(DPBEY)-750, (c) poly(PyPDO)-800, and (d) PHDO-800. The solid and dot lines correspond to the first and second cycle, respectively.](image-url)
Table 4
Charge/discharge capacity and cyclic efficiency of poly(MPBEY)-750, poly(DPBEY)-750, poly(PyPDO)-800, and PHDO-800

<table>
<thead>
<tr>
<th>Materials</th>
<th>Capacity (mA h/g)</th>
<th>Irreversible Capacity (mA h/g)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Discharge</td>
<td>Charge</td>
<td>1st</td>
</tr>
<tr>
<td>poly(MPBEY)-750</td>
<td>1040 520</td>
<td>495 435</td>
<td>545</td>
</tr>
<tr>
<td>poly(DPBEY)-750</td>
<td>710 300</td>
<td>275 260</td>
<td>440</td>
</tr>
<tr>
<td>poly(PyPDO)-800</td>
<td>820 340</td>
<td>355 295</td>
<td>470</td>
</tr>
<tr>
<td>PHDO-800</td>
<td>940 305</td>
<td>320 255</td>
<td>620</td>
</tr>
</tbody>
</table>

*a* Electrolytes used in the test: 1.0 M LiPF<sub>6</sub>/EC + DMC (2:1). Abbreviations: EC (ethylene carbonate); DMC (dimethyl carbonate).

*b* Irreversible capacity in the 1st cycle.

rived polymers because fused aromatic structure cannot be formed easily from the pendant olefin groups during pyrolysis. Besides, poly(MPBEY) and poly(DPBEY) have bulky phenyl moieties adjacent to the polyacetylene backbone causing fragmentation into small molecules such as ethylene, benzene, etc. As a result, both poly(MPBEY) and poly(DPBEY) are converted into disordered carbon having many defect sites. Mesophase carbon, however, can be obtained from poly(DPBEY) because this has sterically much more hindered structure than that of poly(MPBEY).

The defect sites can be oxidized by exposure to air in the process of fabrication of carbon electrodes to give carboxyl groups, carboxylic anhydrides, lactones, lactols, hydroxyl groups, ether-type oxygen, carbonyl groups, etc. [23,24]. It is well known that lithium forms a very wide range of complexes with amines, ethers, carboxylates, alkoxydes, and many other ligands [25,26]. The reversible interaction between lithium and surface functional group can play an important role for extra charge capacity especially in poly(MPBEY)-750 compared to other carbons derived from diacetylenes because poly(MPBEY)-750 has relatively large amounts of defect sites. On the other hand, small charge capacity is observed in poly(DPBEY)-750 because mesophase carbon which is partially soluble in electrolyte and cannot react with lithium reversibly is formed as mentioned above.

The irreversible capacity observed usually in the first discharge step is defined as the difference in capacity between the first discharge and the subsequent charge. It is generally accepted that a part of the irreversible capacity is caused by the formation of a so-called solid electrolyte interface (SEI) on the surface of carbons due to the decomposition of electrolyte [27]. The samples studied in this report show enormously large irreversible capacities.

Fig. 6. Cyclic voltammograms of the carbon samples: (a) poly(MPBEY)-750, (b) poly(DPBEY)-750, (c) poly(PyPDO)-800, and (d) PHDO-800.
between 470 and 620 mA h/g (see Table 4). Lithium can also irreversibly react with surface functional groups such as hydroxyl and carboxyl groups [28]. These samples have many defect sites where surface oxides may be formed as shown in Scheme 1. The large irreversible capacity is conclusively caused by the many defect sites.

Cyclic voltammograms (CV) of the carbon samples and the plots of discharge capacity (Q\textsubscript{dis}, cathodic scan) and charge capacity (Q\textsubscript{ch}, anodic scan) calculated in each cycle vs. cycle number are shown in Fig. 6 and Fig. 7, respectively. Poly(PyPDO) displays very large capacity on CV tests compared to other carbon samples (Fig. 7). These results indicate that the kinetics of lithium insertion/deinsertion in poly(PyPDO)-800 is faster than those of other carbons. Poly(PyPDO) have incorporated nitrogen functional groups [23] which are different from any other nitrogen containing carbonaceous materials (e.g., PAN-based carbons). The incorporated quaternary nitrogen in poly(PyPDO)-800 makes the single layers spherical and prohibits the particle from maturing compared to other carbonaceous materials indicating that lithium can rapidly diffuse in poly(PyPDO)-800.

4. Summary

Four kinds of synthetic carbons were prepared by vacuum pyrolysis of black polyacene-based polymers. The electrochemical properties of carbons were dependent on the precursor polymers. Precursor polymers from enynes yielded synthetic carbons having many defect sites because the olefin pendant group cannot form honeycomb structures through aromatization unlike most of precursor polymers having acetylene pendant groups as verified by the TEM studies. The poly(DBPBEY)-750, poly(PyPDO)-800, and PHDO-800 show smaller charge capacities than that of graphite (372 mA h/g), while a large charge capacity of 496 mA h/g is observed from poly(MPBEY)-750 in the first cycle. Our samples show enormously large irreversible capacities between 470 and 620 mA h/g due to the additional irreversible reaction of lithium with surface functional groups such as hydroxyl and carboxyl groups besides electrolyte decomposition. Poly(PyPDO)-800 displays very large capacity on CV tests compared to other carbon samples indicating that the kinetics of lithium insertion/deinsertion in poly(PyPDO)-800 is faster than those of other carbons.

Acknowledgements

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References