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Electrochemical characteristics of lithium intercalation into natural gas coke serving as the negative electrode of a lithium battery

Qin-min Pan, Zheng-hua Deng [*], Xiao-zheng Zhang, Guo-xiang Wan

Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, 610041, China

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Abstract

The electrochemical characteristics of a new type of coke for the negative electrode of a lithium ion battery are investigated. This coke is prepared from natural gas by means of thermoplasma technology. The initial discharge–charge properties of natural gas coke of several kinds are discussed. The effects of surface modification of cokes on the characteristics of lithium intercalation during the first cycle are also explored. The properties of lithium intercalation into carbon electrodes show that the electrochemical behaviour is determined by the nature of the carbon material. The results also demonstrate that the surface properties of carbon electrodes remarkably influence the efficiency of the first cycle. Surface modification of coke electrodes with polymer can increase the initial coulombic efficiency but reduces the initial discharge capacity. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Natural gas coke; Lithium intercalate; Chemical surface modification

1. Introduction

Carbon is a promising candidate material for negative electrodes in lithium-ion batteries. Extensive efforts have been directed to the development of different carbonaceous materials which are able to deliver high specific capacity, high coulombic efficiency, and long cycle life. The structure of the carbon exerts a major influence on lithium intercalation, it determines how much can be intercalated and at what voltage [1,2]. Thus, many studies have attempted to define the relationship between the structure and the electrochemical properties of carbon. For example, there have been reports [3,4] of the variation in capacity with structural parameters of the carbon host. It has been concluded that these parameters profoundly affect the attainable energy of a practical lithium ion cell. In summary, the lattice constant, graphitization, the layer spacing (d_{002}) and the size of the crystalline domains (L_a and L_c) are major factors which influence the capacity of carbon. It is difficult, however, to produce a theoretical model which explains the change in capacity with structure. In part, this is because carbon structure is difficult to quantify. Recently, Dahn et al. [4] developed a model for the structure of disordered carbons and a corresponding structure-refinement program for power X-ray data that allows accurate quantification of the structural parameters (L_c, L_a, etc.). According to this model, high-capacity carbons can be found near $P = 0$ (P is the fraction of turbostratic disorder in carbon) with small (002) half width. These are very graphitic carbons with flat voltage curves near 0.1 V. Carbons with a large (002) half width and large P also yield large capacity. These are low-temperature carbons with significant fractions of unorganized carbon and sloping voltage profiles. In this paper, we have prepared carbonaceous material from a natural gas precursor by means of thermoplasma technology. The coke obtained is a typical hard carbon. Different cokes were prepared under different synthesis conditions and the effect of structural factors on the electrochemical behaviour of lithium-ion batteries is examined.

2. Experimental

2.1. Carbons

Natural gas coke (NGC) samples were synthesized from natural gas at 2000 to 3000°C by means of thermoplasma technology. Pyrolysis of natural gas was performed at 2000 to 3000°C under plasma atmosphere and the free

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[*] Corresponding author. E-mail: gxwanioc@mail.sc.cninfo.net

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radicals produced were polycondensated into coke. Different cokes were obtained according to reaction conditions. The products were then ground, using a pulverizer, to below 280 mesh. The samples are termed CH-1, CH-2 and CH-3, respectively.

2.2. Sample preparation and electrochemical measurements

The carbon electrodes consisted of a mixture of coke and polytetra-fluoroethylene (PTFE, 5 wt.%) and were pressed into tablets of 10 mm diameter under a pressure of 14 MPa and oven-dried at 120°C for 4 h. The negative electrodes were then weighed to determine the active mass of carbon. The counter electrode was a lithium metal foil disc of 10 mm diameter and 1 mm thickness. The electrolyte was a 1.0 M solution of $LiClO_4$ in a 1:1 volume percent mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Each laboratory cell was constructed using the electrodes described above, Celgard 2400 microporous film and a disc of lithium foil. Cell assembly was carried out in a glove box filled with dry argon. All cell testing was carried out with computer-controlled constant-current cyclers at a constant temperature of 25°C. Each test was performed in duplicate. The cut-off voltage was 0.01 V in discharge and 2.0 V in charge. The characteristics of intercalation of lithium into coke were measured by cyclic voltammetry.

2.3. X-ray diffraction

Powder X-ray diffraction (XED) profiles were collected for each type of coke using a Philips diffractometer equipped with a copper target X-ray tube and a diffracted beam monochromator. The L_c structural parameter was estimated from the 002 Bragg peak using the Scherrer equation, i.e.,

$$L_c = k\lambda/\beta\cos\theta \tag{1}$$

The parameter L_a was determined from the Warren–Bodenstein equation, viz.,

$$L_a = 1.77\lambda/\beta\cos\theta \tag{2}$$

where: λ is the X-ray wavelength, θ is the Bragg angle, β is the full-width at half-maximum of the peak, κ is the correctness factor.

3. Results and discussion

3.1. Structural characteristics of natural gas cokes

There are large differences between the properties and the structures of carbon anode materials used in lithium ion batteries because of different precursors and methods employed in their preparation [5]. It is necessary to understand the influence of structure on the properties of carbon electrodes in order to develop improved lithium-ion batteries. In this paper, we have synthesized three types of cokes from a natural gas precursor by thermoplasma technology. The cokes (NGC) have different structural parameters. The XRD patterns of the NGC samples are presented in Fig. 1. The shape, intensity and full-width at half maximum (FWHM) of the peak are different for the coke samples. A general structural feature of these materials is their very similar interplanar spacing which has a d_{002} value between 3.45 and 3.53 Å. The lattice parameters and the initial cycle data of each carbon sample are summarized in Table 1.

A disordered (turbostratic) structure is present in these samples as indicated by the data of Fig. 1 and Table 1. It is the degree of short-range order (SRO) that causes the difference in XRD patterns and lattice parameters. The micro-morphology of coke grains is revealed by transmission electron microscope (TEM), see Fig. 2. The micro-

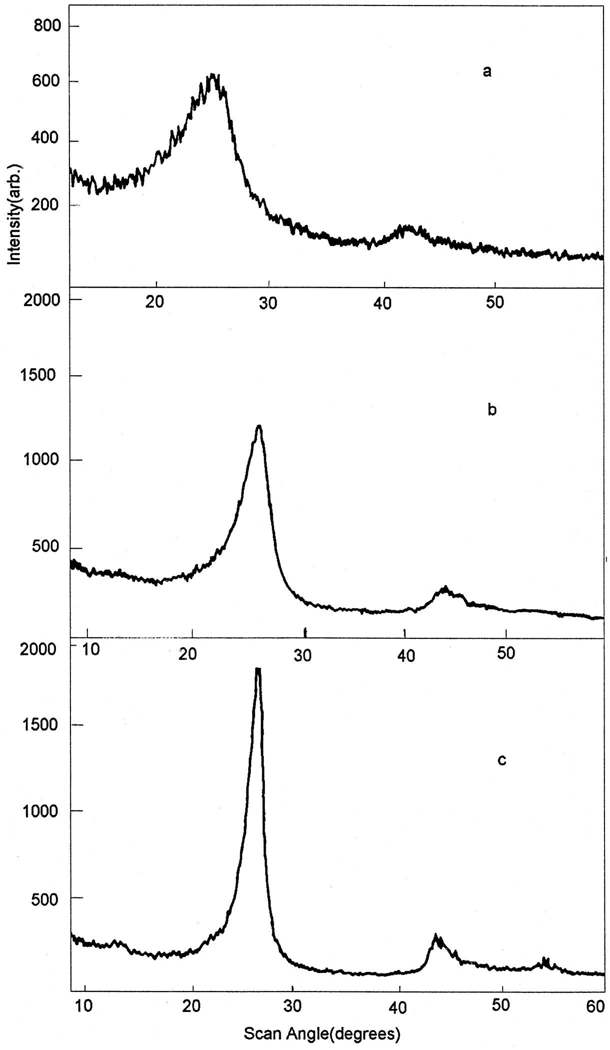

Fig. 1. X-ray diffraction patterns of natural gas coke samples: (a) CH-1; (b) CH-2; (c) CH-3.

Table 1
Summary of structural and electrochemical data for natural gas coke samples

Sample	CH-1	CH-2	CH-3
d_{002} (Å)	3.531	3.489	3.450
L_c (Å)	18.0	58.3	106.8
L_a (Å)	31.9	103.2	189.0
(002) FWHM (degrees)	5.0	3.1	1.7
BET (m^2 g^{-1})	175	82	44
Size of coke grain (μm)	20 ~ 80	120 ~ 400	200 ~ 600
Capacity of first discharge (mAh g^{-1})	990	480	380
Capacity of the first charge (mAh g^{-1})	70	145	190
Coulombic efficiency (%)	7.1	30.2	50
Capacity loss at 3.0 to 0.6 V (mAh g^{-1})	540	150	100
Capacity loss at 0.6 to 0.01 V (mAh g^{-1})	370	185	80
Capacity loss at 3.0 to 0.01 V (mAh g^{-1})	910	335	180

graphs show that there are nanotubes in the CH-1 sample. The CH-3 coke is an aggregation of nanometric particles. The structure of sample CH-2 lies between CH-1 and CH-3.

3.2. Discharge–charge and voltammetric properties of coke samples

The initial discharge–charge curves and cyclic voltammograms of CH-1 and CH-3 electrodes are shown in Figs. 3 and 4, respectively. During the first cycle, the discharge capacity of sample CH-1 exceeds 1000 mAh g^{-1} while the charge capacity is only 70 mAh g^{-1} (coulombic efficiency = 7%). This means that most of the lithium ions intercalated into coke electrode during the first discharge are used to form an irreversible intercalation compound. The discharge–charge curve of CH-1 displays a large plateau with a large irreversible capacity loss at potentials around 0.8 V. The plateau is due to decomposition of the solvent on the surface of the coke electrode; the potential range of the plateau corresponds to the decomposition voltage of carbonate reduction on the coke surface. The cyclic voltammograms of CH-1 also clearly indicate that the current of the reduction peak is greater than that of the oxidation peak, which is due to the removal of lithium ions from the coke electrode. After several cycles, the CH-1 electrode exhibits a distinct oxidation peak while the polarization of coke electrode is obvious (the voltage of oxidation peak is around 1.5 V). Although the discharge capacity of the

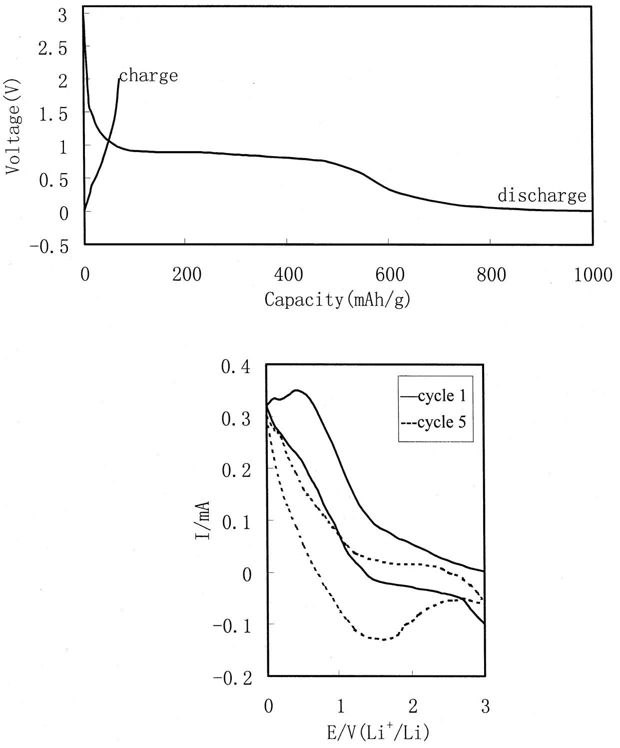

Fig. 3. Voltage profile of first cycle and cyclic voltammograms for CH-1 electrode in 1 M $LiClO_4$ EC/DEC; current density: 0.2 mA cm^{-2}; sweep rate: 1 mV s^{-1}.

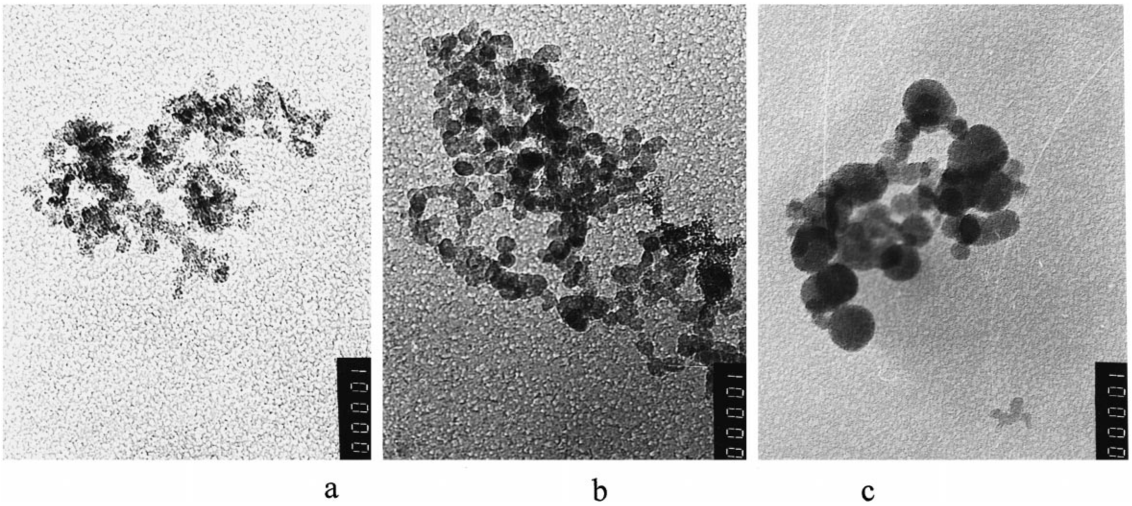

Fig. 2. Transmission electron micrographs of natural gas coke samples: (a) CH-1; (b) CH-2; (c) CH-3.

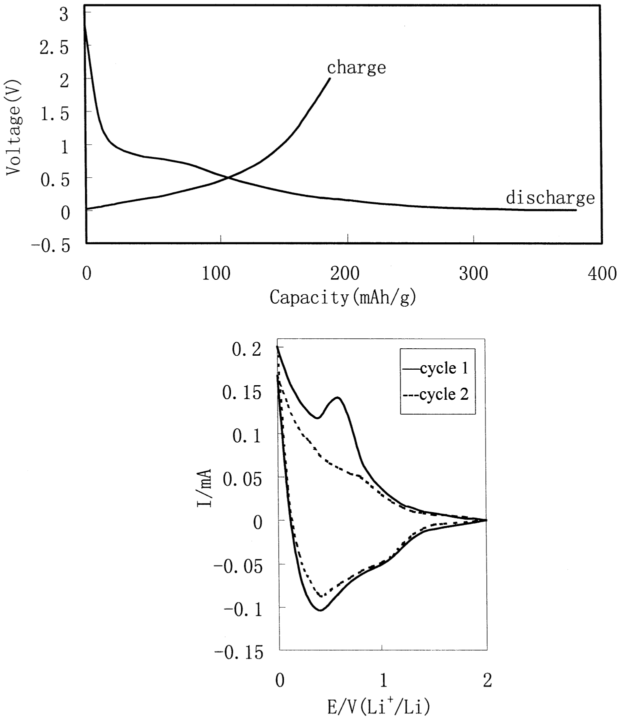

Fig. 4. Voltage profile of first cycle and cyclic voltammograms for CH-3 electrode in 1 M $LiClO_4$ EC/DEC; current density: 0.2 mA cm^{-2}; sweep rate: 1 mV s^{-1}.

CH-3 sample is only about 360 mAh g^{-1}, its charge capacity is 180 mAh g^{-1}, i.e., the coulombic efficiency is 50%. The voltammograms for CH-3 also illustrate that there is a reduction peak (~0.8 V) which is due to decomposition of solvent. This peak disappears after the first cycle. The main difference between CH-1 and CH-3 samples is those large oxidation peak displayed by the latter. The results demonstrate that CH-3 has a greater lithium storage ability than CH-1.

3.3. *Correlation of electrochemical characteristics and structure of natural gas cokes*

The above studies reveals that there are in the major differences discharge–charge behaviour of CH-1 and CH-3 and that this is an influence of microstructure on the electrochemical properties of natural gas coke. The data in Table 1 reveal some relationships between the electrochemical properties and the microstructure. The reversible capacity and coulombic efficiency of coke increases with increase in BET area, L_c and L_a but decreases with decrease in d_{002} and full width at half-maximum of the peak. This means that the reversible capacity of coke is determined by the size of the graphite domains. The most remarkable effect of structure on the lithium-storage ability of coke is the irreversible capacity loss during the first cycle. As it has been pointed out [6,7] that the irreversible capacity loss during the first cycle is caused by decomposition of the solvent to produce a solid electrolyte interface (SEI) on the surface of carbon electrode and by reaction of lithium ions with the active sites in the bulk of the carbon [6,7]. Generally, the solvent decomposition reaction occurs at ~0.8 V (Li/Li^+). Therefore, it is possible that the irreversible capacity loss shown in Table 1 is due mainly to solvent decomposition, and the irreversible capacity loss in the range of 0.6 to 0.01 V is produced by side reactions of lithium ion with active sites in the bulk of the coke electrode. Sample CH-1 is a nanometric coke with a large specific areas (175 m^2 g^{-1}) while CH-2 and CH-3 have a greater grain size and lower specific area than CH-1. The irreversible capacity loss caused by decomposition of solvent on CH-1 is 3 to 5 times greater than that on CH-2 or CH-3. Furthermore, since natural gas coke is the product of pyrolyzed natural gas using thermoplasma technology at 2000 to 3000°C and is a typical glassy carbon, the texture of natural coke is in a state of thermodynamical instability and there are many active sites in the bulk. The data given in Table 1 demonstrate that a decrease in the grain size of coke and an increase in BET specific area increase the irreversible capacity loss caused by reaction of lithium ions with the active sites. In an earlier work [8], we found that the texture of natural gas coke is unstable and the graphitic structure collapses as insertion and removal of lithium ion proceeds. Thus, the method of preparation of the coke is an important factor which affects both the irreversible capacity loss and the stability of the carbon structure.

4. Effect of surface modification on lithium intercalation into coke

As discussed above, the coke prepared from natural gas by thermoplasma technology has deficiencies such as high chemical activity on the surface and a large number of active sites in the bulk of the coke. In order to decrease the irreversible capacity loss and increase the coulombic efficiency during the first cycle, we modified the surface of the CH-3 sample. The effects of modification on the electrochemical properties of coke have been investigated.

The discharge–charge curves of coke and modified coke are compared in Fig. 5. Curve (b) for a CH-3 sample

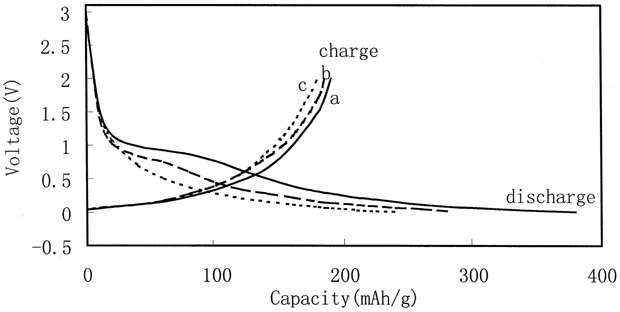

Fig. 5. Comparison of the character of the first cycle between treated and untreated coke electrodes made from sample CH-3. Current density: 0.2 mA cm^{-2}. (a) Untreated coke, (b) treated by H2O2, (c) treated by polymer.

treated with H_2O_2 under acidic conditions and then neutralized by Li_2CO_3. Curve (c) is for a CH-3 sample encapsulated with polymer which is polymerized from the monomer absorbed on the surface of the coke. The initial discharge capacity of modified coke decreases while the initial charge capacity remains unchanged. As a result the coulombic efficiency of the first cycle is increased. Results show that different methods of preparation induce remarkable differences in the properties of the coke. A goal of surface modification is to reduce the degree of decomposition of solvent by reducing the activity and organic groups on the surface of the coke and by decreasing the number of active sites in the bulk of the coke. Thus, modification using a polymer causes a greater decrease in the decomposition of solvent than treatment with H_2O_2. The plateau at about 0.8 V due to decomposition of solvent in curve (c) disappears during the first discharge. As a result, the coulombic efficiency of the initial cycle increases to 65 and 75% on H_2O_2-treated and polymer-treated coke samples, respectively.

5. Conclusion

Studies of natural gas coke prepared from natural gas precursor by means of thermoplasma technology shows that: (i) the decomposition of solvent on the surface of nanometric coke is serious because of its high activity and specific area; (ii) the lithium ions intercalate into nanometric coke mainly to form electrochemical irreversible compounds with low reversible capacity and low first coulombic efficiency. As the size of the graphite domains increases, the initial efficiency and the reversible capacity also increases. Surface modification of natural gas coke, especially by polymer, passivates the surface of coke and thus reduce the decomposition of solvent and increases the coulombic efficiency.

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