

Short communication

Influence of active surface on electrochemical properties of mesocarbon microbeads powders

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Abstract

Mesocarbon microbeads (MCMB) powders were treated in Ar–H₂–SF₆ radio frequency inductively coupled thermal plasma. The structure, chemical composition and related electrochemical property changes have been studied. The results demonstrated that the active surface area has a great influence on the electrochemical properties of MCMB powder, and the specific irreversible capacity loss decays non-linearly with the increase of active surface area.

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1. Introduction

Carbonaceous materials have been proven to be an inexhaustible source for scientific research and technological development, such as electrode of lithium ion rechargeable battery [1,2]. Surface and chemical modifications are usually the first step for the application of carbon materials [3,4]. The modifications can change surface composition and structure, active surface area (ASA) and total surface area (TSA), which all play important roles in carbon chemical reactions and applications. The concept of ASA was firstly introduced by Laine and his co-workers in 1963 [5]. The way used to characterize the ASA was to remove surface defects by heat treatment and then measuring the amount of oxygen subsequently chemisorbed. The extent of ASA was thought to be a function of such properties of the carbon as crystallite size, crystallite orientation, vacancy concentration in the basal plane, and impurity concentration, type, and location.

For battery applications, the electrochemical lithium intercalation and de-intercalation capacities are important characteristic of carbon materials, which strongly influence the energy density. While, during the first charge and discharge cycle, an irreversible capacity loss (ICL) always exists, and

the ICL has been attributed to the solid electrolyte interphase (SEI) formation and other side reactions. Carbon surface structure has a great influence on the ICL of electrodes [6].

Radio frequency inductively coupled thermal plasma (RF-ICP) treatment has been proved to be a successful way to modify carbon surface for its high temperature, high energy density, high chemical reactivity properties and high heating and cooling rate ($\sim 10^6$ K/min) [7]. The aim of this work is to study the effect of Ar–H₂–SF₆ plasma treatment induced active surface of MCMB powder on the electrochemical properties of the anodes made from these materials.

2. Experimental procedure

The carbon used in this investigation was mesocarbon microbeads (MCMB), which is a kind of artificial graphite. The RF induction plasma generating and powder feeding apparatus have been shown elsewhere [8]. The plasma conditions were set as follows: Power (40 kW), plasma gas (Ar 15 l/min), sheath gas (Ar 60 l/min), and H₂ (3 l/min). The powder carrier gas was a mixture of Ar and SF₆, and its total flow rate was set as 10 l/min, in which the SF₆ flow rate was changed from 0.4 to 1.0 l/min. The plasma was generated at

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the reactor pressure of 27 and 53 kPa. Surface morphology of MCMB powders was observed using scanning electron microscopy (SEM, HITACHI S-5000). Surface area was measured by N₂ adsorption using the Brunauer–Emmett–Teller (BET) method (BEL JAPAN, BELSORP18). Oxygen content measurement was performed on an oxygen/nitrogen analyzer (HORIBA, EMGA-650). Sulfur content measurement was carried out on a carbon/sulfur analyzer (LECO CS-444). Fluorine content was measured by ion chromatography. Fourier transform infrared (FTIR) experiments were carried out on a BIO-RAD FTS-65 FTIR spectrometer.

Electrochemical properties were measured in non-aqueous solvents containing 1 M LiClO₄. Sample electrodes were prepared by the following way: Poly vinylidene fluoride was used as the binder and slurry was spread on copper foil and dried at 150 °C under vacuum for 1 h, a 1 mol/cm² solution of LiClO₄ in a 50:50 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was used as the electrolyte; the electrochemical cell was set up in a dry box under argon atmosphere and the charge/discharge behavior of the cell was measured galvanostatically at the current density of 0.25 mA/cm² between 0 and 3 V versus Li/Li⁺ at 25 °C.

3. Results and discussion

Fig. 1 shows typical surface morphologies of the original MCMB and the plasma treated MCMB powders. The original MCMB in Fig. 1a has polyhedral shape, while Fig. 1b reveals that some particles have a lot of holes after plasma treatment. Fig. 2 gives the FTIR results on the original and the plasma treated powders. The peak at 1716 cm⁻¹ in plasma treated sample represents the C=O double bond stretching vibration in the form of C–C=O, and peaks at 1222, 1364 and 984 cm⁻¹ represent the C=S bonds, which are attributed to the chemical reactions of carbon and sulfur. Figs. 1 and 2 prove that the surface structure and chemical composition of MCMB have changed greatly after plasma treatment, which should be responsible for the change of the electrochemical properties.

Table 1 shows the relationship between the plasma conditions and the properties of plasma treated powders. From the table, it can be seen that the surface area and chemical

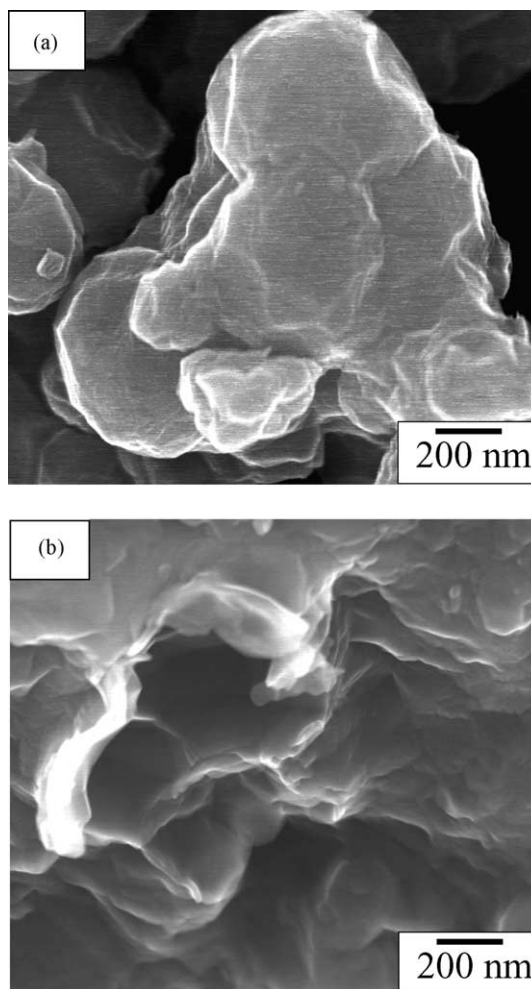


Fig. 1. Surface morphologies of original and plasma treated MCMB. (a) Original MCMB and (b) plasma treated MCMB.

composition have a relationship with the plasma condition. Fig. 3 shows the first charge/discharge curves of the original and the plasma treated MCMB powders (SF₆ flow rate: 0.5 l/min; reactor pressure: 27 kPa). It can be seen that the plasma treatment gave the great increase of discharge capacity at the first charge/discharge cycle. Fig. 4 shows the relationship between the specific ICL and the BET surface area. This figure demonstrates that the specific ICL (the

Table 1

Comparison of plasma conditions, surface area, elemental compositions and electrochemical properties

Conditions or Properties	Original	1	2	3	4
Powder carrier gas (1): Ar (l/min)		4.5	4.6	4	4.5
Powder carrier gas (1): SF ₆ (l/min)		0.5	0.4	1.0	0.5
Reactor pressure (kPa)		53	53	27	27
BET (m ² /g) (N ₂ adsorption)	1.4	2.21	1.86	0.99	1.75
Oxygen contents (%)	0.047	0.105	0.089	0.068	0.082
Sulfur contents (%)	0	0.30	0.16	0.07	0.08
Fluorine contents (%)	0	0.011	0.0081	0.003	0.0055
Reversible capacity (mAh/g)	280	302	300	317	312
Irreversible capacity (mAh/g)	30.1	27.3	28.2	29.4	27.9

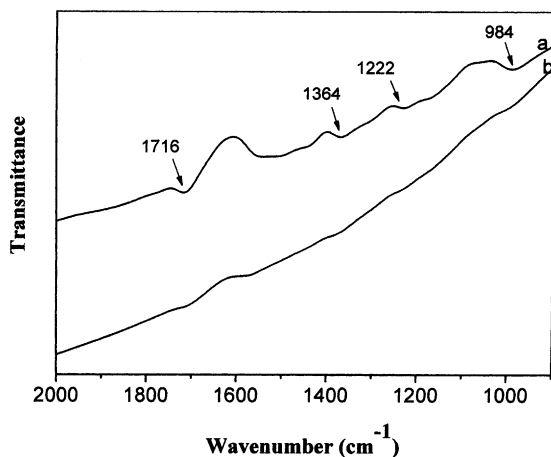


Fig. 2. FTIR results of original and plasma treated MCMB. (a) Original MCMB and (b) plasma treated MCMB.

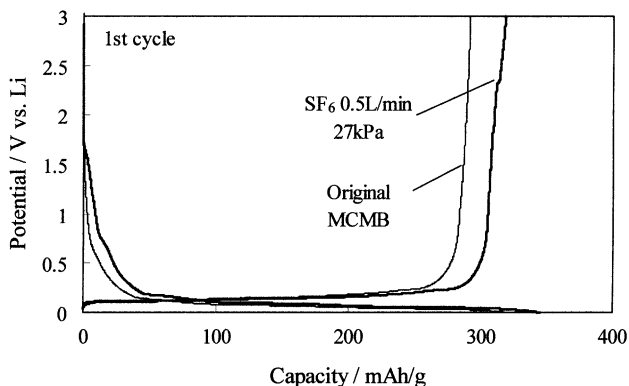


Fig. 3. First charge/discharge curve of original MCMB and plasma treated MCMB (SF_6 flow rate: 0.5 l/min; reactor pressure: 27 kPa).

calculation method is dividing ICL by TSA) decreases with the increase in BET surface area, and the relationship is approximately exponential. The curve also suggests that the carbon surface is not uniformly active for irreversible capacity loss. Fig. 5 shows the relationship between the specific ICL (the calculation method is dividing ICL by the content

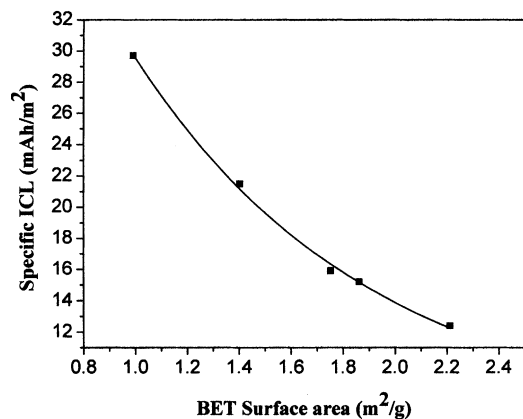


Fig. 4. The relationship between the specific irreversible capacity loss (in respect to the BET surface area) and BET surface area.

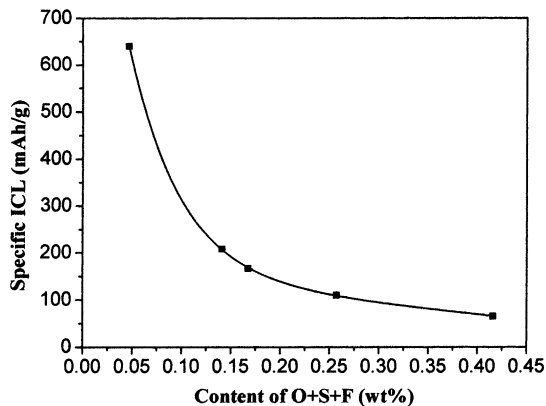


Fig. 5. The relationship between the specific irreversible capacity loss (in respect to the content of O + S + F) and the content of O + S + F.

of O + S + F) and the content of O + S + F. Since the content of active site of O + S + F can be an indicator of the ASA, this figure demonstrates that that the ASA is not the only reason to be responsible for the ICL. Fig. 5 also shows that within certain extent of ASA, the specific ICL decreases with the increase in ASA.

4. Conclusions

In summary, we have demonstrated that the electrochemical properties of MCMB as an anode of lithium-ion rechargeable battery have a great relationship with the surface area and active surface area. Within certain extent, the specific irreversible capacity loss decays non-linearly with the increase of surface area and active surface area.

Acknowledgements

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