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Characterization of Carbon Powders Prepared by Induction Plasma Treatment of Glassy Carbon Powders

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Spherical glassy carbon powders were treated in Ar-H_2, Ar-N_2 and Ar-H_2-CO_2 induction plasmas under a reduced pressure of 400 Torr. The plasma-treated powders were characterized by scanning electron microscopy (SEM), X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy[XPS]. BET surface area and the content of carbon, hydrogen, oxygen and nitrogen were also measured. Electrochemical measurements as an anode of lithium rechargeable battery were performed in 1M $LiClO_4$/(ethylene carbonate[EC] + diethyl carbonate[DEC]). Pseudo equilibrium potential profiles in the intermittent charge/discharge data indicated the plasma-treated powders have higher capacity than the untreated sample, which would be due to the modification subject to chemical composition and morphology as well as crystal structure on the surface of powders induced by plasma treatment.

1. INTRODUCTION

The carbonaceous materials as an anode of lithium secondary batteries have been studied by many researchers extensively, in order to obtain high performance such as high capacity, good cycle life and so on. Graphite, as a highly ordered carbonaceous material, has the theoretical capacity of 372 mAh/g, in which Li content should corresponds to that of a graphite intercalation compound (GIC), C_6Li. Recently, it has been reported that some kinds of disordered carbonaceous materials have a higher capacity than the theoretical value of 372 mAh/g. Some different mechanisms of lithium storage from the formation of GIC have been proposed to explain the high capacity.

Carbonaceous materials derived from polymer precursors and heated at low temperature contain some functional groups , such as =CO, -OH, -COOH groups. It has been reported the residual functional groups and hydrogen are related to the high capacity and that the functional groups and/or hetero atoms in carbonaceous materials can affect strongly its electrochemical properties as an anode of lithium rechargeable batteries.

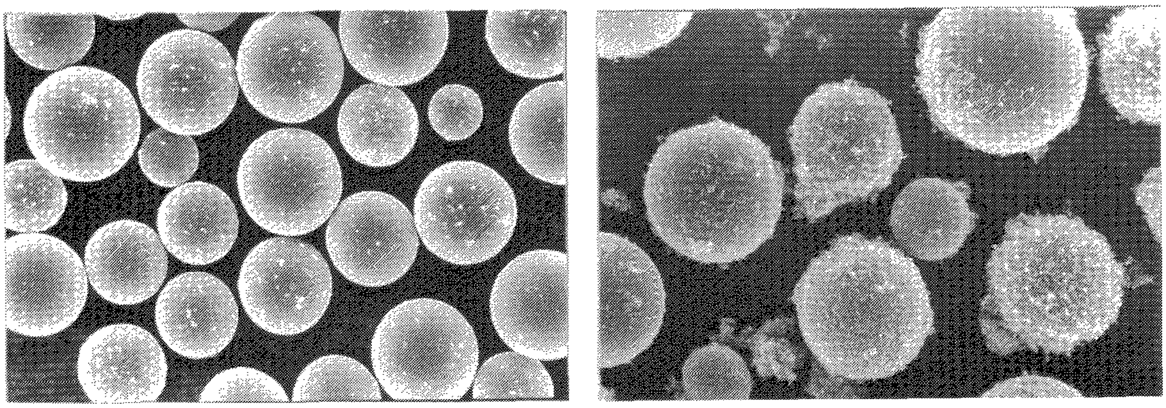
The thermal plasma is known to have very high temperature and to contain chemical reactive species. The powders introduced into the plasma are modified subjected to surface morphology and chemical composition as well as bulk microstructure. The present authors have reported that the thermal plasma treatment gave rise to the improvement of lithium storage capacity in glassy carbon powders[1]. In this work, spherical glassy carbon powders treated in Ar-H_2, Ar-N_2 and Ar-H_2-CO_2 induction thermal plasmas under reduced pressure with the intention of surface modification on carbon powders were characterized, and their electrochemical properties were investigated as an anode for lithium rechargeable battery.

2. EXPERIMENTAL

Spherical glassy carbon powder derived from phenolic resin (Yunitica, GCP-30H, 12 μm in average particle size) was used as the original carbon powder. It is well known that the pyrolysis of phenolic resins gives disordered carbon (hard carbon)[2]. Zheng and his co-investigators have reported that the pyrolyzed phenolic resin shows a specific capacity of much higher than 372 mAh/g[3]. The induction plasma torch and reactor chamber used in this study were described elsewhere[4]. The plasma generating and powder feeding conditions are summarized in Table I.

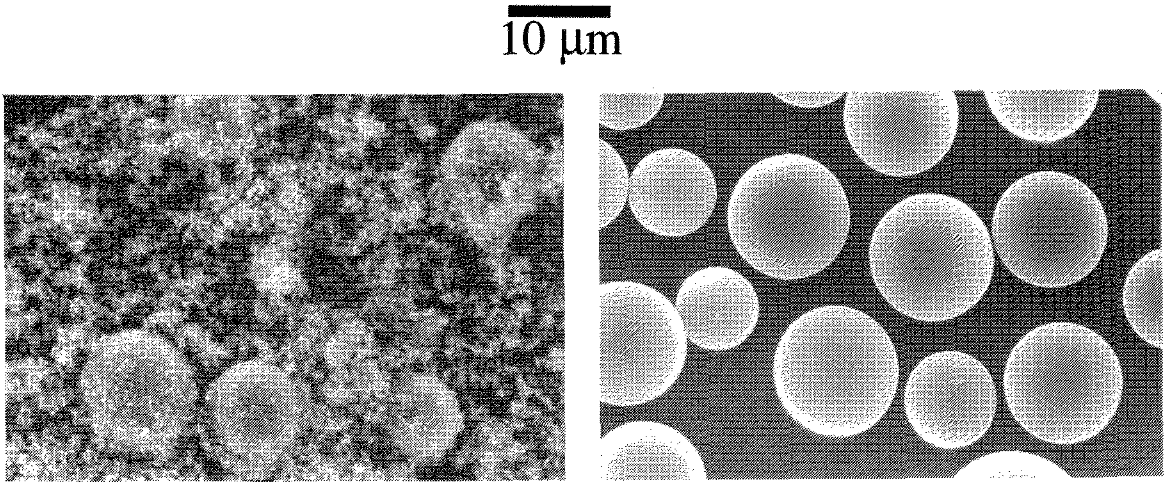
Table I. Plasma generating and powder feeding conditions

Plasma gas flow rate[slpm]	(a)	(b)	(c)
Central gas;	Ar / 6	Ar / 6	Ar / 6
Sheath gas (1):	Ar / 30	Ar / 30	Ar / 30
Sheath gas (2):	H_2 / 3	N_2 / 3	H_2 / 3
Powder carrier gas (1):	Ar / 5	Ar / 5	Ar / 4.5
Powder carrier gas (2):			CO_2 /0.5
R.F. frequency[MHz]	2		
Plate power[kW]	40		
Reactor pressure[Torr]	400		
Powder feed rate[g/min]	1.4		



(a) Original powder

(b) Ar-H_2 plasma treated powder



(c) Ar-N_2 plasma treated powder

(d) Ar-H_2-CO_2 plasma-treated powder

Fig. 1 Morphology of original and plasma-treated glassy carbon powders.

Sample electrodes were prepared as follows. Carbon powder was mixed with polyvinyldene fluoride in the weight ratio of 1:7. The mixture was dispersed in N-methyl-2-pyrrolidinone. The carbon containing slurry was spread on copper foil and dried at 150°C under vacuum for an hour. An 1 mol·cm^{-3} solution of $LiPF_6$ in a 50:50 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was used as an electrolyte. A reversible lithium reference electrode and lithium counter electrode were employed. Galvanostatic charge/discharge measurements were performed at a current density of 0.25 mA/cm^2 between the limit of 0 to 3 V vs. Li/Li^+ at 25°C (in this work, charge and discharge mean cathodic reduction and anodic oxidation, respectively). Pseudo-equilibrium potential as a function of the lithium concentration x (C_6Li_x at charging, C_6Li_{max-x} at discharging, and max in C_6Li_{max} means maximum value of each sample) were determined as the open-circuit voltage an hour after the current was switched off in galvanostatic intermittent 1-hour charge/discharge cyclings.

3. RESULTS AND DISCUSSION

Figure 1 shows the surface morphology of original and plasma-treated glassy carbon powders. Surface of original spherical particles were smooth as shown in Fig. 1(a). The surface of Ar-H_2 and Ar-N_2 plasma-treated powders in Figs. 1(b) and (c) was attacked by plasma and became rough. Partial evaporation occurred and the fine condensate below some tens of nanometer in size was formed. In the Ar-N_2 treatment, more condensate was formed than the Ar-H_2 treatment. The Ar-H_2-CO_2 plasma gave an oxidative atmosphere. Particles remained spherical shape, however, the surface morphology becomes appreciably rough and no fine condensate was formed (Fig. 1(d)).

Corresponding to the change of morphology, the BET surface areas for plasma-treated samples increased from 0.5 m^2/g for the virgin sample to 1.9, 23 and 220 m^2/g for Ar-H_2-CO_2, Ar-H_2 and Ar-N_2 plasma-treated samples, respectively. From the XRD data, the inter-layer spacing d(002) of plasma-treated samples decrease from 0.361 nm for virgin sample to 0.348, 0.347 and 0.345 nm for Ar-N_2, Ar-

H_2-CO_2 and Ar-H_2 plasma-treated samples, respectively. In the Ar-H_2 plasma treatment, the graphitization proceeded most rapidly because Ar-H_2 plasma with high thermal conductivity is able to heat particles most efficiently.

The chemical composition, which was determined by the gas analysis evolved from fused samples, is as follows: original powder, C: 64.05, H: 35.22, O: 0.43, N: 0.30 mol%; Ar-H_2 plasma-treated powder, C: 81.97, H: 17.21, O: 0.48, N: 0.34 mol%; Ar-N_2 plasma-treated powder, 63.61, H: 33.72, O: 1.40, N: 1.27 mol%; Ar-H_2-CO_2 plasma-treated powder, 86.15, H: 12.92, O: 0.57, N: 0.36 mol%. By the treatment of Ar-H_2 and Ar-H_2-CO_2 plasmas, in which much heat was absorbed to pyrolyze carbon powders, hydrogen contents decreased considerably. The Ar-N_2 plasma treatment gave the nitrogen incorporation.

Nitrogen incorporation was recognized on the surface of powder. Figure 2 shows the XPS spectra on the surface of Ar-N_2 plasma-treated powders. N1s peak was observed in XPS spectra, and the element peak relating to carbon-nitrogen bonding is also recognized in C1s spectrum.

Pseudo-equilibrium potential curves are shown in Fig.3(Figures 3(a) and (b) are for the first charge and discharges, respectively). Change in pseudo equilibrium potential of virgin sample is similar to typical potential curve of hard carbon[5], and no plateau was observed in the discharging curve. Average potential in the virgin sample is 0.40 V and there is no capacity over 1.3 V, as shown in Fig 3(b). On the other hand, the plasma treated samples have a capacity over 1.3 V, and the higher total capacity than the virgin sample in the both potential region under and over 1.3 V. Especially, total capacity of Ar-N_2 plasma treated sample is about 2.5 times higher than that of virgin sample and have a highest capacity in the range over 1.3 V.

In the Ar-H_2 and Ar-H_2-CO_2 plasma-treated samples, the increase in capacity was obtained in the potential range under 1.3 V. The potential curves of Ar-H_2 and Ar-H_2-CO_2 plasma treated samples showed stepwise profiles with the plateaus at ~0.1, ~0.65 and over 1.3 V. Since the plateaus under 1.3 V indicates the reversible intercalation of Li in graphite[6], which has the capacity only in the range under 1.3 V, and the plasma treated samples are more graphitized than virgin samples, the increase in capacity under 1.3 V could be due to the increase in degree of graphtization. In the case of Ar-N_2 plasma treated sample, the potential curves for discharging shows linear increase and the average potential, 0.68 V, in the range under 1.3 V is higher than those of Ar-H_2 and Ar-H_2-CO_2 plasma-treated and the virgin samples.

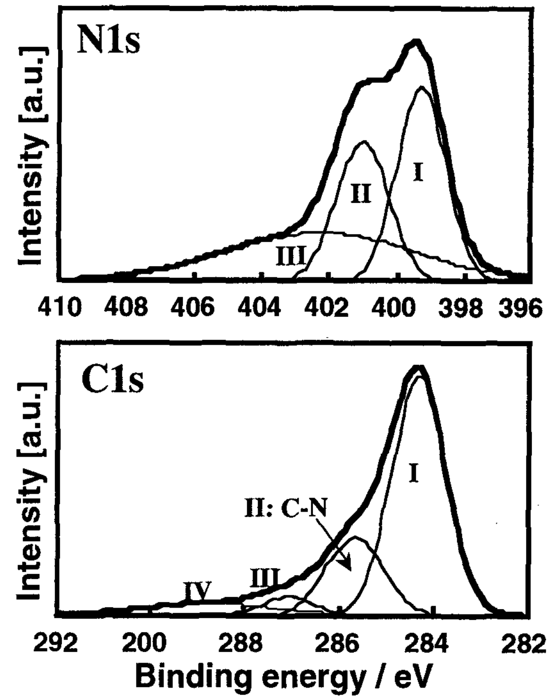


Fig. 2 XPS spectra on Ar-N_2 plasma-treated glassy carbon powder.

The effects of containing hetero atoms such as hydrogen, nitrogen and oxygen in carbonaceous materials on its electrochemical properties have been investigated by many research groups. Dahn and his co-workers[5] showed linear relationship between capacity and H/C atomic ratio in

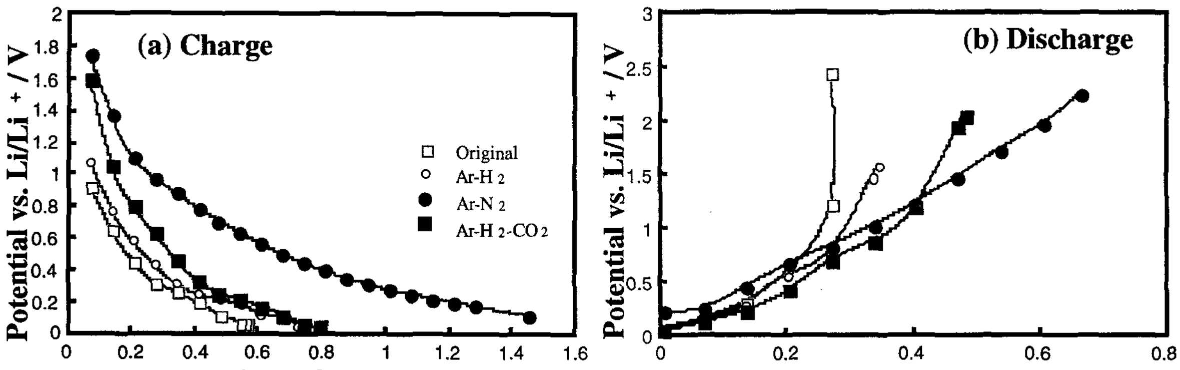


Fig. 3 Pseudo-equilibrium potential profiles for 1st charge and discharge with lithium content x.

carbonaceous materials pyrolyzed at temperatures between 550 and 1100℃, and explained that the extended capacity in carbonaceous materials heated at lower temperature is caused by some lithium atoms bound on the hydrogen-terminated edges of hexagonal carbon fragments during lithium insertion. By nitrogen doping into carbon, the sites for lithium insertion can be modified. Nitrogen in carbon is substitutional electron donor. As for boron, substitutional electron acceptor, it has been reported that boron-substituted carbons show the increase in voltage for a given lithium concentration compared to that in pure carbon because of the presence of boron acting as an electron acceptor in carbon lattice[7]. Thus nitrogen-substitutional carbon is expected to decrease in voltage compared to that in pure graphite.

Also, large surface area and fine particles could be related to the increase in capacity by plasma treatment. It has been reported that the mechanical grinding in graphite and soft carbons(graphitizable carbons) gave a large surface area (>150 m^2/g) and the increase in d(002), resulted in high reversible capacity exceeded theoretical value without increasing hydrogen or oxygen content, and lithium insertion at higher potential than ungrounded powders[8]. When we look at Ar-N_2 plasma-treated sample, which showed the increase in capacity, the existence of capacity over 1.3 V and the highest average potential under 1.3 V, the powder has a large surface area and a large amount of fine particles. The nitrogen incorporation in powders was observed and the amount of oxygen increased, while the hydrogen content decreased. Further investigation is necessary for understanding the complicated effect of plasma treatment.

In summary, glassy carbon powder was modified by the induction thermal plasma. The powders were partially evaporated, and then subjected to modifications in its chemical composition, morphology and crystal structure on the surface. The modification gave rise to the higher capacity than the untreated sample as an anode of lithium rechargeable batteries.

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