ELECTROCHEMICAL PROPERTIES OF PAN(polyacronitrile)-BASED CARBON FIBER FOR RECHARGEABLE LITHIUM ION BATTERY ANODE

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Introduction

Carbonaceous material used in this study is poly-acrylonitrile(PAN)-based carbon fibers which were prepared at various kinds of conditions. The carbon fibers were employed as anode active materials for lithium ion rechargeable battery. We investigated the effects of tension during oxidative stabilization, heat treatment temperature(HTT) and gas atmosphere during carbonization on the properties and charge-discharge characteristics of carbon fiber anode.

Experimental

PAN fiber (Courtaulds Co.) in the form of continuous yarn composed of 6,000 filaments was used as a precursor in this work. The oxidative stabilization of the PAN fiber was carried out at 230°C for 2 hours in a forced-convection oven. The tension applied to the fiber bundle was varied from zero to 15.03 MPa. Sequentially, the stabilized PAN fiber was carbonized in a tubular furnace under argon, hydrogen, nitrogen and vacuum atmosphere at HTT range of 700~1500°C in a tubular furnace for 2 hours.

The galvanostatic charge-discharge was performed in a mixture of ethylene carbonate(EC), dimethyl carbonate(DCE) and propylene carbonate(PC) containing 1M $LiPF_6$ salt.

Results and Discussion

As shown in the Table 1, variation of physical properties such as diameter and density was insignificant, but electric conductivity was significantly changed with preparation conditions such as stabilization tension and HTT. Tension during stabilization affected charge-discharge curve patterns as shown in Figure 1. Over the range of applied tensions, the specific capacity of carbon fiber prepared at 10.97Mpa was the highest.

As shown in Figure 2, the discharge capacity of the carbon fibers prepared at low HTT was sharply decreased, but the higher HTT of the fibers showed relatively low but steady discharge capacity values during cycles. The results indicated that the fibers prepared at low HTT have more sites for intercalation while having small conductivity. As the conductivity of carbon fiber decreased, the current-potential distribution became less uniform within the electrode. It leads to decrease in the discharge capacity, which may caused by side reaction at the local region of the electrode. However, the carbon fibers prepared at higher HTT have the small intercalation sites but high conductivity and they showed small, but steady discharge values. It can be concluded that the effect of HTT on discharge capacity is due to combination of the amount of intercalation site and the conductivity of the prepared carbon fiber.

Figure 3 shows the charge-discharge curves for carbon fibers prepared under different gas atmosphere. The carbon fiber carbonized under N_2 atmosphere showed the highest specific capacity. In Figure 4, measured diffusion coefficient values are proportional to specific capacity of the carbon fibers treated at various atmospheres as in Figure 3. This means that electrochemical intercalation which is dependent on mass transfer of lithium ion to carbon layer is rate determining.

Table 1. Preparation conditions and properties of PAN-based carbon fibers

Stabilization Tension(Mpa)	Carbonization atmosphere	HTT (°C)	Diameter (μm)	Density (g/cm³)	Conductivity (Scm⁻¹)
0	Nitrogen	1,100	11.7 ~12.7	1.75 ~1.77	220 ~ 260
4.87	Nitrogen	1,100	8.3 ~ 9.5	1.76 ~ 1.78	410 ~ 460
10.97	Nitrogen	1,100	7.8 ~ 8.3	1.79 ~ 1.81	430 ~ 480
15.03	Nitrogen	1,100	6.8~ 8.0	1.78 ~1.80	440 ~470
10.97	Nitrogen	700	8.8 ~ 9.3	1.76 ~ 1.78	1.0 ~ 1.3
10.97	Nitrogen	900	8.2 ~ 8.8	1.78 ~ 1.80	150 ~ 160
10.97	Nitrogen	1,300	7.6~ 8.0	1.79 ~1.81	560 ~ 600
10.97	Nitrogen	1,500	7.6~ 8.0	1.79 ~1.81	570 ~ 620
10.97	Hydrogen	1,100	7.8 ~ 8.3	1.79 ~1.81	460 ~ 500
10.97	Argon	1,100	7.8 ~ 8.3	1.79 ~1.81	460 ~ 480
10.97	Vacuum	1,100	7.8 ~8.3	1.79 ~ 1.81	460 ~490

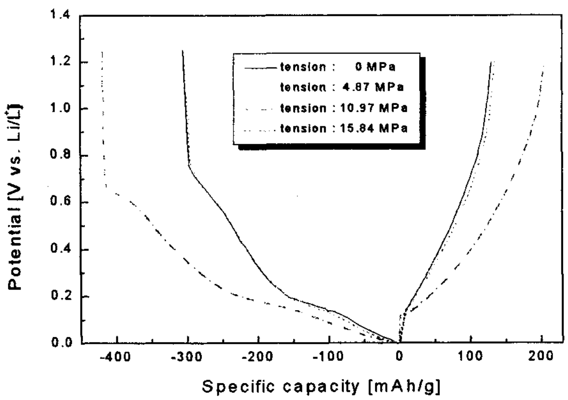

Figure 1. First cycle charge-discharge curves of PAN based carbon fibers prepared with various stabilization tensions. 1M $LiPF_6$ in EC/DCE/PC electrolytes at current density of 50 mA g^{-1}.

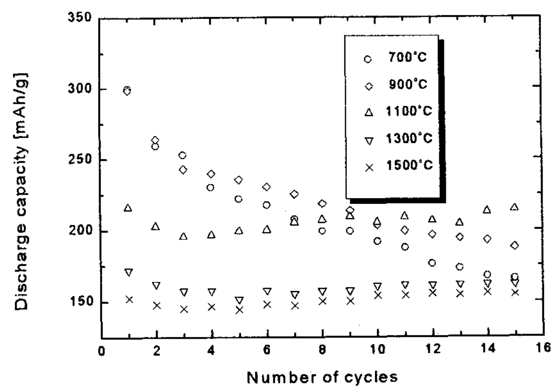

Figure 2. Discharge capacity curves of PAN based carbon fibers prepared with various HTTs. 1M $LiPF_6$ in EC/DCE/PC electrolytes at current density of 25 mA g^{-1}.

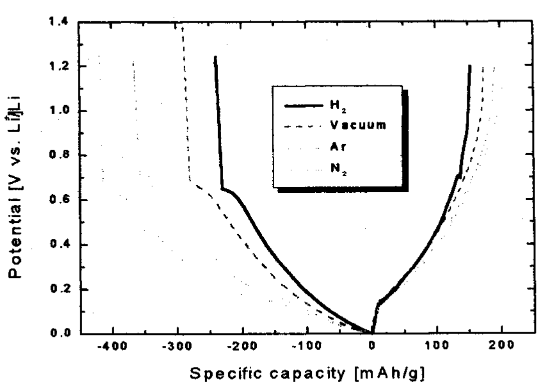

Figure 3. Charge-discharge characteristic curves of the carbon fibers prepared with various gas atmospheres. 1M $LiPF_6$ in EC/DCE/PC electrolytes at current density of 25 mA g^{-1}

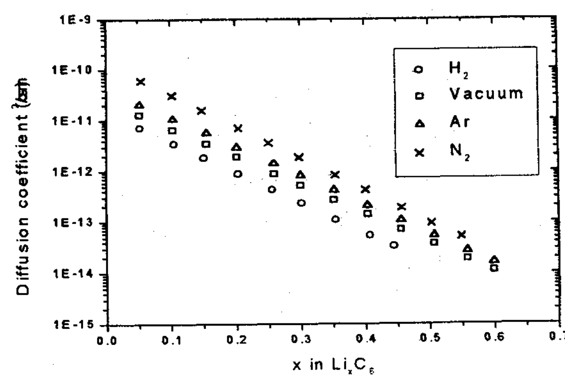

Figure 4. The variation of lithium ion diffusion coefficient of the carbon fibers anodes prepared by various gas atmospheres