PREPARATION OF THE HIGH RATE GRAPHITIC CARBON MATERIALS FOR THE ANODE OF LI-ION BATTERY

Yuzo Ohata[1], Jin Miyawaki[2], Seong-Ho Yoon[2] and Isao Mochida[3]

[1]Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
[2]Institute of Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
[3]Research and Education Center of Carbon Resources, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

Introduction

Graphite materials have been considered as the best anodic material for Li-ion battery from their performances such as large discharge capacity, small irreversible capacity long life, and low discharge potential for obtaining high voltage [1, 2]. Recently, high rate property at charge and discharge attract another attention to meet a desired performance for the application to EV and/or HEV.

Hyper coal (HPC) derived from the solvent extraction of low rank coals has many advantages as a feedstock for the anodic material of Li-ion battery because it has low contents of ashes, high carbonization yield and low cost [3]. So far, HPC alone can not have suitable performances as an effective precursor for the anode of Li-ion battery even if it was treated at higher temperature than 2800 °C [4].

In this study, we tried to develop the anodic material with high rate property using HPC as a starting feedstock through the co-carbonization of HPC with coal tar derived soft pitch (SP). We have investigated the correlation between the texture and high rate property of resultant graphitized cokes.

Experimental

HPC and SP were supplied from Kobe Steel Co.Ltd. and OCI Co. Ltd., respectively. HPC and SP were mixed with different mixing ratios (9/1, 7/3, 5/5, and 3/7). After removing solvent (THF), the mixture was co-carbonized at 500 °C or 530 °C for 1 h under N_2 atmosphere. Obtained green coke was pre-heated at 800 °C for 30 min and then graphitized at 2800 °C for 10 min under Ar atmosphere. For comparison, graphitized cokes from HPC alone and SP alone were also prepared by the same procedures.

Texture and crystallinity of obtained graphite cokes were evaluated with polarizing microscope and X-ray diffractometer (XRD, Ultima-III, Rigaku, Japan; CuKα radiation), respectively.

The electrochemical properties of obtained graphite cokes for Li-ion battery were evaluated as follows; For the preparation of anodic electrode, a slurry of graphitized coke (90 wt%) with 7 wt% styrene-butadiene rubber (SBR, 40 wt% solution) and 3 wt% carboxymethyl celullose (CMC, 1.0 wt% solution) was coated on copper foil (18 um thick). The obtained electrode was dried at 105 °C for 12 h under vacuum and pressed by a roll-type mill at 100 MPa. The pressed electrode was cut into disc (12 mm diameter and around 90 um in thickness) and carefully weighed using ultra-fine balance to set the exact amount of active material. Coin-type half cell of CR2032 were assembled in a glove-box using lithium foil, poly-ethylene film (16 um thick) separator, active material disc, and electrolytes of 1 M $LiPF_6$ in ethylene carbonate (EC) / diethyl carbonate (DEC) (1/1 vol.%. Ube Kosan, Japan). Charging was performed under constant current and constant voltage method (CC-CV) with the current density of 35 mAh/g (charge cut-off current is 3.5 mA) in the potential range of 0-1.5 V versus Li/Li^+. Discharging was performed under CC method (0.1 C 3 times, 0.2 C, 0.5 C, 1.0 C, 2.0 C) using galvanostatic charge discharge apparatus (Toscat-3100, Toyo-system, Japan). All the electrochemical experiments were carried out at room temperature.

Results and Discussion

Green cokes obtained had some amounts of porosity which increased with increasing HPC contents. Graphitized cokes did not show a remarkable morphological change.

The optical textures of graphitized cokes from HPC, SP and HPC/SP mixtures are shown in Fig. 1. The graphitized coke from HPC alone showed an ultra fine-mosaic texture (Fig. 1a), whereas that from SP alone did a developed flow domain (Fig. 1f). The size of textures of the graphitized cokes from HPC/SP mixtures went to be larger with increasing the contents of SP amounts. Graphitized cokes from the mixtures of 5/5 and 3/7 showed well defined coarse-mosaic textures (Figs. 1d and 1e).

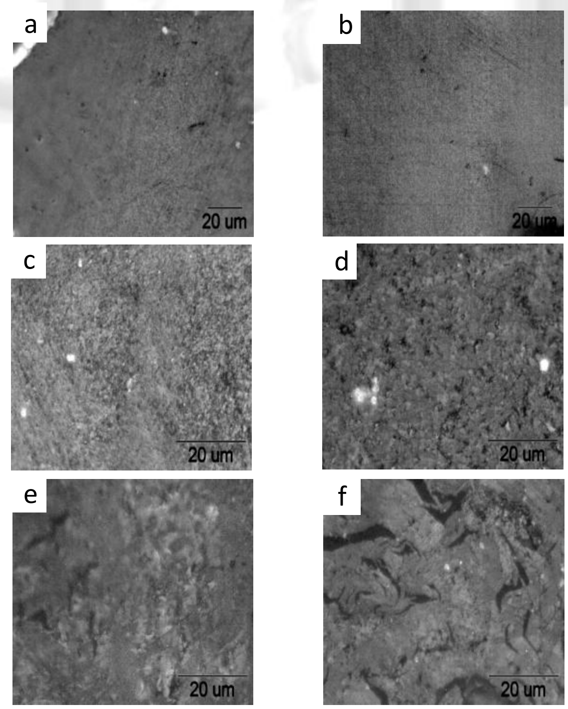

Figure 1 Textures of graphitized cokes from (a) HPC only, (b) mixture of 9/1, (c) 7/3, (d) 5/5, (e) 3/7, and (f) SP only.

Fig. 2 showed the values of d_{002} and Lc(002) which were calculated from XRD measurements of the graphitized cokes. The higher HPC contents, the larger values of d_{002} were obtained. Lc values gradually increased up to 30 wt% of HPC contents. The value of Lc of the graphitized coke from SP alone showed sudden jumped up to 183 nm.

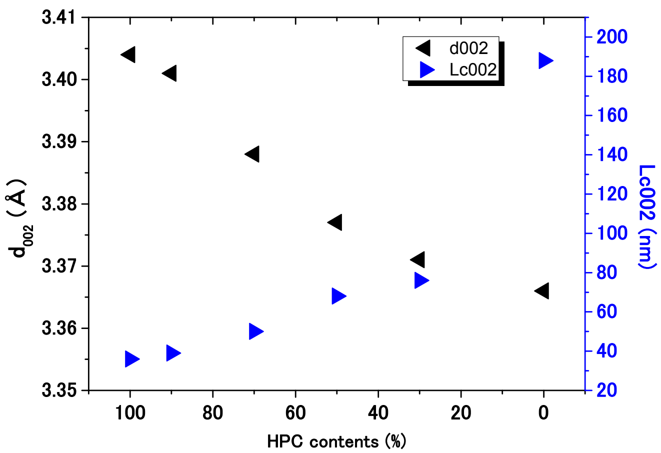

Figure 2. Values d_{002} or Lc(002) of graphitized cokes from HPC, SP and HPC/SP mixtures

Fig. 3 shows the charge / discharge profiles in the 1st cycle of graphitized cokes from HPC alone, SP alone and various mixtures. The graphite-like charge - discharge profiles with the discharge amounts of 213 ~ 323 mAh/g appeared. Discharge capacity increased with increasing contents of SP. The 1st cycle coulombic efficiencies were located in the ranges of 84-90 %.

Fig. 4 shows the discharge amounts at different rates from 0.1 C to 2.0 C. The discharge amounts of 0.1C ~ 1.0 C showed constant values regardless of discharge rate. However, at 2.0 C, the discharge amount started to decrease. Especially, the graphitized coke from SP alone which had a developed flow texture showed large decrease of discharge amount at 2.0C. The graphitized coke from the 5/5 mixture showed the highest retention efficiency of 2.0 C / 0.1C of 90 %, suggesting its coarse mosaic texture might be suitable for high rate property of the resulted coke.

Acknowledgment We give our great thank to Kobe Steel Co. Ltd. and OCI Co. Ltd. for their kind supplies of samples. We also give out thanks to G-COE of Kyushu University for the financial support of this study.

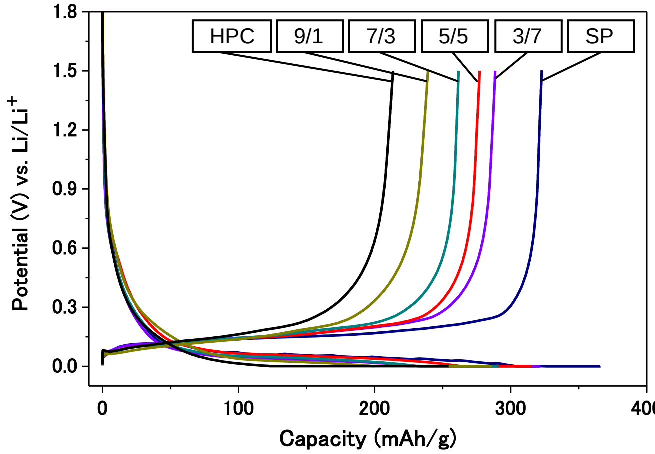

Figure 3 Charge / discharge profiles of graphitized cokes at 0.1C.

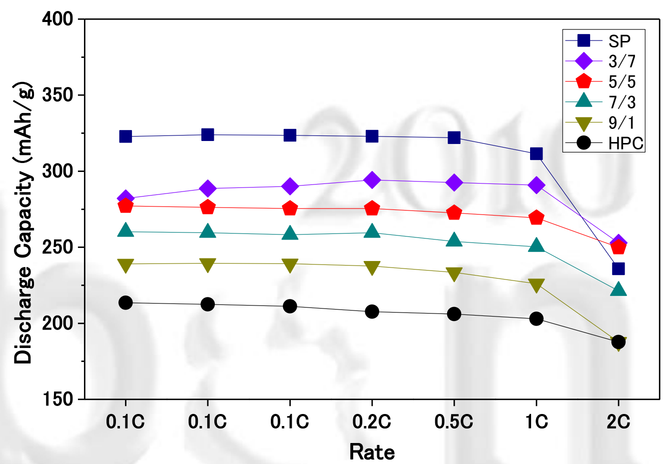

Figure 4. Discharge rate performances of the graphitized cokes at discharge rate from 0.1 C to 2.0 C.

References

[1]SH Yoon, CW Park, HJ Yang, Y Korai, I Mochida, RTK Baker, Nelly M. Rodriguez. Novel carbon nanofibers of high graphitization as anodic materials for lithium ion secondary batteries. Carbon 2004;42(1):21-32.

[2]SM Jang, J Miyawaki, M Tsuji, I Mochida, SH Yoon, K Fei-yu, preparation of a carbon nanofiber/natural graphite composite and an evaluation of its electrochemical properties as an anode material for a Li-ion battery, New Carbon Materials, 2010;25(2):89-96.

[3]N Okuyama, N Komatsu, T Shigehisa, T Kaneko, S Tsuruya, Hyper-coal process to produce the ash-free coal. Fuel Processing Tech. 2004;85:947-67.

[4]Y Ohata, J Miyawaki, SH Yoon, I Mochida, The conference of the Carbon Society of Japan, 2009;338-9.