PREPARATION AND PERFORMANCE OF COKE FROM COALS AS AN ANODE OF LITHIUM ION SECONDARY BATTERY.

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Introduction

Lithium ion batteries have stimulated extensive search because their high energy density enables smaller and lighter batteries in consummer electronics. Since its energy density depends mainly upon the performance of carbon anode, extensive study on carbons of a large variety has been attempted in recent years. So far hard carbon(non-graphitizable carbon), graphite and soft carbon(graphitizable carbon) are examined as the anode, exploring the larger capacity, efficiency and rate of charging, and discharging potential. Another approach is to reduce the cost of carbon anode at reasonable performance. Coke from coal can be a cadidate of very reasonable cost when it is carbonized in the coke oven, Dahn et al reported peformances of some cokes[1].

In this study, cokes from coals of various ranks were examined as an anode of the lithium ion secondary battery because they are variable in their optical texture, graphitizibility, oxgen content, and porosity.

Experimental

Coal was carbonized in a Pyrex glass tube at 500 °C for 1 h under nitrogen flow at a heating rate of 1 °C/min. The semi-coke was further heat-treated at 700 °C or 1100 °C for 1 h in a tube furnace under Ar flow at a heating rate of 1 °C/min. The optical texture of coke was observed under a polarized reflected light microscope(Olympus B061) after conventional mounting and polishing. The electrolyte used was 1M $LiPF_6$- EC/DEC(1:1). Coke calcined at 700 °C was charged and discharged in the voltage range of 0.0 to 2.0 V vs. Li/Li^+ by a constant current density of 0.16 mA/cm^2 while that of 1100°C coke was first charged to 0.0 V vs. Li/Li^+ by a constant current density of 0.16 mA/cm^2 and then short-circuited for 40 h. Discharge was measured to 2.0 V vs. Li/Li^+ by a constant current density of 0.16 mA/cm^2.

Results

Figure 1. shows the discharge voltage profiles of the first cycle with cokes calcined at 1100 °C. The coke from Tanitoharum coal exhibited discharge at 0 V by 150 mAh/g where the potentail started to increase to 1.5 V, discharging further by 326 mAh/g. Witbank and Goonyella showed similar discharge profiles. Such profiles are common to that of hardcarbons.

Figure 2. shows the discharge profiles of coke calcined at 700 °C. The profiles were common to that of the soft carbons calcined at a similar temperature. Goonyella coke showed discharge capacity was 373 mAh/g at the first cycle while the undischargeable capacity was as high as 318 mAh/g. Cokes from Witbank and Tanitoharum showed small discharge and large undischargeable capacity according to the rank.

Figure 3. shows microphotogragh of cokes calcined at 1100 °C. Goonyella coke showed domain and mosaic textures in the major grains. Witbank coke showed mosaic texture in some grains while major grain stayed isotropic. Tanitoharum coal provided isotropic texture in whole grains.

Discussion

The coke from coals of rather low ranking showed discharge profiles of soft carbon and hard carbon according to the calcined temperature. The cokes calcined at 700 °C showed the increase of capacity and decrease of undischargeable capacity with the increasing rank, while those at 1100 °C, did with the decreasing rank.

The discharge and undischargeable capacities of the former cokes may reflect the increasing graphitizibility and decreasing H or O contents. The capacity of the coke calcined at 1100 °C may reflect the volume of void which reflects the coking value, lower ranking coal tending to carry more voids.

In conclusion, the coke from coals showed reasonable capacity and profiles of discharge. Careful control of the carbonization including co-carbonization and selection of coal expected to give better anode at very reasonable cost. Mineral contaminants in the coal can be roved.

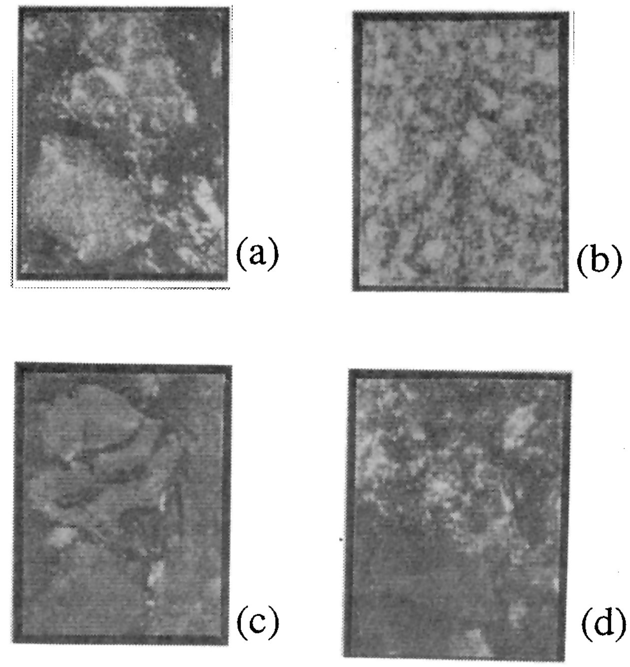

Fig. 3 Microphotographs of cokes calcined at 1100 °C
(a) Goonyella (b) Tanitoharum (c) Witbank
(d) Goonyella + Witbank

Reference

1. T. Zheng, X. Xing and J. R. Dahn, *Carbon* **34**, 1501(1996)

Table 1. Heat Treatment and Capacity of various Coals.

	Carbon Content (%)	HTT	1st Charge Capa. (mAh/g)	1st Discharge Capa. (mAh/g)	Irrevesible Capa. (mAh/g)
Goonyella Coal	88.1	700 °C	691	373	318
		1100 °C	(289)	309	---
Tanitoharum Coal	71.6	700 °C	626	258	368
		1100 °C	(267)	326	---
Witbank Coal	82.7	700 °C	626	292	334
		1100 °C	(242)	315	---
Goonyella +Witbank	85.4	700 °C	633	318	315
		1100 °C	(264)	307	---

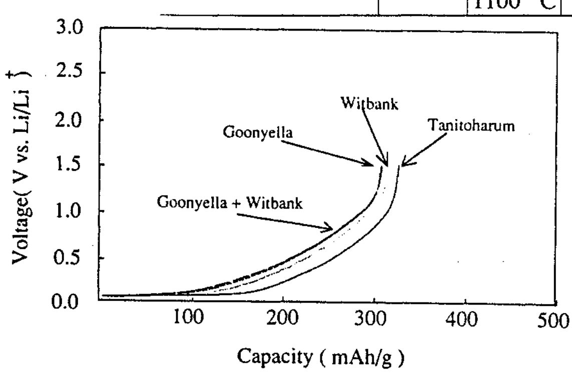

Fig. 1 Discharge Voltage Profile of Various Coals Carbonized at 1100℃

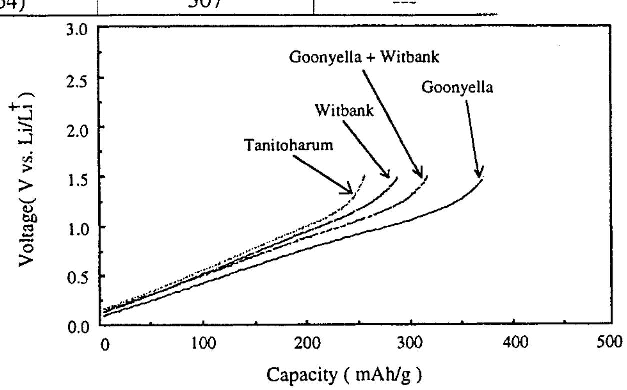

Fig. 2 Discharge Voltage Profile of Various Coals Carbonized at 700℃