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Journal of Power Sources 54 (1995) 425–427

JOURNAL OF POWER SOURCES

A modification in the preparation process of a carbon whisker for the anode performance of lithium rechargeable batteries

K. Tatsumi [a,*], K. Zaghib [a], H. Abe [b], S. Higuchi [a], T. Ohsaki [b], Y. Sawada [a]

[a] *ONRI-AIST, 1-8-31, Midorigaoka, Ikeda, Osaka 563, Japan*

[b] *R&D Center-Shizuoka Plant, Nikkiso Co., Ltd., 498-1, Shizutani, Haibara-gun, Shizuoka 421-04, Japan*

Abstract

In general, a carbon whisker is prepared from hydrocarbons using a vapor-grown method and chopped to a suitable length. Two procedures were examined to prepare the whiskers: in the normal procedure (1A), whiskers were graphitized after the chopping process, and in the other process (2A), they were chopped after the graphitization. The carbon whisker of 2 μm in length by the 1A procedure (2GWH-1A) showed an average capacity of 248 mAh g^{-1}. On the other hand, the whisker of the same diameter by the 2A process (2GWH-2A) showed a much higher capacity of 363 mAh g^{-1}: this value is 1.6 times of that of 2GWH-1A. This modification method may open a new probability to higher performance carbon materials for the anode.

Keywords: Rechargeable lithium batteries; Carbon; Anodes

1. Introduction

Carbon materials have been developed as alternative anode materials of lithium rechargeable batteries, so-called lithium-ion 'rocking-chair' batteries [1–3]. Although low or non-graphitized carbons are interesting because of their large capacity over 372 mAh g^{-1} [4,5], well-graphitized carbons show capacity in the potential range near 0 V (potential will be shown against lithium electrode) [6,7]. However, there has been no paper reporting on a method that improves the capacity of well-graphitized carbons. A vapor-grown carbon whisker is one of the soft carbons and has a special texture showing concentric orientation of graphite crystallites along its cross section. The concentric texture is important to prepare well-graphitized carbon fibers that have enough stability during the charge/discharge cycling [8]. In addition, the styles of fiber and whisker are practical to prepare a sheet-style electrode that is convenient to be stacked in batteries. In this paper, it is reported that the chopping process showed a novel effect on the capacity of a well-graphitized carbon whisker. This phenomenon is quite new and difficult to be explained at present. The structural characteristics of this material are also discussed.

* Corresponding author.

SSDI 0378-775394)02116-K

2. Experimental

Well-graphitized carbon whiskers (2GWH, Nikkiso Co., Ltd.; heat-treated at 2800 °C, 2 μm in diameter) were used for the electrode. The carbon whiskers are prepared from hydrocarbons using the vapor-grown method and are chopped to about 10 μm in length by hybridizer. Two procedures were examined to prepare the whiskers: in the normal procedure (1A), the carbon whiskers were graphitized after the chopping process; in the other process (2A), they were chopped after the graphitization. Structural characteristics of the pristine carbon whiskers were investigated by X-ray diffraction (XRD), Raman scattering spectroscopy and the BET analysis (N_2 gas). A carbon electrode was prepared by mixing a carbon material with poly(vinylidene fluoride) (PVDF) of 10%. This composition of the binder showed the best performance in capacity and stability during cycling [9]. The carbon paste was spread on an expanded nickel metal and was dried under vacuum for 24 h at 120 °C. Then, the electrode was transferred to a dry box without exposing to air and was set in a three-electrode cell with 1 M $LiClO_4$ solution in a 50:50 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Lithium metal was used as counter and reference electrodes. The specific capacity of the carbon electrode was measured by a galvanostatic charge/discharge examination in the potential range between

0 and 2.5 V. The current density was 25 mA g^{-1} (about 15 h for the theoretical capacity of LiC_6). The measurements were done at ambient temperature (27 °C). In this study, the carbon electrodes were positive against the lithium counter electrode and this means that the carbon electrodes were used as cathode in our cell system. Thus in this paper, discharging is considered as the storage of lithium into the carbon electrode and charging as the evolution of lithium. The charge/discharge examination of the electrodes were started at discharging.

3. Results and discussion

Fig. 1 shows the potential change of 2GWH during the first cycle of the galvanostatic charge/discharge examination. The initial potential of each carbon electrode was about 3.2 V. After the potential decreased immediately to 0.8 V, the curve had a shoulder-like profile at 0.7 V only in the first discharging like other carbon materials. This irreversible shoulder probably corresponds to the formation of the passivating layer [6]. There were, however, no plateaus above 0.3 V after the second cycle. Next to the shoulder-like profile, the curve had 3 plateaus at 200, 100 and 75 mV. These plateaus also appeared in the charging process: these electrochemical reactions were reversible. Those characteristics in the curves are almost equal to those of artificial graphite [6] or natural graphite [7]. The charging capacity and the cycle efficiency of each carbon whisker in the charge/discharge cycling test are summarized in Table 1. 2GWH-1A showed a capacity of 248 mAh g^{-1} in the first charging. However, the charging capacity was decreasing during cycling. On the other hand, the 2A method improved clearly the performance of the whisker. Compared with 2GWH-1A, 2GWH-2A

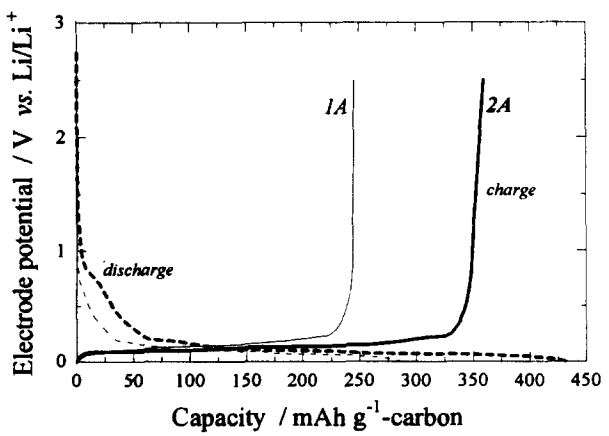

Fig. 1. Change in potential during the first cycle of the discharge/charge examination in 1 M $LiClO_4$/EC–DEC (1:1 in volume ratio) at 25 mA g^{-1} of current density; (——) prepared by 1A method and (——) prepared by 2A method; (– – –), charging and (- - - - -) discharging.

showed an improvement of 1.6 times in charging capacity. 2GWH-2A had a high capacity (363 mAh g^{-1}) and the value is almost equal to the theoretical value for LiC_6 (372 mAh g^{-1}). Moreover, the charge capacity of 2GWH-2A was almost constant during the initial cycles. These results indicate that the chopping process has a strong effect on the electrochemical performance of the well-graphitized whisker. This is a novel phenomenon because it is thought that the graphitization states of carbon materials are hardly changed by the chopping process.

Furthermore, the large capacity of 2GWH-2A cannot be explained only by the lithium intercalation into the graphitic structure, because the volume ratio of the graphitic structure (P_1) in 2GWH-2A was about 0.7 by the Fourier analysis of the (*hk*) lines [10]: the capacity of 2GWH-2A should be about 260 mAh g^{-1} when lithium is intercalated into the graphitic structure [11]. In order to investigate the structural differences between 2GWH-1A and 2GWH-2A, the structure of the pristine whiskers were examined by XRD and Raman spectroscopy. Lattice parameters of the whiskers are summarized in Table 2 and show clearly the effect of the 2A method on the crystal structure. The R value of 2GWH-2A was higher than that of 2GWH-1A: this means the crystal defects have been increased by the 2A method. Thus, the lattices of the well-graphitized whisker were changed during the chopping process. However, the graphitization state of 2GWH-2A also developed is higher than that of 2GWH-1A: the d spacing became closer to that of natural graphite and $L_{d_{112}}$ increased. In the other words, these results mean that the graphitization state was developed during the chopping process, though the 2A method induced the disorder structure in the graphite crystallites. Thus, a new structure that affects the electrochemical characteristics seems to be introduced during the chopping process. It is possible that such a structure appears in the well- graphitized carbon whiskers during the process. That is because the novel development of the graphitization state by the chopping process become possible with some structural changes in the whiskers. The progress in graphitization seems to be explained by the release of the residual strains in the well-graphitized whiskers. Graphite crystallites in carbon materials are often distorted by the residual strains in themselves. In particular, it is sure that the strains remain inside of the whiskers, because the carbon whiskers have a concentric texture in their cross section: graphite crystallites are bent in this texture. Thus, the graphitization state developed probably with the release of the residual strains during the chopping process, and some structures, i.e. new grain boundaries that could not be detected by the XRD probably appeared in the whiskers during the release of the strains. In fact, specific surface area of 2GWH-2A was higher than that of 2GWH-1A

Table 1
Discharge capacity and cycle efficiency of 2GWHs in the discharge/charge cycling test between 0 and 2.5 V at 25 mA g^{-1} (C/15)*

	Capacity (mAh g^{-1})			Cycle efficiency (%)		
	1st cycle	2nd cycle	4th cycle	1st cycle	2nd cycle	4th cycle
2GWH-1A	248	235	220	85	94	96
2GWH-2A	363	363	363	83	96	99

* About 15 h for full discharge.

Table 2
Lattice parameters of the carbon whiskers by the X-ray diffraction and Raman spectroscopy

	c-direction		a-direction		Stacking order		R value*
	c_0 (2 nm)	L_c (nm)	a_0 (nm)	L_a (nm)	d_{112} (nm)	L_{d112} (nm)	
2GWH-1A	0.3367	43	0.2461	45	0.1156	4	
2GWH-2A	0.3359	63	0.2462	90	0.1156	8	0.073

* The R value was calculated with the intensity ratio of the disorder band (about 1360 cm^{-1}) against the E_{2g2} band of graphite crystal (about 1580 cm^{-1}).

Table 3
Specific surface area of the carbon whiskers and the irreversible capacity in the first discharging

	Specific surface area (m^2 g^{-1})	
	Observed	Calculated*
2GWH-1A	1.2	1.1
2GWH-2A	10.7	1.1

* These values were calculated on the assumption that the whisker has an ideal cylinder style and flat surface.

(Table 3): the bulk of 2GWH-2A was damaged by the chopping process. Anyhow, the novel characteristics of 2GWH-2A are very interesting not only for the battery with high voltage and large capacity but also for a possibility of a new site of lithium storage in well-graphitized carbon materials.

Acknowledgement

The authors acknowledge Dr Norio Iwashita for the measurement of the P_1 value of 2GWH-2A.

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