Development of Negative Electrode for Calcium-Ion Battery Using Marimo Nano Carbon

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The problem of calcium-ion batteries (CIBs) using graphite electrodes is that the charge/discharge capacity cannot be sufficiently obtained due to the poor reactivity of Ca^{2+} . In this study, we investigated Marimo Nano Carbon (MNC) as a new negative electrode material for CIBs. MNC was an aggregate of carbon nanofilaments (CNFs) and it was synthesized by decomposition of ethylene using oxidized diamond-supported Pd catalyst. When the charge and discharge capacity using MNC as negative electrode was larger than that of the natural graphite. In addition, the intercalation of Ca^{2+} between the graphene layers was confirmed by XRD measurement.

Introduction

Calcium-ion batteries (CIBs) use Ca^{2+} for charge carriers instead of Li^+ and have great potential as alternatives to lithium-ion batteries (LIBs) (1-3). Since it uses divalent cations, it has the potential to obtain twice the capacity of LIBs. In addition, compared with Mg^{2+} , the standard electrode potential of Ca is approximately 0.5 V lower (-2.87, -2.37 V vs. SHE for Ca, Mg), and it can use a high operating voltage.

However, there are some problems in the development of CIBs. Since divalent cations such as Ca^{2+} have a stronger Lewis acidity than Li^+ , they form a strong solvation structure with solvent molecules in the electrolyte, and also have large desolvation energy (4, 5). Therefore, Ca^{2+} are less reactive than Li^+ .

For this reason, we used Marimo Nano Carbon (MNC) as a new negative electrode material. MNC is an aggregate of carbon nanofilaments (CNFs) (6). This CNFs have coin-stacked structure in which graphene layers are stacked similar to graphite and the edge plane is exposed. Generally, graphite used for LIBs has a spheroidizing treatment on the edge plane in order to suppress excessive decomposition of the electrolytes, and as a result, reactivity is suppressed (7). Hence, we expected that MNC negative electrode would more intercalate Ca^{2+} between the graphene layers of CNFs and indicated larger charge/discharge capacity than that of the graphite negative electrode.

In this paper, we synthesized CNFs oxidized diamond-supported catalyst on decomposition of ethylene by chemical vapor deposition (CVD) method, and We evaluated the performance of MNC electrodes as negative electrode materials for CIBs.

Experimental

Preparation of catalyst for synthesis CNFs

Oxidized diamond (Diamond Innovations Co., Ltd.) was used as the catalyst supports. Oxidized diamond has oxygen-containing functional groups arranged regularly, so that nano metal particles can be highly dispersed on it (8). Therefore, oxidized diamond-supported Pd catalyst (Pd loading: 5 wt%) for CNFs synthesis was prepared by the metal nano-colloidal method (9). Diamond oxide was added to deionized water and stirred for 30 min under ultrasonic treatment. PdCl_2 as a precursor and citric acid as a dispersing agent were added, and this solution was stirred for 30 min under ultrasonic treatment. NaBH_4 as a reducing agent was added to the solution. After stirring for 30 min under ultrasonic treatment, the supernatant was removed from the solution by centrifugation and dried at 333 K. Supported catalysts were calcined at 723 K for 5 h in N_2 prior to the reaction.

CNFs were synthesized by the CVD method using a horizontal rotating fluidized bed reactor (10). Oxidized diamond-supported Pd catalyst was used 200 mg and uniformly distributed in a quartz boat. After inserting quartz boat into the center of the quartz tube, the reactor was elevated temperature at 873 K, under N_2 atmosphere. Afterwards, 30 mL/min C_2H_4 was introduced at 873 K. The reaction time was 1 h.

Characterization of MNC

Surface structures of MNC were observed using field emission scanning electron microscopy (FE-SEM; Hitachi, Ltd. S-4800), and internal structures of synthesized CNFs were observed using transmission electron microscopy (TEM; JEOL Ltd. JEM-2010K). The degree of graphitization of synthesized CNFs were measured by Raman spectroscopy (Raman; JASCO, NRS-3000). The rate of surface functional group of CNFs was measured by X-ray photoelectron spectroscopy (XPS; JEOL Ltd. PS-9000MX). The interlayer spacing (d_{002}) of synthesized CNFs were measured by X-ray diffraction (XRD; Rigaku, SmartLab). The specific surface area and the ratio of the mesopore volume to the total volume of synthesized CNFs were measured by the nitrogen adsorption method at 77 K (BELSORP-mini; Nippon Bel, Japan).

Electrochemical measurements

MNC were used as a working electrode and an activated carbon fiber cloth (Kynol; Gunee Chemical Industry, Ltd.) was used as a counter electrode. Spherical natural graphite (CGB-10; Nippon Graphite Industries, Ltd.) was used as comparative material. Cellulose fiber (ADVANTEC No.5, Toyo, Ltd.) was used as a separator. The electrolytes were prepared by dissolving a $\text{Ca}(\text{ClO}_4)_2$ at 1 M concentration in ethylene carbonate (EC): diethyl carbonate (DEC) = 1:1 (vol/vol), and γ -butyrolactone (GBL). These were purchased from FUJIFILM Wako Pure Chemical Ltd.

In order to calculate charge/discharge capacity of each electrolyte, charge and discharge measurement was performed (HZ-7000, Hokuto Denko). The measurement was conducted out at a scanning potential of 0 to 3.5 V and performed 3 cycles. In addition, intercalation of Ca^{2+} into graphene layers of MNC anode was measured by XRD.

Results and Discussions

Characterization of MNC

Fig. 1 shows SEM images of synthesized CNFs over oxidized diamond-supported Pd catalyst. From these images, it can be seen that CNFs are densely generated and there are many pores between the fibers. The diameters of CNFs were approximately in the range of 5-100 nm.

Figure 1. SEM images of synthesized CNFs.

Fig. 2 (a) shows TEM image of synthesized CNF over oxidized diamond-supported Pd catalyst and model of coin-stacked structure CNF. It seems that Synthesized CNFs had coin-stacked structures which is stacked graphene wall perpendicularly to the nanofilaments axis. Fig 2 (b) shows model diagram of coin-stacked CNF.

Figure 2. (a) TEM image of synthesized CNF and (b) model of coin-stacked structure CNF.

TABLE I. Characteristic data of MNC and Spherical natural graphite.

Samples	I _G /I _D [-]	C-C [%]	d ₀₀₂ [Å]	S _{BET} [m ² /g]	V _{meso} [cm ³ /g]
MNC	1.14	78.1	3.45	188	0.287
Spherical natural graphite	3.36	81.0	3.35	7	0.019

TABLE I shows Characteristic data of MNC and Spherical natural graphite. First, I_G/I_D was calculated by Raman spectroscopy. The peaks at 1580 cm^{-1} and 1350 cm^{-1} correspond to the G (graphite)-band and the D (disorder)-band, respectively, and the I_G/I_D is represented by the ratio of the intensity of the G-band to the D-band (11). The values of I_G/I_D for MNC and Spherical natural graphite were 1.14 and 3.36, respectively. This result is because CNFs are synthesized at a relatively low temperature, so that the crystal structure is not sufficiently developed and the edge plane has defects such as oxygen-containing functional groups.

Second, the surface functional group ratio of the synthesized CNFs and Spherical natural graphite were measured by XPS. The values in the TABLE I indicate the ratio of C-C bonds (sp^2 , 284.4 eV) in the C1s spectrum. The rate of C-C bond of CNF and Spherical natural graphite was 78.1 % and 81.0 %, respectively. This result coincided with the result of Raman measurement. From the result of Raman and XPS, it was able to confirm that there was a correlation between the degree of graphitization and the rate of surface functional group. Therefore, CNFs are considered to have more exposed edge plane than that of spherical natural graphite.

Third, d-spacing (d_{002}) of synthesized CNFs and Spherical natural graphite were measured by XRD. From the results of XRD, the values of d_{002} of each sample were 3.45 Å and 3.35 Å, respectively. Therefore, synthesized CNFs had similar d-spacing of graphite.

Finally, the specific surface area (S_{BET}) and the ratio of the mesopore volume to the total volume (V_{meso}) of synthesized CNFs and Spherical natural graphite were measured by the nitrogen adsorption method at 77 K. The synthesized CNFs had a larger specific surface area and the mesopore volume than that of Spherical natural graphite.

Electrochemical measurement

TABLE II. Charge/discharge capacity of MNC and Spherical natural graphite electrodes in each electrolyte.

Solvent	EC-DEC		GBL	
Samples	Charge [mAh/g]	Discharge [mAh/g]	Charge [mAh/g]	Discharge [mAh/g]
MNC	6.3	4.9	98.9	20.2
Spherical natural graphite	3.8	3.0	34.1	15.3

TABLE II shows the charge/discharge capacity of MNC and spherical natural graphite electrodes in each electrolyte. The order of charge/discharge capacity was $MNC > \text{Spherical natural graphite}$ for each electrolyte. It is considered that this is because the MNC negative electrode with the highly active edge plane exposed reacted with Ca^{2+} in the electrolytes more than the Spherical natural graphite negative electrode. Further, the difference in charge/discharge capacity of each solvent may be due to the solution structure in each electrolyte.

Fig. 3 shows X-ray patterns of MNC negative electrode before and after charge in each organic electrolyte. In the GBL based electrolyte, the peak of (002) plane shifted after charging, confirming that the interlayer distance had expanded from 3.45 Å to 4.29 Å. Recently, it has been reported that electrochemical intercalation of Ca^{2+} into graphite is possible (3,12). Therefore, it was confirmed that Ca^{2+} intercalation proceeded between the graphene layers of CNFs after charging the MNC negative electrode. Furthermore, there

was a correlation between the height of the peak after charging with each electrolyte and the charge/discharge capacity.

Figure 3. X-ray patterns of MNC negative electrode before and after charge in each electrolyte.

Conclusions

Synthesized CNFs had coin-stacked structures. Electrochemical measurements indicated that MNC negative electrode exhibits more charge/discharge capacity than that of graphite negative electrode. Result of XRD measurements, the peak of (002) plane of MNC negative electrode shifted after charging. Therefore, it was shown that Ca^{2+} can be intercalated between graphene layers of CNFs.

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