Li/Na Storage Properties of Disordered Carbons Synthesized by Mechanical Milling

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ABSTRACT

Impact of structural disorder induced by mechanical milling on electrochemical properties of carbonaceous materials is systematically examined. Carbonaceous materials with different structural disorder are prepared by mechanical milling with different rotation speeds. Thus prepared carbons show sloping voltage profiles in Li/Na cells, which resemble those of soft carbons. The disordered carbon material prepared at 600 rpm shows a reversible capacity of >500 mA h g⁻¹ in a Li cell. In addition, the disordered carbon also delivers 200 mA h g⁻¹ in a Na cell with high Coulombic efficiency for continuous cycles. Heat treatment of the disordered carbon results in the formation of hard carbon with nanopores, and thus Li/Na storage properties are significantly changed.

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1. Introduction

Graphite is widely used as a negative electrode material of rechargeable lithium batteries. Lithium ions are reversibly intercalated/de-intercalated into/from graphite with low electrochemical potential, which is similar to Li plating potential. Li intercalation into graphite highly depends on interfacial reactions at graphite and electrolyte. For instance, graphite easily exfoliates when a graphite electrode is electrochemically reduced in the electrolyte with propylene carbonate. ¹ Such exfoliation of graphite originates from co-intercalation of solvated propylene carbonate and lithium ions, and instantaneous electrochemical reduction and decomposition of solvents. This unfavorable reaction is effectively suppressed by modification of the surface of graphite by forming a solid-electrolyte interphase (SEI).² Highly reversible lithium storage with graphite is realized in electrolyte containing ethylene carbonate associated with the formation of a chemically/electrochemically stable SEI layer on the surface of graphite.³

In contrast, sodium ions cannot be intercalated into a graphite electrode, and graphite is known as electrochemically inactive in Na cells.⁴ Instead of graphite, hard carbon, which contains nanopores in the structure, is often used for Na storage applications.⁵,⁶ Sodium ions are reversibly inserted into hard carbon, and large reversible capacities (200–400 mA h g⁻¹, depending on nanostructures of hard carbons) are obtained in Na cells.⁷ Two characteristic features are observed on a reduction voltage profile; a sloping region followed by a plateau region near to 0 V versus metallic sodium.⁸ Recent ab initio studies have suggested that Na ions with an ionic nature are trapped at defects sites on carbon for the sloping region,⁹ and clustering of Na ions and the formation of Na-Na bonds in nanopores at the plateau region.¹⁰ The formation of metallic-like Na in hard carbon has been also evidenced by operando¹¹ Na solid-state NMR study.¹² Nevertheless, solvated Na ions by diglyme are reversibly inserted into graphite, forming staging compounds.¹³ Recently, electrochemical intercalation of Na ions without co-intercalation of solvent into graphite has been successfully reported, and the formation of a stage 7 Na/graphite intercalation compound has been first evidenced.¹⁴ In this study, carbonaceous materials with different disordered structures are prepared from graphite by mechanical milling, and lithium/sodium ions storage properties are systematically examined. Mechanical milling is an effective method to synthesize structurally disordered materials by applying mechanical energy, including friction and shear stress.¹⁵ Moreover, the extent of structural disorder is easily modulated by changing a milling speed and time, and thus Li/Na storage properties also alter depending on the structures of carbon. From these results, factors affecting Li/Na insertion/extraction in carbonaceous materials with different structural disorder are discussed.

2. Experimental

Carbonaceous materials with different structural disorder were prepared by mechanical milling of graphite (Wako Pure Chemical Corp. Ltd.) with different milling speeds. Mechanical milling was conducted using a planetary ball mill (PULVERISETTE 7; FRITSCH). 1.5 g of graphite was milled using a zirconia pot (45 mL) and zirconia balls (60 g) at 200–600 rpm for 12 h. The zirconia pot was sealed in an Ar-filled glove box to avoid the oxidation of samples during mechanical milling. X-ray diffraction (XRD) patterns of the samples were collected using an X-ray diffractometer (D2 PHASE; Bruker Corp., Ltd.) equipped with a one dimensional X-ray detector using CuKα radiation generated at 300 W (30 kV and 10 mA) with a Ni filter. Composite positive electrodes, comprising 80 wt% graphite and 20 wt% polyvinylidene fluoride (KF 1100; Kureha Co. Ltd.) dispersed in N-methylpyrrolidone, were pasted on copper foil used as a current collector. The electrodes were dried at 80°C for 2 h in vacuum, and then heated at 120°C for 2 h. Metallic lithium and sodium were used as negative electrodes. The electrolyte solutions used were 1.0 mol dm⁻³ LiPF₆ dissolved in ethylene carbonate:dimethyl carbonate (EC:DMC = 3:7 by volume, battery grade; Kishida Chemical Corp., Ltd.) and...
1.0 mol dm$^{-3}$ NaPF$_6$ dissolved in propylene carbonate (PC, battery grade; Kishida Chemical Corp., Ltd.). Two-electrode cells (TJ-AC; Tomcell Japan) were assembled in the Ar-filled glovebox. The cells were cycled at a rate of 20 mA g$^{-1}$ at room temperature.

3. Results and Discussion

Structural changes of graphite induced by mechanical milling were examined by X-ray diffraction method. Figure 1 shows structural evolution of carbonaceous materials from graphite by mechanical milling. Before milling, a clear peak at 26° in a two-theta range is observed, which corresponds to a 002 diffraction line of graphite. After mechanical milling at 200 rpm, a profile of the 002 diffraction line is broadened, and it is expected that some extent of structural disorder, including stacking disorder of graphene layers and surface defects, is induced in graphite. After mechanical milling at 300 rpm, a broad 002 peak is noted, and the structure of graphite seems to be lost. Further reduction of crystallinity is realized at 600 rpm, and some new peaks are also observed, which can be assigned into the peaks from ZrO$_2$ used for milling. Moreover, a peak width of 002 line is further broadened. A crystallite size along c-axis direction is calculated to be ca. 1 nm, which is estimated from full width at half-maximum of 002 line. An average interlayer distance is also estimated to be 3.53 Å. Defects created in carbon increase interlayer distances. Similar to the impact of milling speed shown in this study, milling time also influences structural disorder of graphite.$^{18,19}$ Longer milling time results in reduction of crystallinity, and similar crystallinity with the sample milled at 600 rpm for 12 h is obtained after milling at 150 rpm for 40 h.$^{19}$

Local structures of carbonaceous materials with different crystallinity obtained by mechanical milling of graphite were also studied by Raman spectroscopy. For graphite before milling, a strong G band originating from an $E_{2g}$ vibration mode was observed with a minor contribution of a D band from $A_{1g}$ ring breathing mode, which is forbidden in graphite without defects.$^{19}$ As milling time increases, it was reported that the intensity of the D band relative to the G band is enhanced, indicating enrichment of defect concentration by milling. In addition, a peak width of the D bands is increased as a function of milling time, suggesting that carbonaceous materials contains structural disorders with different domain sizes, including turbostratic structures.$^{19}$

Changes in particle morphology were also observed by SEM as shown in Fig. 2. Graphite features plate-shaped morphology, and these plates are stacked for each other, forming large plates. Nanometer-sized particles are formed by milling at 200 rpm, but agglomerated and micrometer-sized secondary particles are also found. After milling at 600 rpm, primary particle sizes of the sample are further reduced, and better uniformity of particle sizes is noted as clearly shown in magnified SEM images for 200 and 600 rpm (Fig. 2e and f). Thus prepared nanosized carbonaceous materials are tightly agglomerated for each other, forming micrometer-sized secondary particles. It has been reported that surface area observed by BET measurement increased $\sim$400 m$^2$g$^{-1}$ by milling.$^{19,20}$ and surface area analysis indicated that nonporous structures were produced by milling.$^{20}$ Detailed nanostructures of carbonaceous materials prepared by milling were also directly observed by TEM.$^{19,21}$ The layered structure of graphite with high crystallinity was lost after milling, and nanostructured carbons with misoriented nanodomains were observed,$^{21}$ which is also consistent with the data shown in Fig. 1.

Electrochemical reactivity of these carbons with different structural disorder was further examined and compared (Fig. 3). Graphite before milling shows highly reversible reaction for the Li intercalation/de-intercalation process, and the sample delivers a reversible capacity of nearly 360 mAh g$^{-1}$ as a negative electrode material in a Li cell. In contrast, electrolyte decomposition and no intercalation into graphite are observed in a Na cell. Cell voltage does not reach 0 V vs. metallic Na because of continuous electrolyte decomposition and no passivation on the graphite surface. In this study, EC/DMC co-solvent was used for Li cells and PC monosolvent is used for Na cells because DMC is known as electrochemically unstable in the Na cells.$^{4}$ In contrast, PC is known as stable solvent for Na cells.$^{22}$ Moreover, graphite is electrochemically inactive with EC/DMC solvent in the Na cell.$^{12}$ Structural disorder induced by milling clearly changes the intercalation behavior of Li ions into carbon. A voltage plateau observed for graphite in gradually disappears as increase in a rotation speed of mechanical milling, and voltage profiles change into a more sloping one. Charge/discharge profiles of the sample milled at 600 rpm resemble

**Figure 1.** Evolution of X-ray diffraction patterns of carbonaceous materials from graphite during mechanical milling at different rotation speeds for 12 h. Average interlayer distances of carbonaceous materials are also shown.

**Figure 2.** Particle morphology of graphite before (a) and after mechanical milling at 200 (b), 300 (c), and 600 rpm (d). Magnified images of the samples prepared at 200 (e) and 600 rpm (f) are also shown.
those of soft carbon in Li cells. A large reversible capacity of >500 mA h g⁻¹ suggests that the presence of hydrogen in the carbon surface and interaction with Li ions on electrochemical reduction. Na storage properties are also changed after milling at 200 rpm. After milling at 200 rpm, defects are created at the graphite surface, and thus passivation may be also promoted by the presence of defects. Voltage reaches nearly 0 V vs. metallic Na for the 2nd cycle even though a negligible amount of Na ions is inserted into carbon, which is estimated from a discharge (oxidation) capacity. A reversible capacity of approximately 200 mA h g⁻¹ is observed in a Na cell for the disordered carbonaceous material prepared at 600 rpm, and a similar voltage profile is reported for a Na cell with soft carbon used as a negative electrode.

Capacity retention and Coulombic efficiency of the carbonaceous materials prepared by mechanical milling in Li and Na cells are summarized in Fig. 4. Among the tested carbonaceous materials, the samples ball milled at 200 and 300 rpm show lower initial Coulombic efficiency in both Li/Na cells. Relatively improved Coulombic efficiency is noted for the sample milled at 600 rpm for both Li/Na cells. Charge (reduction) capacities of the sample at 600 rpm in the Li cell are gradually reduced for initial several cycles, good capacity retention and high Coulombic efficiency are achieved after 10 cycles. However, Coulombic efficiency for the 30th cycle is limited to 97.8%, which is much smaller than that of 99.0% for graphite without milling. Although the reversible capacity is much smaller for the Na system, good capacity retention is achieved for

Figure 3. Galvanostatic charge/discharge curves of graphite before and after milling at different speeds in Li cells (a–d) and Na cells (e–h) at a rate of 20 mA g⁻¹. The maximum charge capacity for the measurement was set to 1450 mA h g⁻¹.
the sample at 600 rpm, and high Coulombic efficiency of 99.1% is achieved for the 30th cycle, which is comparable to that of graphite in the Li cell.

Because disordered carbons prepared by mechanical milling contain surface defects in the structure, heat treatment of the sample at 1000°C for 12 h was further conducted to reduce excess irreversible capacities observed for the initial cycle. Heat treatment was conducted in a quartz tube furnace under Ar flow. After heat treatment of the sample prepared by mechanical milling at 600 rpm, crystallinity of both carbon and ZrO$_2$ is slightly increased, but disordered structures of carbon are still observed as shown in Fig. 5a. It is also noted that an average particle size is slightly grown by heat treatment as observed by SEM (Fig. 5b), and nanosized carbon is still observed after heat treatment. An irreversible structural change of the carbonaceous material prepared by milling was also reported in the literature. Graphitization was impossible by heat treatment of low crystallinity carbon obtained from graphite by milling, and carbonaceous materials with many nanoporous were obtained after heating at 2800°C.$^{21}$

Impact of heat treatment on electrochemical reactivity was examined in both Li and Na cells. An initial irreversible capacity is successfully reduced by heat treatment from approximately 600 to 300 mA h g$^{-1}$ in a Li cell, but a reversible capacity is also decreased to 300 mA h g$^{-1}$ as shown in Fig. 6. Heat treatment at 1000°C possibly eliminates the surface hydrogen species from the sample,$^{24}$ leading to a smaller reversible capacity. Similarly, a reversible capacity is also reduced after heat treatment for the Na system, but much smaller reduction of a reversible capacity is noted. Moreover, changes in charge/discharge profiles are noted, and voltage plateaus at 0.1 V appear for both Li and Na systems. This fact suggests that carbonaceous materials are changed into hard carbon by heat treatment. Mechanical milling induces many defects into the structure, leading to the formation of disordered carbons with lower density compared with graphite. Heat treatment partially removes these defects, and forming nanopores and dense graphitized regions in the structure, which is consistent with the finding by TEM.$^{21}$ Therefore, Li/Na clusters are accumulated into nanopores near Li/Na plating voltages, resulting in the change in the voltage profiles by heat treatment. However, the formation of Li/Na clusters is expected to result in inferior rate-capability as electrode materials.

![Graph showing capacity and efficiency vs. cycle number for Li and Na cells](image)

Figure 4. Comparison of capacity retention (a and c) and Coulombic efficiency (b and d) for the carbonaceous materials with different structural disorder in Li (a and b) and Na (c and d) cells.

![X-ray diffraction patterns](image)

Figure 5. (a) X-ray diffraction patterns of the sample milled at 600 rpm for 12 h, and after heat treatment at 1000°C for 12 h. Particle morphology of the sample after heat treatment with different magnifications is also shown in (b).
In this study, the disordered carbonaceous materials with different nanostructures were prepared by mechanical milling. It is expected that differences in milling speed influence the concentration of defect sites of disordered carbons, and differences in these nanostructures of carbons, including pore sizes, would be responsible for the enhancement in reversible capacity as electrode materials. Moreover, these nanostructures would influence rate-capability as electrode materials in Li/Na cells. Further studies on the factors affecting electrochemical properties of carbonaceous materials with different nanostructures are currently in progress in our group, and these results will be published elsewhere.

4. Conclusions

Influences of mechanical milling on structures of carbonaceous materials are systematically examined. Carbonaceous materials with different structural disorder synthesized by mechanical milling are tested as electrode materials. Sloping voltage profiles with large reversible capacities (500 mA h g⁻¹ in a Li cell and 200 mA h g⁻¹ in a Na cell) are observed for disordered carbons as electrode materials, and such characters are found to be similar to those of soft carbons.

Heat treatment of the disordered carbon leads to the formation of hard carbon with nanopores, resulting in the appearance of voltage plateaus at low electrochemical potential during Li/Na storage.

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Figure 6. Galvanostatic charge/discharge curves of the milled sample after heat treatment at 1000°C for 12 h in a Li (a) and Na (b) cell at a rate of 20 mA g⁻¹.