ECS Electrochemistry Letters, **4** (2) A22-A23 (2015)
2162-8726/2015/4(2)/A22/2/$31.00 © The Electrochemical Society

Excellent Rate Capability of MgO-Templated Mesoporous Carbon as an Na-Ion Energy Storage Material

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MgO-templated mesoporous carbon was investigated as an anode material for Na-ion storage. The mesoporous carbons exhibited a discharge capacity of 180 mAh g^{-1} at a current density of 0.1 A g^{-1} in a potential range of 2.00–0.01 V vs. Na^+/Na. This capacity was comparable to that of commercial hard carbon materials. They also showed an outstanding rate capability: 70 mAh g^{-1} at 4 A g^{-1}, which was 10-fold greater than the corresponding capability of commercial hard carbons. These results indicate that MgO-templated mesoporous carbon is a potential new anode material for high-power-density Na-ion batteries and capacitors.
 [DOI: 10.1149/2.0051502eel]

Manuscript submitted November 13, 2014; revised manuscript received December 1, 2014. Published December 10, 2014.

Lithium-ion batteries (LIBs) are one of the most promising energy storage systems because of their excellent properties such as high energy densities.[1,2] However, alternative energy storage systems are required to alleviate demand for LIBs in the near future because Li resources are limited and unevenly distributed throughout the world. Thus, sodium (Na) is an attractive material with the potential to replace Li in energy storage systems; unlike Li, Na is an inexpensive and abundant natural resource.[3] Recently, hard carbons have attracted interest as anode materials for Na-ion batteries and capacitors.[4–10] These previous studies have demonstrated that hard carbons are promising anode materials for Na-ion insertion. However, hard carbons exhibit poor rate capability.[7] Because a high rate capability is one of the most important properties for the practical use of hard-carbon electrodes, to enable their use in Na-ion batteries and capacitors, an enhancement of their rate performance is required. Nitrogen doping and nanostructuring have been investigated as approaches to improve the rate capability of hard carbons.[11,12] Wenzel et al. reported an improved rate capability when silica-templated carbons were used as anode material in Na-ion batteries.[11] The authors stated that the rate performance was enhanced through minimization of the Na diffusion length by interconnected pore structures. Fu et al. attributed the excellent rate performance of nitrogen-doped porous carbon fibers to their fiber-like morphology and to charge transfer facilitated by nitrogen functionalities.[12] In both cases, highly ordered nanoporous structures supported the high-rate performance of the batteries.

In the present study, MgO-templated mesoporous carbon was examined as an anode material for high-rate Na-ion storage. MgO-templated mesoporous carbons have recently attracted attention as electrode materials for electric double layer capacitors (EDLCs) because of their unique properties, which include mesopore-dominated structures and high specific surface areas.[13] In addition, MgO-templated mesoporous carbons are now produced on an industrial scale due to their simple and cheap production method (e.g., unlike silica-templated carbons, hydrofluoric acid is not necessary). However, the use of these carbons as electrode materials is mainly limited to EDLCs, although their application in other energy storage systems such as Na-ion batteries and capacitors is important from both scientific and industrial viewpoints. In this work, we demonstrate the surprisingly enhanced rate performance of MgO-templated mesoporous carbon as a Na-ion storage material.

Experimental

MgO-templated mesoporous carbons (CNovel, annealed at 1000°C, Toyo Tanso Co., Ltd.) and, for comparison, commercial hard carbons (BELLFINE, LN-0001, AT Electrode Co., Ltd.) were examined as active anode materials. For the electrochemical measurements, the mesoporous-carbon or hard-carbon powders were mixed with 6 wt% styrene-butadiene rubber (BM-400B, Zeon Co.) and 4 wt% carboxymethyl cellulose (D2200, Daicel FineChem, Ltd.) in distilled water. The obtained solution was cast onto an aluminum current collector. All electrodes were fabricated with a diameter of 10 mm and were used after being dried at 150°C overnight under vacuum. Three-electrode cells were assembled using carbon electrodes and glass-fiber filters (GA-55, Toyo Roshi Kaisha, Ltd.) that had been immersed in an electrolyte for 30 min under reduced pressure. The electrolyte was a solution of 1 M sodium hexafluorophosphate ($NaPF_6$, Wako Pure Chemical Industries, Ltd.) in propylene carbonate (PC, Kanto Chemical Co., Ltd., electrochemistry grade). Electrochemical measurements were performed with a BioLogic VMP3 multichannel galvanostat–potentiostat in a three-electrode configuration. The carbons were used as the working electrode, and Na foil was employed as the counter and reference electrodes. Charge–discharge tests were performed in a potential range of 2.00–0.01 V vs. Na^+/Na. The cyclability tests were conducted at 0.1 A g^{-1} between 2.00–0.01 V in the electrolyte containing 4 vol% of fluoroethylene carbonate (FEC, Tokyo Chemical Industry Co., Ltd.) with a coin type two electrode cell.

The morphology and pore structures of the carbons were characterized by transmission electron microscopy (TEM, TOPCON EM002B, 120 kV) and by N_2-gas adsorption/desorption isotherms measured at 77 K using a BELSORP-Max (BEL JAPAN, Inc.). The total pore volume, V_{total}, was determined from the amount of N_2 adsorbed at $P/P_0 = 0.95$. The micropore volume, V_{micro}; the total surface area, S_{total}; and the external surface area, S_{ext}, were estimated by the αs method. The mesopore size distributions were calculated according to the Barrett–Joyner–Halenda (BJH) and the non-local density functional theory (NLDFT) method.

Results and Discussion

The morphology and pore structures were characterized prior to the electrochemical measurements. TEM observations indicated that the pore structure was uniformly distributed (Fig. S1). As shown in the N_2 isotherm in Fig. S2, the adsorption amount increased in the high-pressure regions, indicating the formation of mesopores. The total surface area reached almost 2000 m^2 g^{-1} and consisted primarily of external surface area, likely as a consequence of mesopore formation. Notably, the presence of micropores was also indicated by an increase in N_2 adsorption in the low-pressure region. In addition, BJH and NLDFT analysis indicated that the mesopore size distribution peaked at approximately 4 nm (Fig. S3). On the other hand, the total surface area of the hard carbon (LN-0001) is approximately 20 m^2 g^{-1}, and the amount of pores is negligibly small.

Electrochemical measurements were subsequently performed with the mesoporous carbons and, for comparison, commercial hard carbons. Figure 1 shows cyclic voltammograms collected at a scan rate of 0.1 mV s^{-1}. In both cases, the reduction/oxidation peaks were observed at approximately 0.1 V vs. Na^+/Na. These peaks are attributed to Na insertion into the carbon layers. Clearly, the peaks were much sharper for the hard carbon than for the mesoporous carbons. This

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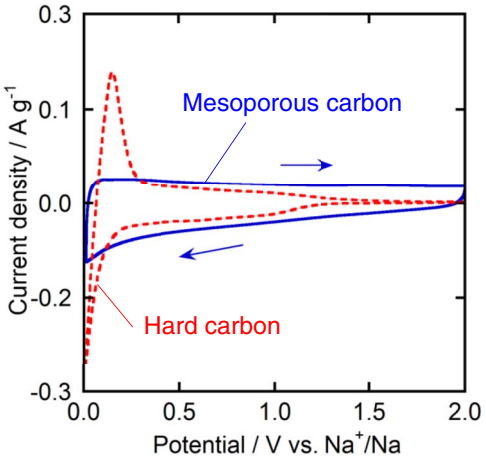

Figure 1. Cyclic voltammograms (3rd cycle) for the mesoporous carbons and commercial hard carbon (LN-0001) in a potential range of 2.0–0.01 V vs. Na^+/Na in 1M NaPF6/PC electrolyte. Scan rate is 0.1 mV s^{-1}.

increased sharpness is due to the difference in the annealing temperatures used to prepare the carbons. Because the mesoporous carbon was annealed at a relatively low temperature (1000°C), its carbon layers contained few Na-insertion sites compared to the carbon layers of the hard carbon. Another insertion mechanism likely occurred in the case of the mesoporous carbon, such as the formation of Na clusters in the mesopores.[14] In addition, capacitive contributions were significant for the mesoporous carbon due to its large specific surface area. Figure 2a shows the charge/discharge curves measured at 0.1 A g^{-1}. The mesoporous carbons exhibited a discharge (Na-deinsertion) capacity of 180 mAh g^{-1}, which is comparable to that of the hard carbon. The most remarkable result was the excellent rate capability, as shown in Fig. 2b. The charge/discharge curves at different current densities are shown in Fig. S4. The capacity was 70 mAh g^{-1} at 4 A g^{-1}, which was 10-fold greater than the corresponding capacity of the hard carbon. This greater capacity is ascribed to minimization of the diffusion length by mesoporous structures and significant capacitive contributions. The durability of the mesoporous carbon was evaluated using the FEC-containing electrolyte in a coin-type two-electrode cell. Figure 3 shows the capacity retention and coulombic efficiency. The retention decreased at the beginning of the cycle, but exhibited an almost constant value of 90%; the coulombic efficiency reached 99.9% after 100 cycles. However, the coulombic efficiency of the first cycle was very poor. Irreversibility is caused by the formation of solid electrolyte interface layers and is related to the large

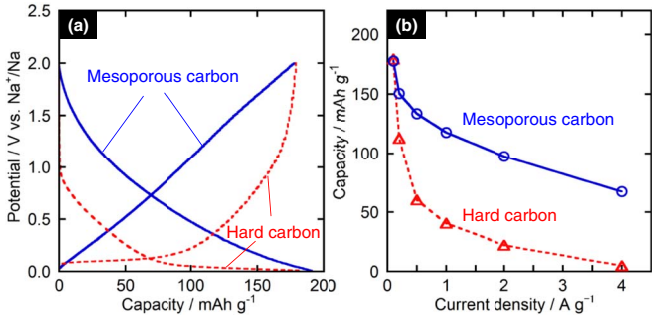

Figure 2. (a) Charge/discharge curves (5th cycle) measured at 0.1 A g^{-1} and (b) the rate performance for the mesoporous carbons and commercial hard carbons (LN-0001) in a potential region of 2.0–0.01 V vs. Na^+/Na in 1 M $NaPF_6$/PC electrolyte.

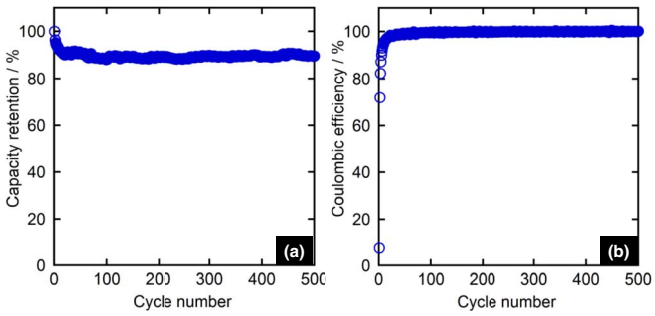

Figure 3. (a) Capacity retention and (b) coulombic efficiency for the mesoporous carbons measured at 0.1 A g^{-1} in a potential region of 2.0–0.01 V in 1 M $NaPF_6$/PC-FEC (4 vol%) electrolyte.

surface area of carbons. The literature contains few studies on reducing the irreversible capacity of Na-ion storage materials. However, by analogy, several strategies used in the development of Li-ion batteries could also be applicable to Na-based systems; these strategies include modifications of the electrolyte compositions, and the surface chemistry and nanostructures of carbons.[14–16] Thus, although further investigations on reducing the irreversible capacity of carbons are required to enable their practical use, the outstanding rate performance of MgO-templated mesoporous carbon as a Na-ion storage material is noteworthy given that this material is now produced on an industrial scale.

Conclusions

An MgO-templated mesoporous carbon was investigated as an anode material for Na-ion energy storage. Both Na insertion and capacitive contributions were significant for the mesoporous carbon. A drastically enhanced rate capability was observed, which we ascribed to minimization of the diffusion length by mesopores and to a capacitive contribution resulting from the carbon's large specific surface area. Although the large irreversible capacity is a challenging problem, we believe that the present work represents a positive step toward the use of industrially produced mesoporous carbons as Na-ion energy storage materials in batteries and capacitors.

Acknowledgment

We thank Dr. T. Morishita, Toyo Tanso Co. Ltd. for supplying the MgO-templated mesoporous carbons.

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Erratum: Excellent Rate Capability of MgO-Templated Mesoporous Carbon as an Na-Ion Energy Storage Material [*ECS Electrochem. Lett.*, 4, A22 (2015)]

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On page A23, left column, Figure 1 should be

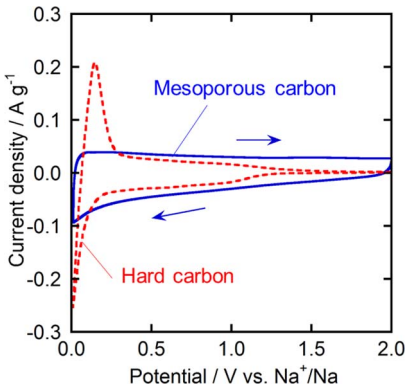

Figure 1. Cyclic voltammograms (3rd cycle) for the mesoporous carbons and commercial hard carbon (LN-0001) in a potential range of 2.0–0.01 V vs. Na^+/Na in 1M NaPF6/PC electrolyte. Scan rate is 0.1 mV s^{-1}.