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The global demand for the large-scale energy storage is rapidly growing, especially for the load leveling in electrical grids. Lithium batteries have potential applications for energy storage within electrical grid systems to effectively use electricity from power plants, solar cells and wind turbines. However, lithium resources do not seem particularly limited but the access to this essential resource could be potentially uncertain. Moreover, the cost of lithium keeps increasing with the prospect of future demand of Li-ion batteries. Thus, Na-ion batteries are promising candidates because sodium resources are unlimited everywhere. In the Na-ion battery, hard carbon is utilized as a negative electrode material. Our group first demonstrated the satisfactory practical performance for the Na-ion battery by using a commercialized hard carbon [1]. However, the hard carbon was extensively studied and optimized as a negative electrode material for the Li-ion battery not for Na-ion battery [2]. In this study, we examine the influence of pyrolysis temperatures on the structures and electrochemical performance of hard carbon in Li and Na cells. Furthermore, the Li/Na insertion mechanisms for the hard carbon are studied.

Hard carbon was prepared by pyrolysis of sucrose. De-watered sucrose was heated at between 900 and 1500 °C in Ar. The structures of the samples were examined by wide angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS) and Raman spectroscopy. Physical properties of the samples were also studied by Brunauer-Emmett-Teller (BET) surface area analysis and electron spin resonance spectroscopy (ESR). The broad diffraction peaks of 002 and 10/ Bragg diffraction lines are observed in all the WAXS patterns of the samples and the 002 peak shifted to high angle with increase in the pyrolysis temperature. The results suggest a disordered structure with locally ordered hexagonal carbon layers and the layer distance decreases as the pyrolysis temperature increases. These results are also in a good agreement with that reported by Dahn’s group [2].

The number of stacked hexagonal carbon layers calculated from the full width at half maximum (FWHM) of the 002 peak increased with pyrolysis temperatures. The analysis results of SAXS show a formation of micropores in the disordered structure and their size increased with the pyrolysis temperatures. Additionally, Raman spectroscopy of hard carbon shows that G-band and D-band peaks appear at around 1600 cm⁻¹ and 1350 cm⁻¹, respectively. The G-band peaks show no significant changes in the hard carbon prepared at different pyrolysis temperatures, which implies that the structure of hexagonal carbon layer does not change. However, the D-band peaks are relatively wide at lower pyrolysis temperatures, which is probably due to defects in the structure and the existence of functional groups on the hard carbon. Electron spin resonance spectroscopy (ESR) suggests that more pores with less surface area are formed at higher pyrolysis temperatures. The detailed structural dependence of hard carbon on the pyrolysis temperatures by combined analysis of WAXS, SAXS, Raman and ESR spectroscopy, BET surface area analysis and TEM observation will be discussed.

We also evaluated the electrochemical properties for the hard carbon with different structures synthesized at different pyrolysis temperatures. Charge/discharge curves (Figure 1) for all the samples show a sloping profile region at relatively high voltage in Li and Na cells where Li and Na ions insert into the hexagonal carbon layers [3]. Moreover, a flat plateau region at low voltage near to the equilibrium potential of Li and Na metals is observed, where Li and Na ions insert into the micropores. The reversible capacity delivered in the two voltage regions is significantly influenced by the pyrolysis temperatures. The temperature dependence on the reversible capacity is different between Li and Na cells. This fact also supports the difference in the structure of hard carbon synthesized at different pyrolysis temperatures, and Na/Li insertion mechanisms related to the micropores size.

The details of the correlation between pyrolysis temperatures and the electrochemical performance of hard carbon as negative electrode materials in Li and Na cells will be presented.

Figure 1: Galvanostatic charge-discharge curves of hard carbon electrode at different pyrolysis temperatures in a Na cell at a rate of 25 mA g⁻¹.

Reference:

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