MINIMIZATION OF THE IRREVERSIBLE Li+ CAPACITY OF HARD CARBONS

S. R. Mukai, T. Masuda, T. Tanigawa, T. Harada and K. Hashimoto
Division of Chemical Engineering
Graduate School of Engineering, Kyoto University
Kyoto 606-8501, Japan

Introduction

The demand for lithium ion batteries is rapidly increasing, due to their higher energy densities and longer shelf lives. In these batteries, carbon materials that can store a significant amount of lithium ions are used as the anode. Presently, graphitic carbons are widely used for this purpose in commercial batteries. However, as there is a limit in the lithium ion capacity in these types of carbon (372 mAhg^{-1}), worldwide scale research is in progress to find alternative anode materials that possess higher capacities.

Among various types of carbon materials, hard carbons, which are predominantly formed by graphene sheets stacked like a "house of cards" [1], is a potential alternative. However, although most hard carbons possess large lithium ion reversible capacities, their irreversible capacities are also rather large. Therefore it is difficult to apply such materials to commercial batteries. Part of this irreversible capacity arises from the formation of a passivation layer on the outer surface of the carbon [2]. In hard carbons, this layer is also likely to be formed within its pores. Previously, we showed that the irreversible capacity of hard carbons highly depends on their pore structures, and hard carbons which pore openings are small enough so that CO_2 cannot penetrate into them tend to have smaller irreversible capacities [3]. However, the pore volume of such hard carbons tends to be small, and it is hard to expect large reversible capacities from these materials.

In this work, hard carbons were synthesized by carbonizing various combinations of phenolic resins in order to obtain a hard carbon with large pore volume and small pore openings. The lithium ion capacities of thus obtained carbons were also measured. From the obtained results, strategies to obtain hard carbons with large reversible capacities and small irreversible capacities are proposed.

Experimental

Phenolic resins are usually synthesized via various stages. First phenols react with formaldehyde by the catalysis of an acid catalyst and novolac resin is formed. These novolacs are usually cured with agents such as hexamethylenetetramine and a thermosetting resin is obtained. Hard carbons can be obtained by carbonizing this thermosetting resin.

A wide variety of hard carbons can be obtained by carbonizing mixtures of phenolic resins derived from different phenols that are at different synthesis stages. In this work, first various phenolic resins were synthesized from combinations of different phenols and formaldehyde. The phenols employed were pure phenol, o-cresol and 3,5-xylenol. Note that the relative reactivities of these phenols with formaldehyde are 1:0.26:7.55, respectively. Next mixtures of phenolic resins derived from different phenols that are at different synthesis stages were combined and carbonized at 1273 K for 1 h, and various types of hard carbons were obtained.

The pore volumes of the obtained hard carbons were measured using the molecular probe method. Adsorption isotherms of the probe molecules were measured at 298 K using an adsorption apparatus (Bel Japan, Belsorp 28). The employed probe molecules were CO_2, C_2H_6, n-C_4H_{10} and i-C_4H_{10} (minimum molecular dimensions: 0.33, 0.40, 0.43 and 0.50 nm, respectively). Using the isotherms, the limiting micro-pore volume corresponding to the minimum size of the adsorbed molecules was determined using the Dubinin-Astakhov equation.

Electrochemical measurements of the samples were conducted using a two-electrode cell at a constant current of 25 mAg^{-1} and cut off voltages of 0 and 2.5 V. Lithium metal was used as the counter (reference) electrode. The carbon electrodes were constructed by supporting ball-milled carbon to copper foil using PVDF. The electrolyte used was a 1 M LiClO4-EC/DEC (1:1) solution (Mitsubishi Chemicals). Celgard 2400 (Hoechst Celanese) was used as the separator.

Results and Discussion

Previously, we showed that the pore structures of carbonized phenolic resins differ significantly when different phenols are used for synthesis. If the reactivity of the phenol with formaldehyde is high, the resulting carbon tends to have small pore openings, and if low the

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pore volume tends to become large. Therefore the carbonization of mixtures of phenolic resins derived from phenols with high reactivity and low reactivity are expected to give hard carbons with large pore volume and small pore openings.

Among various combinations, it was found that the carbonization of a mixture of o-cresol derived phenolic resin at the thermosetting stage (OCN-R) with the 3,5-xylenol derived phenolic resin at the novolac stage (3,5XN) gave a hard carbon with large pore volume which pore openings are small.

Figure 1 shows typical micro-pore volume distributions of the carbonized mixtures along with those of carbons obtained from the carbonization of o-cresol derived phenolic resin (OCN-RC) and 3,5-xylenol derived phenolic resin (3,5XN-RC). OCN-RC has a large pore volume but the sizes of the pore openings are rather large. On the other hand, the pore openings of 3,5XN-RC are extremely small, and it is assumed that its pore volume is also small. These structures reflect the reactivity of the phenols used for resin synthesis. By carbonizing a mixture of 10 wt% 3,5XN and 90 wt% OCN-R, the pore openings of the resulting carbon becomes smaller, but it maintains a pore volume close to that of OCN-RC. When the amount of 3,5XN is increased to 20wt%, the pore openings of the resulting carbon also becomes smaller, but a slight decrease in its pore volume is observed.

Figure 2 summarizes the results of the electrochemical measurements of the obtained carbons. OCN-RC has a large lithium ion capacity, but the proportion of the irreversible capacity is large due to its large pore openings. The lithium ion capacity of 3,5XN-RC is not so large, but the proportion of the irreversible capacity is small which also reflects its pore structure. When compared with OCN-RC, a large reversible capacity increase, and a slight irreversible capacity decrease was observed in the carbonized mixture including 10 wt% 3,5XN. When the amount of 3,5XN was increased to 20 wt%, the reversible capacity decreased but there was a significant decrease in irreversible capacity. These results are consistent with the pore structures of the tested carbons.

It is obvious that the narrowing of the pore openings is an effective way to minimize the irreversible capacities of hard carbons. We believe that it is much more feasible to directly synthesize a hard carbon with small pore openings rather than narrowing the pore openings of a synthesized hard carbon. However, the pore volumes of hard carbons which pore openings are small tend to be small when the carbons are synthesized using typical methods. The carbonizing of mixtures of phenolic resins derived from different phenols that are at different synthesis stages gives a wide variety of hard carbons with various pore structures. This method is thought to be a promising method to obtain hard carbons which pore structures lead to large reversible and small irreversible capacities for lithium ion insertion.
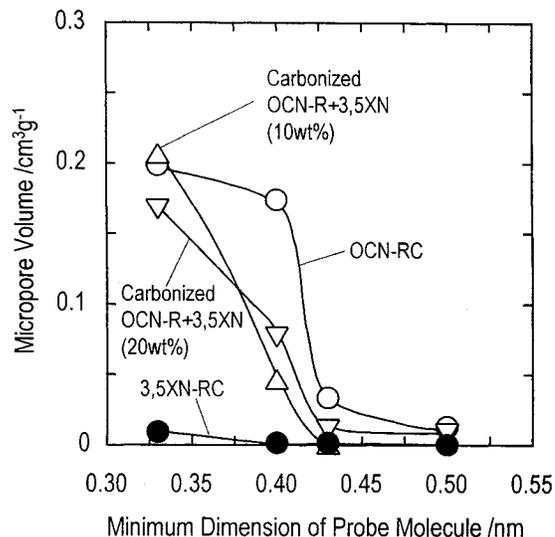

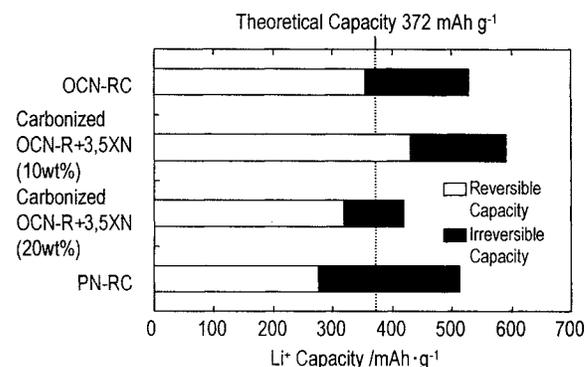Figure 1 Accumulated micropore volume distributions of the obtained samples

Figure 2 Lithium ion capacities of the obtained samples

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