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Synthesis and Electrochemical Characteristics of Pitch Coke Carbon Material for Lithium Ion Battery

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Carbon[1] is chemically very simple compound composed of only one element. But carbon has various structure, which lead versatile usage from structural material to advanced functional material. In the field of lithium ion battery, honeycomb-like layered stacking structure serves lithium ion intercalation site as the host. Guest lithium ion intercalates into the carbon host reversibly under electrochemical process by the following reaction[2]:

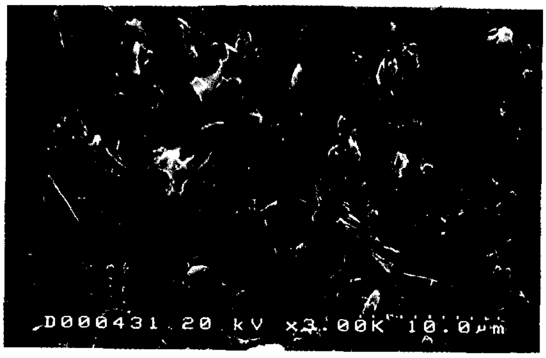
$$C_6 + Li^+ + e^- \rightleftharpoons LiC_6$$

Intercalation characteristics closely depend on the particle size, surface area and stacking structure of carbon material. Fundamental requiring characteristics of carbon material for lithium ion battery are high specific capacity, high 1st Ah efficiency and stable cycling behavior.

Here, we discuss the synthesis and electrochemical properties of pitch coke derived from coal tar pitch by heat treatment under inert atmosphere on the purpose of the investigation of its applicability to lithium secondary battery.

Experimental

Pitch coke 1200 was synthesized by the heat-treatment of coal tar pitch. Coal tar pitch (softening point; 140 ℃) was carbonized at 500 ℃ for 1hour, and then heat-treated at 1200 ℃ for 2 hours under argon atmosphere. Heating rate was 10 ℃/min. Yield of synthesized pitch coke was 41 weight % based on loaded coal tar pitch. Coarse pitch coke was milled with zirconia ball to give pitch coke 1200, which is denoted as P.Coke12. X-ray diffractogram and SEM photographs of P.Coke12 were obtained by PW 1830 model of Phillips and S-2700 model of Hitachi, respectively.



(a) x 3000

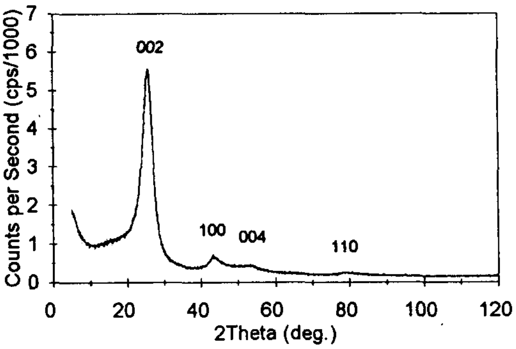
(b) x 10000

Figure 1. SEM photograph of P.Coke12 electrode.

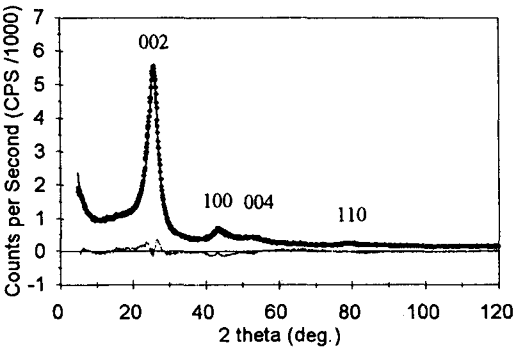
Anode was prepared as 75 μm sheet on one side of 50× 4.15 cm² area of copper foil (12 μm), coating of anode slurry, drying at 100 ℃ and then pressing. Anode slurry was the mixture of P.Coke12, super S. black, polyvinylidene fluoride and 1-methylpyrrolidone (weight ratio; 87 : 3 : 10 : 100). SEM morphology of P.Coke12 electrode in Figure 1 is shown. Particles having bended microstructure were observed in SEM photograph (a) and (b).

Cathode was prepared as 75 μm sheet on one side of 60× 4.2 cm² area of aluminum foil (25 μm) by similar process to anode process. Cathode slurry was the mixture of $LiCoO_2$ (FMC Ltd.), super S. black, polyvinylidene fluoride and 1-methylpyrrolidone (weight ratio; 92 : 3 : 5 : 100). Lithium metal was used as a reference electrode. Laminates of cathode, anode and separator (Cellgard 2500) were wound to make jelly roll by winding machine. Test cell was constructed on Pyrex glass tube using this jelly roll with lithium reference and electrolytic solution of 1 M $LiPF_6$ in ethylene carbonate and diethyl carbonate (1 : 1).

Assembled cell was tested by the galvanostatic charge-discharge by the Maccor series 2000 charge/discharge tester. Here, cut-off potential limits of P.Coke12 electrode were 0.02



(a) XRD pattern of P.Coke12



(b) XRD pattern of measured, calculated and difference of P.Coke12

Figure 2. XRD analysis of P.Cok12.

V for charging and 1.5 V for discharging versus lithium reference electrode. Current density was 65.4 mA/g-carbon (0.482 mA/cm^2).

Results and Discussion

Figure 2(a) represents XRD pattern of P.Coke12 measured from 5° to 120° of 2θ by CuKα radiation monochromated by nickel filter with 0.5°/min scan rate. d_{002}, La and Lc were obtained from Bragg's and Sherrer's equations, respectively.[3,4] A broad d_{002} peak around 25° means irregularity of 002 interplane distances. Low intensity of d002 and absence of some peaks compared with natural graphite due to the low crystalinity of P.Coke12. Average values of d_{002}, La and Lc were calculated as 3.43 Å, 60 Å and 1600 Å, respectively. Average layer stacking number of crystalite domain was 470. P and $(1-g)$ parameters were evaluated as ~1 and 0.38, respectively, from XRD data by using structure simulation program (Carbonxs).[5] Figure 2(b) represents the calculated XRD pattern and the difference between measured and calculated patterns. Here, P is the probability of finding a random shift or rotation parallel to adjacent layers. $(1-g)$ is the fraction of unorganized carbon. Therefore, the structure of P.Coke12 might be turbostratically disordered and buckled layer structure, which show continuous potential sloping in wide potential range during lithium ion intercalation. Maximum specific capacity of P.Coke12 was expected as 185 mAh/g using following relationship between maximum capacity and probabilities of P and g^2;

$$[\text{Specific Capacity}]_{max} = [g((1-P)+0.25P)+0.9(1-g)] \times 372 \text{ mAh/g}$$

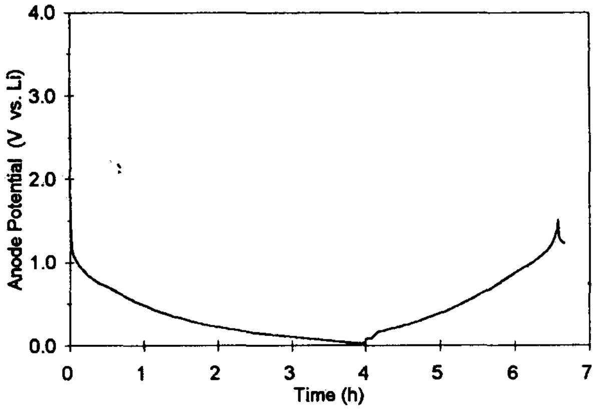


Figure 3. Typical voltage profile of P.Coke12 electrode at galvanostatic charge-discharge condition. current density: 65.4 mA/g-carbon (0.482 mA/cm^2). electrolyte: 1 M $LiPF_6$ in EC-DEC (1 : 1). potential range: 0.02-1.5 V *vs.* Li/Li$^+$.

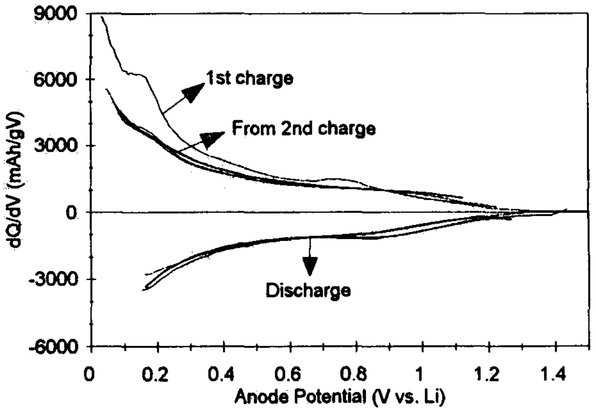


Figure 4. The differential capacity versus anode potential for P.Coke12 electrode. experimental condition: see caption of Figure 3.

Figure 3 represents the 1st charge-discharge characteristics of P.Coke12. At the 1st charge-discharge, specific capacities were 275 mAh/g for charge and 173 mAh/g for discharge yielding 63% of Ah efficiency. During charge-discharge, potential profile of P.Coke12 had ambiguous potential plateau as predicted from structure of P.Coke12.

dQ/dV variations were plotted against anode potential to identify potential plateau in Figure 4. dQ/dV peak at 0.75 V at 1st charge appeared due to irreversible reaction between carbon surface and electrolytic solvent. Also, peak near 0.15 V at 1st charge process disappeared after the 1st discharge process. So, the 1st Ah efficiency was very low (63%) due to this charge-discharge behavior. dQ/dV variations were similar after 2nd cycle. Capacity differences between 1st and 2nd charge process might be related to irreversible intercalation of lithium at 1st cycle. This phenomenon might be results of high initial irreversible capacity (102 mAh/g) due to lithium ion trapped in carbon host.

Figure 5 represents specific discharge capacities and Ah efficiencies with cycle number. Cycleability of P.Coke12 test cell was very good and its specific capacity was 180 mAh/g-

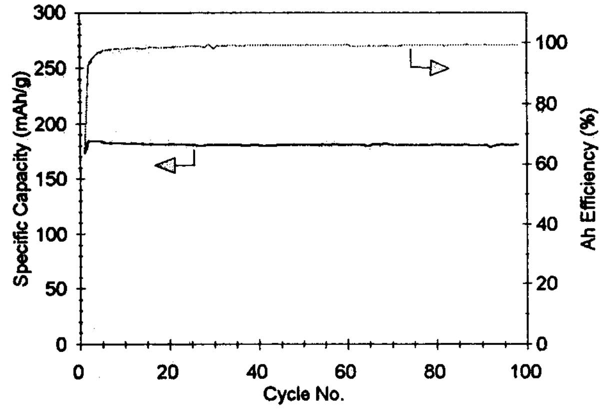


Figure 5. Variation of specific discharge capacity and Ah efficiency of P.Coke12 with charge-discharge cycling. experimental condition: see caption of Figure 3.

carbon from 2nd cycle to 98th cycle. The utilization of P.Coke 12 in this test was 48.4% based on 372 mAh/g of graphite's theoretical specific capacity. Ah efficiency of 63% at 1st cycle was raised to above 98% after 6th cycle. Therefore, the cycling characteristics of P.Coke12 were very stable. Obtained specific capacity of P.Coke12 was corresponding to calculated value from XRD analysis.

Conclusions

Pitch coke was synthesized from coal tar pitch. Synthesized P.Coke12 was found to have turbostratically disordered and buckled layer stack. Average d_{002}, La and Lc were calculated as 3.43 Å, 60 Å and 1600 Å, respectively. In cell test of P.Coke12, Ah efficiency of 63% at 1st cycle was raised to above 98% after 6th cycle. Low Ah efficiency at 1st cycle due to the irreversible intercalation of some lithium ion to carbon. Specific capacity was 180 mAh/g with good cycling behavior. Obtained specific capacity of P.Coke12 was corresponding to predicted value from XRD analysis.

In summary, synthesized P.Coke12 had low specific capacity but good cycling behavior compared, generally, with graphitic carbon.

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Cyclic Dimerization of 2-Piperidylglycine

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2-Piperidylglycine (**1**)[1] was prepared for the first time as a model compound for streptolutin (**2**)[2] which might be converted to antitumor agent DKP 593A *via* cyclic dimerizatioin. DKP 593A was isolated from the soil microorganism *Streptomices griseoluteus* and reported to be effective against certain solid tumors and leukemia.[3]

Piperazinedione ring structures are usually prepared by cyclic dimerizations of amino acids. It was reported that glycine and methyl L-alanine were converted to the corresponding piperazinediones by simple heating.[4] In addition to the thermal treatment, activation of the acid functionality is also available. For example, activation *via* *N*-carboxyanhydride[5] or *N*-hydroxysuccinimide ester[6] successfully gave the piperazinediones.

Relating to the present subject, the corresponding piperazinedione was not given from 2-(5-chloro)pyridylglycine upon heating,[7] while the piperazinedione was successfully formed from a β-lactam upon standing at room temperature in the preparation of racemic DKP 593A.[3] This paper aims to find a good method for preparing a piperazine-2,5-dione moiety from 2-piperidylglycine.

Result and Discussion

The ester **5** was prepared from alcohol **4** by oxidation, esterification, and protection in sequence. The ester **5** was treated with KHMDS and 2,4,6-triisopropylbenzenesulfonyl azide (trisyl azide) to give azide **6**. Simple hydrogenation of the azide **6** with or without di-*tert*-butyldicarbonate gave bis Boc ester **8** or mono Boc ester **7** in good yields.[8] During the hydrogenation of the azido ester **6**, or heating the amino ester,[7] none of the desired piperazinedione was detected. Removal of the Boc group from **7** followed by heating under reflux resulted in the intractable mixture.[7]

The acid **9**, prepared from the ester **8** by hydrolysis, was reacted with *N*-hydroxysuccinimide, and the resulting activated ester was treated with TFA and pyridine to give a solid.[6] Unfortunately, the solid was not the desired piperazinedione, but a mixture of polymeric materials by FAB mass spectral analysis.[9]

The coupling of the acid **9** to the amino **7** using HOBt and BOP gave dipeptide **10**. Finally, removal of all Boc groups from **10** followed by the treatment with NMM resulted in the desired piperazinedione **11** (Scheme 1). When the ring nitrogens in **10** were protected by Cbz instead of Boc, the corresponding piperazinedione was not given.

In conclusion, the cyclic dimerization of 2-piperidylglycine was accomplished *via* the peptide formation followed by the cyclization. *N*-Protecting groups on the piperidine rings should be removed prior to the cyclization. Using this methodology, the cyclic dimerization of streptolutin is currently