

Effect of $ZnCl_2$ on Formation of Carbonized Phenol Resin Anode

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Abstract

For replacing Li metal at Lithium Ion Battery(LIB) system, we used carbon powder material which prepared by pyrolysis of phenol resin as starting material. It became amorphous carbon by pyrolysis through its self condensation by thermal treatment. Amorphous carbon can be doped with Li intercalation and deintercalation because it has wide interlayer. However, it has a problem with structural destroy due to weak carbon-carbon bond. So, we used $ZnCl_2$ as the pore-forming agent. This inorganic salt was used together with the resin serves not only as the pore-forming agent to form open pores, which grow into a three-dimensional network structure in the cured material, but also as the microstructure-controlling agent to form a loose structure doped with bulky dopants. We used SEM in order to find to difference of structure, and can calculate the distance of interlayer by XRD analysis. CV test showed oxidation and reduction.

초 록 : Lithium Ion Battery(LIB)의 음극 활물질로서 리튬을 대체하기 위한 노력으로 phenol resin을 탄화시킨 탄소재료를 사용하였다. Phenol resin을 소성하면 축합반응을 일으키면서 탄화되어 무정형 탄소가 된다. 무정형 탄소는 층간거리가 넓어 리튬의 삽입과 탈리가 용이하지만 탄소간의 결합력이 약하여 구조적 붕괴가 일어난다. 이러한 문제를 해결하기 위해 세공형성제로서 $ZnCl_2$ 를 사용하였다. $ZnCl_2$ 는 생성된 물질에서 3차원적 망상구조로 성장하는 개방세공을 형성하는 세공형성제로서 뿐만 아니라, 벌크 첨가제가 도핑된 느슨한 구조를 형성하는 미세세공 형성제로서 작용하였다. SEM을 통해서 구조적 차이를 알 수 있었으며, XRD 분석으로 층간의 거리를 알 수 있었다. CV 측정을 통해 두 가지 샘플에 대한 산화와 환원 반응의 차이를 알아 보았다.

Key words : Lithium ion battery, Phenol resin, Electrode, Anode, Carbone

1. Introduction

It's getting more important to get high performance, high efficiency and portable convenience for batteries according to advanced science technology. Batteries were classified with solar battery, fuel cell, lithium battery, nickel-cadmium battery, and polymer battery et al. depend on devices used. Especially, secondary batteries have been studied, based on compactness. Among the secondary batteries, lithium battery has been developed extensively. Lithium secondary batteries were classified with lithium metal battery, lithium ion battery using carbon materials instead of lithium metal as anode and lithium polymer battery using polymer as electrolyte. In this work, we used amorphous carbon prepared by pyrolysis of phenol resin as anode material of lithium secondary battery, which is a major product in commercial compact battery.¹⁾

Recently, application of carbon material to anode has been studied. Carbon materials don't cause formation of lithium dendrite, which is one of the most serious problem in applying Li-based materials.²⁾ A high capacity, high operating voltage, good reversibility and long cycle life, these are

essential properties for high performance secondary batteries, can be realized by using carbon materials prepared from appropriate starting materials and heat treatment. There are two main approaches for the formation of carbon anode materials with high electrochemical performance.³⁻⁵⁾ One approach is to use highly graphitic carbon materials, in which Li atoms can intercalate the carbon layers up to the so-called C_6Li state indicated in Fig. 1. In this state, Li atoms are located over every three benzene rings. The theoretical capacity of the fully intercalated graphite is 372 mAh/g.²⁾ Highly graphitic carbons exhibit several advantages such as constant operating voltage and good reversibility. The preparation of highly graphitic carbon materials is technologically not so difficult, which is prepared by heat treatment at high temperature (2000-3000°C) to achieve a high crystallinity.⁶⁾

Another approach is to utilize amorphous carbon materials that have been investigated extensively because of their higher capacity than that of graphite. The electrochemical properties of amorphous carbon materials and highly graphitic carbons were recently reviewed by Dahn *et al.*³⁾ Among them, the hydrogen-containing carbon that is prepared at relatively low temperature (400-800°C) exhibits out-

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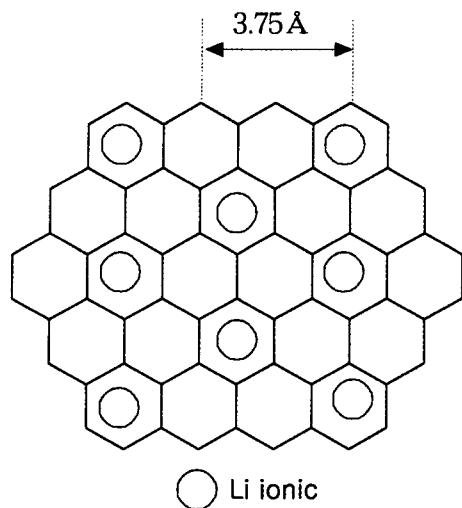


Fig. 1. C6Li configuration observed Li-graphite intercalation compound.

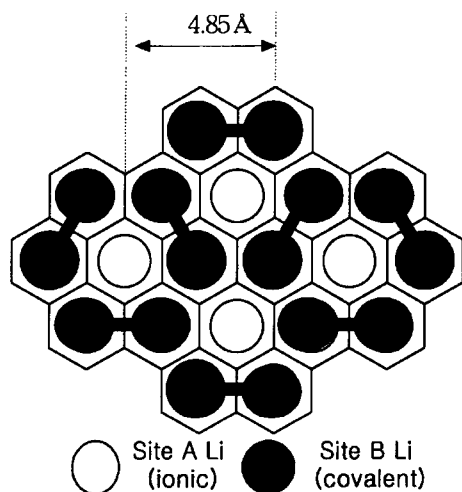


Fig. 2. Co-existence of two kinds of Li dopants, ionic and covalently bonded LiC₂.

standingly high reversible capacity.⁷⁻¹⁰⁾

We have been studying carbonized phenol resin prepared by the pyrolysis of resole-type phenol resin as one of the most promising amorphous carbon materials. An illustrative model of the carbonized phenol resin is shown in Fig. 2.¹²⁾ Owing to such a loose structure, the carbonized phenol resin can accommodate a large number of dopants compared with graphite. Therefore, carbonized phenol resin has been intensively examined toward the application to the electrodes of Lithium secondary batteries. However, it has a problem with structural destroy due to weak carbon-carbon bond. So, we used ZnCl₂ as the pore-forming agent. This inorganic salt used together with the resin serves not only as the pore-forming agent to form open pores, which grow into a three-dimensional network structure in the cured material, but also as the microstructure-controlling agent to form a loose structure doped with bulky dopants.

So, we compared pure phenol resin with phenol resin added ZnCl₂. In order to understand fundamental aspects of

the carbonized phenol resin, a variety of studies have been carried out based on X-ray diffraction (XRD),¹¹⁾ Scanning electron microscope (SEM), and Cyclic Voltammetry (CV).

2. Experimental

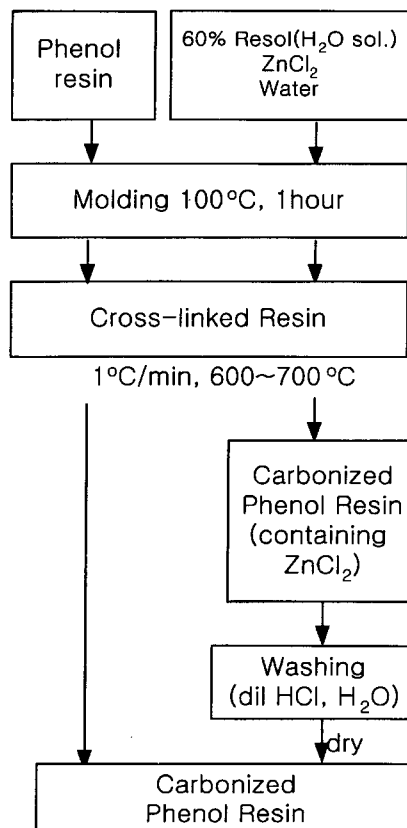
2.1. Sample preparation

Samples were prepared by two types of methods. One is the pyrolysis of pure resin, the other is the pyrolysis of resin added ZnCl₂ as metal catalyst. Former method used resole-type phenol resin as starting material and resin was molded in vacuum oven for about 2 hours at 100°C. After molding, it was carbonized by pyrolysis in Lenton's furnace in argon atmosphere at a temperature-elevating rate of 1°C/min in the range of 600-700°C. Latter method are prepared by pyrolysis of phenol resin molded with ZnCl₂, which removed in a last step. The sample-making solution prepared by mixing a 60% aqueous solution of resole-type phenol resin, ZnCl₂ and water in a weight ratio of 10:25:4 was poured onto a glass plate to form a film. This solution was heated and cured at about 100°C for 1 hour, and the rest process was the same as former method. All these process were shown in scheme I.

2.2. Electrode preparation

Prepared samples were shattered and meshed 45 μm size powder using 325 mesh. Binder solution prepared by mixing a 10% NMP solution of PVDF combined carbonized phenol resin as anode material. Ketjen black was used as electron conductor. Carbonized phenol resin, 10% binder solution,

Scheme I



ketjen black in a weight ratio of 85:10:5 was mixed. After solution changed into slurry type used NMP as solvent, it was made a sheet by blade method. Prepared sheet was heated and pressed on copper foil as anode collector.

2.3. Cell fabrication

In aluminum cell, carbonized phenol resin electrode was used as working electrode. Lithium metal was used as counter and reference electrode. Polypropylene (Celgard 1400) was used as separator. 1M LiPF₆/EC:DEC (1:1) was used as electrolyte. All experiments were undergone in glove box in order to prevent oxidizing.⁴⁾

2.4. Electrochemical test

Above mentioned cell was tested by cyclic voltammetry using EG&G 273A in the range of voltage 1.0-4.0 versus Li/Li⁺. Scan rate was 10 mV/s and open circuit voltage was 3.49V. In the charge-discharge test, We used charge/discharge battery test system (TOSCAT-3000U). Current density was 0.5 mA/cm² and working voltage was 0.01-2.00V.

3. Results and Discussions

3.1. SEM analysis

In order to observe morphology of carbonized phenol resin, we analyzed it by SEM(Hitachi S-2500C). Line was stated by size of 5 μm (×6000) and 10 μm (×3000). Fig. 3 shows morphology of carbonized phenol resin. We could observe ZnCl₂ located among carbonized phenol resins. Fig. 3(a) shows that resin containing ZnCl₂. Fig. 3(b) shows resin eliminated ZnCl₂. Fig. 3(c) shows carbonized phenol resin

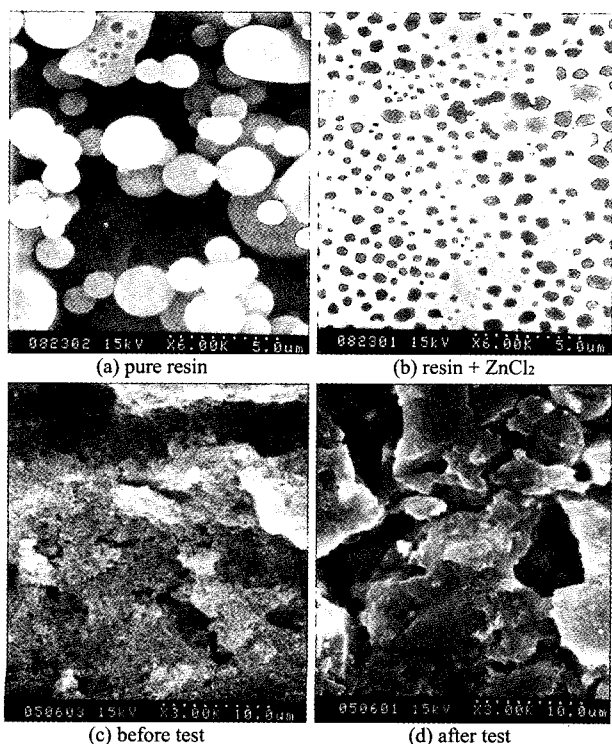


Fig. 3. SEM image of carbonized phenol resin.

electrode before charge-discharge test. PVDF as binder and ketjen black as electron conductor are shown in it. Fig. 3(d) shows carbonized phenol resin electrode after charge-discharge test, representing scar of Li intercalation and deintercalation.

3.2. XRD analysis

Fig. 4 shows results of XRD, main peak was found at 2θ = 20.5-23.5° and 2θ = 41-46° and most of all were spline

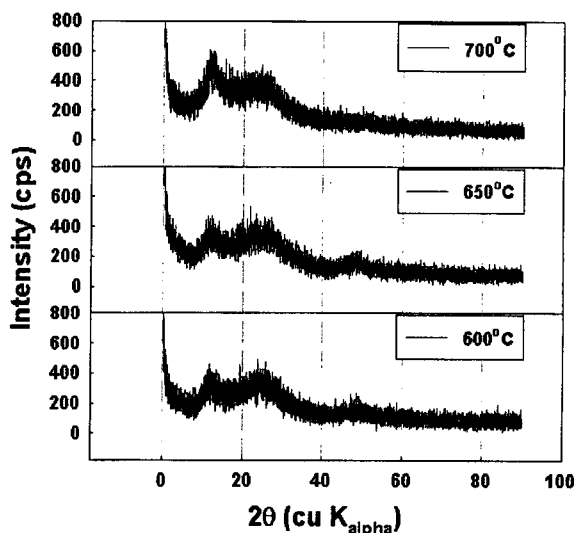


Fig. 4. XRD of carbonized phenol resin.

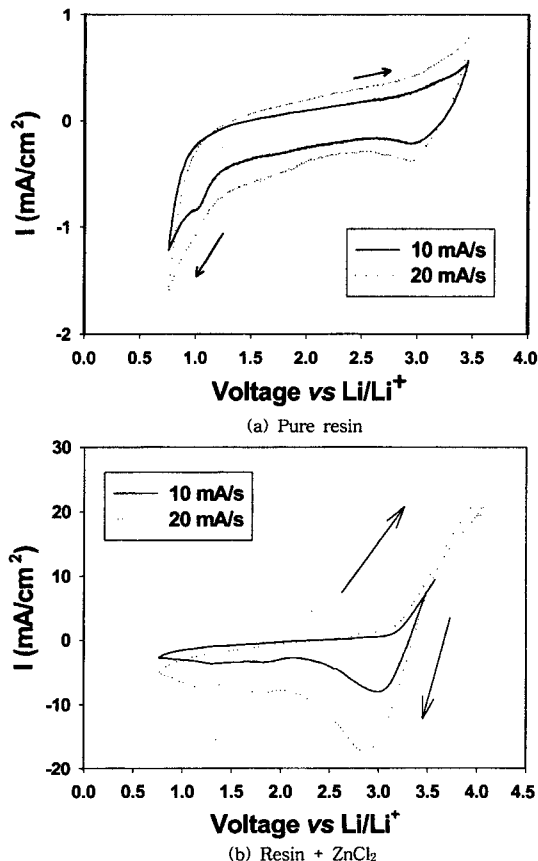


Fig. 5. CV curves of carbonized phenol resin.

curves. This indicates that carbonized phenol resin is amorphous structure. By increasing thermal decomposition temperature, (001) plane doesn't exhibit any change but (002) plane has a little tendency of increase. (002) plane is a distance of resin molecular. (100) plane is a growth of carbonized phenol resin structure to form benzene ring connected each other. Also, peak of 2θ below 25° was affected by remainder that wasn't decomposed during pyrolysis of phenol resin, and it was considered that the factor was determined by purity degree of phenol resin.

3.3. Cyclic voltammetry test

Shape of CV curves were shown as static state in Fig. 5. Fig. 5(a) is a result of pure phenol resin. The reaction around 3.5V was considered as p-type doping that PF_6^- ion from electrode was reversible intercalation and deintercalation. This indicates that carbonized phenol resin can be doped with bulk ions. Fig. 5(b) is a result of resin added ZnCl_2 . This shows p-type doping around 3.0-3.5V. As a voltage of Lithium metal is 3.045V, it would perform 3.6V of battery in case of using other cathode material.

3.4. Profiles of charge-discharge test

Cell was constructed with carbonized phenol resin as anode material. Li metal was used as reference electrode and counter electrode. Fig. 6 shows results of charge-discharge test. Fig. 6(a) shows result of charge-discharge for sample carbonized at 550°C . First discharge capacity was 600 mAh/g

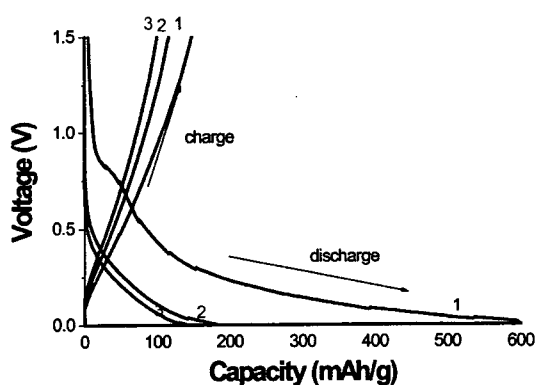
and first charge capacity was 150 mAh/g. Fig. 6(b) shows result of charge-discharge for sample carbonized at 600°C . First discharge capacity was 900 mAh/g and first charge capacity was 300 mAh/g. Reaction around 0.8V is the decomposition reaction of electrolyte and SEI formation at surface of phenol resin electrode. Curve below 0.8V decreased slope of curve by intercalation of solvated lithium ion (Li-intercalated compounds content solvent of electrolyte) to surface of carbonized phenol resin electrode. Because reaction of solvated lithium doesn't occur after forming solid electrolyte interphase (SEI) that has constant thickness at surface of electrode formed, it doesn't occur after second cycle.

4. Conclusion

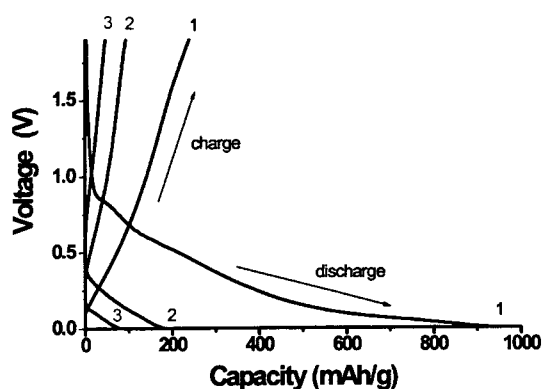
We obtained electrochemical results of carbonized phenol resin throughout the above experiments. As results of XRD, carbonized phenol resin has amorphous structure. It is similar to that of graphite but the distance of layer wider and could be doped easily Li-intercalation and deintercalation, which can increase to capacity of battery. Throughout SEM analysis, we knew that ZnCl_2 serves as not only pore-forming agent but also microstructure controlling agent to form a loose structure doped with bulky dopants. As results of CV test, the reaction around 3.5V was considered as p-type doping that PF_6^- ion from electrode was reversible intercalation and deintercalation. This indicates that carbonized phenol resin can be doped with bulk ions. The study of the Li ion storage mechanism and the electronic structure of such highly doped amorphous carbon materials is very interesting not only from engineering but also from scientific viewpoints. However, using amorphous carbon materials for Li ion rechargeable batteries, it has been suggested that there are some disadvantages such as Li ion loss in the first charging-discharging cycle and a large hysteresis in electrode potential vs. capacity profile.

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(a) 650°C



(b) 600°C

Fig. 6 Charge-discharge potential profile of carbonized phenol resin.

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