

리튬 이온 전지의 충방전 탄소전극의 특성

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Charge/Discharge Characteristics of Carbon Electrodes
in Lithium Ion Rechargeable Battery

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Introduction

Reversibility of lithium ion intercalation into carbon has been known to depend on the nature of electrolytic solution as well as to the structural variations of the host [1,2]. It is now well known that the solution components other than lithium ions participate in irreversible side reactions at the first charge curve; their by-product, either gas or surface film, influences and often interferes with the lithium ion intercalation. These side reactions and their resulting by-products are currently recognized as inevitable; but attempts at the research and development level usually focus on understanding and controlling these side-reaction phenomena. In this paper, these side reactions as well as the lithium intercalation phenomena are further explored with a focus on the role of physical properties of the active electrode material: Electrochemical interactions of three different carbons, petroleum coke, natural and artificial graphites, with electrolytic solutions are compared with a focus on the effects of particle size, surface area, and ohmic resistance of the carbon electrodes.

Experimental

The carbons tested in this work were petroleum coke (Karam Carbon, Inc.), Brazilian Natural Graphite (JEC-sample), and Treated Artificial Graphite (TC-01S). Lithium (Cyprus, 125 micron foil) was used as the reference and counter electrodes separated from the carbon electrode by Celgard 2400 separator. Electrolytic salts used were LiClO_4 , LiBF_4 , LiPF_6 , and/or LiAsF_6 . Solvents used were propylene carbonate (PC) and/or ethylene carbonate (EC) as high permittivity solvents (HPS); and diethyl carbonate (DEC), 1,2-dimethoxy-ethane (DME), 2-methyl-tetrahydrofuran (2-MeTHF), or dimethyl carbonate (DMC) as low viscosity solvents (LVS) (Aldrich). In some experiments, additives Al_2O_3 and/or 12-Crown-4 ether were also used

Characterization of the carbon material included Scanning Electron Microscopy (SEM), X-Ray Diffraction analysis (XRD), BET surface area analysis, and particle size distribution.

For electrochemical characterization, chronopotentiometric testing involved 16-channel battery tester (JEC Model PSG 102), and cyclic or pulse voltammetry experiments were performed on either PAR 273 or Schlumberger Electrochemical Interface SI 1286 in conjunction with SI 1260 Frequency Response Analyzer.

Results and Discussion

Effect of Carbon Structure

Figure 1 compares the X-ray diffraction patterns of raw petroleum coke, natural, and artificial graphites. Figure 2 shows the corresponding comparisons of first charge and discharge curves among the three types of carbons from Fig. 1. Going from the disordered (coke) to the more graphitic carbons, the potential range for the intercalation reaction narrows within 0.2 V vs Li/Li^+ , displaying a flat plateau at specific capacity region between 100 to 400 mAh/g. Natural and artificial graphites are compared by their (004) peak at about 54.5° , revealing a more ABCABC hexagonal close packing in natural graphite [3,4]. The discharge curve of the natural graphite occurred comparatively lower than its charging capacity (60% coulombic efficiency). Furthermore, other XRD measurements of the natural graphite after the first charge cycle showed that the (004) peak was reduced once the lithium ions have intercalated. These results suggest initial lithium ion intercalation, excluding the irreversible plateau near +0.8 V vs Li/Li^+ , was also *not* as reversible during the first cycle.

Effect of Surface Area

Surface areas of the three carbons were measured by the BET method to be 7.19, 14.33, and 17.15 m^2/g for coke, natural, and artificial graphites, respectively. The irreversible plateau occurring near +0.8 V vs Li/Li^+ in the first charge curve for the disordered coke was less clearly defined. However, better defined plateaus in the two graphites, were calculated to be 30 and 40 mAh/g, for natural and artificial graphites, respectively. This difference in the irreversible side reaction, in terms of specific capacity, corresponded to the difference in the surface areas between natural and artificial graphites. However, it is recognized that the irreversible side reaction is dependent not only on the surface area, but involves complex coupling of phenomena occurring at two different length scales: first a co-intercalation of solvent species (at an angstrom (10^{-10}m) scale): then

cracking or fracturing of the lamellar graphite leading surface film formation on the newly exposed surfaces (at a micron (10^{-6} m) length scale) of graphite.

Effects of Particle Size and the Addition of Carbon Black

Figure 3 compares the irreversible plateaus for the TAG electrode fabricated at four different conditions: two different particle size distributions (one sieved less than 500 mesh (26 micron) diameter, the other 325 mesh (45 microns) diameter), and with and without carbon black (Ketjen Black 600-JD) at the two particle sizes. Figure 4 shows their discharge capacities upto first 50 cycles for the four TAG electrodes in the solution of 1M LiPF_6 in EC:DEC. From fig. 4, electrode with smaller particles began with a slightly higher discharge capacity values in the range of 240 mAh/g. However the rate of fall in the capacity was the dramatic, decreasing to about 120 mAh/g after 40th cycle. Graphite electrode containing 5% carbon black initially displayed lower overall discharge capacity (~210mAh/g), however, maintained a more stable capacity at higher cycle (> 40 cycles). Since the carbon black used had surface area in the range of 1200 m^2/g , a hundred times the surface area of the graphite particles, the higher degree of side reaction is likely due to higher surface area provided by the electrode. Figure 3 shows a significantly larger irreversible capacity plateau. Higher degree of side reaction consequently lowered the electrode efficiency, thus the discharge capacity values. However, with the incorporation of these carbon black particles can act as sinks to scavenge the side reaction components, while the lithium ions can be directed towards the graphite particles. It has been reported by Shu *et al*[2] that the carbon black enhances electrode's both electronic and ionic conductivity by their higher surface area and higher degree of interdispersion among the active material. As the carbon electrode undergoes a gradual reduction in capacity due to exfoliation of the graphitic particle as well as loss in electronic conduction between the particles due to surface insulating films, carbon black can better distribute and connect to the exfoliated active material and lower the increasing resistance of the electrode.

Reference

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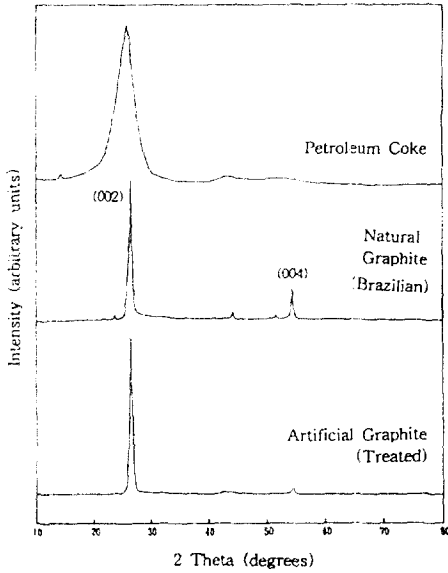


Fig.1 X-Ray diffraction patterns of (a) Petroleum Coke (KC-12), (b) Brazilian Natural Graphite, and (c) Treated Artificial Graphite (TDC-01S).

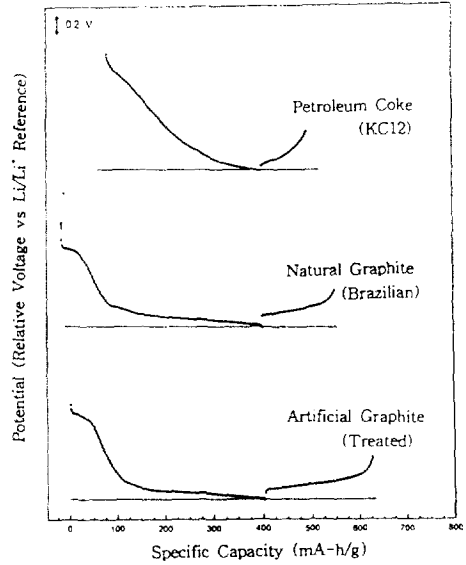


Fig.2 First charge-discharge characteristics of three different carbons in 1M LiPF₆ in EC:DEC.

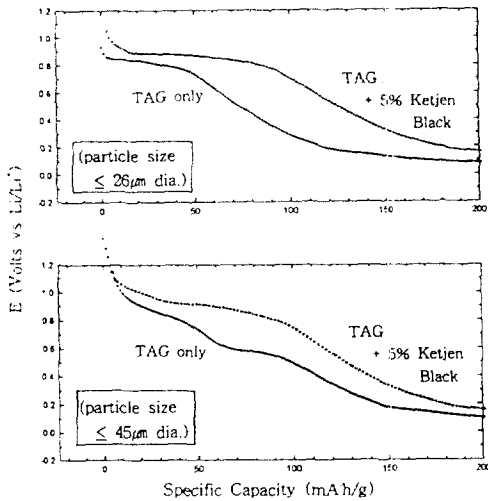


Fig.3 Comparison among the irreversible plateaus occurring during the first charge curve of TAG electrodes of two different particle sizedistributions and carbon black contents. (Electrolytic Solution 1.2M LiPF₆ in PC:EC:DMC).

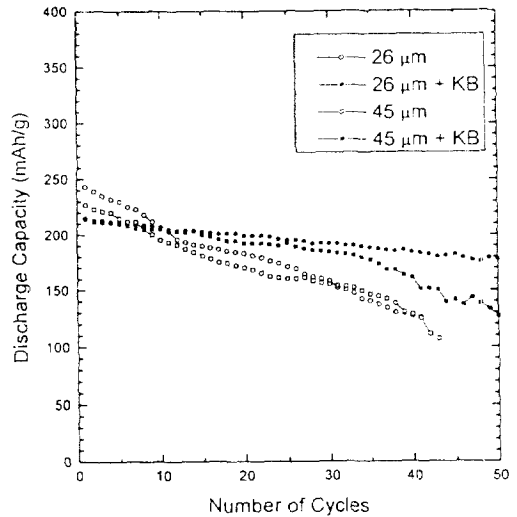


Fig.4 Discharge capacities of TAG electrodes of two different particle size distributions and carbon black contents. (Electrolytic Solution 1.2M LiPF₆ in PC:EC:DMC).