

Short Communication

Electrochemical behaviour of carbon electrodes in some electrolyte solutions

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Abstract

The electrochemical properties of coke and natural graphite in some electrolyte solutions containing diethylcarbonate (DEC) are studied. It is found that natural graphite exhibits an excellent performance, such as high discharge capacity ($370 \text{ mAh}^{-1} \text{ g}$), when a mixed solvent composed of ethylene carbonate (EC) and DEC is used. The charge/discharge characteristics of the coke electrode are not influenced by the species of the electrolyte solution, but those of the natural graphite electrode are very much influenced by the species of the electrolyte solution. It is confirmed that there are three patterns in the behaviour of the graphite electrode in the electrolyte solutions tested in this investigation. In the first pattern, natural graphite can be charged to C_6Li and then discharged. In the second pattern, the charging and discharging of the natural graphite electrode is impossible and destruction of the natural graphite crystal structure is observed. In the third pattern, lithium is intercalated into the graphite layer but the de-intercalation of lithium does not take place.

Keywords: Lithium; Lithium-ion batteries; Carbon; Graphite; Electrolyte

1. Introduction

Lithium secondary batteries offer excellent features, such as high specific energy, and high voltage. When lithium metal is used as the negative electrode, the cycle life of the battery is insufficient due to the production of dendrites.

In recent years, lithium secondary batteries with carbon negative electrodes have been actively studied because this type of battery offers superior characteristics in terms of charge/discharge cycle life. Carbon materials with intermediate crystallinity, such as petroleum coke and pitch coke, have been investigated as negative electrode materials. The capacity of these carbon, however, is small (200 to 250 mAh g^{-1}) [1–5]. It is therefore necessary to find carbon materials with a larger capacity in order to develop a lithium secondary battery with high specific energy.

The synthesis of C_6Li by a chemical reaction of graphite and lithium metal was reported by Guerard and Herold in 1974 [6]. The theoretical capacity of C_6Li as a negative electrode is 372 mAh g^{-1} . Day and Sullivan [7] reported that lithium ions could not intercalate into a graphite electrode electrochemically when using propylene carbonate (PC) as a solvent.

The authors investigated [8] many kinds of solvents for electrolytes in lithium secondary batteries, and found that C_6Li was electrochemically synthesized when EC was used as a solvent. There was a problem, however, in that the melting point of EC is high (36.4°C). It is necessary to develop an electrolyte containing a low-viscosity solvent with a low melting point in order to improve the charge/discharge characteristics. The electrochemical characteristics of a graphite electrode in EC and 1,2-dimethoxyethane (DME) have been reported by Ohzuku et al. [9].

In this study, DEC is selected as a low-viscosity solvent, and the charge/discharge characteristics are measured for carbon negative electrodes in a mixed solvent composed of DEC and typical solvents such as PC, butylene carbonate (BC), γ -butyrolactone (γ -BL), sulforan (SL), and EC.

2. Experimental

Pitch coke and natural graphite were examined as carbon materials. Pitch coke was prepared by heat-treating coal tar pitch at 1200°C in a nitrogen atmosphere. Refined natural graphite with a purity of more than 99.9% was used.

Table 1 shows the physical properties of the carbon materials examined. The crystalline parameters of the carbon materials were measured by the X-ray powder diffraction (XRD) method. The crystallite size along the *c*-axis (L_c) was calculated from the peak intensity and full width at half-maximum (FWHM) using the following relationship

$$L_c = \kappa \lambda / \beta \cos \theta \quad (1)$$

where κ is a constant, λ the wave length, β the FWHM, and θ the Bragg angle.

As natural graphite has a larger crystallite size (L_c) and smaller interlayer distance (d value) than pitch coke, the crystallinity of the natural graphite is higher than that of pitch coke. Moreover, the density of natural graphite is higher than that of pitch coke.

These carbon materials were mixed with polytetrafluoroethylene (PTFE) powder (5 wt.%) as a binding agent, and this mixture was then pressed onto a copper mesh to form a square shape (20 mm × 20 mm, thickness 0.1 mm).

A mixed solvent composed of DEC and a typical solvent (PC, EC, BC, γ -BL or SL) that contained LiPF₆ as the electrolyte. The mixture volume ratio was 1:1.

Charge/discharge tests were performed on experimental cells that used lithium metal for both the counter and the reference electrodes. Charging and discharging were con-

ducted at a constant current density (0.2 mA cm⁻²) over potential ranges between 0 and 1 V versus Li/Li⁺.

3. Results and discussion

3.1. Charge/discharge characteristics of coke electrode

The coke electrodes could be charged and discharged in all of the electrolytes used in this study. The charge/discharge characteristics are shown in Fig. 1, while the capacity and initial efficiency are given in Table 2. The initial efficiency is the charge/discharge coulombic efficiency at the first cycle. The discharge capacity of the coke electrodes is between 244 and 248 mAh g⁻¹ for these electrolyte solutions. The initial efficiency of the coke electrodes is between 81 and 82%. The initial efficiency after the second cycle is 100%.

There is no correlation between the discharge capacity and the kind of electrolyte solution. Likewise, the initial efficiency of the coke electrodes does not depend on the kind of electrolyte solution. It is found that all of the solvents can be used as electrolyte solutions when employing a coke electrode as the negative electrode.

3.2. Charge/discharge characteristics of natural graphite electrodes

The charge/discharge characteristics of natural graphite electrodes in several electrolytes are presented in Fig. 2. The capacity and initial efficiency of natural graphite electrodes are shown in Table 3.

In the case of employing SL/DEC and γ -BL/DEC as the solvent, natural graphite can be charged, but not discharged. In PC/DEC and BC/DEC, natural graphite cannot be

Table 1
Physical properties of carbon materials

Carbon materials	Density (g cm ⁻³)	L_c	d value (Å)
Pitch coke	2.02	26	3.47
Natural graphite	2.20	2291	3.35

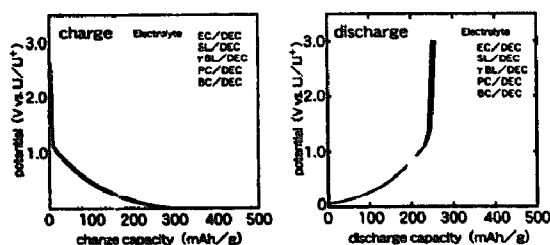


Fig. 1. Charge/discharge characteristics of coke electrode in several electrolytes.

Table 2
Capacity and initial efficiency of the coke electrodes

Electrolytic solvent	Charge capacity (mAh g ⁻¹)	Discharge capacity (mAh g ⁻¹)	Initial efficiency (%)
EC/DEC	304	248	82
PC/DEC	305	247	81
BC/DEC	304	246	81
SL/DEC	301	245	81
γ -BL/DEC	300	244	81

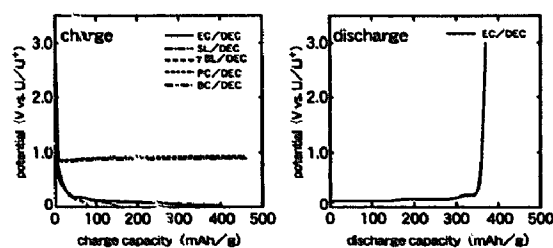


Fig. 2. Charge/discharge characteristics of natural graphite electrode in several electrolytes.

Table 3
Capacity and initial efficiency of natural graphite electrodes

Electrolytic solvent	Charge capacity (mAh g ⁻¹)	Discharge capacity (mAh g ⁻¹)	Initial efficiency (%)
EC/DEC	404	370	92
PC/DEC	(gas evolution)	0	0
BC/DEC	(gas evolution)	0	0
SL/DEC	153	0	0
γ -BL/DEC	82	0	0

charged, and gas evolution occurs during charging. Butylene and propylene gases were detected (by gas chromatography) in the case of using BC/DEC. This is understandable given the fact that the BC used in this investigation contained 2,2-butylene carbonate and 2,3-butylene carbonate. Propylene gas was detected when using PC/DEC. From these results, it is considered that the gases were produced by the decomposition of PC and BC.

The natural graphite electrode can be charged and discharged only in EC/DEC. The discharge capacity of the natural graphite electrode in EC/DEC is 370 mAh g^{-1} , which is nearly equal to the theoretical capacity of C_6Li . The natural graphite electrode shows a larger discharge capacity than that of the coke electrode. The natural graphite electrode also has a flat charge/discharge curve and a base charge/discharge potential. The initial efficiency of natural graphite, which (92%) is superior to that of the coke electrode. The efficiency of the natural graphite electrode after the second cycle is 100%, the same as that of the coke electrode.

The charge/discharge characteristics of natural graphite are thus influenced by the type of electrolyte solution. Natural graphite is considered to be suitable as a negative electrode material for lithium secondary batteries because it yields excellent charge/discharge characteristics when using EC/DEC.

3.3. Charge/discharge mechanism of natural graphite electrodes

The crystal structure of natural graphite in various states was analysed by XRD. The XRD patterns of natural graphite are given in Fig. 3. The (002) peak of natural graphite before charging was 26.5° . The (002) peak shifted to lower angles (24.0°) by charging in EC/DEC. This indicated an expansion of the inter-layer along the *c*-axis caused by the intercalation of lithium into the van der Waals gap. As the (002) peak angle of C_6Li is 24.0° , it was considered that the formation of C_6Li occurred by charging natural graphite in EC/DEC. In the case of charging in SL/DEC and γ -BL/DEC, the (002) peak of natural graphite shifted to the lower angles of 25.6 , 24.5 and 24.0° . As each peak angle of C_{24}Li , C_{12}Li and C_6Li corresponded to 25.6 , 24.5 and 24.0° , it was considered that the formation of C_{24}Li , C_{12}Li and C_6Li occurred by charging in SL/DEC and γ -BL/DEC. That is, the lithium ions intercalated into natural graphite, but not all of the graphite crystals changed to C_6Li by charging in SL/DEC and γ -

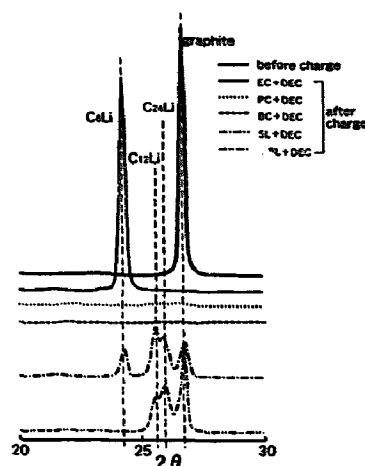


Fig. 3. X-ray diffraction patterns of natural graphite.

BL/DEC. In PC/DEC and BC/DEC, no peak of charged natural graphite was observed. This revealed the destruction of the natural graphite structure. In the case of using PC/DEC and BC/DEC, it was confirmed that these solvents were decomposed and the structure of the natural graphite was destroyed.

The results concerning the charge/discharge characteristics and the change in the crystal structure of the natural graphite electrode are shown in Table 4. The electrochemical behaviour of natural graphite can be classified into three patterns. In pattern A, both charging and discharging are possible and the structure of the graphite is stable. In pattern B, neither charging nor discharging is possible and the structure is destroyed during charging. In pattern C, graphite can be charged but cannot be discharged and the structure is stable. It is concluded that the electrolyte is decomposed during charging in pattern C because the graphite electrode cannot be discharged. As the decomposition of the electrolyte is not accompanied by gas evolution, it is considered that the products of the decomposition are solid state and disturb the deintercalation of lithium ions during discharging. In pattern A, it is thought that lithium is intercalated into graphite and almost no decomposition of the electrolyte occurs.

On the other hand, destruction of the natural graphite structure and gas evolution while charging appear in pattern B. The destruction of the natural graphite structure is attributed to gas evolution produced by the decomposition of the solvents in the natural graphite crystal layer.

Table 4
Charge/discharge characteristics and change in structure of natural graphite electrodes

Pattern	Electrolytic solvent	Charge	Discharge	Structure of graphite
A	EC/DEC	possible	possible	stable
B	PC/DEC	impossible	impossible	destroyed
B	BC/DEC	impossible	impossible	destroyed
C	SL/DEC	possible	impossible	stable
C	γ -BL/DEC	possible	impossible	stable

4. Conclusions

It is found that the charge/discharge characteristics of coke electrodes are not influenced by the species of electrolyte solution, but that those of natural graphite electrodes are very much influenced by the species of electrolyte solution. It is confirmed that there are three patterns in the behaviour of graphite electrodes in the several electrolyte solutions. In EC/DEC, natural graphite can be charged to C_6Li and discharged. Natural graphite exhibits the highest discharge capacity of 370 mAh g^{-1} in EC/DEC. In PC/DEC and BC/DEC, the charging and discharging of the natural graphite electrode are impossible and destruction of the natural graphite crystal structure is observed. It is thought that gas evolution causes the destruction of the natural graphite structure. In SL/DEC and γ -BL/DEC, lithium intercalates into the graphite layer but the de-intercalation of lithium is impossible. It is considered that the products of the sub-reaction while charging are

solid in these solvents and disturb the de-intercalation of lithium ions.

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