



An X-ray photoelectron spectroscopy study on the surface film on carbon black anode in lithium secondary cells

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Abstract

The property of the surface film formed on the carbon black anode of a lithium cell at the initial reduction stage was investigated. About 90% of the carbon black surface was covered with a smooth film about 10–15 Å in thickness after five cyclic voltammetry cycles. The X-ray photoelectron spectroscopy analysis revealed that this film contained oxygen atom bonding directly to the carbon atoms and was formed by decomposition of the solvent. The inhibiting effect of the surface film against further solvent decomposition reaction disappeared after washing with ethanol or heat treatment above 200 °C. The surface film was confirmed to form also by chemical reduction using lithium naphthalide, where lithium insertion in the carbon black took place. The inhibiting effect of a chemically formed surface film against the solvent decomposition was less marked than that of an electrochemically formed film.

Keywords: Lithium secondary cells; Carbon black; Anodes; Surface films

1. Introduction

Various carbon materials had so far been investigated as a possible anode material for the so-called lithium-ion secondary battery having a long cycle life and the reliable safety [1–4]. The amount of lithium inserted/extracted reversibly into/from a carbon matrix and the charge/discharge potentials are the most important factors to achieve a high energy density and efficiency of the cell.

Meanwhile, the irreversible initial reduction process consisting of the solvent decomposition and the succeeding surface film formation [1] were suspected to lower a reversible capacity of the cell. The detailed mechanisms of these phenomena, however, are not yet clear at present.

In this work, the electrochemical behaviour of a carbon black anode was investigated in a non-aqueous electrolyte solution. The surface film formed at the initial reduction stage was observed by transmission electron microscopy (TEM) and analysed by X-ray photoelectron spectroscopy (XPS). The inhibiting effect

of this film against the further solvent decomposition was examined in a reconstructed cell after various treatments such as heating at 100 to 300 °C, washing with ethanol, and so on. Moreover, the surface film formed during chemical reduction was also investigated.

2. Experimental

Carbon black used in this work was prepared by the oil furnace method and then heat-treated at 1200 °C in an inert atmosphere. The carbon black sheet was then obtained by hot pressing the mixture of a carbonaceous active material (90%) and a poly(tetrafluoroethylene) (PTFE) binder (10%). The working electrodes were prepared by pressing a nickel foil current collector on to these sheets and finally dried under vacuum at 200 °C. The beaker-type three-electrode cells were constructed with flooded electrolyte in an argon-filled dry box.

All the measurements were carried out at 25 °C. The counter electrode was a lithium foil with a large surface area and the reference electrode was a lithium chip. The electrolyte was a 1 M LiPF₆/EC-DME (50/50 by vol.) solution from Mitsubishi Petrochemical Co.,

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Ltd. Cyclic voltammetry (CV) was mainly used to examine the reversibility between 2 and 0 V (versus Li/Li⁺).

Before TEM and XPS analyses, the sample electrodes, after the electrochemical experiments, were rinsed with ethanol using soxhlet extractor in air, or with dimethoxyethane (DME) 5 times on a filter paper in argon atmosphere.

On the other hand, the carbon black was reduced chemically in the argon-filled dry box as follows: 6.7% w/v naphthalene was dissolved in DME [4,5] and then lithium chips were added to this solution yielding a green solution of lithium naphthalide. Chemical reduction was carried out by immersing a sample electrode into the solution under agitation.

3. Results and discussion

3.1. Electrochemical aspects of the carbon black anode

Typical CVs during initial five cycles are shown in Fig. 1. The cathodic peak at 650 mV was observed only at the first cycle and the CVs were quite reproducible for the second to fifth cycles. There were two couples of redox peaks at about 0.2 and 0.9 V, as already mentioned in a previous paper [6]. In a propylene carbonate (PC)–DME solution, the evolution of propylene (C₃H₆) gas, a reduction product of PC, was confirmed by gas chromatographic analysis combined with the potentiostatic reduction at <900 mV [6]. The analogous irreversible cathodic peak at 650 mV appearing only on the first sweep in an ethylene carbonate (EC)–DME solution, furthermore, suggested that this peak would be concerned with the formation of a surface film on carbon black which inhibited the subsequent reduction of solvent molecules.

3.2. Analysis of the surface film on carbon black

The surface of carbon black particles after five CV cycles was covered with a smooth film about 10–15 Å in thickness as seen on a TEM view in Fig. 2(a). At least about 90% of the carbon black surface was covered with this film, which did not form after open-circuit immersion for the same period as the CV experiments (Fig. 2(b)). Therefore, the surface film should form electrochemically and it seemed stable in the atmosphere prepared this sample.

Both C(1s) and O(1s) XPS spectra from these two samples were compared in Figs. 3 and 4, respectively. In addition to the main C–C peak at 284 eV, another weak peak at 292 eV probably due to the C–F bond in a PTFE binder could be detected in an immersed sample before argon etching. The disappearance of the peak at 533 eV after slight argon etching implied the

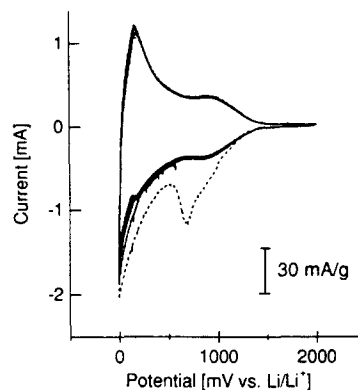


Fig. 1. Cyclic voltammograms of a carbon black electrode at 3 mV/min: (---) 1st cycle, and (—) 2nd to 5th cycles.

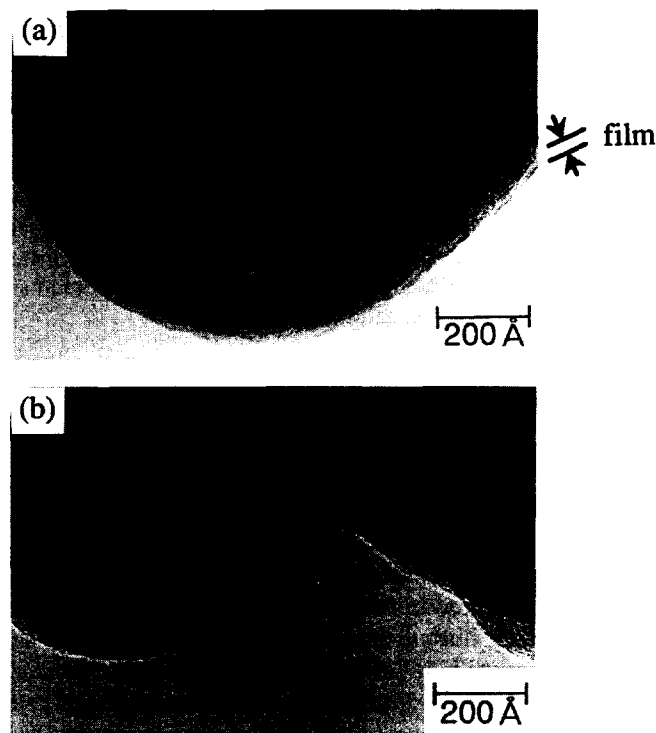


Fig. 2. Transmission electron microscopy photographs of carbon black after (a) five CV cycles, and (b) immersed under open circuit for 195 h.

adsorption of some O-containing species from the electrolyte. As for CV-cycled sample, on the other hand, O(1s) peak at 530–535 eV was strong, whereas C–C peak at 284 eV was relatively weak. The broad O(1s) peak should arise from several different bonding states of oxygen which were poorly resolved in this case. With increasing the argon etching time, O(1s) and C(1s) peaks became weaker and stronger, respectively.

From these results, the surface film formed after CV cycles was considered to contain oxygen atoms bonding directly to the carbon atom and to originate from the decomposition of EC and/or DME.

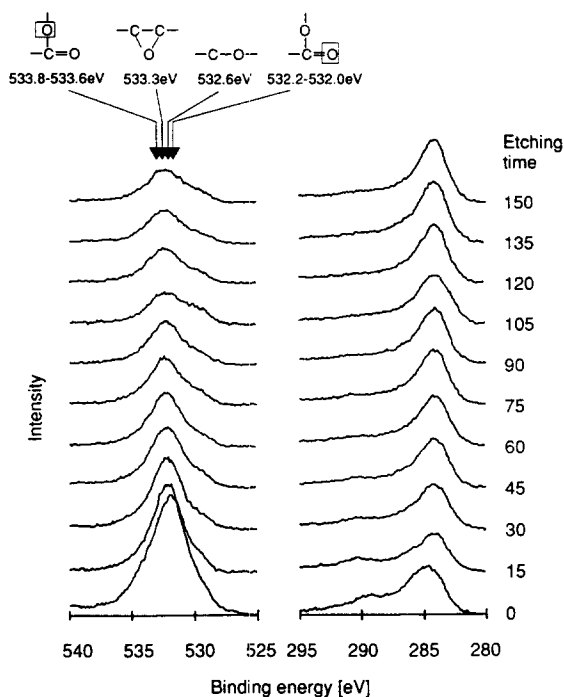


Fig. 3. O(1s) and C(1s) X-ray photoelectron spectroscopy spectra after five cyclic voltammetry cycles.

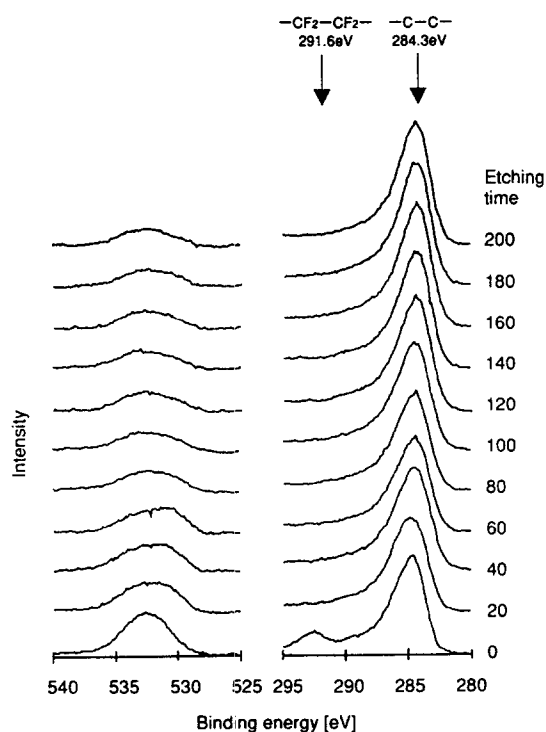


Fig. 4. O(1s) and C(1s) X-ray photoelectron spectroscopy spectra after immersion under open circuit for 195 h.

3.3. Inhibiting effect of the surface film on the solvent decomposition

After five CV cycles, the sample electrode was rinsed with ethanol in air, and then the cell was reconstructed

with a fresh electrolyte solution. In such a case, the irreversible current peak at 650 mV (Fig. 1) again appeared on the first cathodic sweep. On the contrary, when the electrode was heat-treated below 200 °C under vacuum after being rinsed with DME in dry argon, this irreversible peak was not observed clearly in the renewed electrolyte, see Fig. 5. With increasing the heat-treatment temperature, furthermore, the irreversible cathodic peak at 650 mV on the first sweep became clear and the surface film tended to be easily removable by rinsing with water as seen from TEM observations. These experimental results suggested that the inhibiting effect of the surface film against the solvent-decomposition reaction disappeared after contacting with a trace amount of water or oxygen in the atmosphere or after the heat treatment leading to some transformation of this film.

Moreover, when the electrolyte LiPF_6 was replaced with LiClO_4 in a renewed cell, the initial irreversible peak did not appear, almost like as in Fig. 5(a). This fact probably suggested that the insertion/extraction of lithium occurred almost reversibly through this Li^+ -ion conducting surface film.

3.4. Chemical reduction by lithium naphthalide

The surface of chemically lithiated carbon black was covered with a film similar to that observed in Fig. 2(a) after electrochemical lithiation. This film was confirmed to consist of a certain compound insoluble in DME. These chemically reduced electrodes showed the open-circuit potential of about 1.0 V after construction of a cell with a fresh electrolyte solution.

CV curves of chemically reduced samples in an $\text{LiPF}_6/\text{EC-DME}$ solution were given in Fig. 6, where the anodic current peak appeared at about 1150 mV on the first anodic sweep ensuring the preceding chemical lithium insertion by lithium naphthalide. The reduction peak attributable to the irreversible solvent decomposition was slightly present on the subsequent cathodic sweep, and the CVs were reproducible for the second to fifth cycles. The small charge/discharge capacity compared with that of original carbon black tended to decrease with the immersion time of a sample electrode in a lithium naphthalide solution.

4. Conclusions

The surface film on carbon black formed electrochemically in an $\text{LiPF}_6/\text{EC-DME}$ solution at the initial reduction stage has an inhibiting effect against further solvent decomposition. This film contains oxygen bonding directly to the carbon atoms and its inhibiting effect disappears after contacting with traces of water or oxygen or heat treatment over 200 °C. Though analogous

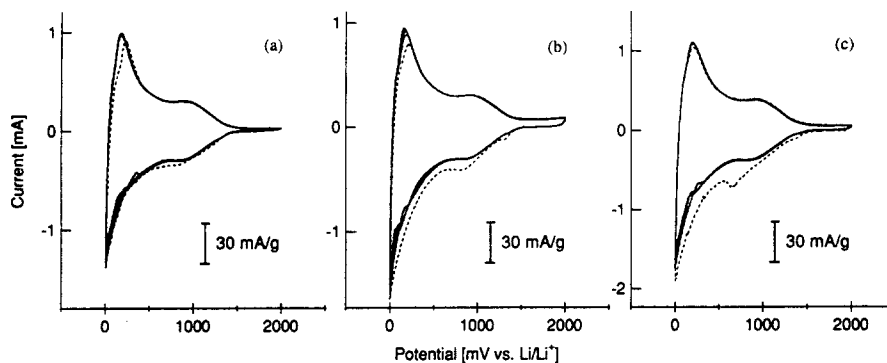


Fig. 5. Cyclic voltammograms (3 mV/min) in a renewed solution of previously five cyclic voltammetry cycled electrodes after treated for 24 h at: (a) 100 °C; (b) 200 °C, and (c) 300 °C. (---) 1st cycle, and (—) 2nd to 5th cycles.

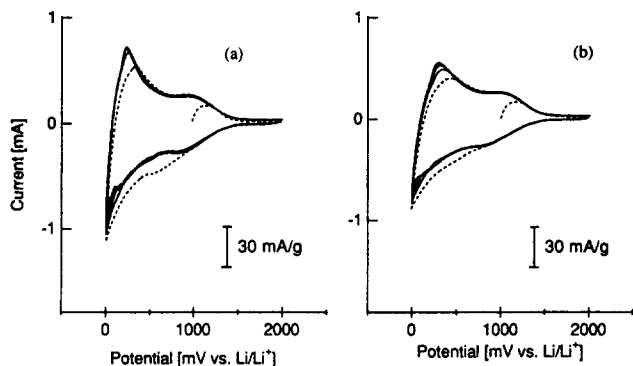


Fig. 6. Cyclic voltammograms (3 mV/min) of chemically pre-reduced carbon black electrodes by immersing in a lithium naphthalide solution: (a) for 1 day, and (b) 5 days. (---) 1st cycle, and (—) 2nd to 5th cycles.

surface film is formed by the chemical reduction with lithium naphthalide, its inhibition effect against solvent decomposition was less marked compared with that of an electrochemically formed film.

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References

- [1] R. Fong, U. von Sacken and J. Dahn, *J. Electrochem. Soc.*, **137** (1990) 2009.
- [2] N. Imanishi, S. Ohashi, T. Ichikawa, Y. Takeda and O. Yamamoto, *J. Power Sources*, **39** (1992) 185.
- [3] A. Sleight and U. von Sacken, *Solid State Ionics*, **57** (1992) 99.
- [4] Z. Shu, R. McMillan and J. Murray, *J. Electrochem. Soc.*, **140** (1993) 922.
- [5] K. Abraham, Ambient temperature secondary lithium batteries using LiAl or lithium insertion anodes, *LBL-24647 UC-210*, Lawrence Berkeley Laboratory, University of California, 1987, p. 9.
- [6] K. Takei, K. Kumai, T. Iwahori, T. Uwai and M. Furusyo, *Denki Kagaku*, **61** (1993) 421.