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Direct evidence on anomalous expansion of graphite-negative electrodes on first charge by dilatometry

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Abstract

Dilatometer was fabricated and applied to measure change in electrode thickness of the graphite-negative electrode for lithium-ion batteries. Anomalous expansion was observed in the initial part of the first reduction, i.e. so-called irreversible capacity region in voltages of 1.1–0.5 V versus Li. During further reduction to 0 V versus Li, the thickness of electrode increased monotonously as the lithium-intercalation reaction proceeded. The observed change in electrode thickness was larger than that of 10% expected from XRD data, due mainly to the expansion at the initial part of the first reduction. One-to-one correspondence between the electrochemical and dilatometric data was observed. The acoustic events occurring inside the Li/graphite cells were also measured. The effect of electrolyte on the anomalous expansion was also examined by dilatometry in relation to the irreversible capacity for the first reduction of graphite, and the significance of introducing the dilatometry together with acoustic emission technique to insertion materials research for advanced lithium-ion batteries was discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dilatometry; Graphite; Acoustic emission; Lithium battery; Intercalation compound

1. Introduction

A graphite is of particular importance as a negative electrode material for lithium-ion batteries, because of the lowest operating voltage among insertion materials [1–4], excellent rechargeability, and the highest volumetric capacity of ca. 600 mAh g⁻¹ calculated from the observed density and rechargeable capacity [1,4]. A characteristic feature of lithium-graphite intercalation compounds is a staging phenomenon with a periodic sequence of lithium-intercalated layers between graphite sheets. When lithium is intercalated into graphite matrix, the interlayer distance between graphite sheets increases about 10% by XRD [1]. However, a change in electrode thickness visually inspected on the first reduction of graphite (first charge as a negative electrode) is usually larger than that expected by XRD. The capacity for the first reduction of graphite is larger than that of subsequent cycles, so that a part of charge capacity in the first cycle is missing, so-called irreversible capacity. Such a capacity loss has been reported [5–9] with

emphasizing on reductive decomposition of electrolytes, protective film formation, solvent co-intercalation, and so forth. Less attention has been paid to the relation between the change in electrode thickness and irreversible capacity.

In this paper we report a dilatometer to monitor the change in electrode thickness and show direct evidence on anomalous expansion of graphite negative electrode in relation to so-called irreversible capacity during the first charge by dilatometry.

2. Experimental

A schematic illustration of a dilatometer used in this study is shown in Fig. 1. The electrochemical cell consisted of graphite electrode and lithium electrode, separated by a porous polypropylene membrane. The graphite electrode in measuring change in thickness was a compressed pellet (11.3 mm diameter, 10³ kg cm⁻² of forming pressure) of natural graphite (NG-7, Kansai Coke and Chemical Co., Ltd., Japan) without the addition of any binder. The electrodes were under a constant load by a weight (2 kg in this study) attached to a spindle. The change in total thickness of both electrodes was transmitted to a spindle and was

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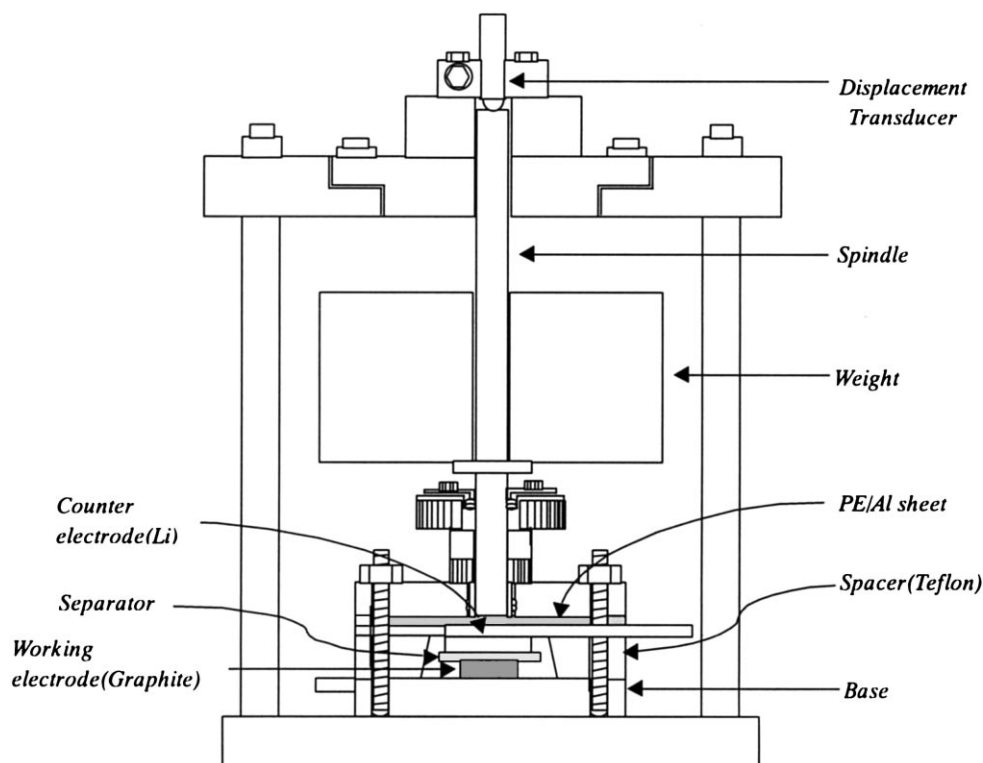


Fig. 1. Schematic illustration of a dilatometer used to monitor change in electrode thickness.

measured using a linear voltage displacement transducer (AT2-51, Keyence) mounted on a rigid frame.

The details of electrochemical cells and data acquisition system used for the electrochemical tests were the same as those described previously [10]. Acoustic events occurring inside the cell were also measured by a method described previously [11–13]. In measuring acoustic events, we used the graphite electrodes identical with those for dilatometry. Electrolytes used in this study were 1 M LiClO_4 in propylene carbonate (PC), 1 M LiClO_4 in PC/dimethoxy ethane (DME) (1/1 by volume), and 1 M LiClO_4 in ethylene carbonate (EC)/DME (1/1 by volume) solutions. All procedures for handling and fabricating the cells were performed in an argon-filled glove box. Other sets of conditions were described in Section 3.

3. Results and discussion

The open-circuit voltages of freshly fabricated cells were about 3 V versus Li. When the Li/graphite cell with 1 M LiClO_4 PC solution was discharged, the voltage stayed at ca. 0.9 V versus Li, as shown in Fig. 2(a). The change in graphite electrode thickness in Fig. 2 was calculated by subtracting the thickness of lithium electrode ($4.85 \mu\text{m mAh}^{-1} \text{cm}^{-2}$) from the observed change in the total thickness of graphite and lithium electrodes. As seen in Fig. 2(a), the graphite electrode in 1 M LiClO_4 PC continuously expanded during discharge, and the voltage did not

approach 0 V unless the electrolyte was entirely consumed. The extraordinary degree of expansion was observed. Consequently, no reversible capacity was observed for the Li/graphite cell with PC electrolyte. However, when we add other solvents, such as DME or equivalent, to PC electrolyte, the situation is dramatically changed, as shown in Fig. 2(b). The Li/graphite cell with PC/DME (1/1) electrolyte shows the operating voltages below 0.25 V versus Li. When the current was switched on, the voltage dropped from ca. 3 to ca. 1.1 V and then showed shoulders in the voltages of 1.1–0.5 V, which were observed only once for the first reduction. As can be seen in Fig. 2(b), the reaction can be divided into four regions. In the voltages of ca. 1.1–0.95 V, the graphite electrode expanded quickly. The electrode expansion at ca. 0.95 V (ca. 20 mAh g^{-1} of discharge) was ca. $50 \mu\text{m}$ in this region, where the number of acoustic events increased (not shown). Then the graphite electrode expanded almost linearly until the voltage reach ca. 0.85 V with drawing a sloping line. On further discharge to ca. 0.65 V (ca. 125 mAh g^{-1}) with changing the slope of discharge curve, the graphite electrode thickness was nearly constant, while the total number of acoustic events continuously increased (not shown). Then the graphite electrode expanded linearly again in the range of discharge voltages of 0.65–0.5 V. During further discharge in the voltage below 0.5 V, graphite electrode thickness increased gradually, where the lithium intercalation reaction proceeded. The graphite electrode reduced down to 0 V showed beautiful golden yellow in color which is characteristic of the first-stage lithium–graphite

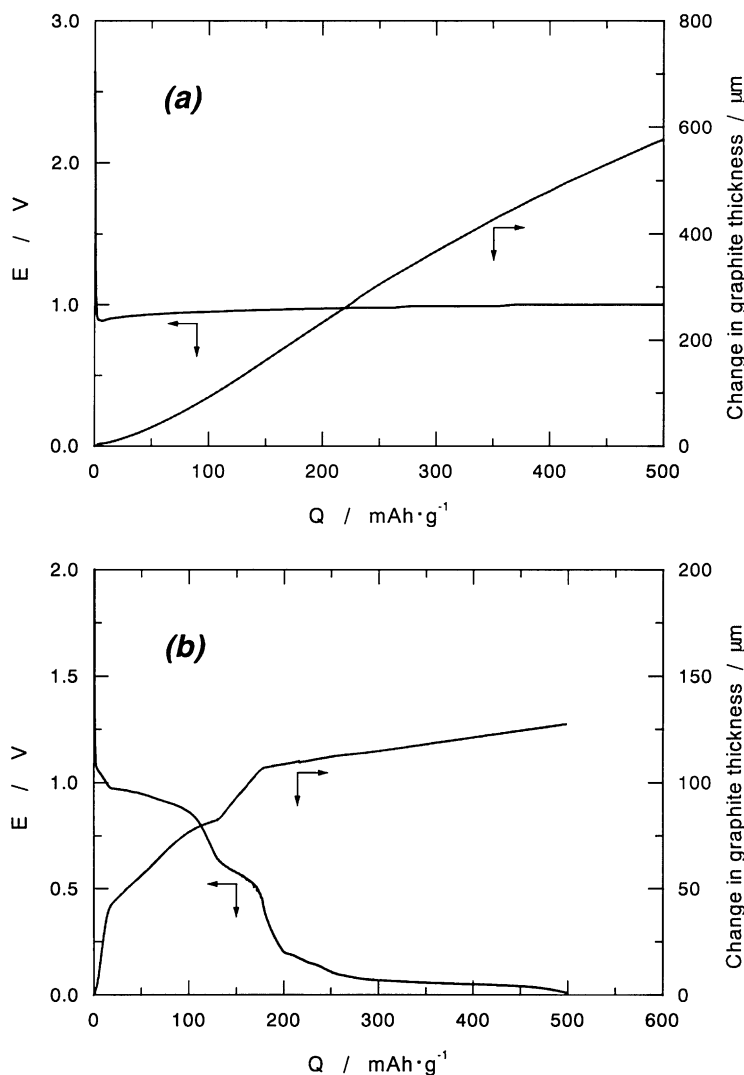


Fig. 2. Change in graphite electrode thickness during the first discharge in 1 M LiClO₄ dissolved in (a) PC; and (b) PC/DME (1/1 by volume) at a rate of 0.15 mA cm⁻². The graphite electrodes were compressed pellets (1 cm²) of natural graphite without any binder. Thickness and weight of compressed pellets were 120 μm and 19.8 mg before cell fabrication.

intercalation compounds. The graphite electrode once reduced to 0 V is reversibly operated as a negative electrode for lithium-ion batteries even in PC-based electrolyte, as was already shown in a previous paper [14], although the great loss of capacity for the first cycle is observed.

As is clearly seen in Fig. 2(b), we can describe as to when lithium-intercalation reaction begins by dilatometry. By applying this technique, we examine the difference between PC- and EC-based electrolytes in terms of the expansion of graphite electrode in relation to irreversible capacity. Fig. 3 shows the change in graphite electrode thickness and the number of acoustic events observed during the first reduction of graphite in 1 M LiClO₄ EC/DME (1/1 by volume) solution. The expansion of graphite electrode at the beginning of the reduction was less pronounced comparing with that in PC-based electrolyte. The expansion of graphite in the voltages between 1.1 and 0.8 V was about 10 μm . Then the electrode gradually expanded in the voltages 0.8–0.5 V

with drawing a sloping curve. On further reduction below 0.5 V, the electrode expanded monotonously as lithium-intercalation reaction proceeded. As can be seen in Figs. 2(b) and 3(a), the electrode expansion and the irreversible capacity in the initial part of the first reduction is closely correlated to each other, i.e. larger the expansion, larger the irreversible capacity. In the voltages below ca. 0.5 V, the slope of the dilatometric signals as a function of the degree of reduction was almost the same both in PC/DME (1/1) and EC/DME (1/1) electrolytes.

Specific description on reactions in the irreversible capacity under consideration is difficult at moment, because the acoustic events concurrent with anomalous expansion of graphite electrode are observed mainly in this region, as was shown in Fig. 3(b). The acoustic events in this region are predominantly due to gas bubble, which is identified by power spectra of acoustic signals. During lithium-intercalation reaction into graphite, the acoustic events were

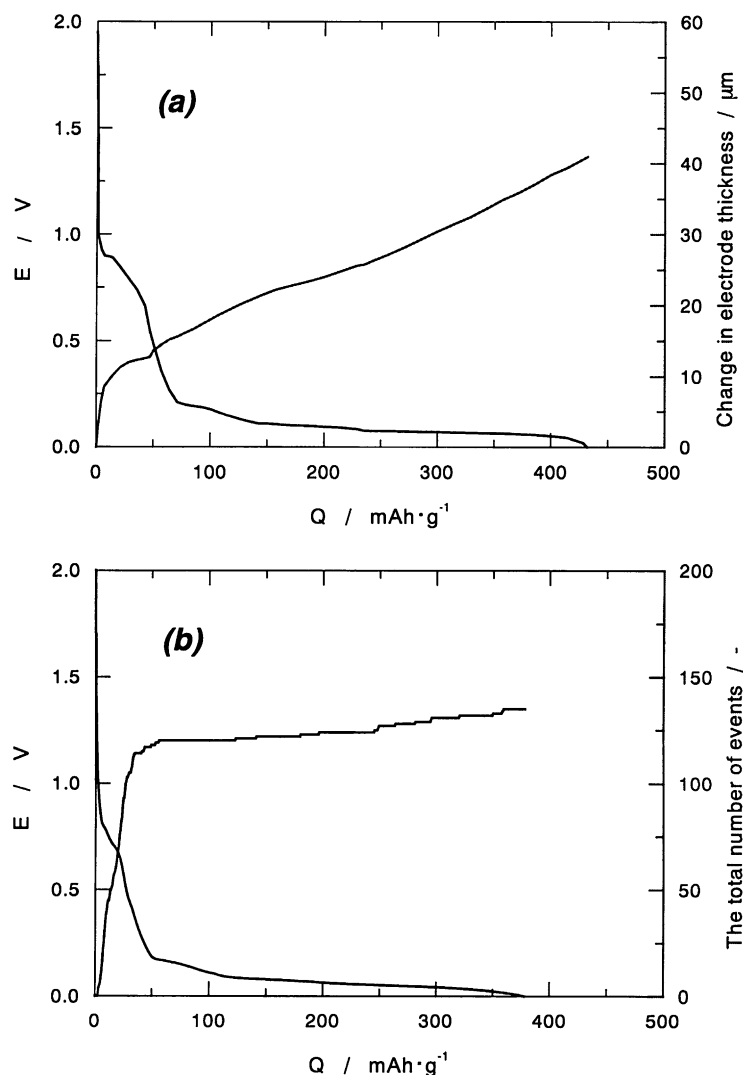


Fig. 3. (a) Change in graphite electrode thickness; and (b) the total number of events of Li/natural graphite(NG-7) cell during the first discharge in 1 M LiClO₄ EC/DME (1/1) at a rate of 0.15 mA cm⁻². The graphite electrodes were compressed pellets (1 cm²) of natural graphite without any binder. Thickness and weight of compressed pellet used in (a) was 130 μm and 21.0 mg before cell fabrication.

scarcely detected. In subsequent charge and discharge, the Li/graphite cell gives the featureless results in terms of acoustic emission.

As were briefly described above, we confirmed the one-to-one correspondence between the electrochemical and dilatometric signals for the reduction of graphite in PC- and EC-based electrolytes. Although the improvement of the dilatometer including the electrochemical cells with respect to sensitivity and accuracy is necessary, we believe that dilatometry and acoustic emission histometry are powerful methods to investigate materials for advanced lithium batteries. Such trials are under way in our laboratory.

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