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In situ diagnosis of the electrolyte solution in a laminate lithium ion battery by using ultrafine multi-probe Raman spectroscopy

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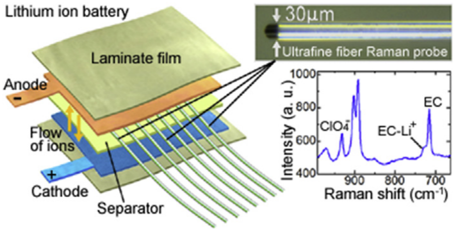
HIGHLIGHTS

- In situ analysis of the electrolyte in a laminate lithium ion battery was conducted.
- Eight micro Raman probes were placed at different positions in the battery.
- The concentration of ions changed differently at the positions during operation.
- Local dry up and local refilling of the electrolyte solution were observed.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium ion batteries have attracted much attention due to their high power density. The change in concentration of salt in the electrolyte solution and local shortage of electrolyte solution in batteries cause serious degradation of battery performance. In this work, in situ Raman spectroscopy of the electrolyte solution at different positions in a laminate lithium ion battery (a typical practical battery) was simultaneously conducted by using ultrafine multi-probes. Eight probes were aligned in deep narrow spaces between two electrodes at intervals of about 2.5 mm in a plane parallel to the surfaces of electrodes. The concentration changed differently at the positions during charging and discharging. In addition, local dry up and local refilling of the electrolyte solution were observed. These phenomena were sometimes observed at the same time at the positions of two adjacent probes, indicating that the phenomena occurred in a millimeter scale. The method used in this study is useful for in situ analysis of the electrolyte solution in deep narrow spaces in other electrochemical devices under conditions close to those in practical devices.

1. Introduction

The development of superior electrochemical devices, such as batteries, capacitors and fuel cells, is an urgent social task. Lithium ion batteries have attracted considerable interest for use in vehicles and portable electronics due to their high energy densities [1–4]. The development of methods for in situ analysis inside batteries is also needed in order to obtain information necessary for understanding phenomena in batteries and for the development of superior batteries [5–9].

During charging and discharging of lithium ion batteries, lithium ions flow through the electrolyte solution between two electrodes. In situ analysis of the concentration of ions in the

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electrolyte solution is requisite since the concentration changes during charging and discharging, reflecting the resistance to ion diffusion and the positions of diffusion barriers [10–13]. Changes in the concentration lead to various negative effects including lowering of the reaction rate, voltage drop and temperature rise, resulting in poor performance and deterioration of batteries.

In situ observation of the concentration of ions by using nuclear magnetic resonance (NMR) has been conducted with model cells [14–19]. The distribution of ions in a direction perpendicular to the surfaces of electrodes was clearly observed, providing important parameters of salt diffusivity and Li$^+$ transport number [14,15,17,19]. It was also shown that microscopic morphology of electrodeposited lithium at an Li electrode surface is influenced by the concentration of Li$^+$ [16] and that the local concentration of Li$^+$ at the interface between an electrode and electrolyte solution increased during formation of the surface film (SEI) on the electrode [18], indicating a strong relation between phenomena at surfaces of electrodes and concentration of ions in the electrolyte solution. Elucidation of the concentration of ions in practical batteries is also necessary for the development of superior practical batteries. However, in situ analysis of the electrolyte solution under conditions close to those in practical batteries is very difficult because the electrolyte solution in practical batteries is confined in deep narrow spaces between two electrodes, of which the distance is typically several tens of micrometers. Raman spectroscopy inside deep narrow spaces has been conducted by using fiber probes in the fields of biomedical diagnostics [20–26]. However, the diameters of probes so far reported were larger than 600 μm, and these probes were too large for studies inside batteries. Recently, we have developed the world's thinnest (cross-sectional area of about 30 μm × 60 μm) ultrafine fiber Raman probe with the highest spatial resolution of 23 μm [27]. By using this probe, in situ multi-microprobe Raman spectroscopy of the electrolyte solution inside model batteries, in which the distance between the two electrodes was accurately controlled, was conducted [28]. The structures and dimensional accuracy of practical batteries such as laminate cells and winding-type batteries are still different from those of model batteries. Therefore, in situ analysis inside practical batteries is still strongly required for the development of superior batteries.

In this work, in situ Raman spectroscopy of the electrolyte solution at different positions in deep narrow spaces in a laminate lithium ion battery, which is a typical practical battery, was simultaneously conducted by using ultrafine multi-microprobes. Eight probes were inserted between two closely faced electrodes, and the ends of the probes were aligned at intervals of about 2.5 mm to study the difference between concentrations of ions in the electrolyte solution at different positions in a plane parallel to the electrodes. The concentration of ions changed differently at the positions during charging and discharging. In addition, local dry up and local refilling of the electrolyte solution were observed. The method used in this study is useful for monitoring the electrolyte solution in deep narrow spaces in other electrochemical devices including capacitors and fuel cells under conditions close to those in practical devices.

2. Experimental

The probe consists of two optical fibers of 30 μm in diameter, an excitation fiber to guide excitation laser light and a collection fiber to guide signal light (Fig. 1a). [26] The end of the excitation fiber was cut at an angle of 45° and mirror-coated. Excitation laser light was reflected by the mirror and only signals from the analysis area could be detected, resulting in a high spatial resolution of about 23 μm. Eight probes were inserted into the cell through eight 25G stainless tubes (outer and inner diameters of 0.51 mm and 0.26 mm, respectively), as shown in Fig. 1b–d. A piece of commercial LiFePO$_4$ composite electrode (40 mm × 40 mm) and a piece of commercial graphite composite electrode (42 mm × 42 mm) were used as the cathode and anode, respectively (see supporting information). Two separator sheets (50 mm × 50 mm) (Cell guard 2500) were inserted between the cathode and anode, and the eight probes were inserted between the two separator sheets, as shown in Fig. 1c and d. The ends of the eight probes were aligned with intervals of about 2.5 mm. The ends of probes 1 to 7 were between the cathode and anode, but the end of probe 8 was outside the electrodes, as shown in Fig. 1c and d. Thus, the probes were distributed almost uniformly from the center to the edge of the electrodes to elucidate the concentration change of electrolyte salt in the cell. An electrolyte solution of 1 mol dm^{-3} LiClO$_4$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1 was injected in the cell, and the cell was heat-sealed in vacuum. The cell was tightly sandwiched between very flat faces (±5 μm) of stainless blocks, and the distance between the two faces was controlled by four micrometers, as shown in Fig. 1d and e (see supporting information Figs. S1–S4). The two flat faces were kept as parallel as possible (see Fig. S4). Fig. 1f shows a

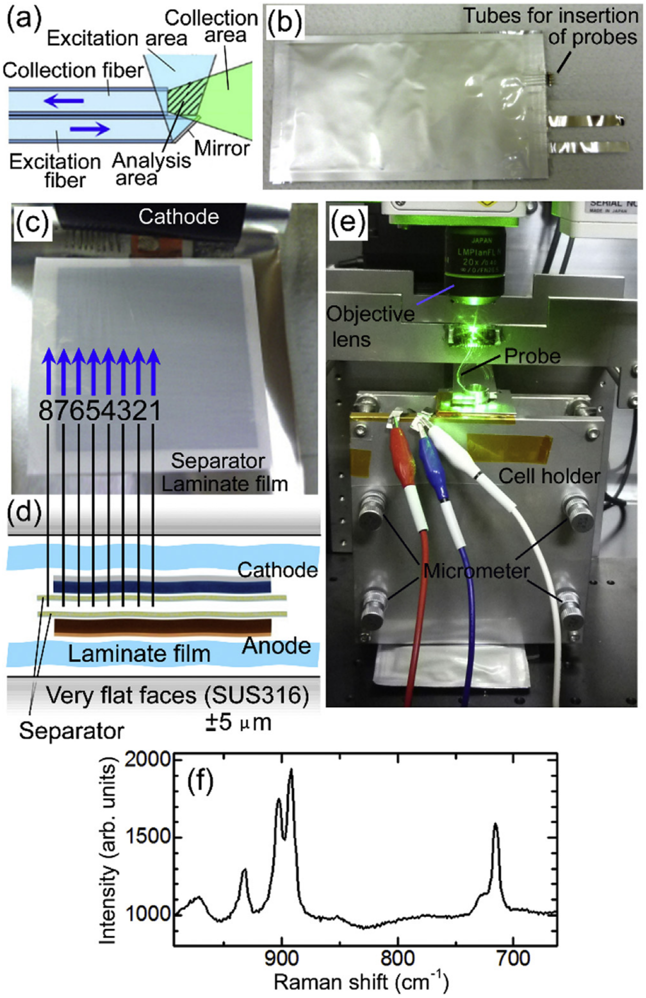

Fig. 1. Raman spectroscopy inside a laminate cell using multiple microprobes. (a) Structure of the probe. (b) Photograph of the laminate cell with eight probes. (c) Inside of the laminate cell. (d) Cross-sectional view of the laminate cell sandwiched by two flat faces of stainless blocks, indicating the positions of the probes. (e) Photograph of the set-up for in situ multi-microprobe measurements. (f) A typical Raman spectrum of the electrolyte solution inside the laminate cell.