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Lithium batteries: application of neutron radiography

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Abstract

Several kinds of primary and secondary commercial lithium batteries, such as CR1/3·1H (Fujitsu), CR1220 and BR435 (Panasonic), ML1220 (Sanyo Excel) were investigated using neutron radiography; the variation of the lithium distribution inside these batteries upon discharging (and charging) were clarified by analyzing their visualized images. It was demonstrated that neutron radiography is a potential and useful method, especially in evaluating the reversibility of rechargeable batteries, which have been used under different discharging/charging conditions. © 1997 Elsevier Science S.A.

Keywords: Lithium batteries; Neutron radiography; Non-destructive detection, Lithium distribution

1. Introduction

Although neutron radiography (NR) has been used for many purposes, for example non-destructive inspection of aircraft or rocket components [1,2], visualization of two phase flows in fluid mechanics [3–5], and research on ancient arts [6], this technique has not been exploited widely in the field of electrochemistry. The authors have studied the visualization of the results of the motion of lithium ions in lithium-ion conductors such as $Li_{1.33}Ti_{1.67}O_4$ at high temperatures using NR, and have demonstrated that NR is very effective in ^{6}Li-containing systems [7]. This means that NR may be used as a non-destructive method to study the electrode reactions and the mass transfer in lithium batteries.

In this work, it was tried to visualize nondestructively the distribution of lithium in primary and secondary commercial lithium batteries before and after discharge using NR. the obtained images will be presented along with a brief explanation on the principle of this technique.

2. Principle of neutron radiography

Although the principle of NR is the same as that of X-ray or gamma-ray radiography, the images are completely different because the interaction of neutrons with materials is quite different from that of X-rays or gamma-rays as shown in Fig. 1 [8]. Neutrons interact with the nuclei of the substances whereas X-rays or gamma-rays interact with the electrons around the nuclei. This means, while the magnitude of interaction of X-rays with materials increases with the atomic number of the constituent element, such a simple relation cannot be found in case of neutrons. Consequently NR has the distinctive feature that materials composed of light elements such as H and Li can be visualized easily even in some heavy materials such as Fe and Pb.

The NR facility used in this work is installed at the exposure tube E2 of Kyoto University reactor in the Research Reactor Institute, Kyoto University. The vertical cross sectional view of the facility is illustrated in Fig. 2, while the detailed characteristics of the facility have been reported elsewhere [9]. The sample and the vacuum film cassette are irradiated with the neutron beam from the tube as illustrated in Fig. 3. The neutrons which have passed through the sample are absorbed by gadolinium atoms on the converter (an aluminum plate coated with gadolinium with thickness of 25 μm) and cause the following nuclear reactions

$$^{155}Gd + n \rightarrow {}^{156}Gd + \gamma \quad (1)$$

$$^{157}Gd + n \rightarrow {}^{158}Gd + \gamma \quad (2)$$

The X-ray film in the vacuum cassette is exposed to the internal conversion electrons or the orbital electrons emitted with gamma-rays from reactions (1) and (2).

3. Experimental

Three types of primary and one type of rechargeable lithium battery were used in this study. The first one is CR1/

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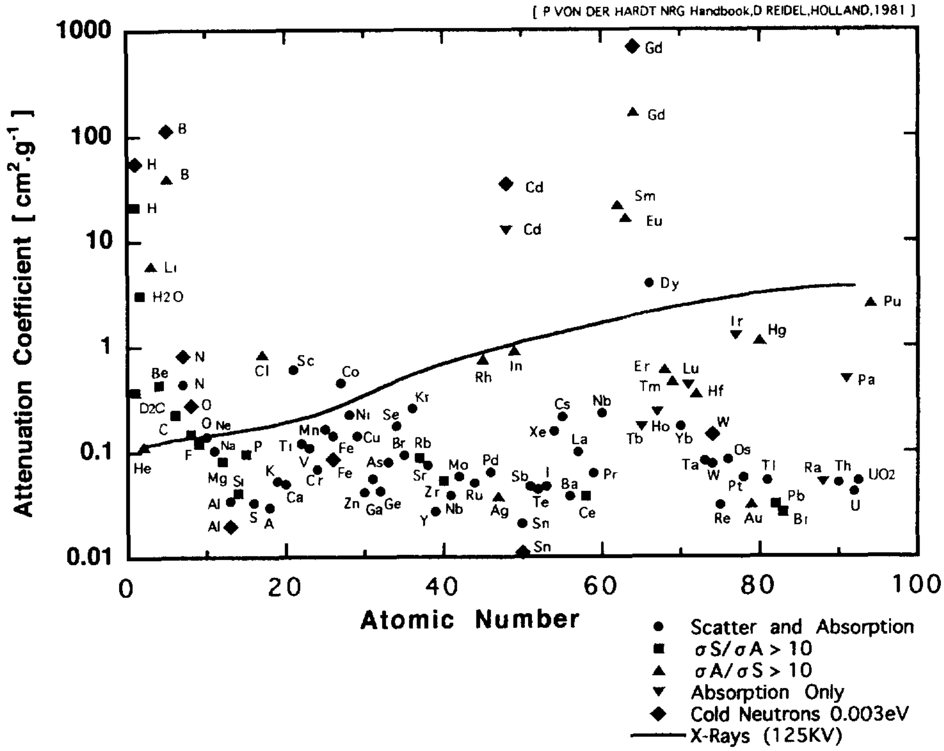

Fig 1 Neutron and X-ray mass attenuation coefficients for the elements.

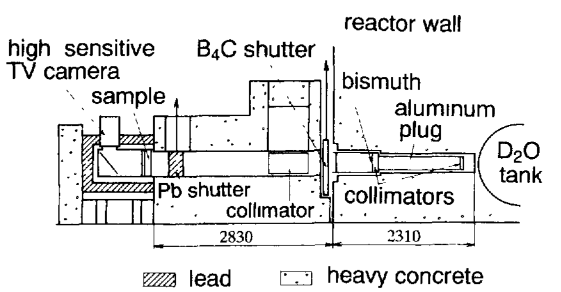

Fig. 2. Neutron radiography facility of the Kyoto University Reactor

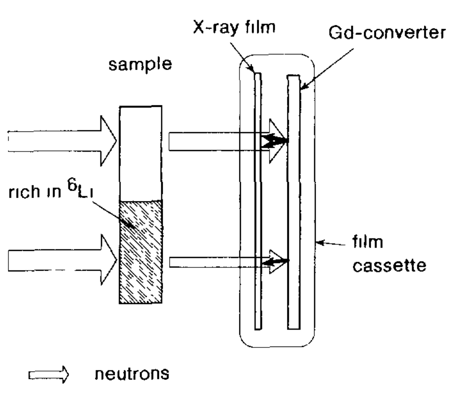

Fig 3. Schematic illustration of the neutron radiography arrangement

3 · 1H (Fujitsu) with a cylindrical shape whose diameter is 11.5 mm and height is 10 mm. A laminate cell is rolled and packed in the case (cf. Fig. 4). The second one is a coin-type battery CR1220 (Panasonic); its diameter is 12.5 mm and height is 2 mm. In these two batteries, lithium metal and MnO_2 are used as the anode and cathode material, respectively, and $LiClO_4$ and PC + DME are used as the electrolyte and solvent, respectively. The third one is a pin-type battery BR435 (Panasonic); its diameter is 4.2 mm and length is 35.9 mm. In BR435, lithium metal and $(CF)_n$ are used as the anode and cathode material, respectively, and $LiBF_4$ and γ-butyrolactone are used as the electrolyte and solvent. The last one, which is rechargeable, is ML1220 (Sanyo Excel). The shape and the size of ML1220 are the same as that of CR1220. In this battery, aluminum alloy containing lithium and MnO_2 are used as the anode and cathode material, respectively, while $LiClO_4$ and PC + DME are used as the electrolyte and solvent.

CR1/3 · 1H was placed on the surface of the vacuum film cassette so that its axis was perpendicular to the film, while the other three batteries were mounted with their axes parallel to the film. They were irradiated during 16 to 18 min in the NR facility of the Research Reactor Institute, Kyoto University and the same NR procedures were repeated after the secondary batteries had been discharged and charged.

4. Results and discussion

NR images obtained for CR1/3 · 1H are shown in Fig. 4, a schematic illustration of the structure and the film density profiles (gray level obtained using CCD camera) along the radial direction is also given. As neutrons strongly interact with ^6Li and cannot penetrate through ^6Li-rich regions, the white region in the left photograph (before discharge) cor-

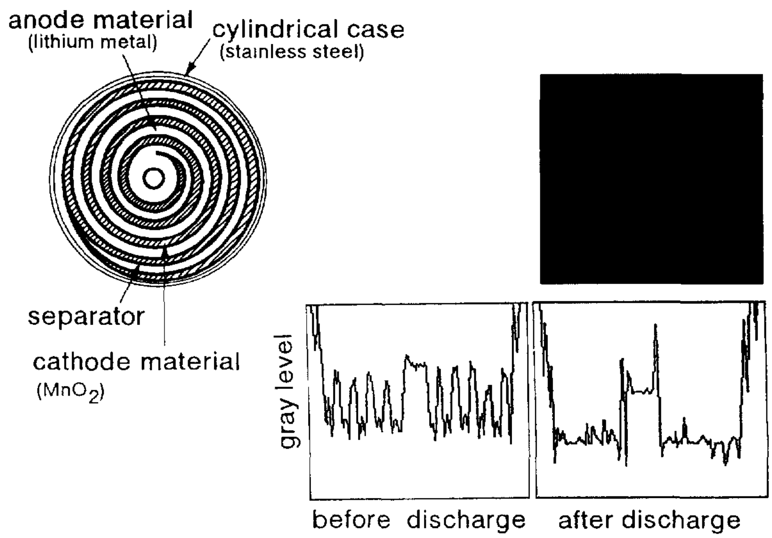

Fig. 4 Neutron radiography images of CR1/3 1H before and after discharge.

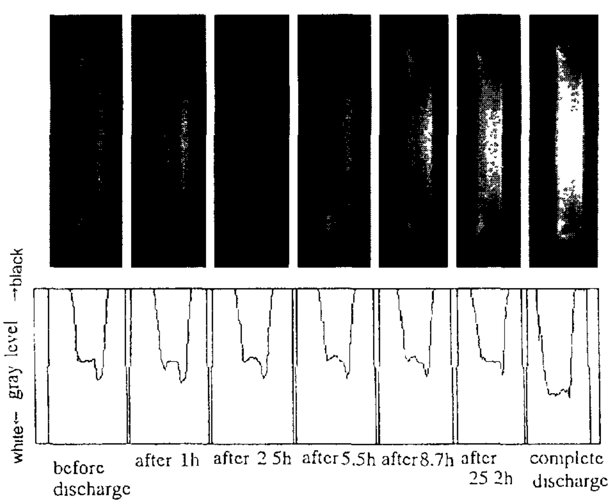

Fig. 5 Variation of neutron radiography images of CR1220 with discharge using LED.

responds to the anode material and the separator wetted with the electrolyte solution. These are lithium metal and propylene carbonate containing $LiClO_4$. The black or exposed region indicates the presence of the cathode material MnO_2. When the battery is discharged, the black region becomes gray. This means that lithium ions moved to and reacted with the cathode material as the lithium metal was consumed.

As far as these images are concerned, the ratio of lithium metal to MnO_2 near the center of the cell seems to be smaller than that in the surrounding region, which is based on the fact that unreacted lithium metal after discharge can be recognized near the cylindrical wall of the battery. It should be noted here that if some standard samples are prepared to simulate the components of commercial lithium batteries, a quantitative discussion on the lithium content in the cathode material, or that on local discharge efficiency will be possible.

The NR images obtained for CR1220 are presented in Fig. 5 with the film density profiles near the central axis along the axial direction. The white region near the right (anode) sidewall of the cell is lithium metal and the left gray region is MnO_2 in the first photograph (before discharge). As these images were taken from a radial direction, the length of neutron penetration is not constant along this direction, and, therefore, quantitative analysis of these images is rather difficult. Yet, consumption of lithium metal can be firmly recognized from changes in profiles of film density under corresponding NR images.

The NR images obtained for BR435 are presented in Fig. 6 with a schematic illustration of the inner structure. As these images were also taken from a radial direction, their quantitative analysis is rather difficult. Moreover, the electrolyte solution of this battery is γ-butyrolactone containing $LiBF_4$ and the boron atoms in it prevent to obtain clear NR images.

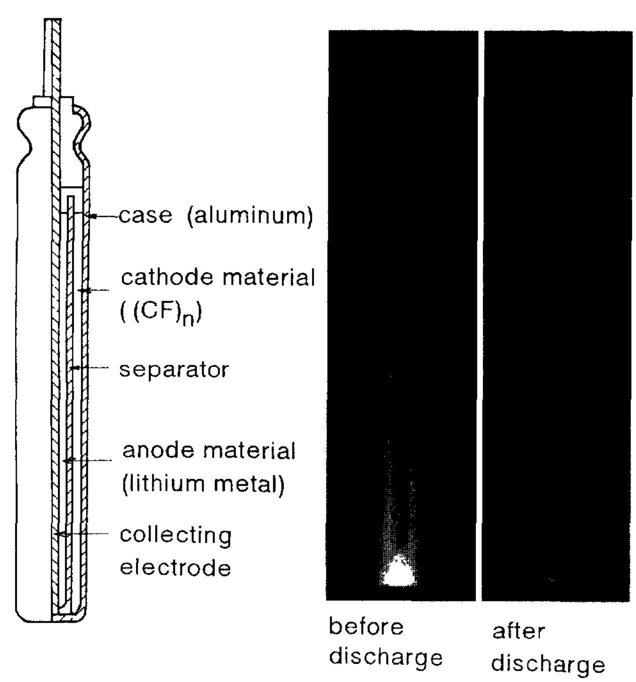

Fig. 6 Neutron radiography images of BR435 before and after discharge

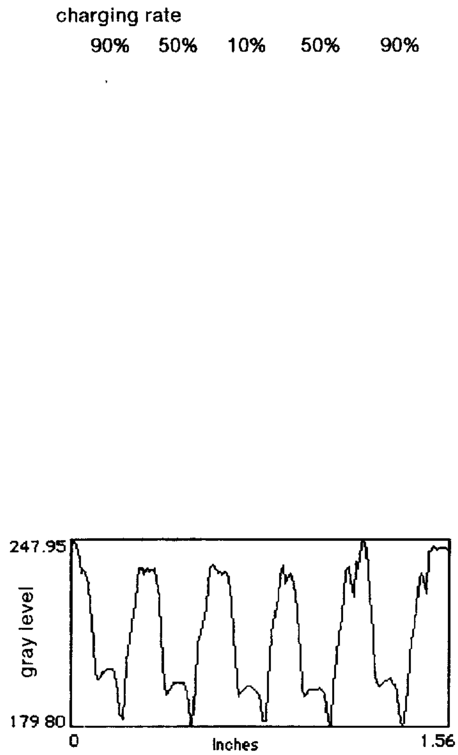

Fig. 7. Neutron radiography images of ML1220 for different charging rates.

Yet, the change of the lithium distribution in the battery can be recognized in these radiographs.

The NR images of ML1220 for different charging rates are presented in Fig. 7 with the film density profiles near the central axis along the axial direction. The reversibility of lithium movement between the anode and cathode materials can be recognized from the film density profiles under corresponding images. However, the change in contrast between the anode and cathode material one was very limited because the capacity of ML1220 is approximately one third of that of CR1220.

5. Conclusions

Since the purpose of this study was to demonstrate the possibility to apply the NR technique to the research of lithium batteries, quantitative discussions were not carried out here. But if some standard samples are prepared to simulate the components of commercial lithium batteries, the quantitative discussions on the lithium content in the cathode material or those on local discharge efficiency will be possible. In addition, NR is a nondestructive testing method. This means that the superiority of this technique over other methods will be further recognized, if it is applied to the study of the reversibility of rechargeable lithium batteries under different discharging and/or charging conditions.

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