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Li-Ion Transfer at positive electrode / Electrolyte Interface

Izumi Yamada, Takeshi Abe, Yasutoshi Iriyama and Zempachi Ogumi
Department of Energy & Hydrocarbon Chemistry, Graduate school of engineering,
Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
Fax: 81-075-383-2488, e-mail: izumi@elech.kuic.kyoto-u.ac.jp

To clarify interfacial reactions at interface between positive electrodes and electrolyte for lithium-ion batteries, thin film electrodes of $LiCoO_2$ and $LiMn_2O_4$ were prepared by pulsed laser deposition. Lithium ion transfer at structurally ordered interface between positive thin film electrode / electrolyte was studied by AC impedance method. As a result, resistances due to the lithium ion transfer, namely, the charge transfer resistances at the interface were observed. The charge transfer resistances on $LiMn_2O_4$ thin film electrode were much smaller than those on c-axis orientated $LiCoO_2$ thin film electrode, indicating charge transfer resistances should be regulated by the number of Li-ion-insertion sites at the interface. As cycled, the charge transfer resistances on $LiMn_2O_4$ thin film almost remained unchanged, but those on $LiCoO_2$ thin films markedly increased.

Key words: Thin film electrode, Pulsed laser deposition, Lithium-ion transfer, Li-ion batteries

1. INTRODUCTION

Li-ion batteries are expanding their production and application areas in the field of portable electronic devices such as cellular phone, notebook computer, and the others. Recently, Li ion batteries are thought to be one of the candidates of power supply for electric vehicles and hybrid electric vehicles [1-3]. While Li ion batteries should play an important role in the trend of miniaturization of electronic devices, large-scale Li ion batteries have been also developing.

High rate performances, namely, fast charge and discharge reactions are essential for the practical use of Li ion batteries as power sources in hybrid vehicles. Therefore, kinetics of Li-ion transfer at positive and negative electrodes should be understood. Lithium ion transfer in Li-ion batteries includes three different steps, Li-ion transfer across the interfaces between electrolyte / active materials, Li-ion diffusion through active materials, and Li-ion migration through electrolytes. Latter two issues have been well investigated so far [4-6]. To decrease of the internal resistance of Li ion batteries, diffusion path through active materials can be shortened by use of smaller size powders and electrolyte resistances can be decreased by use of thinner electrolyte layer. On the other hand, the effective surface area of electrodes becomes smaller and then the interfacial reaction plays very important role in the total rate of battery reactions, namely rate performance of lithium ion batteries. However, this interfacial Li-ion transfer has not been well understood yet.

For elucidation of interfacial Li ion transfer at interface, structurally ordered interface is essential. The use of flat and homogeneous thin film electrode makes detailed research possible, without contribution of binder and conductive additives. We have prepared $LiCoO_2$ thin films and $LiMn_2O_4$ thin films by pulsed laser deposition [7-10]. Li ion transfer at electrolyte / electrode interface should be influenced by the condition of the interface such as electrode structures, electrolytes, etc. $LiCoO_2$ has a layer-typed 2-dimentional structure; on the other hand, $LiMn_2O_4$ shows a spinel-typed 3-dimentional structure. Therefore, it is very interesting to use the above electrode to compare how charge transfer resistances are influenced by the structures of the electrode. In this paper, we report Li-ion transfer at positive thin film electrodes by AC impedance spectroscopy.

2. EXPERIMENTAL

Positive thin film electrodes of $LiCoO_2$ and $LiMn_2O_4$ were prepared by pulsed laser deposition using KrF excimer laser of a wavelength of 248 nm (Japan Storage Battery, EXL-210). Substrate was polished Pt plate whose temperature was kept at 873 K for $LiCoO_2$ and at 973 K for $LiMn_2O_4$. Detailed preparation conditions were reported elsewhere [7,10]. X-ray diffraction (XRD) measurement was conducted by Rint-2500 (Rigaku) equipped with a graphite monocrometer with a scintillation detector. Typical working conditions were 40 kV and 250 mA with a scanning speed of 0.125 s.

Electrochemical properties of $LiCoO_2$ and $LiMn_2O_4$ thin film electrodes were studied by cyclic voltammetry employing a three-electrode cell (lithium metal was used as counter and reference electrode) by HSV- 100 (HOKUTO DENKO Inc.). Unless otherwise stated, potentials are referred to lithium metal.

Li ion transfer at positive thin film electrodes was studied by AC impedance spectroscopy using Radiometer, Voltalab40 over frequency region from 100 kHz to 10 mHz employing the same three-electrode cell.

All experiments were conducted under Ar atmosphere.

3. RESULTS AND DISCUSSION

3.1. Characterization of thin films

3.1.1. $LiCoO_2$ thin film

Figure 1 shows XRD pattern of a $LiCoO_2$ thin film deposited on Pt plate at 973 K for 1h. Except for substrate peaks, only one peak at $2\theta = 18.95$ was observed, which is indexed as the 003 reflection of hexagonal $LiCoO_2$. This result indicates that the $LiCoO_2$ thin film had a preferred c-axis orientation to the substrate surface.

Redox behavior of $LiCoO_2$ thin film was examined in liquid electrolyte system of 1 mol dm^{-3} $LiClO_4$ / PC. As is shown in Fig.2, large anodic and cathodic peaks were seen at around 3.9 V. Since electroactive species are deposited on electrode surface, the species should show the redox behavior of adsorbate, i.e., oxidation and reduction peaks are symmetrical. However, this voltammogram shows somewhat diffusional behavior. The peak separation was not zero but about 40 mV. This is because the amount of active species ($LiCoO_2$) deposited on the electrode (current collector) is too much and the diffsional behavior of Li^+ through $LiCoO_2$ layer was observed. This small peak separation means that the ohmic drop is small and therefore the electric conductivity of the $LiCoO_2$ layer is high enough for electrochemical measurements.

3.1.2. $LiMn_2O_4$ thin film

Figure 4 shows XRD pattern of a $LiMn_2O_4$ film deposited on Pt at 973 K for 1h. Number on peaks denotes index *hkl*. XRD pattern indicates that single-phase spinel $LiMn_2O_4$ was obtained. Very sharp peaks appear in Fig.4; therefore the resultant $LiMn_2O_4$ thin film is well crystallized.

Redox behavior of $LiMn_2O_4$ thin film electrode was examined by cyclic voltammetry in 1 mol dm^{-3} $LiClO_4$ / PC. As is shown in Fig.5, $LiMn_2O_4$ thin film shows redox behaviors with two couples of redox peaks at around 4.0 and 4.1 V. The voltammogram shows not the redox behavior of absorbate bur somewhat diffusional behavior. Mentioned above with $LiCoO_2$, this is because the amount of active species ($LiMn_2O_4$) deposited on Pt is too much and the diffusional behavior was observed. The peak separation was about 30 mV, which means that the ohrmic drop is small and therefore the electric conductivity of the $LiMn_2O_4$ thin film electrode is high enough for electrochemical measurements.

3.2 Impedance measurements

3.2.1. $LiCoO_2$ / electrolyte interface

AC impedance measurements were carried out. In Fig.5 are shown Niquist plots at given potentials ranging 3.6-4.2 V. At potential below 3.80 V, no semi-circle but only blocking electrode behavior appeared. No oxidation and reduction currents were observed in cyclic voltammogram given in Fig.2 below 3.8 V, and therefore, blocking electrode behaviors below 3.8 V are quite valid. One semi-circle appeared in the higher frequency region followed by a diffusional behavior in the lower frequency region at potentials above 3.92 V. Resistances evaluated from semi-circle are dependent on electrode potentials and also on salt concentration of electrolytes used, which indicates that the process responsible for the semi-circle is closely related with the process including Li-ion. It is now reasonable to consider that the resistance is ascribed to the interfacial Li-ion transfer.

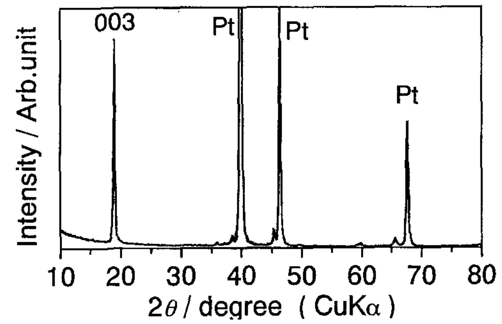

Fig.1. X-ray diffraction pattern of $LiCoO_2$ thin film on Pt disk. Number on peaks denotes index *hlk*.

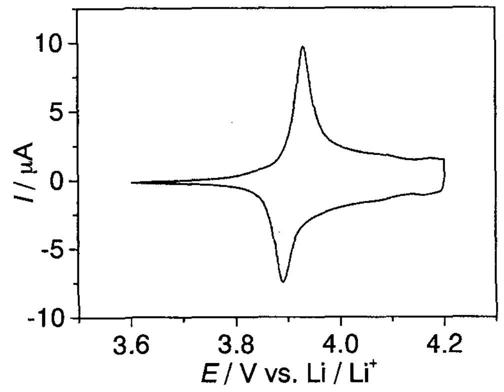

Fig.2. Cyclic voltammogram of $LiCoO_2$ thin film electrode in 1 mol dm^{-3} $LiClO_4$/PC. Scanning rate, 0.1

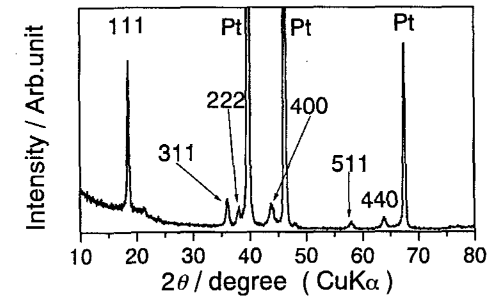

Fig.3. X-ray diffraction pattern of $LiMn_2O_4$ thin film on Pt disk. Number on peaks denotes indec hkl.

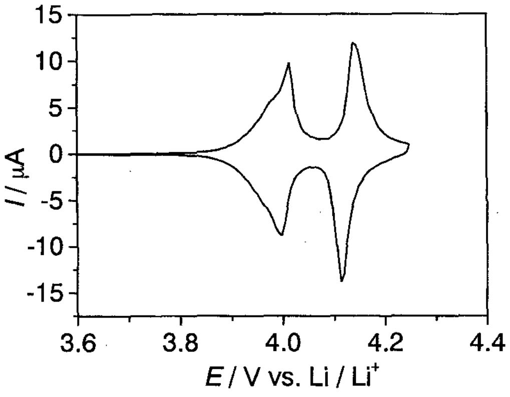

Fig.4. Cyclic voltammogram of $LiMn_2O_4$ thin film electrode in 1 mol dm^{-3} $LiClO_4$/PC. Scanning rate, 0.1 mV s^{-1}.

3.2.2. $LiMn_2O_4$ / electrolyte interface

Similarly to $LiCoO_2$ thin film electrode, AC impedance measurements were carried out on $LiMn_2O_4$ thin film electrode. In Fig.6 are shown Niquist plots at given potentials ranging 3.6-4.2 V. At electrode potentials of 3.60 V, no semi-circle appeared and capacitive behavior was observed, indicating no lithium ion insertion and extraction occur at $LiMn_2O_4$ thin film electrode. That is consistent with the cyclic voltammogram given in Fig.4, in which no oxidation and reduction currents were observed at 3.60 V. At potential between 3.80 and 4.20 V, one semi-circle in the high frequency region and linear line in the lower frequency were appeared. Resistances evaluated from semi-circles are dependent on electrode potentials, indicating the impedance should be ascribed to the resistances of interfacial Li-ion transfer.

3.3. Li-ion transfer resistances

Figure 7 shows the Li-ion transfer resistances against electrode potentials in 1 mol dm^{-3} $LiClO_4$ / PC of $LiCoO_2$ thin film (open circles) and $LiMn_2O_4$ thin film (closed squares). The behaviors of Li-ion transfer are different by positive electrode materials. For $LiCoO_2$ thin film electrode, Li-ion transfer resistance appeared at 3.9 V and decreased with increasing electrode potential up to 4.0 V and then kept constant with increasing electrode potential up to 4.2 V. On the other hand, Li-ion transfer resistance with $LiMn_2O_4$ appeared 3.8 V and decreased with increasing electrode potential up to 4.0 V and then increased with increasing electrode potential. These behaviors can be explained as follows; decrease of the resistance is due to the increase of vacant site of Li-ion in positive materials. At higher potentials, the site of Li-ion will decrease leading to the increase of Li-ion transfer resistances. In addition, electrolyte decomposition may take place to form passivation film on positive thin film electrode at higher potentials. This passivation film could cause the increase of impedance for Li-ion transfer. Since electrolyte decomposition is irreversible, the two factors causing the increase of the resistances can be explicit, which is mentioned later.

It should be noted that minimum values of Li-ion transfer resistance are very different by positive electrode materials. At 4.0 V, the value of resistance on $LiMn_2O_4$ electrode was 150 ohm; on the other hand, that of $LiCoO_2$ was 1500 ohm, which is ten times larger than that of $LiMn_2O_4$. Since the surface areas are regulated to be the same by o-ring, this big difference should be caused by structures of positive electrode materials. As described above, $LiCoO_2$ has a layered-typ 2-dimentional structure; on the other hand, $LiMn_2O_4$ has spinel-typed 3-dimentional structure.

Li ion inserts and extracts at the reactive site of the interface. The number of reactive sites influence on the value of charge transfer resistances. The working electrode area is controlled by the o-ring, and therefore, the effective area of $LiCoO_2$ for Li-ion insertion and extraction is only defect of $LiCoO_2$. In contrast, $LiMn_2O_4$ has 3D structure and insertion and extraction of Li ion can be possible at the surface of $LiMn_2O_4$ thin film electrode. Therefore, charge transfer resistances differ by these electrodes

Figure 8 shows the Li-ion transfer resistances of $LiCoO_2$ thin film electrode against electrode potentials as cycled. In charge direction, Li-ion transfer resistances decreased with increasing electrode potentials and then kept constant with increasing electrode potential. On the other hand in discharge direction, Li-ion transfer resistances increased with decreasing electrode potentials; Li-ion transfer resistance becomes larger with the increment of cycles. And the behavior of Li-ion transfer resistances in both charge and discharge direction was unchanged irrespective number of cycles.

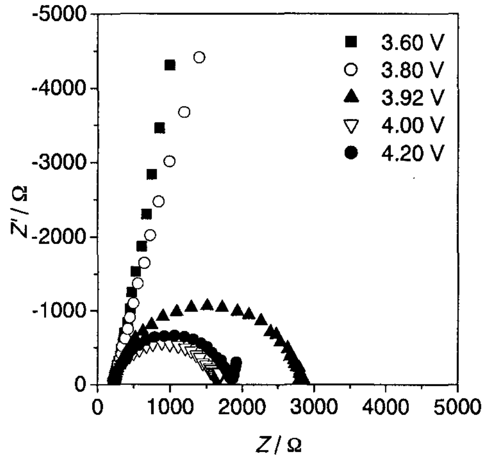

Fig.5. Impedance spectra of $LiCoO_2$ thin film electrode in 1 mol dm^{-3} $LiClO_4$/PC at potentials of 3.60, 3.80, 3.92, 4.00 and 4.20 V.

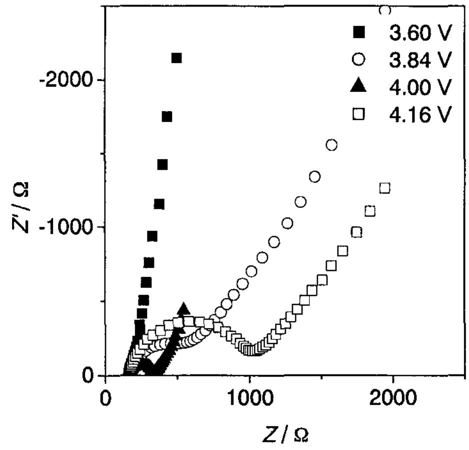

Fig.6. Impedance spectra of $LiMn_2O_4$ thin film electrode in 1 mol dm^{-3} $LiClO_4$/PC at potentials of 3.60, 3.84, 4.00, and 4.16 V.

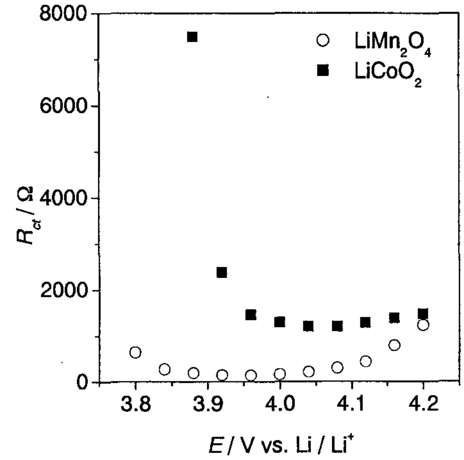

Fig.7. Variation of charge transfer resistances against electrode potentials. ■, $LiCoO_2$; ○, $LiMn_2O_4$.

At more positive electrode potentials Li-ion transfer resistance did not decrease in discharge direction, indicating irreversible reaction occurred and passivation film should be formed on electrode, leading to increase of resistances.

In Fig. 9, the Li-ion transfer resistances of $LiMn_2O_4$ thin film against electrode potentials as cycled are shown. The behaviors of Li-ion transfer resistance were almost the same in charge and discharge direction except for the first charge. At positive electrode potential, Li-ion transfer resistances decreased in discharge direction, indicating that reversible reaction should occur.

Different behaviors were obtained by $LiCoO_2$ and $LiMn_2O_4$ as cycled in terms of reversibility at positive electrode potential. The irreversible behavior is due to electrolyte decomposition. Catalytic activity toward decomposition reaction could be different by transition metals, and cobalt has higher catalytic activity than manganese.

4. CONCLUSION

Fabrication of structurally ordered interface consisting of $LiCoO_2$ and $LiMn_2O_4$ thin film electrodes and electrolyte gives precise studies on Li-ion transfer at positive electrodes. Li-ion transfer resistances at interface between electrolyte and positive thin film were elucidated. Li-ion transfer resistances of $LiMn_2O_4$ were smaller than that of $LiCoO_2$ due to their material structure.

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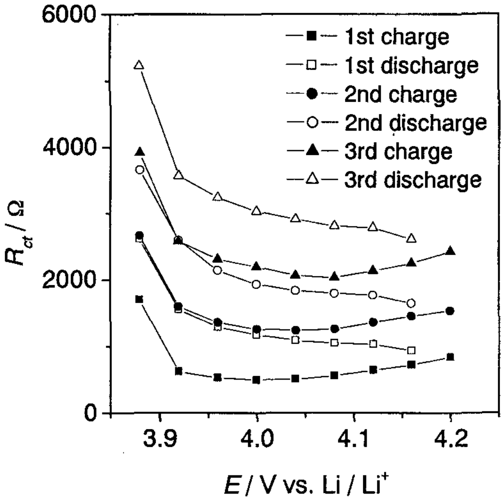

Fig.8. Variation of charge transfer resistances on $LiCoO_2$ thin film electrode against electrode potentials with cycles.

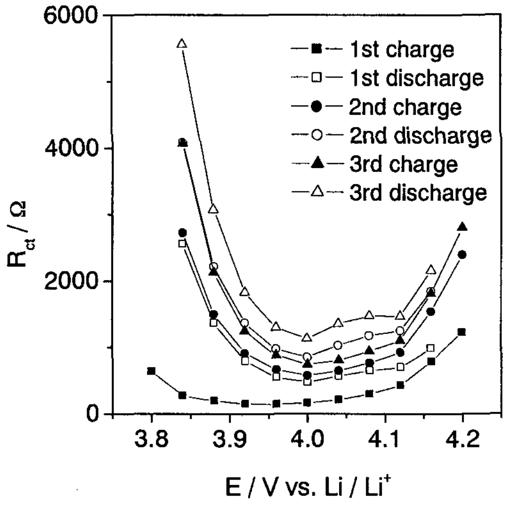

Fig.9. Variation of charge transfer resistances on $LiMn_2O_4$ thin film electrode against electrode potentials with cycles.

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