



Short communication

Determination of lithium ion diffusion in lithium–manganese-oxide-spinel thin films by secondary-ion mass spectrometry

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ABSTRACT

Lithium ion chemical diffusion coefficients in ⁶LiMn₂O₄ thin sputtered films (~2 μm) were determined by the depth profiles of ⁷Li concentration after adopting the potential step in ⁷LiClO₄/propylene carbonate solution by using secondary-ion mass spectrometry (SIMS). Lithium chemical diffusion coefficient via bulk (D_{bulk}) and grain boundary diffusion coefficient normalized with width (dD_{gb}) were determined as $1.23 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ and $6.55 \times 10^{-20} \text{ m}^3 \text{ s}^{-1}$, respectively.

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1. Introduction

Insertion electrode materials have widely been studied as electrodes for lithium ion batteries. Among the insertion cathode materials, LiMn₂O₄-based spinel type oxides are one of the most promising materials because of their low fabrication cost and high theoretical energy density [1–6]. The electrochemical reaction of the intercalation cathode involves charge transfer reaction at the interface between cathode and electrolyte, coupled with diffusion of lithium ions into the cathode structure. In many cases, the rate-determining step of the electrochemical reaction is controlled by lithium ion diffusion. Therefore, determination of the lithium ion diffusion coefficient may provide basic information to understand the electrochemical reaction mechanism, which is important in designing practical lithium battery systems. Measurement of chemical diffusion coefficients has been performed by various electrochemical techniques including current pulse relaxation technique [7], complex impedance technique [8], potential step chronoamperometry [9], and galvanostatic intermittent titration technique [10]. In order to obtain precise data with these electrochemical methods, many factors, such as active electrode area or particle size of the oxide should be considered. The influ-

ence of lithium ion diffusion through electrolyte solution, influence of the existence of surface layer on the particle should also be considered.

This paper reports on the direct method using secondary-ion mass spectrometry (SIMS) in order to measure lithium ion diffusion profile in LiMn₂O₄ spinel oxide, which makes it possible to determine both bulk and grain boundary diffusion coefficients by assuming a single boundary condition [11–13]. SIMS has been used to obtain elemental depth profiles of the electrode materials [14,15], however, determination of lithium ion diffusion coefficients have not been carried out. The thin film of ⁶Li-enriched LiMn₂O₄ was prepared by sputtering. A potential step measurement was applied to the film in lithium perchlorate (isotopic abundance; ⁷Li = 92.5, ⁶Li = 7.5) in propylene carbonate solution, which resulted in the lithium ion depth profile in LiMn₂O₄ spinel oxide, and SIMS was used to determine depth profiles.

2. Experimental

⁶Li_{1.8}Mn₂O₄ as the target powder for RF sputtering was prepared by the following method; ⁶LiNO₃ aqueous solution was prepared by reaction with ⁶Li (Aldrich Chem. Co., 95 at.% ⁶Li enriched) and nitric acid aqueous solution. Mn(NO₃)₂·6H₂O (Wako Chem. Co., guaranteed reagent grade) was dissolved in the ⁶LiNO₃ aqueous solution. The solution was dropped on an alumina dish heated to 200 °C, and the resultant powder was calcined at 400 °C for 6 h in air to obtain

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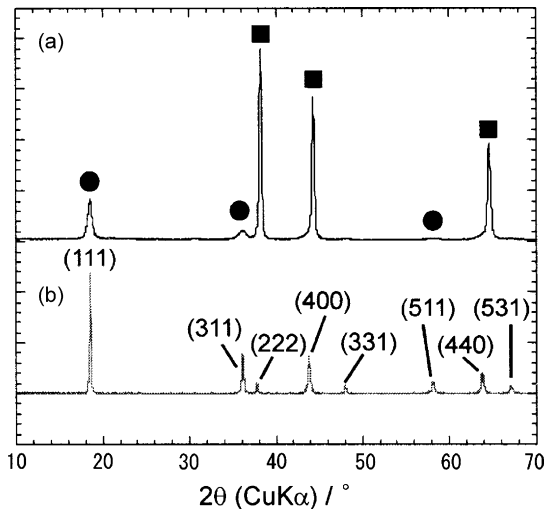


Fig. 1. X-ray diffraction patterns of the synthesized LiMn_2O_4 thin film (a) and the powder LiMn_2O_4 (b). (●) LiMn_2O_4 and (■) Au substrate.

the target powder. RF sputtering was carried out in a stainless-steel reactor equipped with capacitively coupled inner electrodes to which an alternating voltage was applied at a frequency range of 13.56 MHz. A gold plate was used as a substrate. Argon gas was introduced into the reactor and the pressure was maintained at 5.0×10^{-2} Torr. The RF sputtering was carried out at an RF power of 50 W. The sputtered thin film was annealed at 600°C for 6 h in air. The film was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and inductively coupled plasma spectrometry (ICP).

Electrochemical measurement was carried out by using the ${}^6\text{Li}_{1.01}\text{Mn}_2\text{O}_4$ annealed film as a working electrode, and lithium metal was used as counter and reference electrodes. The electrolyte was 1 mol dm^{-3} lithium perchlorate (LiClO_4 ; isotopic abundance; ${}^7\text{Li}=92.5$, ${}^6\text{Li}=7.5$) in propylene carbonate solution. Open circuit voltage (OCV) of the film was 3.6 V vs. Li^+/Li . The potential step in which interdiffusion of ${}^6\text{Li}$ and ${}^7\text{Li}$ was occurred was adopted from the OCV to 4.0 V vs. Li^+/Li for 90 s. After the potential step, the thin film was cooled in liquid nitrogen to quench the concentration profile of ${}^7\text{Li}$ and ${}^6\text{Li}$. The depth profile of lithium isotope fraction was obtained by Cs^+ monitoring the intensity of ${}^6\text{Li}^-$ and ${}^7\text{Li}^-$ secondary ions using SIMS (ims5f, CAMECA instruments Co., France) equipped with a 10 keV primary ion source and a secondary ion imaging unit. The depth of etched area was subsequently measured by using surface profiler (Dektak3 Veeco/Sloan Co. Ltd. USA).

3. Results and discussion

SEM observation shows that the thin film after annealing was polycrystalline and has nearly random orientation. The cross-sectional SEM showed that the thin film after annealing had a thickness of about $2 \mu\text{m}$ and that at least within the scale of SEM observation it was free of pinholes. ICP measurement indicated that the composition of the thin film after annealing was $\text{Li}_{1.01}\text{Mn}_2\text{O}_4$.

XRD of the thin film before annealing indicated that the film was amorphous. Fig. 1 shows XRD patterns of X-ray diffraction patterns of LiMn_2O_4 thin film prepared by sputtering after annealing ($\sim 2 \mu\text{m}$ in thickness) (a) and the powder LiMn_2O_4 (b) in the 2θ region from 10° to 70° . The LiMn_2O_4 powder possessed a cubic structure with $Fd-3m$ symmetry (Fig. 1b) [2]. As shown in Fig. 1a, peaks of the sputtered film on gold substrate at 18.6° , 36.1° , and 58.1° correspond to the (1 1 1), (3 1 1), and (5 1 1) reflections of cubic LiMn_2O_4 spinel phase, respectively. Peaks marked ■ correspond to

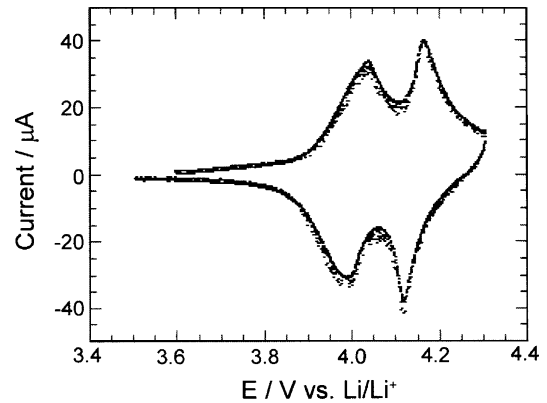


Fig. 2. Cyclic voltammogram of the thin sputtered film after annealing. Electrolyte: 1 mol dm^{-3} LiClO_4 /Propylene carbonate. Scan rate: 1 mV s^{-1} .

the diffraction lines of gold substrate. Except for the diffraction lines of cubic LiMn_2O_4 spinel phase and gold, anomalous peaks were not observed in Fig. 1a. In conclusion, the thin film after annealing was indexed to a cubic lattice, and no second phase was observed.

Fig. 2 shows the cyclic voltammogram of the LiMn_2O_4 film. This figure indicates the two-step reversible intercalation/deintercalation of lithium ions, which located 4.03 V and 4.16 V on the anodic sweep (deintercalation) and 3.99 V and 4.12 V on the cathodic sweep (intercalation). The shape of the cyclic voltammogram is well in agreement with that reported for cubic LiMn_2O_4 [2,16].

Fig. 3 shows the depth profile of the thin film before adopting the potential step obtained by SIMS. This figure indicated that the film has about $2 \mu\text{m}$ in thickness that is in good agreement with SEM observation. The constant intensity of ${}^6\text{Li}^-$, ${}^7\text{Li}^-$, and ${}^{55}\text{MnO}^-$ ion indicates the uniform structure of the prepared film. The ratio of ${}^6\text{Li}$ to ${}^7\text{Li}$ in the film was determined as 95.5–4.5.

The film was immersed in electrolyte of 1 mol dm^{-3} lithium perchlorate (LiClO_4 ; isotopic abundance; ${}^7\text{Li}=92.5$, ${}^6\text{Li}=7.5$) in propylene carbonate solution for 12 h at room temperature. The depth profile of ${}^7\text{Li}$ isotope fraction in the film was unchanged before and after immersion. Lithium ion diffusion would normally be expected to take place immediately on contact with the electrolyte. However, this result indicates that the surface exchange rate between ${}^6\text{Li}$ and ${}^7\text{Li}$ at the interface between LiMn_2O_4 and electrolyte is slow under no potential gradient.

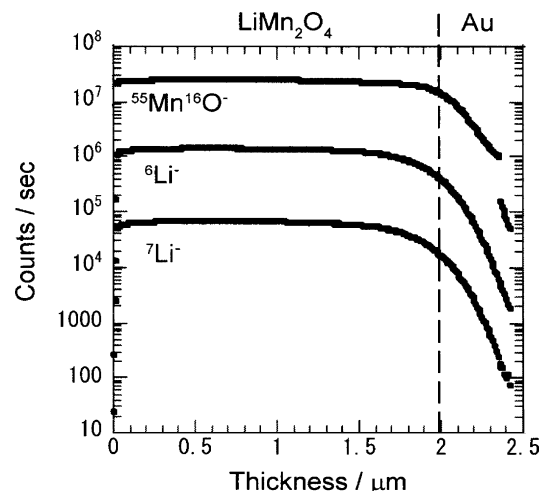


Fig. 3. Depth profile of the thin sputtered film after annealing.

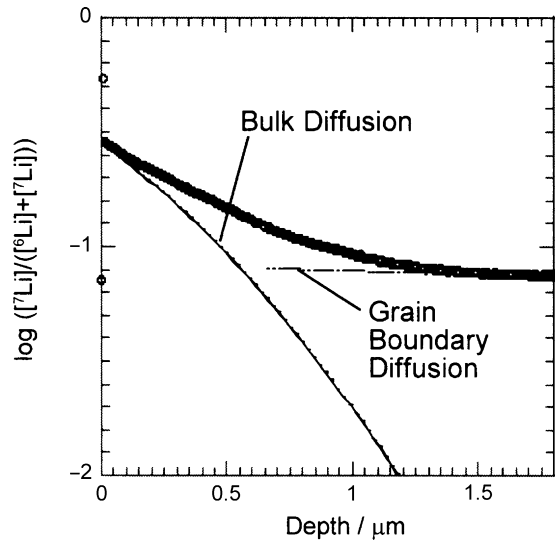


Fig. 4. ${}^7\text{Li}$ depth profile of the thin films of the thin sputtered film after potential step from OCV to 4.0V vs. Li^+/Li for 90 s.

Table 1
Lithium chemical diffusion coefficient determined by SIMS for LiMn_2O_4 .

D_{bulk} ($\text{m}^2 \text{s}^{-1}$)	1.23×10^{-15}
dD_{gb} ($\text{m}^3 \text{s}^{-1}$)	6.55×10^{-20}

D_{bulk} : lithium bulk chemical diffusion coefficient, D_{gb} : lithium grain boundary chemical diffusion coefficient and d : width of grain boundary phase.

Fig. 4 shows the depth profile of ${}^7\text{Li}$ isotope fraction in the film after adopting the potential step from OCV to 4.0V vs. Li^+/Li for 90 s. The steep slope in the shallow region indicated the bulk diffusion of ${}^7\text{Li}$ ions which was introduced from LiClO_4 during potential step. However, the observed ${}^7\text{Li}$ fraction did not reach to initial value (=4.5%), which indicates the contribution of fast Li ion diffusion along grain boundary. The contribution of lithium ion diffusion via grain boundary is found as a long tail of the depth profile. The lithium ion diffusion coefficient via bulk (D_{bulk}) was estimated by fitting the data to Eq. (1) [17] and the grain boundary diffusion coefficient normalized with the width of grain boundary (dD_{gb}) was estimated by Eq. (2) [18].

$$C = \left[\text{erfc} \frac{z}{2\sqrt{D_{\text{bulk}}t}} \right] - \exp(hz + h^2 D_{\text{bulk}}t) \text{erfc} \left(\frac{z}{2\sqrt{D_{\text{bulk}}t}} + h\sqrt{D_{\text{bulk}}t} \right), \quad h = \frac{\alpha}{D_{\text{bulk}}} \quad (1)$$

$$\left(\frac{\partial \ln C}{\partial z^{6/5}} \right)^{-5/3} = \left(\frac{dD_{\text{gb}}}{0.66} \right) \left(\frac{4D_{\text{bulk}}}{t} \right)^{-1/2} \quad (2)$$

where C is the ${}^7\text{Li}$ concentration at the depth z from the interface between the film and the electrolyte solution (m), t is the

potential step time (s), and α is the surface reaction coefficient (m s^{-1}). The obtained D_{bulk} and dD_{gb} are shown in Table 1. Several groups determined lithium chemical diffusion coefficients in $\text{Li}_x\text{Mn}_2\text{O}_4$ samples, e.g. Li^+ chemical diffusion coefficient of $\text{Li}_x\text{Mn}_2\text{O}_4$ powder of 10^{-8} to $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ [19–21], Li^+ chemical diffusion coefficient of $\text{Li}_x\text{Mn}_2\text{O}_4$ film by pulse laser deposition of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ [22], Li^+ chemical diffusion coefficient of $\text{Li}_x\text{Mn}_2\text{O}_4$ film by electron beam deposition of $10^{-14} \text{ cm}^2 \text{ s}^{-1}$ [23]. The Li^+ chemical diffusion coefficient determined in this work is relatively small compared with that in other groups. The difference of small amount of defect in the oxide may affect the Li^+ chemical diffusion coefficient.

4. Conclusion

The direct method using SIMS to obtain depth profile of lithium ion can determine the bulk diffusion coefficient and the grain boundary diffusion coefficient separately. Therefore, a wide range of application of this method to other cathode and anode active materials of lithium ion battery is promising.

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