Short communication

High rate discharge capability of single particle electrode of LiCoO$_2$

Kaoru Dokko [a,*], Natsuko Nakata [b], Kiyoshi Kanamura [b]

[a] Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
[b] Department of Applied Chemistry, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan

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ABSTRACT

The electrochemical properties of a single particle of LiCoO$_2$ (8 μm in diameter) in an organic electrolyte were characterized using a microelectrode technique, and the high rate capability of commercially available micron-sized LiCoO$_2$ was examined in this study. A Pt microfilament (10 μm in diameter) was attached to the single LiCoO$_2$ particle in the electrolyte during optical microscope observation, and galvanostatic charge-discharge tests were carried out. The discharge capacity of the single LiCoO$_2$ particle (8 μm diameter) was 0.157 nA h in the potential range of 3.0–4.2 V vs. Li/Li$^+$, which was close to the theoretical capacity. The discharge rate capability of the single LiCoO$_2$ particle was excellent, and the particle exhibited its full-discharge capacity up to a high rate of 30 C (5 nA). The discharge reaction of the single particle was not controlled by the solid-state diffusion of Li$^+$, but by the charge transfer process at a rate lower than 30 C. The discharge capacity of the particle measured at a high rate of 300 C (50 nA) was 0.12 nA h, which was more than 75% of the full capacity of a single particle.

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1. Introduction

LiCoO$_2$ is the most popular cathode material for lithium ion batteries [1]. Obtaining an insight into the kinetic properties of LiCoO$_2$ for Li$^+$ ion extraction and insertion is important for determining the power density of lithium batteries. So far, most studies have used porous composite electrodes prepared by mixing the battery active material with an organic polymeric binder, and a high surface area carbon. However, additives of the porous electrode have been reported to affect the charge/discharge properties [2,3]. Moreover, the porous structure of the electrode must be taken into account in order to analyze its electrochemical response, because there are distributions of potential, current density, and concentration of the electrolyte salt within the porous electrode during charging and discharging [4]. These distributions become particularly significant in the case of high rate charge–discharge, and the electrochemical reaction does not take place uniformly within the porous electrode.

In this study, the electrochemistry of a single LiCoO$_2$ particle was investigated using a microelectrode technique. Uchida et al. have developed this technique in order to investigate the electrochemical properties of micron-sized single particles of battery active materials [5–7]. As shown in Fig. 1, by bringing a metal microfilament in contact with a micron-sized particle in an electrolyte, we can characterize the electrochemical properties of the parti-

cle. In the case of a single particle electrode, the current is small enough (nA level), and the iR potential drop can be neglected even if the material is highly resistive. Then, the distributions of potential and current density are almost uniform at the particle surface. Therefore, by employing the single particle electrode, we can investigate the electrochemistry of the redox material in detail. In this study, the high rate charge–discharge capability of a single LiCoO$_2$ particle was examined. The electrode process including charge transfer at the interface and Li$^+$ ion diffusion within the particle are discussed.

2. Experimental

The experimental setup for electrochemical measurements is similar to that reported elsewhere [5,6]. A glass-sealed Pt microfilament (10 μm in diameter) was attached to a LiCoO$_2$ particle in an organic electrolyte using a micromanipulator during optical microscope observation; then, electrochemical measurements were performed. The Pt microfilament sealed with glass was utilized to minimize the background current. The detailed procedure for fabricating the glass-sealed Pt microfilament is reported elsewhere [8]. The LiCoO$_2$ particle was supplied by Nippon Chemical Industrial Company and used as received. The electrolyte was a mixed solvent of propylene carbonate and ethylene carbonate (1:1 in volume) containing 1 mol dm^{-3} LiClO$_4$. The counter electrode was Li foil with an area of 1 cm^2, and electrochemical measurements were performed with the two-electrode system. Charging and discharging were carried out using a galvanostat (ALS Model

* Corresponding author. Tel.: +81 45 3393942; fax: +81 45 3393942.
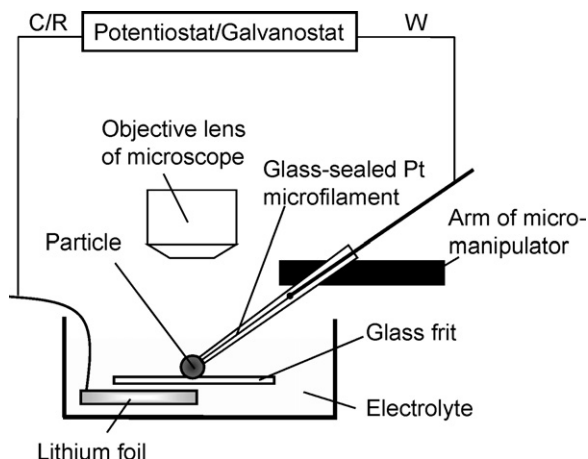E-mail address: dokko@ynu.ac.jp (K. Dokko).

Fig. 1. Schematic illustration of electrochemical cell for single particle electrode.

660A) in the potential range of 3.0–4.2 V vs. Li/Li$^+$. All electrochemical measurements were carried out at room temperature in a glove box filled with dry argon.

3. Results and discussion

Fig. 2 shows charging and discharging curves during the initial three cycles of the single LiCoO$_2$ particle (8 μm in diameter) measured at 1 nA. The single particle showed a potential plateau at 3.9 V and two small plateaus around 4.1 V corresponding to the order–disorder phase transition [9]. This electrochemical behavior is characteristic of LiCoO$_2$ and agrees with that in previous studies [1,9]. Although a small irreversible capacity was observed in the first cycle, the coulombic efficiency after second cycle was more than 99%. The single LiCoO$_2$ particle exhibited excellent reversibility, and the iR potential drop was very small. It was considered that the contact resistance between the Pt microfilament and the LiCoO$_2$ particle was negligibly small, because the electrical conductivity of partially delithiated Li$_{1-\delta}$CoO$_2$ was as high as 10^{-3} S cm^{-1} [10]. Dokko et al. performed AC impedance measurements of the single LiCoO$_2$ particle and reported that the contact resistance did not have any significant effect on the electrochemical behavior of the particle [7]. The theoretical capacity of Li$_x$CoO$_2$ ($x = 0.5$) is 140 mA h g^{-1}, and the theoretical capacity of a single LiCoO$_2$ particle with a diameter of 8 μm can be calculated as 0.19 nA h under the assumptions that the particle is spherical and has a theoreti-
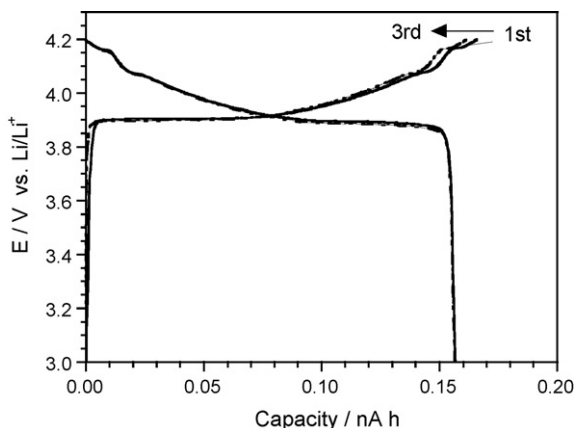

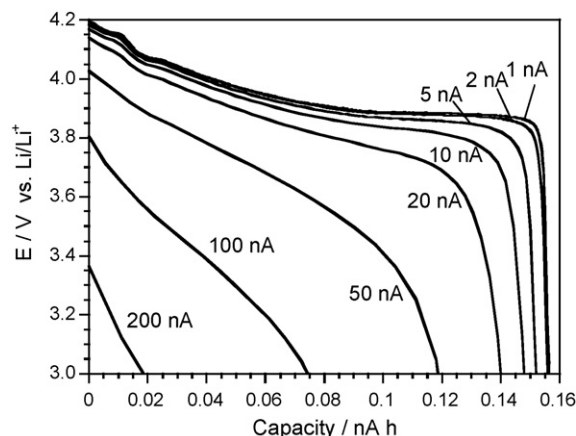**Fig. 2.** Charge and discharge curves of single LiCoO$_2$ particle (8 μm in diameter) measured at 1 nA.

Fig. 3. Discharge curves of single LiCoO$_2$ particle (8 μm in diameter) measured at various currents. Prior to each discharge, the LiCoO$_2$ particle was charged up to 4.2 V at a low current of 1 nA.

cal density of 5.05 g cm^{-3}. The measured discharge capacity of the LiCoO$_2$ particle was 0.157 nA h, which was slightly smaller than the theoretical capacity. The actual LiCoO$_2$ particle was not perfectly spherical, and it was considered that the small deviation from the theoretical capacity was due to the error of particle size estimation. Therefore, it was inferred that the redox reaction of Co$^{3+/4+}$ occurred in the entire particle.

In order to evaluate the discharge rate capability of the single LiCoO$_2$ particle, discharge measurements were carried out at various currents. Fig. 3 shows the rate capability of the single LiCoO$_2$ particle. Prior to each discharge measurement, the LiCoO$_2$ particle was charged galvanostatically to 4.2 V at a constant current of 1 nA. As shown in Fig. 3, the single particle showed excellent discharge rate capability. In the case of LiCoO$_2$, a rate of 1 C corresponds to a current density of 140 mA g^{-1}. A current of 1 nA corresponds to a rate of 6.5 C for the single LiCoO$_2$ particle. The discharge capacity measured at 50 nA, which corresponded to a rate of 300 C, was 0.12 nA h and was more than 75% of the full capacity of the single particle. The discharge reaction of the Li$_x$CoO$_2$ particle consists of several processes: (i) the solvated Li$^+$ ion in the electrolyte diffuses to the surface of the particle, (ii) interfacial charge transfer (Li$^+$ ion transfer) takes place at the interface, (iii) the Li$^+$ ion diffuses from the surface to the center of the particle, and (iv) crystallographic structural change occurs as x varies in Li$_x$CoO$_2$. In general, the diffusion coefficient of Li$^+$ ion in the liquid electrolyte is higher than that for solid-state diffusion. Therefore, it seems that the reaction rate of the Li$_x$CoO$_2$ single particle is controlled by the charge transfer process, solid-state diffusion, and/or crystallographic structural change. The rate-determining step of charge–discharge reaction at the LiCoO$_2$ particle will be discussed in the following sections.

As shown in Fig. 4, at currents lower than 5 nA, the LiCoO$_2$ particle exhibited a constant discharge capacity, although the overpotential increased with the current. It was considered that the solid-state diffusion of Li$^+$ ion did not control the reaction rate at currents lower than 5 nA. If there were a large gradient of the Li$^+$ ion concentration in the particle during the discharge reaction, the electrode potential would have dropped to the cut-off potential rapidly when x (x in Li$_x$CoO$_2$) reached 1 at the particle surface [11], while x at the center of the particle did not reach 1, and the full-discharge capacity would not have been attained. Therefore, it was inferred that the interfacial charge transfer process controlled the reaction rate at currents lower than 5 nA, and there was hardly a gradient of the Li$^+$ ion concentration in the particle during the discharge. It should be noted that 5 nA corresponds to a rate of
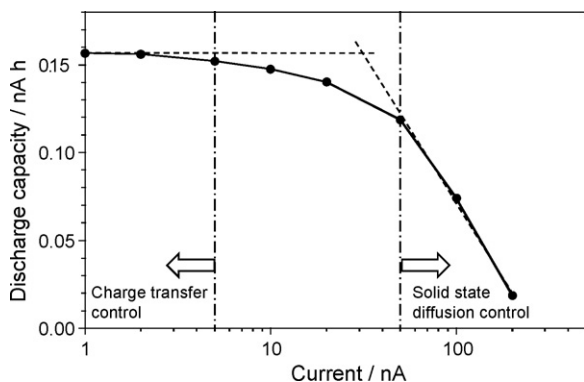
Fig. 4. Dependence of discharge capacity of single LiCoO$_2$ particle (8 μm diameter) on discharge current.

30 C for the single LiCoO$_2$ particle (8 μm diameter); therefore, the discharge reaction of a LiCoO$_2$ particle in a lithium ion battery is not controlled by solid state diffusion, but by the charge transfer process under usual operating conditions.

On the other hand, at currents higher than 10 nA, the discharge capacity of the LiCoO$_2$ particle decreased gradually with increasing discharge current. As mentioned above, the electrode potential dropped to the cut-off potential, because x reached 1 at the particle surface before the full capacity of the particle was achieved. It seems that the solid-state diffusion of Li$^+$ ion becomes a significant factor controlling the reaction rate at currents higher than 10 nA. The Li$^+$ ion concentration gradient (in solid) at the particle surface becomes steeper with increasing current. The solid-state diffusion probably controls the reaction rate completely at currents higher than 50 nA, as shown in Fig. 4. In this study, we did not take into account the effect of the crystallographic structural change on the solid state Li$^+$ ion diffusion. It is difficult to discuss the influence of the crystallographic change on the reaction rate, on the basis of only electrochemical data.

Assuming that the diffusion of Li$^+$ ion in the particle takes place three-dimensionally, the apparent diffusion coefficient of Li$^+$ ion in the particle can be roughly estimated. In the case of three-dimensional diffusion, the diffusion length L can be expressed as $L = (6Dt)^{1/2}$, where D is the apparent diffusion coefficient and t is the time [11]. The diffusion length L of Li$^+$ ion in the solid is equal to the particle radius (4 μm), and the diffusion time is the time required by the particle to attain full-discharge capacity. When the particle was discharged at 5 nA, the discharge duration was 110 s. Therefore, Li$^+$ ion can diffuse from the particle surface to the particle center within 110 s. Then, the apparent diffusion coefficient of Li$^+$ ion in Li$_x$CoO$_2$ should be larger than 10^{-10} cm^2 s^{-1}. It should be noted that the D value estimated in this study is an average value in the entire discharge potential range (3.0–4.2 V). Imanishi et al. calculated the diffusion coefficient (D) of Li$^+$ ion in a LiCoO$_2$ thin film electrode

using the AC impedance method; they reported that the D value changed depending on x (x in Li$_x$CoO$_2$) and was on the order of 10^{-9} to 10^{-12} cm^2 s^{-1} [12]. Furthermore, the crystallographic structural change of Li$_x$CoO$_2$ may affect the reaction rate. However, the apparent diffusion coefficient of the practical battery active material may be useful for the cell design of the lithium battery and simulation of the charge–discharge behavior [13–16].

4. Conclusions

The electrochemical properties of a single particle of LiCoO$_2$ (8 μm in diameter) were characterized using a microelectrode technique. The charge and discharge measurements revealed good reversibility of the LiCoO$_2$ cathode. The discharge capacity of the single LiCoO$_2$ particle was 0.157 nA h in the potential range of 3.0–4.2 V, which was close to the theoretical capacity. The discharge reaction of the single LiCoO$_2$ particle was not controlled by the solid-state diffusion of Li$^+$, but by the charge transfer process at a rate lower than 30 C (5 nA). The discharge capacity measured at a rate of 300 C (50 nA) was 0.12 nA h, which was more than 75% of the full capacity of the single particle. Therefore, it can be stated that commercially available micron-sized LiCoO$_2$ has a higher charge–discharge rate capability than that required for practical application in batteries for electric vehicles and plug-in hybrid vehicles.

Acknowledgement

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