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Short communication

In situ measurement of lithium mass transfer during charging and discharging of a Ni–Sn alloy electrode

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Abstract

The charging (lithiation) and discharging (delithiation) of a Ni–Sn alloy electrode was examined by means of holographic interferometry and laser scanning confocal microscopy (LSCM). The developing concentration profile of Li^+ ion during discharging (delithiation) of the Ni–Sn alloy electrode agreed reasonably well with the prediction based on transient diffusion theory, indicating that the cell configuration successfully suppressed natural convection due to the electrochemical reaction. The morphological variation of Ni–Sn alloy electrode during charge/discharge cycle could be observed very clearly by in situ LSCM. It was found that the contraction of active material during the discharge (delithiation) initiates cracks in the Ni–Sn alloy electrode.

Keywords: Ni–Sn alloy; Holographic interferometry; In situ LSCM; Concentration profile

1. Introduction

Lithium-ion batteries are widely used as power sources for portable electronic devices. In the future, they may be adopted also as power supply for the hybrid electric vehicle (HEV) and fully electric vehicle (EV). For applications such as HEV and EV, improvement of power density and cycle life is indispensable. At present, mainly graphite and graphitic materials are used for the anode in commercially available lithium-ion batteries. The coulombic capacity of these materials is practically limited by the theoretical capacity of graphite ($372\,\mathrm{mAh\,g^{-1}}$). Therefore, it is desirable to develop an alternative anode material.

The most promising alternative materials for the anode of a next-generation Li-ion battery are Sn-based or Si-based alloy materials [1–10]. The capacity of pure Sn metal is $994\,\mathrm{mAh\,g^{-1}}$, assuming formation of $Li_{4.4}Sn$ alloy, however the volume change due to phase transformation exceeds 300%, relative to Sn metal, during charging and discharging. Thackeray et al. examined the possibility of Cu–Sn alloy from the viewpoint of crystal structure [2–4]. The electrochemical characteristics of this material have been reported by other groups [5,6]. Dahn et al. are systematically studying tin-based and Si-based alloys as anode candidate materials, using combinational techniques [7–9]. Mukaibou et al. proposed Ni–Sn alloy, in which the volume change is restricted by formation of a Ni matrix around the Sn atoms, and reported the electrochemical characteristic of this alloy [10]. They reported that charging and discharging caused cracks in the electrode, which indicates that the volume change is still significant or at least that the differential volume change during part of the cycle is excessive.

Our previous research focused on the ionic mass transfer of Li^+ ion near a lithium electrode during charging and discharging and its determination by in situ holographic interferometry [11–14]. From the viewpoint of lithium battery technology the ionic mass transfer phenomena in the electrolyte are especially relevant when fast charging and discharging takes place and lithium dendrite formation occurs. Also, the passivating layer called solid electrolyte interphase (SEI) is formed on the Li metal electrode, and this SEI plays a role in the occurrence of dendrite. However, even at low current density some remarkable phenomena were observed. In the case of a Li metal electrode, the start of the interference fringe shift indicating the onset of transient diffusion is noticeably delayed when electrolysis (charging, or lithiation) occurs at low current density. We have ascribed this

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to SEI formation [11–13] and correlated the time delay with the rate of SEI formation.

We have also studied, again by in situ holography, the transient concentration profile of Li^+ ion near an electrodeposited Ni–Sn alloy electrode during lithiation [14]. Differently from the Li metal electrode, the interference fringes begin to shift as soon as the electrolysis starts, and we ascribed this to the SEI layer at the interface between alloy material and electrolyte being much thinner than at a Li metal electrode.

From these studies we concluded that it is possible to analyze quantitatively the rate and extent of SEI formation at the metal/electrolyte interface from accurate measurement of transient liquid-phase concentration profiles during the charging process.

The purpose of the present study is to further examine the ionic mass transfer phenomena during discharging (delithiation) of a Ni–Sn alloy electrode in PC electrolyte. Two experiments are carried out to elucidate the interfacial phenomena. First, the development of the Li^+ concentration profile during discharge is compared with that observed at a Li metal electrode. Thus, the effect of the alloy electrode material is isolated. Second, the morphology of the lithiated thin-film alloy electrode is observed during charging and discharging by in situ LSCM. The electrode is monitored for the occurrence of cracks.

2. Experimental

A Ni–Sn thin-film was prepared by simultaneous electrodeposition of Ni and Sn on Cu foil from a pyrophoric acid bath of $NiCl_2{\cdot}6H_2O$ (0.075 M), $SnCl_2{\cdot}2H_2O$ (0.175 M), $K_4P_2O_7$ (0.5 M), glycine (0.125 M), and NH_4OH (5 mL L^{-1}). The temperature of the plating bath was maintained at 50 °C (323 K). The characterization of the electrodeposits was described in a previous paper [14]. The Ni–Sn thin-film electrode was used as the working electrode in the measurement described below. The electrolyte was propylene carbonate (PC) containing a predetermined concentration of 0.5 M $LiClO_4$ was used as received from Kishida Chemical Co. Ltd. Their analysis indicates the initial water content of the solution to be less than 30 ppm.

2.1. Holographic interferometry measurement

Lithium foil of 200 m thickness (Honjo Metal Co. Ltd.) was used for the reference electrode and counter electrode. The effective area of the working electrode was 10 mm × 6 mm. The working electrode and counter electrode surfaces were placed face to face, separated by a 2 mm thick electrolyte layer. Details of the electrolytic cell are as described in a previous paper [13]. The electrolytic cell was assembled in a glove box filled with highly pure Ar gas circulating continuously through molecular sieves 4 Å 1/16 (Nacalai Tesqu, Co. Ltd.) to remove water contaminant. The electrolytic cell was next horizontally installed in the holographic interferometer arrangement. The optical arrangement was as described earlier [11,12].

The electrolytic cell configuration was designed to eliminate as much as possible any natural convection due to the insertion of Li metal (depletion of Li^+ ion in the electrolyte) during charging, and the extraction of Li metal (enrichment in Li^+ ion of the electrolyte) during discharge. Therefore, the Ni–Sn alloy electrode was installed horizontally and facing downward during the insertion of Li in the Ni–Sn alloy, and upward during Li extraction. A constant current density of 0.3 mA cm^{-2} was applied to the Ni–Sn alloy electrode as a step function. This current density corresponds to about 0.5C rate in practical battery terminology.

2.2. LSCM measurement

The morphological history of the Ni–Sn electrode surface during lithiation and delithiation was in situ observed by LSCM. The cell design for this measurement is the same as that in the holographic interferometry described in (a), above. However, the configuration is such that the horizontally installed electrode surface faces upward in the electrolyte so that it can be observed directly by LSCM. The electrolytic cell body is of glass such as in a spectrophotometric cell. The distance between electrode surface and electrolytic cell wall was made as short as possible because the working distance of objective lens (LEICA, C PLAN L 40*x*/0.50) is rather short. The microscopic images were recorded by VHS video and analyzed later.

3. Results and discussion

3.1. Interferometric measurements

The main focus of this paper is the transient interference fringe pattern during the discharging (delithiation) of the lithiated Ni–Sn electrode. It is because cracks are suspected to occur during the discharge half-cycle of charge/discharge cycling. The transient behavior of the interference fringe pattern during charging (lithiation) was first measured with the lithiated Ni–Sn electrode. The electrolytic cell was then reinstalled upside down in the holographic interferometry arrangement and the transient fringe pattern during the discharge recorded as shown in Fig. 1. In both cases, the ionic mass transfer during the electrochemical reaction is governed by the one-dimensional transient diffusion equation with constant-flux boundary condition.

Fig. 1 shows that the interference fringe pattern before the start of electrolysis is perpendicular to the electrode. Once the electrolysis starts, the fringes start to shift immediately in both cases, insertion and extraction. The number of fringes shifted, S, can be converted to the refractive index in the electrolyte based on the interference equation

$$\Delta n d = S\lambda \tag{1}$$

where Δn is the difference of refractive index, d the optical path in the electrolytic cell, S the fringe shift, and λ is the wavelength of the laser beam (632.8 nm in this case). In a previous paper we reported the dependence of refractive index on the LiClO4 concentration, which is linear [12]. Therefore, Eq. (1) can be rewritten as

$$\Delta C = \left(\frac{\partial n}{\partial C}\right)\frac{S}{d} \tag{2}$$

where C is the concentration of $LiClO_4$.