Development of newly-designed Li-ion battery using glassy SnO-P₂O₅ anode without pre-doping technique and their safety evaluation

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Introduction

Tin-based materials are attracting a lot of interest as alternative to graphite anode material for LIBs due to their high capacity and energy density. The author's group previously reported that glassy SnO-P₂O₅ (GSPO) anode prepared via glass melting process has high reversible capacity of about 550 mAh/g, high rate capacity and availability from -20°C to 60°C [1,2]. In addition, it was also reported that the cell having outstanding safety performance can be achieved using GSPO anode [3].

However, lithium pre-doping of the anode is required to compensate for its large irreversible capacity of about 650 mAh/g. It poses obstacles to the actual application for the anodes of LIBs.

In the present study, newly-designed cells were developed without pre-doping technique, where GSPO anode was combined with Li-rich layered composite, $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.56}O_2$ (Li-rich NCM) cathode to compensate the irreversible capacity of GSPO anode by that of Li-rich NCM cathode. The cell and safety performance was evaluated for the cells consisting of GSPO anode and Li-rich NCM cathode.

Experimental

GSPO powder was mixed with ketjen black, polyimide resin as a binder, and Si powder to adjust the irreversible capacity of anode for preparing the slurry. The slurry was coated on Cu foil.

Li-rich NCM powder was provided by Nihon Kagaku Sangyo. The slurry prepared from a mixture of the Lirich NCM powder, acetylene black and polyvinylidene fluoride (PVDF) as a binder was coated on Al foil.

The pre-dope free, CR2032-type coin cells (2 mAh) and the laminated cells (1200 mAh) consisting of GSPO-Si anode and Li-rich NCM cathode were fabricated for the measurement of cell and safety performance, respectively. The capacity in the first cycle of the anode was equated to that of cathode to compensate the irreversible capacity of anode by that of cathode. 1 M LiPF₆ in EC/DEC (1/1, v/v) was used as an electrolyte solution for the both measurement. Glass filter and ceramic coated polyolefin non-woven fabric as a separator were used for the measurement of cell and safety performance, respectively.

Nail penetration test were conducted using a safety evaluation apparatus (Toyo system). The fully charged cells were provided for a nail penetration test.

Results and discussion

Figure 1 shows the charge-discharge curves after 10 cycles of the pre-dope free coin cell consisting of GSPO-Si anode and Li-rich cathode. The cell showed the high capacity of 176 mAh g^{-1} for the cathode even without pre-

doping.

Figure 2 shows the cycling performance of the coin cell. The cell had a stable cycling performance during the 50 cycles

Figure 3 shows the cell voltage, nail internal temperature and cell surface temperature profiles of the laminated cell (1200 mAh) for the nail penetration test. The cell was penetrated by a sharp iron nail at a rate of 1 mm/s. The nail internal and cell surface temperatures increased up to 68°C and 43°C, respectively. There were no gas generation and no fire. This result could be due to the electrical insulation of the glass matrix of GSPO.



Figure 1. Charge-discharge curves after 10 cycles of the pre-dope free coin cell (2 mAh) consisting of GSPO-Si anode and Li-rich NCM cathode.



Figure 2. Cycling performance of the pre-dope free coin cell (2 mAh) consisting of GSPO-Si anode and Li-rich NCM cathode.



Figure 3. Cell voltage (left side), nail internal temperature (right side) and cell surface temperature (right side) profiles of the laminated cell (1200 mAh) for the nail penetration test.

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