

Li-doping process for Li_xSiO -negative active material synthesized by chemical method for lithium-ion cells

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Abstract

Li-doped SiO-negative active material (Li_xSiO) has been successfully synthesized by chemical method with immersion in Li-organic complex solution obtained by dissolving naphthalene and metallic Li into butyl methyl ether (BME) solvent. The rest potential of resultant Li_xSiO electrode drastically shifts to less noble value at the beginning of immersion and tends to be stable at around 0.21 V versus Li/Li^+ , which means the progress of Li-doping into SiO-negative active material. Furthermore, this chemical Li-doping process proceeds by the catalysis function of naphthalene and leads to reduce the irreversible capacity of SiO-negative electrode caused by consumption of Li sources provided from positive electrode.

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1. Introduction

The enhancement of energy density has been strongly required for current LiCoO_2/C , LiNiO_2/C , and $\text{LiMn}_2\text{O}_4/\text{C}$ system lithium-ion cells due to increasing demand of power sources for newly developed portable devices and hybrid electric vehicles. However, further increase of energy density has been limited by small theoretical capacity of 372 mAh g^{-1} of graphite-negative electrode. Therefore, the development of large-capacity negative active materials is indispensable to meet its demand. For this reason, the SiO-negative active material has been proposed to be one of promising candidates for the alternative to conventional graphite because of its large capacity over 1200 mAh g^{-1} and relatively low charge–discharge potential [1–5]. The large irreversible capacity of SiO electrode has, however, limited cell designs for the practical use owing to consumption of Li sources provided from positive electrode. The chemical synthesis of Li-doped SiO (Li_xSiO) material by immersion in Li-organic complex solution was found out to overcome the essential problem of the irreversible reaction caused by consumption of Li sources [6–8]. In this report, the detailed

process and reaction mechanism of its method are discussed with the results of XPS analysis and electrochemical measurements.

2. Experimental

Li-doped SiO-negative electrodes were prepared as follows. The electrode with 80 mass% SiO and 20 mass% poly-vinylidene fluoride (PVDF) binder was prepared for the XPS analysis by using a Cu-foil current collector with the needed flat surface. The electrode with additive of acetylene black (AB) as a conductive agent was also prepared by using the mixture of SiO-negative active material, AB, and PVDF with the mass ratios of 75:5:20 for electrochemical measurements by using a foamed nickel substrate as a current collector to prevent from peeling off the active material. Here, the mass of active material was 15 mg in any electrode. These electrodes were then immersed at room temperature for different times into the Li-organic complex solution of 10 cm^3 , which was obtained by dissolving 0.25 mol dm^{-3} naphthalene and metallic Li packed with porous polyethylene film into butyl methyl ether (BME) solvent. The obtained electrode was finally washed with dimethyl carbonate to

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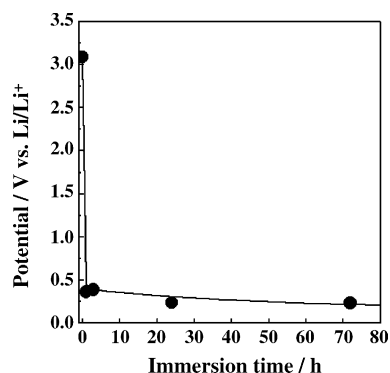


Fig. 1. Change in the rest potential of Li₅SiO electrode obtained by chemical Li-doping method using Li-organic complex solution as a function of the immersion time.

remove the remained solution. The XPS analysis was carried out for the identification of Li-doping by using the Mg K α X-ray source with argon-ion etching to investigate the concentration depth profiles for Li element of electrode. The etching rate was 2.3 nm min⁻¹ for SiO₂ material. The rest potential and initial discharge characteristics of negative electrodes were investigated by using the three terminal test cells with metallic Li foil as the counter and reference electrodes in 1.0 mol dm⁻³ LiClO₄ of ethylene carbonate (EC)–diethyl carbonate (DEC) mixed solution. The rest potential was measured after 30 h of the cell fabrication. Charge was conducted to 0 V versus Li/Li⁺ at the constant current density of 0.5 mA cm⁻². Discharge was also performed to 1.5 V versus Li/Li⁺ at the same constant current density.

3. Results and discussion

The change in rest potential of SiO-negative electrode after Li-doping by chemical method is shown as a function of the immersion time in the Li-organic complex solution in Fig. 1. The potential rapidly shifts to less noble value at the beginning of immersion and tends to be stable at around 0.21 V versus Li/Li⁺. This potential shift toward less noble

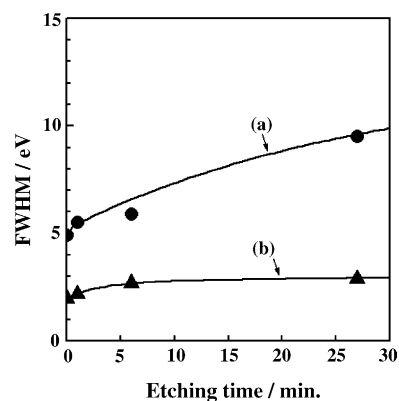


Fig. 3. Change in the FWHM of Li_{1s} spectra analyzed for SiO electrodes with potentials of: (a) 1.82 V and (b) 0.21 V vs. Li/Li⁺.

value means the progress of Li-doping into SiO-negative active material with immersion time.

The Li_{1s} spectra of SiO-negative electrodes with the different rest potentials of 3.08, 1.82, and 0.21 V versus Li/Li⁺ after Li-doping by chemical method are shown with a function of etching time in Fig. 2. In the case of untreated electrode with 3.08 V versus Li/Li⁺, there are no Li peaks at around binding energy of 57 eV in any etching time. The Li peak is, however, apparently detected for the electrode with potential of 1.82 V versus Li/Li⁺ by immersion in the Li-organic complex solution, especially on its surface portion of SiO material. Furthermore, this peak becomes sharp on the electrode with 0.21 V versus Li/Li⁺, even inside portion. In addition, the color of SiO material changes from brown to dark blue with the increase of immersion time. These results mean the direct evidence that Li⁺ ion is doped into SiO material and the content increases with immersion time. Hence, Li-doped SiO-negative active materials are found out to be synthesized by immersion in the Li-organic complex solution. The change in the full-width half maximum (FWHM) of Li_{1s} spectra of the electrodes with potential of 1.82 and 0.21 V versus Li/Li⁺ is shown as a function of etching time in Fig. 3. The FWHM tends to increase with etching time in each case. The Li peak of the SiO electrode with potential

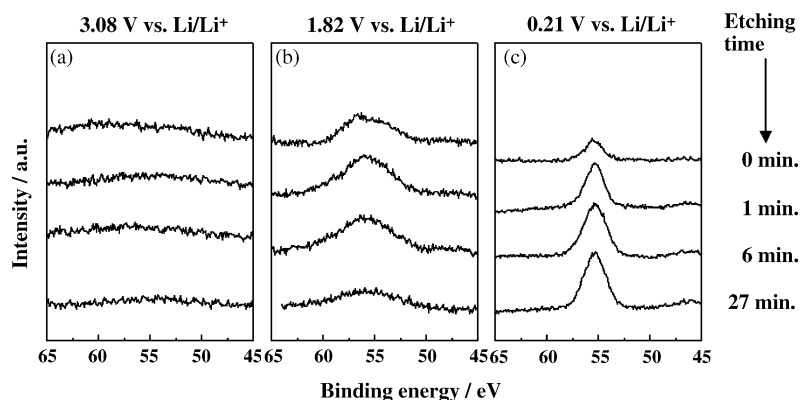


Fig. 2. Li_{1s} spectra of SiO electrodes treated at different immersion times into Li-organic complex solution with BME solvent.

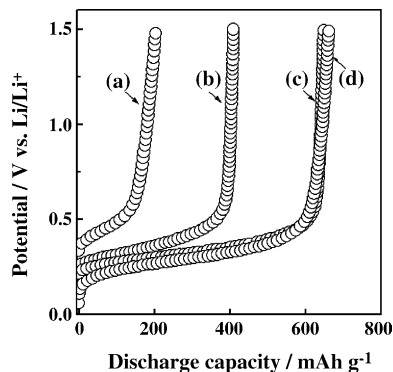


Fig. 4. Initial discharge characteristics of SiO electrodes treated in the Li-organic complex solution at different immersion times of: (a) 3 h; (b) 24 h; (c) 48 h; (d) 72 h.

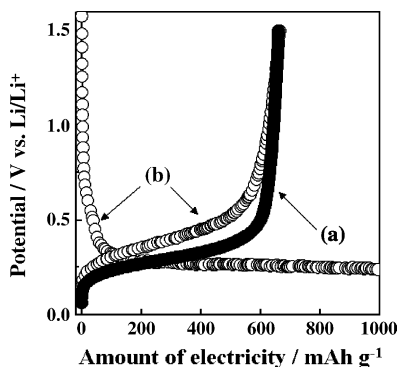


Fig. 5. The charge-discharge characteristics of: (a) SiO-negative electrode treated for 72 h in Li-organic complex solution with BME solvent and (b) untreated one.

of 0.21 V versus Li/Li⁺ shows slight change of FWHM from surface to inside portion. On the other hand, the FWHM of the SiO electrode with potential of 1.82 V versus Li/Li⁺ is larger than that of 0.21 V versus Li/Li⁺, increasing gradually from surface to inside portion. This fact suggests crystallinity of the obtained material becomes lower in the small amount of doped Li.

The initial discharge characteristics of SiO-negative electrodes obtained with various immersion times in the Li-organic complex solution are shown in Fig. 4. The delivered discharge capacity increases with the immersion time and the value reaches the large capacity of 670 mAh g⁻¹ after 72 h immersion. This fact clearly shows that doping of Li⁺ ion into SiO is promoted with the immersion time. Therefore, the amount of doped Li⁺ ion is easily controlled by the immersion time. The initial potential behavior of the treated electrode for 72 h and untreated one are shown in Fig. 5 for comparison. The discharge potential of electrode treated by chemical method shows less noble potential by 200 mV compared with that of the untreated electrode with large irreversible capacity

at initial charging. This result suggests treated electrode leads to reduce irreversible capacity by this Li-doping process.

The chemical Li-doping process into SiO seems to take place as follows. First, Li⁺ ion is dissolved into ether solvent by electron affinity of naphthalene, resulting in the formation of naphthalene radical anion. Li⁺ ion is then solvated with ether solvent and radical anion. After that, radical electron moves into SiO material, which shows recovering to initial state of naphthalene. Finally, Li⁺ ion is immediately doped into this material. Thus, naphthalene is suggested to serve as a catalyst of chemical Li-doping reaction.

4. Conclusions

The potential of Li_xSiO electrode obtained by chemical Li-doping method drastically shifts to less noble value at the beginning of immersion in Li-organic complex solution and tends to be stable at around 0.21 V versus Li/Li⁺, which means the progress of Li-doping into SiO-negative active material with immersion time. Furthermore, XPS analysis revealed the direct evidence that Li⁺ ion is doped into SiO material by this method and the content increases with immersion time. Therefore, the amount of doped Li is easily controlled by the immersion time in the Li-organic complex solution. The delivered discharge capacity of the obtained Li_xSiO electrode increases with the immersion time and the value reaches the large capacity of 670 mAh g⁻¹ after 72 h immersion. This fact clearly shows that doping of Li⁺ ion into SiO is promoted with the immersion time, resulting in the reduction of irreversible capacity. This chemical Li-doping process into SiO material is suggested to take place by using Li-organic complex solution according with the catalysis function of naphthalene.

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