

# Synthesis of Li-doped SiO Negative Active Material by Chemical Method Using Organic Complex Solution for Lithium-ion Cells

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## Abstract

Li-doped SiO as a next-generation negative active material for lithium-ion cells has been successfully synthesized by the new chemical method using Li-organic complex solution prepared by dissolving 0.25 mol l<sup>-1</sup> naphthalene and metallic lithium into butyl methyl ether (BME) solvent for the purpose of the compensation of Li source corresponding to its large irreversible capacity appeared mainly at the first charging process in the practical application of cells. Li<sup>+</sup> ion was found out to be doped into SiO in the complex solution to reach the level of dischargeable capacity of 670 mAh g<sup>-1</sup> as negative electrode with open circuit potential of 0.229 V vs. Li/Li<sup>+</sup>. The amount of doped Li<sup>+</sup> ion was to be easily controlled by immersion time into the solution and measurement of the open circuit-potential of electrode. Furthermore, the detailed reaction mechanism will be discussed with electrochemical measurement and XPS analysis.

## 1 Introduction

The enhancement of energy density has been strongly required for lithium-ion cells such as current LiCoO<sub>2</sub>/C, LiNiO<sub>2</sub>/C, and LiMn<sub>2</sub>O<sub>4</sub>/C systems due to the increasing demand on higher power sources equipped for portable phones and electric vehicles. The utilization of graphite negative electrode used for these cells has already increased up to the value close to the theoretical capacity of 372 mAh g<sup>-1</sup>. Therefore, the development of large-capacity negative active materials is indispensable to meet its demand. Silicon monoxide (SiO) negative active material has been considered to be one of promising candidates for the alternative to conventional graphite because

of its large capacity over 1200 mAh g<sup>-1</sup> and relatively low charge-discharge potential<sup>1,2)</sup>. However, the large irreversible capacity of SiO electrode has limited the design for high-energy-density cells, because the large amount of corresponding Li<sup>+</sup> source has to be provided from positive active material resulting in high cost and low energy density for the practical cell. The new chemical method for synthesis of Li-doped SiO by using Li-organic complex solution has been found to overcome the essential problem caused by this irreversible capacity. The detailed process of its method and reaction mechanism will be reported in this paper.

## 2 Experimental

### 2.1 Preparation of electrode

The SiO electrode was prepared for the capacity measurement of potential behavior and its discharge

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using a foamed-nickel substrate as a current collector to prevent from peeling off the active material from the substrate. The procedure is described as follows. The SiO negative active material with the average particle diameter of  $1\ \mu\text{m}$ , acetylene black (AB) powder as a electro-conductive material, and poly-vinylidene-fluoride (PVDF) as a binder with mass ratios of 75 : 5 : 20 were mixed using N-methyl-2-pyrrolidone (NMP) solvent to prepare a slurry. The substrate was then immersed into the slurry followed by drying at  $150\ ^\circ\text{C}$  under vacuum. The loading level was  $12.5\ \text{mg cm}^{-2}$ . The electrode with no additive of electro-conductive material of AB was also prepared by using the mixture of SiO active material and PVDF with ratio of 80 : 20 with the same procedure as described above for the elimination of effect of Li doping into AB contained in the electrode. The other electrode with no additive was prepared by using a Cu-foil current collector with the flat surface needed for XPS analysis in the place of foamed type substrate.

## 2.2 Chemical method for Li-doped SiO active material

The Li-saturated organic complex solutions with different concentrations of naphthalene from  $0.03\ \text{mol l}^{-1}$  to  $1.0\ \text{mol l}^{-1}$  were prepared by stirring the metallic lithium packed with porous polyethylene film in BME or tetrahydrofuran (THF) organic solvents. The SiO negative electrodes were then immersed in these organic complex solutions followed by washing it with dimethyl carbonate (DMC) (Tomiya Pure Chemical Industries Co., Ltd.) to remove the remained solution in the electrode.

## 2.3 Electrochemical measurements

The electrochemical behavior of electrode after Li doping was investigated in the electrolyte of  $1.0\ \text{mol dm}^{-3}\ \text{LiClO}_4$  of ethylene carbonate (EC)-diethyl carbonate (DEC) mix solution (Tomiya Pure Chemical Industries Co., Ltd.) using metallic Li foil as counter and reference electrodes at  $0.5\ \text{mA cm}^{-2}$  from  $0\ \text{V}$  to  $1.5\ \text{V}$  vs.  $\text{Li/Li}^+$ .

## 2.4 Chemical analysis

The amount of  $\text{Li}^+$  ion in organic complex solution was determined by ion-exchange chromatography using Ion Pac CSRA column (DIONEX Corporation).

The concentration depth profiles for Li element of Li-doped electrode were investigated by XPS analysis using Mg  $K\alpha$  X-ray source with argon-ion etching. The etching rate was  $2.3\ \text{nm min}^{-1}$  for  $\text{SiO}_2$  material.

## 3 Results and discussion

The saturated  $\text{Li}^+$  ion dissolved from metallic Li into the naphthalene-BME organic complex solution is shown in Fig.1 as a function of naphthalene concentration. The saturated  $\text{Li}^+$  ion drastically increases with the addition of naphthalene and the value tends to increase with its concentration. This means that the role of naphthalene is to increase the saturation of  $\text{Li}^+$  ion in the organic complex solution. For the more clear function of naphthalene, the saturated  $\text{Li}^+$  ion in terms of molar ratio to naphthalene is also shown in Fig.2. The value of Li ratio to naphthalene drastically decreases with the slight increment in the concentration of naphthalene of complex solution to reach the turning point at around  $0.25\ \text{mol l}^{-1}$  and tends to the constant value of 0.04 beyond that value. This also means that the activity of naphthalene to increase the saturation of dissolved  $\text{Li}^+$  ion decreases with its concentration.

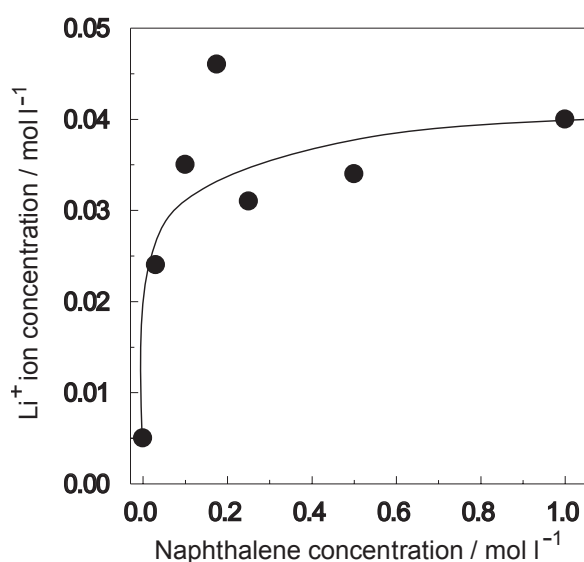


Fig. 1 Effect of naphthalene concentration on the saturated  $\text{Li}^+$  ion in complex solution with BME solvent.

The change in open-circuit potential of electrodes after Li doping by chemical method is shown as a function of the immersion time in the different solvents of BME and THF with naphthalene

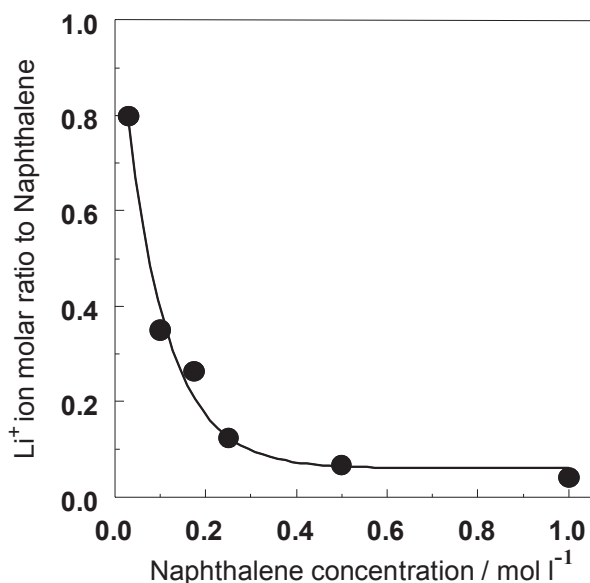


Fig. 2 Effect of naphthalene concentration in the complex solution with BME solvent on molar ratio of Li<sup>+</sup> ion to its naphthalene.

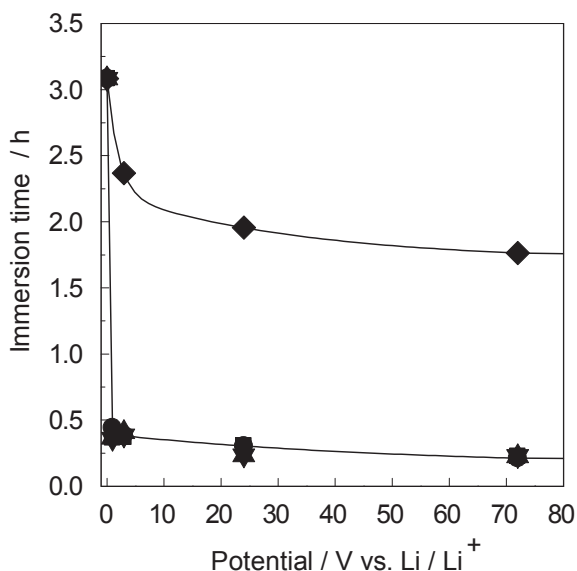


Fig. 3 Change in open-circuit potential of SiO negative electrodes treated in Li-organic solution with BME solvent containing (●) 0.030 mol l<sup>-1</sup>, (▲) 0.100 mol l<sup>-1</sup>, (■) 0.175 mol l<sup>-1</sup>, (▼) 0.250 mol l<sup>-1</sup> naphthalene, and (◆) THF solvent containing 0.250 mol l<sup>-1</sup> naphthalene.

concentration of 0.25 mol l<sup>-1</sup> in Fig.3. Especially for the case of BME, the additional test results of concentration of 0.03, 0.10, and 0.175 mol l<sup>-1</sup> are also shown. The electrode potential rapidly shifts to less noble at the beginning and tends to be stable at around 1.75 V and 0.25 V vs. Li/Li<sup>+</sup> for BME and THF respectively. The potential shift toward less noble shows the progress of Li doping to SiO active material with immersion time. The extent of Li doping to SiO is strongly dependent on the kind of solvents. The BME is found out to accelerate the chemical doping reaction of Li<sup>+</sup> ion to SiO compared with the case of THF. The naphthalene concentration gives no effect on this doping reaction in BME solvent.

The Li<sub>1s</sub> spectra of SiO negative electrode with the different open-circuit potential of 3.084, 1.824, and 0.214 V vs. Li / Li<sup>+</sup> after Li doping by chemical method are shown as a function of etching time in Fig.4. The Li peak at around binding energy of 57 eV is apparently detected for the electrode with potential of 1.824 V vs. Li/Li<sup>+</sup>, especially on its surface portion. This peak becomes sharp on the electrode with 0.210 V vs. Li/Li<sup>+</sup>, even inside portion of the electrode. In addition, the color of SiO material changed from brown to dark blue with the increase of immersion time.

The delivered capacity of negative electrode at the first discharge is shown as a function of the immersion time in Fig.5. The capacity increases with the immersion time and the value reaches the large capacity of 670 mAh g<sup>-1</sup> after 72 h immersion, that is for the electrode with open-circuit potential of 0.210 vs. Li/Li<sup>+</sup>. This fact clearly indicates that Li doping progresses with the immersion time with the change in open-circuit potential and the discharge capacity is controllable by measurement of immersion time and potential. The discharge characteristics of the electrode with the open-circuit potential of 0.210 V vs. Li/Li<sup>+</sup> are also shown in Fig. 6 together with those of the untreated electrode for comparison. The discharge potential of electrode by chemical method shows less noble potential by 200 mV compared with that of the untreated electrode with large irreversible capacity. Therefore, Li-doped

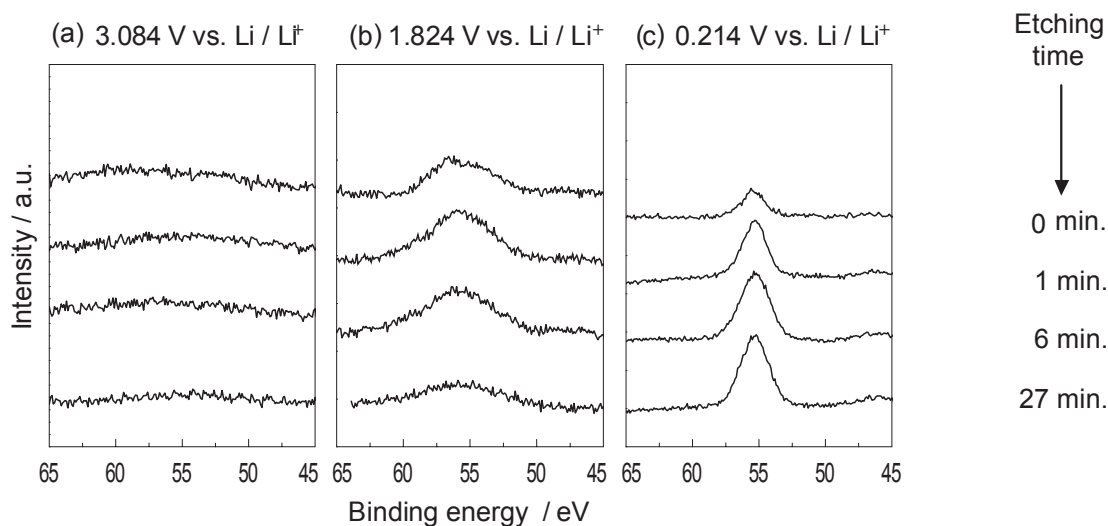


Fig. 4  $\text{Li}_{1s}$  spectra of SiO electrodes treated at various immersion times into Li-organic complex solution with BME solvent containing  $0.25 \text{ mol l}^{-1}$  naphthalene.

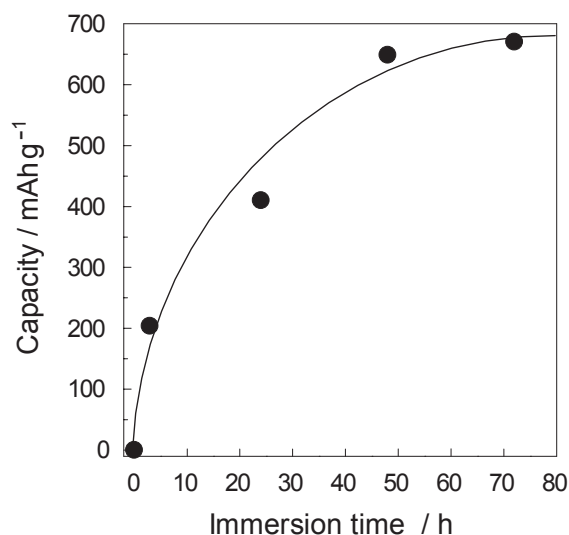


Fig. 5 Delivered capacity of SiO negative electrode treated in Li-organic complex solution with BME solvent containing  $0.25 \text{ mol l}^{-1}$  naphthalene as a function of the immersion time. Discharge:  $0.5 \text{ mA cm}^{-2}$  to  $1.5 \text{ V vs. Li/Li}^+$  in  $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$  of EC-DEC mix solution.

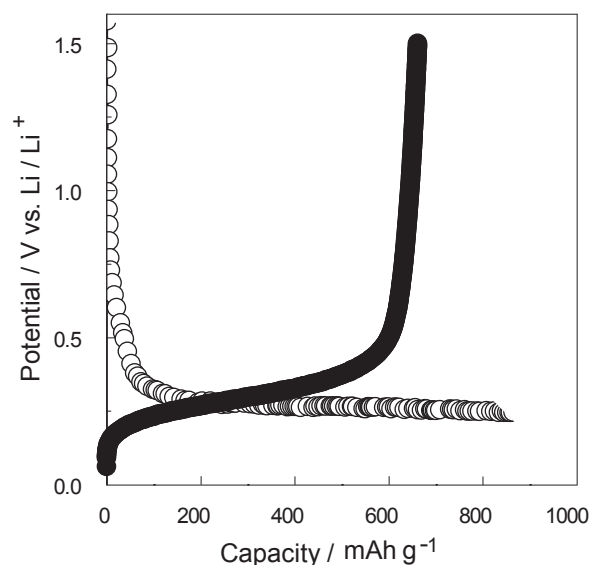


Fig. 6 The discharge characteristics of (a) SiO negative electrode treated for 72 h in Li-organic complex solution with BME solvent containing  $0.25 \text{ mol l}^{-1}$  naphthalene and (b) untreated one. Discharge:  $0.5 \text{ mA cm}^{-2}$  to  $1.5 \text{ V vs. Li/Li}^+$  in  $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$  of EC-DEC mix solution.

SiO negative active material was found out to be synthesized by the chemical method using Li-organic complex solution and the amount of inserted  $\text{Li}^+$  ion is easily controlled by the measurement of open-potential potential, in other words by the immersion time. This method was found out to

overcome the essential problem resulting in the low energy density of the practical cells caused by the irreversible capacity of SiO observed at the first charge.

## 4 Conclusions

The results of this paper are summarized as described below.

- 1) Li-doped SiO as a next-generation negative active material has been successfully synthesized by the new chemical method using Li-organic complex solution.
- 2) The amount of inserted Li<sup>+</sup> ion is easily controlled by immersion time into Li-organic complex solution, selection of the solvent, and measurement of open-circuit potential.
- 3) The extent of the Li doping to SiO is strongly dependent on the kind of solvents. The BME is found out to accelerate the chemical doping

reaction of Li<sup>+</sup> ion to SiO compared with the case of THF. The naphthalene concentration gives no effect on this doping reaction in BME solvent.

## References

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