

Effect of Naphthalene Addition on Solvation of Li-Organic Complex Solution as a Li-Doping Agent for Battery Active Material

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Abstract

Solvation behavior of Li-naphthalene complex organic solution, which is used as Li-doping agent for battery active materials, was examined using ESR and ICP analysis in the range of naphthalene concentration between 0.015 to 0.5 mol dm⁻³. The formation of ion pair of lithium cation and naphthalene was observed in the low naphthalene concentration region of 0.015 and 0.033 mol dm⁻³, where dissolved Li⁺ concentration increases with an increase in naphthalene concentration. At the higher naphthalene concentration of 0.25 and 0.5 mol dm⁻³, it was found that the free naphthalene exists surrounding the ion pair where dissolved Li⁺ concentration was stabilized at 0.2 mol dm⁻³.

Key words: Li-doping; Li-organic complex solution; Naphthalene

1 Introduction

Recently, Li-ion cells have been strongly required to increase the energy density for power sources of portable phones and hybrid electric vehicles. The utilization of graphite negative electrode used for the cells has already increased up to be close to the value of theoretical capacity of 372 mAh g⁻¹. Therefore, negative active material with larger capacity has been required to apply for the new applications. The novel lithium contained material of Li_xSiO (X>0) has been successfully synthesized as one of the promising candidates of negative active material by chemical method using Li-organic complex solution and the reaction mechanism has been cleared by X-ray photoelectron spectroscopy (XPS) and electrochemical measure-

ment.^{1,2)} The amount of doped Li⁺ ion was found out to be controlled by immersion time of SiO starting material in the solution. However, the solvated state of solution has not been identified by the analysis despite the important factor for the Li-doping reaction of chemical method. In this work, the detailed chemical state of complex solution has been investigated to clear the effect of solvent on Li-doping reaction by ESR analysis which can identify the solvation from the signal detected by radical electrons.

2 Experimental

First, naphthalene was dissolved into butylmethylether (BME) solvent of 10 ml with different concentration from 0.015 to 0.5 mol dm⁻³ in a vial container. Metallic Li was then immersed into the mixed solution with stirring by using a rotary shaker for 72 h

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in Ar atmosphere. Finally, Li-organic complex solution was obtained by removing the residual metallic Li. Li^+ ion concentration in the complex solution was determined by inductively coupled plasma (ICP) analysis as reported before.³⁾

ESR analysis was performed to the solution with different naphthalene concentration by using Bruker ESP350E instrument under the condition of 9.8 GHz microwave frequency and 3496×10^{-4} T center magnetic field at room temperature.

3 Results and discussion

The color of solution was changed to be dark violet from transparency after the immersing of metallic Li in the BME solvent dissolved naphthalene, suggesting the formation of complex product. The Li^+ ion concentration of complex solution was analyzed for the control of Li-doping reaction. The concentration change in Li^+ ion dissolved from metallic Li into the solution is shown in Fig. 1 as a function of the amount of naphthalene. The Li^+ ion concentration is found out to increase drastically with the addition of naphthalene and the value becomes to be saturated at around 0.2 mol dm^{-3} . This fact means that the role of naphthalene is to increase the dissolved Li^+ ion in the solution.

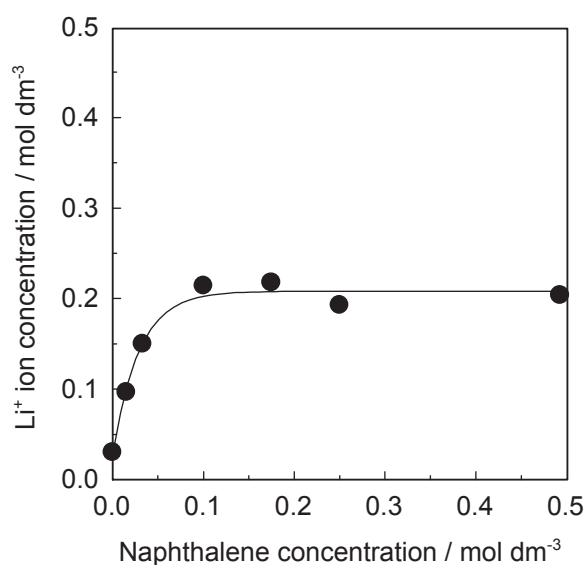


Fig. 1 Effect of naphthalene additive on saturated Li^+ ion concentration for Li-organic complex solution.

ESR analysis was carried out to clear the reason of solvation on the solution with different naphthalene concentration of 0.015, 0.033, 0.25, and 0.50 mol dm^{-3} . The effect of naphthalene additive on ESR spectra is shown in Fig. 2. The sharp ESR spectra with resonance split appear in the low naphthalene concentration at 0.015 and $0.033 \text{ mol dm}^{-3}$ in the range of increasing Li^+ ion content. This behavior is considered to be due to interaction of nuclear spins between lithium and hydrogen in naphthalene. Judging from the result reflected the strong interaction, ion pair between lithium cation and naphthalene anion is suggested to form in the Li-organic complex solution. The spectra are broadened with a further increase of naphthalene additive and its splitting disappears in the high concentration of 0.25 and 0.5 mol dm^{-3} in the range of stabilized Li^+ ion content at 0.2 mol dm^{-3} . The existence of different ESR spectra means that chemical state of ion pair between lithium cation and naphthalene anion changes with naphthalene additive in the Li-organic complex solution. Furthermore, the broadening is considered to be caused by interaction between ion pair and free naphthalene, resulting in the saturation of Li^+ ion concentration at 0.2 mol dm^{-3} .

The change in the concentration of naphthalene

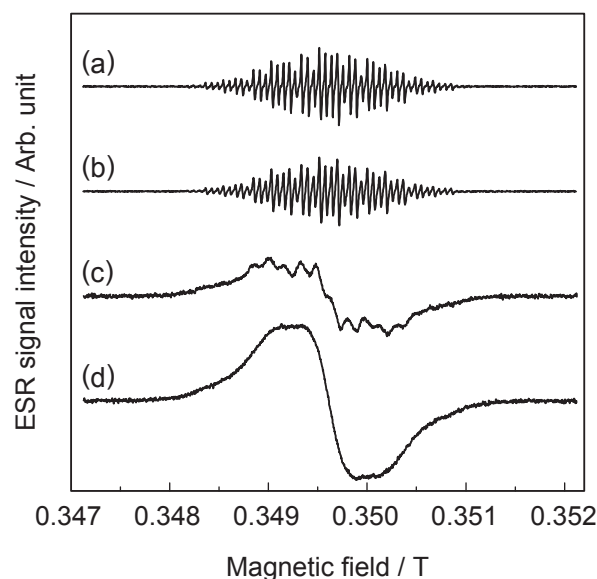


Fig. 2 Effect of naphthalene concentration at 0.015 (a), 0.033 (b), 0.25 (c), and 0.50 mol dm^{-3} (d) on ESR spectra of the Li-organic complex solution.

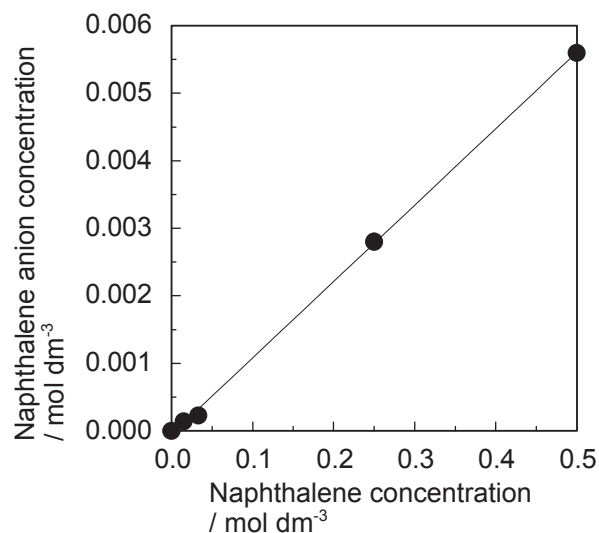


Fig. 3 Change in naphthalene anion concentration calculated from ESR spectra with naphthalene additive in the Li-organic complex solution.

monovalent radical calculated from the peak area of ESR spectra is shown in Fig. 3. The concentration linearly increases with the naphthalene additive and the value is significant small compared with the case of Li^+ ion as shown in Fig. 1. This fact means that there exists little monovalent radical of naphthalene, though ion pair is formed in the complex solution.

4 Conclusions

Sharp ESR spectra with resonance split appeared in the low naphthalene concentration at 0.015 and 0.033 mol dm⁻³ in the range of increasing Li^+ ion content. This is considered to be due to interaction of nuclear spins between lithium and hydrogen in naphthalene, suggesting presence of ion pair in the complex solution. The spectra were broadened with a further increase of naphthalene additive and the splitting disappeared in the high concentration of 0.25 and 0.5 mol dm⁻³ in the range of Li^+ ion content stabilized at 0.2 mol dm⁻³. This fact means that chemical state of ion pair changes by influence of increasing free naphthalene. These results will be useful for the control of Li-doping reaction for chemical method.

References

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