IONIC CONDUCTION IN MESOPOROUS SiO$_2$ THIN FILMS IMPREGNATED WITH Li SOLUTION ELECTROLYTE

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Lithium solution electrolyte was impregnated into mesoporous SiO$_2$ thin film and Li$^+$ ion conductivity of the SiO$_2$ thin film was examined. The mesoporous SiO$_2$ thin films were prepared by spincoating of aqueous solution of tetraethoxysilane and alkyltrimethylammonium chloride on stainless substrates, and subsequent heating at 70℃ or 550℃. Lithium perchlorate/ propylene carbonate solution was used as electrolyte. Impregnation was conducted under vacuum condition. Mesoporous structure of the thin films was confirmed to be cubic Pm3n by low-angle X-ray diffraction. Conductivity estimated from AC impedance plot was 1×10^{-4} Scm^{-1} for thin film calcined at 550℃, which is more than five orders of magnitude higher than that of non-impregnated thin film. However, the conductivity value was about two orders of magnitude lower than that estimated from the conductivity of Li solution and the size of conduction path in mesoporous film. The reason is assumed to be narrow bottle neck of ion conductive path or imcomplete impregnation.

Key words : Self organization, ionic conduction, Electrolyte, Silica thin film, mesoporous material

1.Introduction

Use of lithium batteries is extended in various fields, and many efforts have been made for the improvement of battery performance and the miniaturization of the system. For the electrolyte materials, a high Li$^+$ ion conductivity and formation of thin layer are required to decrease the battery resistance. In addition, safety during and after long-term operation is also demanded. Liquid electrolytes, Li-organic solvents, are now used widely for lithium batteries. It has a high Li$^+$ ion conductivity, but has problems as corrosion of cells and ignition caused by leakage of solvents. It also needs a separator to prevent from short-circuit caused by dendrite formation between electrodes. On the other hand, solid electrolytes are chemically stable and free from leakage problems. Thin-film formation of the solid electrolytes is easier than that of liquid electrolytes, and the thin film also works as the separator. Such a simple cell structure is favorable for miniaturization of the lithium batteries. However, Li$^+$ ion conductivity of solid electrolyte is not high enough for the practical use at present.

Silica mesoporous thin films with pores of several nanometers can be synthesized via self organization process. The self organization process is a method to obtain mesoporous materials using surfactant as template in solution of inorganic precursor and surfactant [1~3]. The mesoporous materials have narrow distribution of diameter of mesopores, and the mesostructure and diameter of mesopore can be controlled by selecting surfactant species and their concentration. Silica mesoporous thin films containing lithium solvent in mesopores are expected as a composite electrolyte having a high conductivity and advantages as a solid electrolyte. In the present study, silica mesoporous thin films impregnated with lithium electrolyte were synthesized and their Li$^+$ ion conductivities were evaluated.

2. Experimental

2.1 Sample preparation

For the preparation of silica mesoporous thin films, tetraethoxysilane (96% TEOS : [Si(OC$_2$H$_5$)$_4$]) was used as the Si source, and hexadecyl-trimethylammonium chloride (C16TAC : [(C$_{16}$H$_{33}$)(CH$_3$)$_3$NCl]) or dodecyltrimethyl-ammonium chloride (C12TAC: [(C$_{12}$H$_{25}$)-(CH$_3$)$_3$NCl]) was used as the surfactant. TEOS and water was stirred for hydrolysis in the ice bath under

acidic condition. Molar ratio of TEOS and water was 2:1. After the solution became homogeneous, 0.3mol/L aqueous solution of surfactant (C16TAC or C12TAC) was added into the solution, and stirred for 10min. Molar ratio of TEOS and surfactant was fixed to be 8:1. The obtained solution was spincoated at a rate of 3000 rpm on stainless (SUS304) substrate. Samples were dried at 70°C for 24h. Some samples synthesized with C16TAC were soaked in ethanol for 24h in order to remove surfactant. After 70°C thermal treatment, samples were calcined at 550°C for 3h in order to remove surfactant completely. Circular electrode of gold, with a diameter of 2 mm, was applied by spattering on the upper surface of synthesized thin films. Samples was impregnated with 1 mol/L Lithium Perchlorate / Propylene Carbonate (PC) solution (Li electrolyte solution). The impregnation was conducted by soaking samples in the Li electrolyte solution for 40h under a reduced pressure using vacuum pump. After impregnation, samples were rinsed by ethanol. The samples, only dried after spincoating and then Li-impregnated, are denoted as "samples without calcination" hereafter, and the samples, soaked in ethanol after drying and then Li-impregnated, are denoted as "ethanol-washed samples". The samples, calcined at 550°C and Li-impregnated, are denoted as "calcined samples".

2.2 Characterization

Mesostructure of the samples was confirmed by low-angle X-ray diffraction using CuK α radiation. Thickness of the samples was measured by probe contact. Ionic conductivity was measured at 20°C by two-probe AC impedance method. Measured frequency was from 5 mHz to 1 MHz (Solartron 1260,1287: TOYO Corporation) and from 5 Hz to 13 MHz (YHP-4192A: Agilent).

3.Results and discussion

3.1 Characterization of synthesized samples

Thickness of the films without calcination was 70nm for the sample using C16TAC and was 60nm for the sample using C12TAC. The X-ray diffraction patterns of samples using C12TAC and C16TAC without calcination are shown in Fig.1. When the main peak is assumed as the (210) diffraction of Pm3n cubic
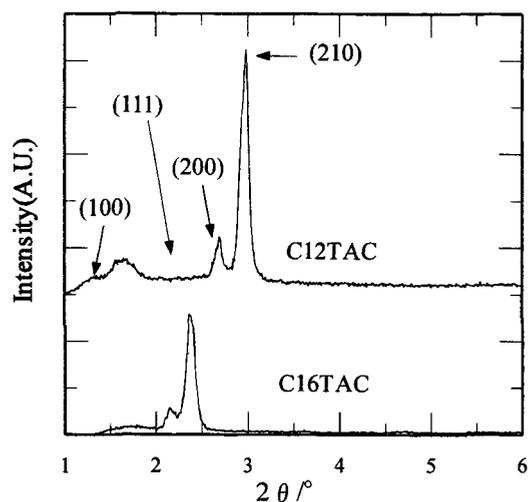
Fig.1 X-ray Diffraction pattern of samples using C12TAC and C16TAC without calcination
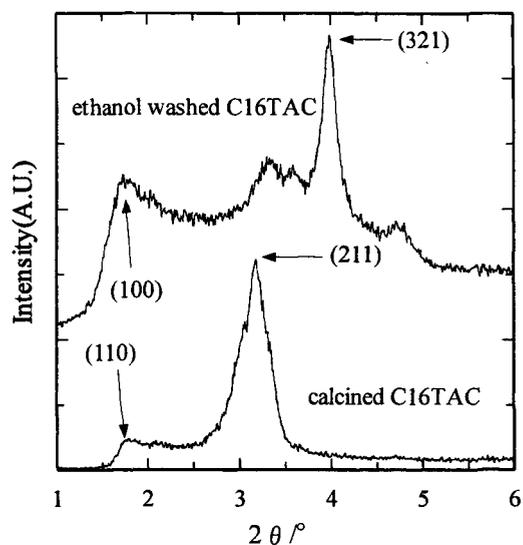
Fig.2 X-ray Diffraction patterns of ethanol washed sample(C16TAC) and calcined sample (C16TAC)

crystal, other measured peak-positions accorded with calculated cubic peak-positions[4]. From this result, the mesostructure of synthesized thin films was judged to be the Pm3n cubic crystal. The unit-cell size, the d-space of (100) diffraction, was 8.3nm for the sample using C16TAC and 6.7nm for the sample using C12TAC. The diameter of the mesopores can be estimated from the diameter of spherical micell of surfactant to be 3.2nm for C16TAC and 2.5nm for C12TAC. The ratio of unit cell sizes of between samples using C16TAC and C12TAC was almost same with that of the diameters of surfactant micells. This indicates that these films have same structure except for sizes of unit cell and mesopore.

The X-ray diffraction patterns of calcined sample (C16TAC) and ethanol washed sample (C16TAC) are shown in Fig.2. Though the intensity of (210) peak became weaker than that of sample before treatment, peak assignment was possible with the Pm3n structure. This indicates that the mesostructure of thin film was not collapsed after calcination or ethanol washing. It is assumed from the unit-cell size and the diameter of mesopores that mesopores are contacted each other or located at very close positions. The connected mesopores are expected to work as the ion conductive path in these thin films.

3.2 Impedances of mesoporous thin films

The impedance plot of the sample before impregnation was characteristic of a capacitor. It is reported that the silica mesoporous materials have low dielectric permittivity about 2 [5], but observed permittivity was about 3 near to that of silica (=4.5). Thus the sample before impregnation was confirmed to be an electrical insulator with a conductivity below 10^{-9} S/cm (the lower limit of measurement system).

Impedance plots of solution-impregnated C16TAC samples are shown in Fig.3. Conductivity was estimated from the cross point of the real axis and the extrapolated line of the impedance plot to the high frequencies, as shown in Fig.4. The conductivity was 1.1×10^{-4} S/cm for the calcined sample, and the 4.5×10^{-5} S/cm for the sample without calcination . Since the sample before impregnation is an electrical insulator, the high conductivity of samples after impregnation is due to the lithium electrolyte impregnated into mesoporous thin film. A semicircle part was observed at high frequencies in the plot of the sample without calcination, and it was not observed in the plot of the calcined sample in Fig.3. In the impedance plot of the ethanol washed sample (Fig.5), a part of semicircle was also observed but it was smaller than that of the sample without calcination. These semicircles are assumed to be attributed to the surfactant molecules left in mesopores. The reason of higher conductivity of the calcined sample than that of the sample without calcination would be due to that the Li^{+} ion
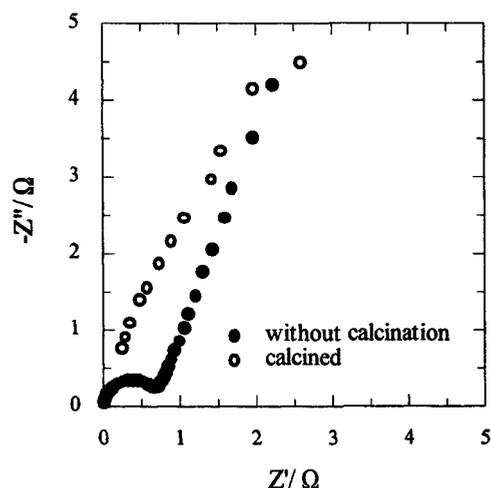
Fig.3   Impedance plot of samples, calcined and without calicination (C16TAC)

Fig.4   Impedance plot of calcined sample (C16TAC) at the high frequency end
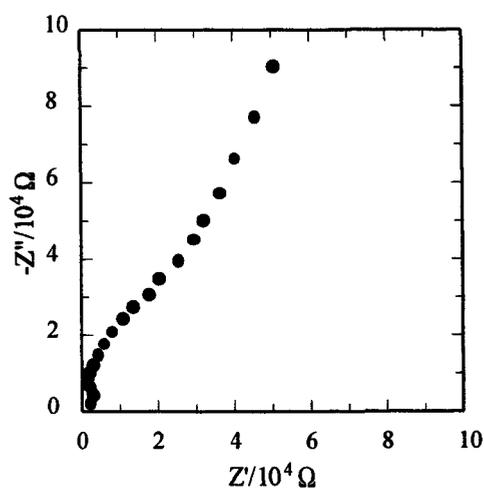
Fig.5   Impedance plot of ethanol washed sample(C16TAC)
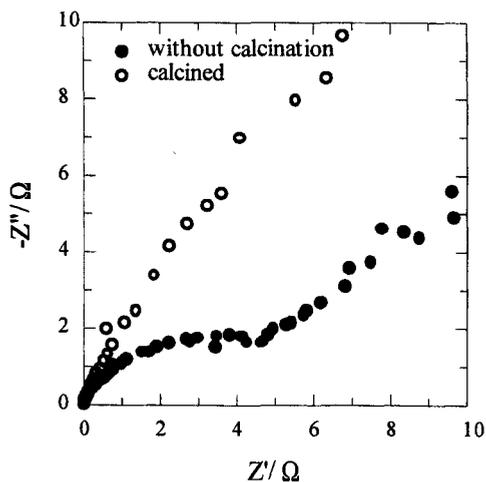
Fig.6 Impedance plot of samples, calcined and without calcination (C12TAC)

movement is free from the prevention by surfactant molecules in mesopores.

Impedance plot of C12TAC samples are shown in Fig.6. Although the shape of plot is somewhat different from those of C16TAC sample(Fig.3), evaluation of conductivity was conducted similar to that for C16TAC samples. The conductivity was 2.7×10^{-6} S/cm for the calcined sample, and 2.0×10^{-6} S/cm for the sample without calcination. The conductivity of calcined samples was higher than that of the sample without calcination. A part of semicircle was also observed in the high frequency region of the impedance plot of sample without calcination. These results are similar to the results of C16TAC samples, and indicate that the surfactant molecules in mesopores prevent the movement of Li^+ ion and lower the conductivity of the thin film. The conductivities of the C12TAC samples were lower than those of the C16TAC samples. This will be caused by a narrow conduction path due to the small size of mesopores in C12TAC samples.

The measured conductivity was lower than the conductivity of liquid electrolyte, about 10^{-2} S/cm for 1mol/L LiClO₄/PC. The average cross sectional area of the ion conductive path was calculated from the volume of unit cell and the volume of micelles of surfactant molecules in one unit cell for C16TAC sample without calcination. Since the cross sectional area of ion conductive path was estimated to be 31% of that of unit cell, the theoretical ion conductivity of

the samples should be 31% of the conductivity of lithium electrolyte solution. However, the evaluated conductivities of solution-impregnated samples were much lower than that. One of the reasons will be the bottle neck of the conduction path. The conduction path is formed by connected, spherical mesopores. Accordingly, the path is not a straight tube and there should be a bottle neck at the interface between neighboring mesopores. The ion conduction path is narrow at this bottle neck position, and it may dominate the ionic conductivity of mesoporous thin films. As another reason, incomplete impregnation of lithium electrolyte can be assummed. Estimation of solution volume impregnated into thin films will be useful to make clear this problem.

4.Conclusions

The conductivity of the silica mesoporous thin film impregnated with lithium electrolyte was measured. The conductivity of calcined C16TAC sample was 1.1×10^{-4} S/cm, which is more than five orders of magnitude higher than that of non-impregnated thin film. The conductivity value was about two orders of magnitude lower than that estimated from the conductivity of lithium electrolyte solution and the size of conduction path in mesoporous film. The reason is assumed to be narrow bottleneck of ion conductive path or incomplete impregnation. The surfactant molecules in mesopores prevent movement of lithium ion. The solution-impregnated thin film that has a larger-size mesopores showed a higher ion conductivity than that with smaller mesopores.

5.References

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