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Co-intercalation of Tetrahydrofuran with Lithium in β-ZrNCl Layered Crystal

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Tetrahydrofuran (THF) is co-intercalated with lithium in β-ZrNCl. Two highly crystalline co-intercalation phases were obtained as single phases by the reaction of the chemically transported β-ZrNCl and lithium-naphthalene in THF. The molecular arrangements in the interlayer spaces were estimated on the basis of the one-dimensional electron-density distribution maps.

Lithium intercalations in layer structured crystals have been extensively studied because of the possible use of these crystals as the electrodes of lithium secondary batteries and electrochromic display (ECD) devices.1,2) It is well known that the intercalated lithium atoms are ionized in the interlayer spaces and often solvated with polar organic solvents;3)

$$[\mathrm{L}] \quad + \quad x\,\mathrm{Li} \quad + \quad y\,(\mathrm{Solv}) \longrightarrow \mathrm{Li}^{+}_{x}(\mathrm{Solv})_{y}[\mathrm{L}]^{x-}$$

where [L] stands for layered crystals such as transition metal dichalcogenides, iron oxychloride, graphite and so on; Solv is solvent molecules. Although the intercalation of small lithium ions alone does not bring in a large increase in the basal spacings, co-intercalation of the solvent molecules with lithium expands the spacing remarkably depending on the way of arrangement as well as the size of the molecules. The formation of such co-intercalation phases does not make good influence on the reversibility of lithium cells, since it may cause the disintegration of the active electrodes.4) It is evident that the better understanding on the formation mechanism of the co-intercalation phases is indispensable for developing the lithium cells with high performance. Studies on the co-intercalation of aprotic solvents, especially tetrahydrofuran (THF) and propylene carbonate (PC) are needed, which are often used for electrolyte solutions in lithium batteries. However, few such studies have been reported. This is because most of these phases are poor-crystalline and labile in air.

A layer structured β-ZrNCl also forms co-intercalation phases by the reaction with n-butyl lithium followed by immersion into solvents such as THF, PC, acetonitrile, formamide, N,N-dimethyl formamide, dimethyl sulfoxide, and pyridine.5) In the present study, highly crystalline co-intercalation phases with different compositions and different structures have been obtained by the reaction of chemically transported β-ZrNCl with lithium-naphthalene (Li-naph) in THF. One-dimensional structural analyses have been carried out on these co-intercalation phases.

β-ZrNCl is a layer structured crystal. Each layer consists of a zirconium nitride double layer sandwiched with two close-packed chlorine layers.6) Such ZrNCl layers (Cl-Zr-N-N-Zr-Cl) are stacked with each other by van der Waals interactions. Highly crystalline β-ZrNCl was obtained by a chemical transport of the powder sample prepared by the reaction of ZrH_2 and NH_4Cl at elevated temperatures.7,8)

A 0.10 M Li-naph solution was prepared by dissolving equimolar amounts of lithium metal and naphthalene into THF. After 20 h, the solution was filtered through a sintered glass disk to remove insoluble impurities. Separate β-ZrNCl samples were dispersed into the varying amounts of 0.10 M Li-naph solution in such a way that the molar ratios of Li-naph/β-ZrNCl were in the range of 1.0 to 18.0. After being allowed to stand for 24 h at room temperature, each sample was separated by filtration and rinsed with THF. All the manipulations of the samples were performed in an argon-filled glove box (Vacuum Atmosphere Co.). The X-ray powder diffraction (XRD) patterns of the separated samples were measured under an argon atmosphere in a cylindrical cover having thin polyethylene windows by using nickel-filtered Cu K_α radiation. The amounts of co-intercalated THF were determined on the basis of the weight loss measured on evacuation at 453 K. The amounts of lithium were determined by flame analysis.9)

The basal spacings and the compositions of the products are listed in Table 1. The amount of lithium intercalated increases with the amount of Li-naph solution used. Single basal spacing phases were obtained only at $x = 0.18$ and 0.20 (x in Li_xZrNCl), the amount of THF co-intercalated (y) being determined to be 0.28 and 0.35, respectively. Although the other products are mixtures of two or three phases, the spacings appear to change in the following order with x:

$$\underset{(\beta\text{-ZrNCl})}{0.92\ \text{nm}} \longrightarrow \underset{(x = 0.18)}{1.49\ \text{nm}} \longrightarrow \underset{(x = 0.20)}{1.85\ \text{nm}} \longrightarrow \underset{(x \approx 0.5)}{2.00\ \text{nm}} \longrightarrow \underset{(x \gtrsim 1.0)}{1.08\ \text{nm}}$$

The two single phases were highly crystalline, and the intensities of the basal reflections up to 12 orders were measured for each sample. One-dimensional electron-density distribution maps were synthesized by using the corrected reflection intensities, and are shown in Fig. 1. As pointed out in a previous

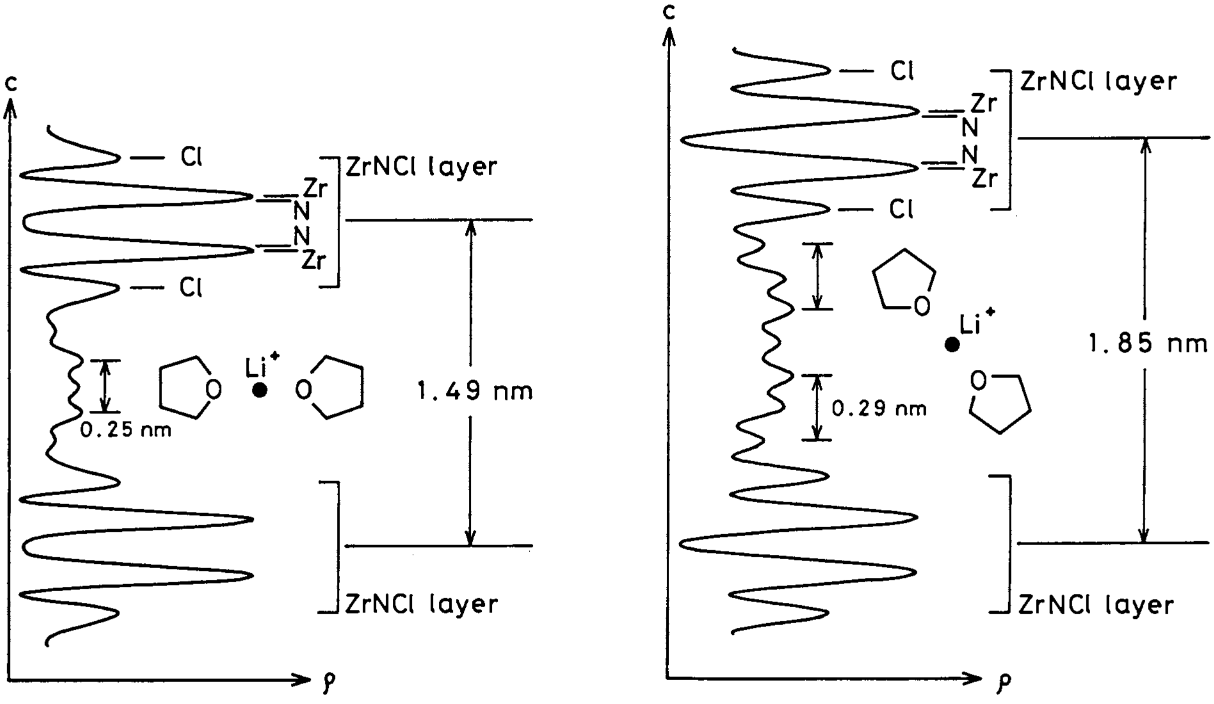
Table 1. Basal spacings and compositions of the products formed by the reaction of β-ZrNCl with varying amounts of 0.10 M Li-naph in THF

Reactants	Products ($Li_x(THF)_yZrNCl$)		
Li-naph/β-ZrNCl	x	ya)	basal spacing / nm
1.0	0.18	0.28	1.49
1.2	0.19	nd	1.49, 1.85
1.5	0.20	0.35	1.85
2.0	0.40	nd	1.08, 1.85
10.0	0.85	nd	1.08, 1.85, 2.00
18.0	1.20	nd	1.08, 2.00

a) nd : not determined.

paper,[10)] β-ZrNCl has two types of interlayers, in between Cl...Cl layers and in between N...N layers. The electron distributions clearly show that the THF molecules are intercalated in between the Cl...Cl layers. The scales attributed to the interlayer electron distributions suggest the following arrangements of the interlayer THF molecules. In the co-intercalated phase with a smaller basal spacing of 1.49 nm, the THF molecules are orientated with the molecular planes perpendicular to the layers and in a mono-layer arrangement. In the phase with a large basal spacing of 1.85 nm, the molecules also seem to be orientated with the molecular planes almost perpendicular to the layers, but in a double-layer arrangement. The R factors were calculated to be 0.23 and 0.27 for the molecular arrangements shown in Figs. 1(a) and 1(b), respectively. The driving force for the co-intercalation of solvent molecules is due mainly to the cation-dipole interactions. The lithium ions are probably located in the center of the interlayer space and coordinated with the THF molecules through the oxygen atoms. The spacing tends to increase with the increase in the amount of THF molecules co-intercalated with lithium ions. In the 2.00 nm phase, much larger amount of THF molecules may be accommodated in the interlayer spaces, enlarging the spacing from 1.85 to 2.00 nm.

It should be noted that when the amount of lithium intercalated exceeds the value x = about 1.0, the spacing collapsed to 1.08 nm. This can be interpreted in terms of the electrostatic interactions between the ionized lithium layers and the negatively charged ZrNCl layers. If the amount of intercalated lithium increased



(a) (b)

Fig. 1. One-dimensional electron-density maps along the direction normal to the ZrNCl layers: (a) $Li_{0.18}(THF)_{0.28}ZrNCl$ and (b) $Li_{0.20}(THF)_{0.35}ZrNCl$.

and the charge density exceeds a critical value, the structure with a collapsed interlayers would be more stable than those with the solvated and expanded interlayers.

When n-buthyl lithium in hexane was used as a lithiation reagent, the maximum amount of lithium intercalated was only 0.16 in x, and the basal spacing was essentially unchanged on the intercalation, showing no co-intercalation of the solvent.9) Li-naph is a stronger reducing agent than n-buthyl lithium, the potentials of which are 0.5 and 1.0 V versus Li^+/Li, respectively.11) The larger amount of lithium intercalated in the Li-naph solution can be attributed to its stronger reducing power. It is strange, however, that though only a part of lithium in the solution is used for the intercalation into β-ZrNCl, much larger amount of Li-naph solution is required to obtain highly intercalated β-ZrNCl. The reason is not obvious, but this is probably due to the partial deactivation or decomposition of Li-naph during the reaction. The final concentration of the solution would be changed depending on the amount of Li-naph used. When Li/β-ZrNCl cell was discharged with $LiClO_4$ in PC electrolyte solution, a co-intercalated phase with a basal spacing of 2.22 nm was obtained.9) If the discharge was continued further, the solvent (PC) was decomposed and no further intercalation of lithium occurred. The small discharge capacity of this cell seemed to be attributed to the hindrance by the co-intercalated PC molecules. The present study, however suggests that even if the interlayer spaces are occupied by the co-intercalated molecules, lithium can be intercalated to the point which is determined by the potential of the reducing agent; the co-intercalated THF molecules are even removed out of the interlayer spaces in the case of the lithium intercalation to the high density level. The decomposition of the solvent may occur by a different mechanism, which would be the subject of a future study. In the system of THF-Li_xZrNCl, no decomposition of the solvent is observed. This would be a more promising system for a lithium battery with a higher energy density. The discharge characteristics of the Li/β-ZrNCl cell with a $LiClO_4$ electrolyte solution in THF are being investigated.

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