2814 © 1991 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 64, 2814—2818 (1991) [Vol. 64, No. 9

Co-Intercalation of Tetrahydrofuran and Propylene Carbonate with Alkali Metals in β-ZrNCl Layer Structured Crystal

Masao OHASHI,* Koji UYEOKA, Shoji YAMANAKA, and Makoto HATTORI†
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Higashi-Hiroshima 724

(Received April 6, 1991)

Alkali metal intercalation compounds of β-ZrNCl were prepared by both chemical and electrochemical processes in tetrahydrofuran (THF) and propylene carbonate (PC), used as solvents. Among the six combinations of alkali metals (Li, Na, and K) with THF and PC, only the Na–THF system did not form a co-intercalation phase. In the other systems, the solvent molecules co-intercalated with alkali metals in mono- and double layer arrangements between the chloride layers of β-ZrNCl, the structures of which were estimated from one-dimensional electron distribution maps along the direction normal to the basal plane. The electrochemical characteristics of β-ZrNCl, used as the cathode of a lithium battery, were greatly influenced by the electrolyte solvent used. The co-intercalation mechanisms are discussed in terms of the energetics of the solvation of alkali metal ions with polar molecules and an expansion of the β-ZrNCl interlayers.

Lithium intercalations in layer-structured crystals have been extensively studied, since such crystals are promising candidates for the electrodes of secondary lithium batteries and electrochromic display (ECD) devices.[1,2] It is well-known that intercalated lithium atoms are ionized in interlayer spaces, and are often solvated with the polar organic solvents used in the preparation,[3]

$$[L] + x\mathrm{Li} + y(\mathrm{Solv}) \rightarrow \mathrm{Li}_x^{+}(\mathrm{Solv})_y[L]^{x-},$$

where [L] stands for layer-structured crystals such as transition metal dichalcogenides, iron chloride oxide, and graphite; Solv represents solvent molecules. Solvent molecules co-intercalated with lithium expand the basal spacing of the host layers. The degree of this expansion depends on the type of arrangement as well as the size of the molecules. Such an expansion of the interlayer spacing is considered to seriously influence the reversibility of lithium cells, since it may cause a mechanical disintegration of the electrode.[4]

β-ZrNCl is a layer-structured crystal. Each layer comprises a zirconium nitride double layer sandwiched between two close-packed chlorine layers. Such layered sequences (Cl–Zr–N–N–Zr–Cl) are stacked with each other by van der Waals interactions.[5] In a series of previous papers[6,7] we showed that β-ZrNCl is an interesting layered host for lithium intercalation, and could be used as a cathode material for the lithium battery and electrochromic devices, although the electrochemical characteristics of the electrodes are not yet satisfactory for practical use.[8] We also showed that β-ZrNCl readily forms co-intercalation phases with a variety of solvents such as THF, PC, acetonitrile, formamide, *N*,*N*-dimethylformamide, dimethyl sulfoxide, and pyridine.[7] It was considered that the formation of co-intercalation phases would have a bad influence on the performance of batteries.[9] A better understanding concerning the formation mechanism of the co-intercalation phases is indispensable for developing secondary batteries with high performance.

In this study we attempted to elucidate the formation mechanism of the co-intercalation phases of β-ZrNCl with THF and PC. The co-intercalation phases are prepared by both chemical and electrochemical processes by changing combinations of the alkali metals and solvents. The mechanisms are discussed in terms of the energetics of the solvation of alkali ions with the polar molecules and the expansion of the interlayer spacing of β-ZrNCl.

Experimental

Materials. β-ZrNCl was prepared by a reaction of $\mathrm{ZrH_2}$ with ammonium chloride in a stream of dry ammonia according to a method reported elsewhere.[10] Highly crystalline β-ZrNCl was prepared by a chemical transport method;[10,11] it was then ground and sieved through a 200 mesh screen.

THF was purified by refluxing with benzophenone and sodium followed by distillation, and then stored with a molecular sieve (4A). Three kinds of 0.1 M alkali dihydronaphthylide solutions (A–Naph, A=Li, Na, and K; 1 M=1 mol dm^{-3}) were prepared by dissolving equimolar amounts of naphthalene and the respective alkali metals into THF. After 20 h, each solution was filtered through a sintered glass filter in order to remove any insoluble impurities. PC was vacuum distilled and then dried with a molecular sieve (4A). The butyllithium (BuLi) used was a 15 wt% solution from Katayama Chemical. Anhydrous alkali perchlorates were dried by evacuation at 393 K for 12 h.

Chemical Intercalation. Lithium intercalation was carried out by reactions with BuLi and Li–Naph. In the case of the former reaction, only a lithium intercalated sample was obtained,[8] which was then soaked in THF and PC in order to convert it to the respective co-intercalation phases. Varying amounts (or volumes) of Li–Naph were added to β-ZrNCl. After being allowed to stand for 24 h at room temperatures, the lithiated samples were separated by filtration in an Ar-filled glove box (Vacuum Atmosphere Co.). Sodium and potassium intercalated samples were prepared by reactions with

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† Present address: Yonago National College of Technology, Hikona-cho, Yonago, Tottori 683.

Na– and K–Naph in a similar manner.

Electrochemical Intercalation. The β-ZrNCl powder sample was pressed onto a stainless-steel mesh of about 8 mm in diameter. Electrochemical cells were constructed by using the pressed sample as the cathode, an alkali metal foil as the anode and a glass filter separator soaked with 1 M Li and Na perchlorate solutions in THF and PC. A $KClO_4$/PC saturated solution was also used for the K/β-ZrNCl cell. The cells were galvanometrically discharged at a rate of 0.2 mA cm^{-2}, and the electrodes were taken out at different stages of discharge to measure the change in the basal spacing of β-ZrNCl.

Analyses. The X-ray powder diffraction (XRD) patterns of all the intercalated samples were measured under an argon atmosphere in a cylindrical cover having thin polyethylene windows by using nickel-filtered Cu $K\alpha$ radiation. The amounts of co-intercalated THF were determined from the weight loss before and after evacuation at 453 K. The amounts of alkali metals intercalated were determined by flame analysis after extraction by a procedure reported elsewhere.[8]

Results

Chemical Intercalation. The basal spacings (d) and some interlayer compositions of the chemical intercalation products are listed in Table 1. The lithium intercalate with a composition of $Li_{0.16}ZrNCl$ and a basal spacing of 0.93 nm was obtained by a reaction with a BuLi solution in hexane.[8] The nonpolar hexane molecules did not co-intercalate with lithium and, thus, the basal spacing is almost unchanged from that of the initial β-ZrNCl (d=0.92 nm). However, when the lithiated sample was dispersed in THF and PC, the basal spacing increased to 1.49 and 2.22 nm, respectively, although β-ZrNCl without lithium did not swell in these solvents. Li–Naph is a stronger reducing agent than BuLi[12] and, as shown in the table, larger amount of lithium can be intercalated by using an appropriate amount of Li–Naph. The amount of lithium intercalated increases with the amount of Li–Naph used.[9] Single-basal-spacing phases were obtained at x=0.18 and 0.20 (x in Li_xZrNCl), the amount of THF co-intercalated (y) being determined to be 0.25 and 0.35, respectively. Although the other products were mixtures of two or three phases with different basal spacing, the spacing appears to vary in the following order with increasing x:

Table 1. Basal Spacings and Interlayer Compositions of the Chemical Intercalation Products of β-ZrNCl

Reagents	Basal spacing (d) d/nm	Stoichiometry/ ZrNCl
(β-ZrNCl	0.92)	
BuLi	0.93	0.16Li
+THF[a]	1.49	0.16Li+yTHF
+$LiClO_4$/PC[a]	2.22	0.16Li+0.64PC
Li–Naph[b]		
1.0	1.49	0.18Li+0.28THF
1.2	1.49, 1.85	0.19Li+yTHF
1.5	1.85	0.20Li+0.35THF
2.0	1.85, 1.08	0.40Li+yTHF
10.0	2.00, 1.85, 1.08	0.85Li+yTHF
18.0	1.08, 2.00	1.20Li+yTHF
Na–Naph[b]		
0.90	0.99	0.40Na
+PC[c]	2.06	0.40Na+yPC
1.0	0.99, 1.06	0.48Na
1.5	1.06	0.75Na
K–Naph[b]		
0.25	1.47	0.20K+0.30THF
0.75	1.30	xK+yTHF
5	—[d]	

a) The lithiated samples by BuLi were immersed in THF or a $LiClO_4$/PC solution. b) Molar ratios of alkali-Naph/ZrNCl are given. c) The $Na_{0.40}ZrNCl$ sample was immersed in PC. d) Only the formation of KCl was observed by XRD analysis.

$$\begin{array}{ccccccccc} 0.92 & \rightarrow & 1.45 & \rightarrow & 1.85 & \rightarrow & 2.00 & \rightarrow & 1.08\ \mathrm{nm} \\ \beta\text{-ZrNCl} & & x=0.18 & & x=0.20 & & x=0.5 & & x>1.0 \end{array}$$

It is interesting to note that the spacing increases up to 2.00 nm with the amount of lithium intercalated and then collapses to 1.08 nm when the amount of lithium (x) exceeds about 1.0.

In reactions with Na–Naph, no co-intercalation phases were obtained; a sample with a small amount of Na showed a basal spacing of 0.99 nm. As the amount of intercalated Na increases, the 0.99 nm phase changes to a 1.08 nm phase. A sample $Na_{0.40}ZrNCl$ with a basal spacing of 0.99 nm swelled in PC and the spacing increased to 2.06 nm, though it did not form any co-intercalation phase with THF.

In the interlayer spaces between the chloride layers of β-ZrNCl, there are 1/2 octahedrally co-ordinated sites and one tetrahderally co-ordinated vacant site on the ZrNCl formula basis. The stoichiometry shown in Table 1 indicates the formation of intercalation phases with $x>0.5$ (x in A_xZrNCl; A=Li and Na); this suggests that alkali metals occupy the tetrahedral as well as the octahedral vacant sites.

K–Naph forms co-intercalation phases with basal spacings of 1.47 and 1.30 nm. If a much larger amount of K–Naph was used, the layer structured phase disappeared and the formation of KCl was observed by XRD analysis. After washing out the KCl with water, the residue was calcined at 1273 K in a vacuum. The resulting compound was found to be ZrN. This finding suggests that K–Naph is a stronger reducing agent than Li- and Na–Naph, so that β-ZrNCl is reduced to ZrN by the following equation:

$$\beta\text{-ZrNCl} + \text{K-Naph} \rightarrow \text{ZrN} + \text{KCl} + \text{Naph}.$$

Electrochemical Intercalation. The discharge curves of alkali/β-ZrNCl cells with THF and PC as electrolyte solvents are shown in Figs. 1 and 2, respectively. The discharges were stopped at different stages of current flow (Q) on separate samples, and the basal spacings of the β-ZrNCl cathodes were measured by an XRD analysis. The spacings listed in Table 2 are coincident with those of the samples obtained by the chemical intercalations up to the same intercalation level. It should be noted that in a battery system with Na–THF, no intercalation of THF occurred, even during the electrochemical process, as found in the chemical intercalation.

In a previous paper[8] it was revealed that in a battery of Li|LiClO$_4$/PC|β-ZrNCl, lithium could not intercalate over the stage of $x\approx0.16$. The current discharged over this stage was used for the decomposition of PC, rather than for Li intercalation; the discharge curve showed a plateau at about 1.0 V vs. Li/Li$^+$. Similar decompositions accompanied by plateaus in the discharge curves were observed for Na– and K–PC systems (Fig. 2). All of the β-ZrNCl cathodes taken out at a discharge level of x=0.10 had very large basal spacings of 2.00—2.22 nm, indicating that PC could co-intercalate with these three kinds of alkali metals in β-ZrNCl.

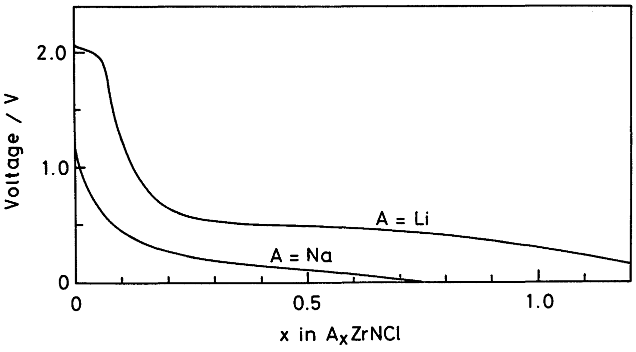

Fig. 1. Discharge curves for A|AClO$_4$/THF|β-ZrNCl cells (A=Li and Na) at a current density of 0.2 mA cm^{-2}.

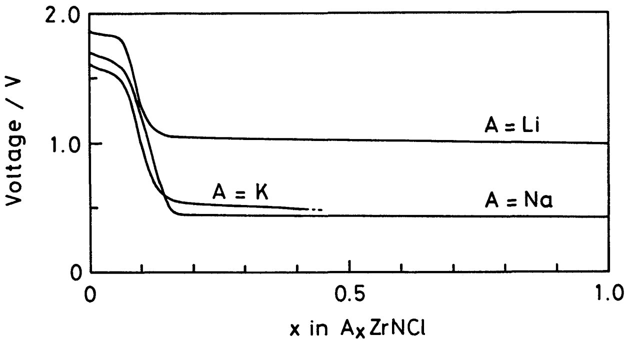

Fig. 2. Discharge curves for A|AClO$_4$/PC|β-ZrNCl cells (A=Li, Na, and K) at a current density of 0.2 mA cm^{-2}.

Interlayer Molecular Arrangements. Most of the co-intercalation phases are highly crystalline and basal reflections up to 12 orders were measured in each XRD pattern. One-dimensional electron-density distribution maps along a direction perpendicular to the basal plane were synthesized on the basis of the corrected reflection intensities on the following three samples; Li$_{0.18}$(THF)$_{0.28}$ZrNCl (d=1.49 nm), Li$_{0.20}$(THF)$_{0.35}$ZrNCl (d=1.85 nm), and Li$_{0.16}$(PC)$_{0.64}$ZrNCl (d=2.22 nm). The presence of a mirror plane was assumed, and the signs of the structural factors were determined on the basis of the β-ZrNCl host structure expanded along the c-axis. The synthesized electron distribution maps are shown in Figs. 3 and 4. The R factors were calculated to be within the range 0.18 to 0.23. The distributions of the figures clearly show that the co-intercalated molecules are located in the Cl···Cl interlayer spaces. In the co-intercalation phase with a smaller basal spacing of 1.49 nm, the THF molecules are oriented with the molecular planes almost perpendicular to the β-ZrNCl layers and in a monolayer arrangement; in the co-intercalation phases with basal spacings of about 2.0 nm, however, the THF and PC molecules are arranged in double layers. It is very likely that the lithium ions seem to be solvated by these molecules through the oxygen atoms.

Discussion

We have examined the intercalations of three kinds of alkali metals coupled with two kinds of solvents for each metal and found that the co-intercalation behaviors are very different, depending on the combinations. In electrochemical intercalations in systems with PC, intercalation compounds A$_x$(PC)$_y$ZrNCl with x>0.16

Table 2. Basal Spacings of the Electrochemical Intercalation Products of β-ZrNCl Separated at Different Stages of Discharge

Anode	Electrolyte	Amount discharged (Q) Q/e/ZrNCl	Basal spacing (d) d/nm
Li	1M LiClO$_4$/THF	0.18	1.49
		0.20	1.85
		1.20	2.00
Na	1M NaClO$_4$/THF	0.40	0.99
K	KClO$_4$ (Satd.)/PC	0.10	2.18
Li	1M LiClO$_4$/PC	0.10	2.22
Na	1M NaClO$_4$/PC	0.10	2.00

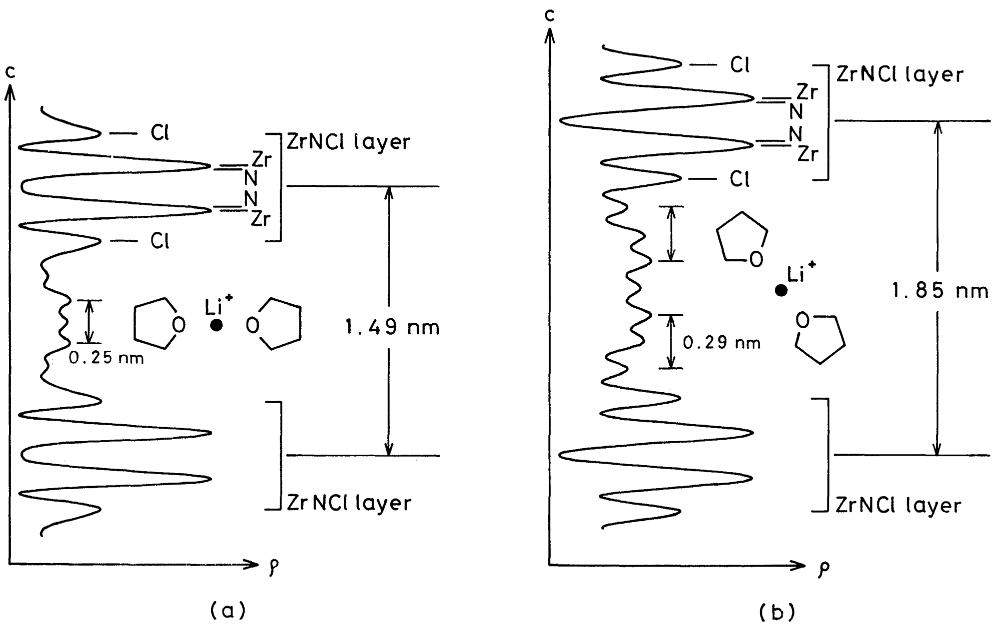

Fig. 3. One-demensional electron-density maps along the direction normal to the β-ZrNCl layers together with the estimated intrlayer molecular arrangements: (a) $Li_{0.18}(THF)_{0.28}ZrNCl$, (b) $Li_{0.20}(THF)_{0.35}ZrNCl$.

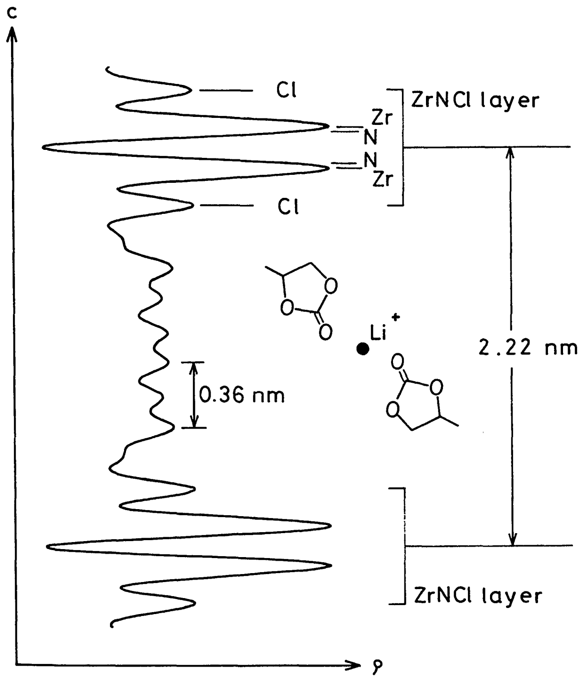

Fig. 4. One-dimensional electron-density map along the direction normal to the ZrNCl layers and the interlayer moleculer arrangement of $Li_{0.16}(PC)_{0.64}ZrNCl$.

were not formed; the current discharged over this point was used for the decomposition of PC rather than for a further intercalation of alkali metals. On the other hand, in electrochemical systems with THF, almost all of the current discharged was used for alkali metal intercalations without being accompanied by a decomposition of THF. In a previous study[8] concerning the characteristics of a $Li|LiClO_4/PC|\beta$-ZrNCl cell, it was expected that the presence of co-intercalated PC molecules in the interlayer spaces might prevent any further intercalation of Li into the interlayer spaces. However, from the comparison of the two electrochemical systems with PC and THF, it is evident that alkali metals can intercalate into the interlayer spaces of β-ZrNCl, even if the spaces are occupied by co-intercalated molecules. An electrochemical system containing PC seems to be rather a special case, in which the surface of the alkali intercalated β-ZrNCl catalyzes the decomposition of PC at relatively high voltages vs. Li^+/Li as seen in Fig. 2. In the case of the Na–THF–ZrNCl system, the intercalation compound Na_xZrNCl did not form any co-intercalation phase. Nevertheless, the cell $Na|NaClO_4/THF|\beta$-ZrNCl experienced a partial polarization for the discharge at the rate same as that used in the cell $Li|LiClO_4/THF|\beta$-ZrNCl, and showed low discharge voltages (Fig. 1). This finding also supports the above conclusion that the co-intercalated molecules do not necessarily hinder the diffusion of alkali metals into the interlayer spaces.

Among the combinations of three kinds of alkali metals (Li, Na, and K) with two kinds of polar solvents (THF and PC), only the Na–THF system does not form co-intercalation phases. In addition, in the Li–THF system, if a larger amount of Li was intercalated, the co-intercalation phase collapsed, releasing solvated THF molecules out of the interlayer spaces. The formation of co-intercalation or collapsed phases seems to be interpreted in terms of the energetics of the solvation of alkali ions with the polar molecules and an expansion of the interlayer spacing as follows:

In the course of intercalation, work must be done by the solvent molecules to make room in the interlayer spaces. The driving force for the intercalation is mainly due to dipole-cation interactions similar to those involved in the solvation of cations in an electrolyte solution. The co-intercalation occurs if such interactions between the polar solvent molecules and the ionized alkali metals in the interlayer spaces are sufficiently strong to compensate for the energy required for expanding the interlayers. The solvation energy or the work of ion dipole interaction ($W_{\text{I-D}}$) is given by the following equation:[13]

$$W_{\text{I-D}} = \frac{Nnz_ie}{(r_i+r_s)^2}\mu_s,$$

where N is Avogadro's number, n is the co-ordination number of the solvent, z_ie is the ionic charge, r_i and r_s are the ionic radius of alkali metals and the radius of the polar solvent, respectively, and μ_s is the dipole moment of solvent molecules. The finding that PC molecules can form co-intercalation phases with all kinds of alkali-intercalated ZrNCl can be interpreted in terms of its exceptionally large dipole moment (μ_s=4.94 D; D=3.3356×10^{-30} C m). THF has a much smaller dipole moment (μ_s=1.75 D), and the systems have a smaller $W_{\text{I-D}}$ than that of the corresponding PC systems. The $W_{\text{I-D}}$ decreases with an increase in the radius of interlayer cations. In THF-containing systems, although the $W_{\text{I-D}}$ decreases in the order Li>Na>K containing systems, only the Na intercalated β-ZrNCl does not form the co-intercalation phase. This suggests that the $W_{\text{I-D}}$ of the Na–THF system would not be large enough to overcome the energy required for the THF molecules to intercalate. The $W_{\text{I-D}}$ in the K–THF system is much smaller than that of Na–THF. However, the K ions are co-intercalated with THF molecules in β-ZrNCl. This can be explained by the large ionic size of K$^+$ as follows: the cation radius of K$^+$ is larger than that of Na$^+$ and the interlayer spacing supported by the K ions is correspondingly larger. Therefore, only a smaller amount of energy would be required for the THF molecules to expand the interlayer spaces in the K–THF system; the K ions can be regarded as acting as pillars.

The degree of interlayer space expansion due to co-intercalation would also be determined energetically. During the early stages of intercalation, the number of co-intercalated THF molecules increases with an increase in the number of intercalated lithium ions. During this procedure, even a small increase in the number of lithium ions causes a large change in the way the intercalated THF molecules are arranged, consequently, resulting in different expansions of the interlayer spacing (Fig. 3). However, if a much larger amount of lithium is intercalated, the electrostatic interactions between the negatively ionized layers and the lithium cations may exceed the solvation energy in the Li–THF system; even if lithium ions are present between the layers, the THF molecules are released out of the interlayer spaces.

This study was partly defrayed by the Grant-in-aid for Scientific Research on Priority Area of the Ministry of Education, Science and Culture.

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