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ABSTRACT. A layer structured crystal  $\beta$ -ZrNCl forms a lithium intercalation compound  $\text{Li}_x\text{ZrNCl}$ . The upper limit for  $x$  determined on the compound prepared by the *n*-butyl lithium technique is  $\approx 0.29$ . In the electrochemical process, a pressed  $\beta$ -ZrNCl cathode is further reduced up to  $x = 1 \sim 1.25$  at potentials as low as  $0.8 \sim 0.6$  V relative to  $\text{Li}/\text{Li}^+$ . The lithium intercalate swells in various polar solvents, increasing the basal spacing. However, in contrast to the salt-like intercalates of transition metal chalcogenides and  $\text{FeOCl}$ , the lithium intercalated  $\beta$ -ZrNCl does not form hydration phases, but reacts with water, evolving hydrogen. These results can be interpreted in terms of the formation of an alloy-like intercalate like the alkali intercalates of graphite. On intercalation,  $\beta$ -ZrNCl is changed from pale yellow-green to black in color, and the electrical conductivity increases by a factor of  $10^6$ .

## 1. INTRODUCTION

Inorganic host lattices which undergo reversible topotactic redox reactions are of interest as rechargeable electrodes for high energy density batteries and electrochromic display (ECD) electrodes. Examples which have been studied are layer structured transition metal dichalcogenides, transition metal trichalcogenides, iron oxychloride, transition metal oxides such as  $\text{WO}_3$ ,  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$  and others.<sup>(1)</sup> Guest species mainly focused in these topotactic reactions is lithium because of the small ionic radius of  $\text{Li}^+$ , high mobility of  $\text{Li}^+$  ions in the host lattices, and high free energy of formation of the complexes with the host lattices. Recently, we have reported in a brief communication that a new type of layer structured compound  $\beta$ -ZrNCl forms a lithium intercalation compound and shows electrochromic behavior.<sup>(2)</sup>

Zirconium nitride chloride  $\text{ZrNCl}$  has two polymorphs; low-temperature  $\alpha$  form with a  $\text{FeOCl}$  type layer structure and high-temperature  $\beta$  form with a  $\text{CdBr}_2$  type layer structure.<sup>(3) (4)</sup> The  $\alpha$  form is very unstable to hydrolysis and easily attacked by moisture in air, whereas the  $\beta$  form used is stable even in water. A schematic structural model of  $\beta$ -ZrNCl is shown in Figure 1. As seen from the figure, the zirconium

nitride layer occupies the equivalent site of  $\text{Cd}^{2+}$  in the  $\text{CdBr}_2$  structure and is sandwiched between two hexagonal close-packed chlorine layers. The stacking sequence of the  $\text{ZrNCl}$  layers are random like that of the bromide layers in the  $\text{CdBr}_2$  structure.

The present paper is concerned with the electrochemical intercalation process of lithium into  $\beta\text{-ZrNCl}$  and the swelling of the lithium intercalated  $\beta\text{-ZrNCl}$  in various nonaqueous solvents which are often used for electrolytes of lithium cells. Changes in the electrical conductivity on lithium intercalation are also mentioned.

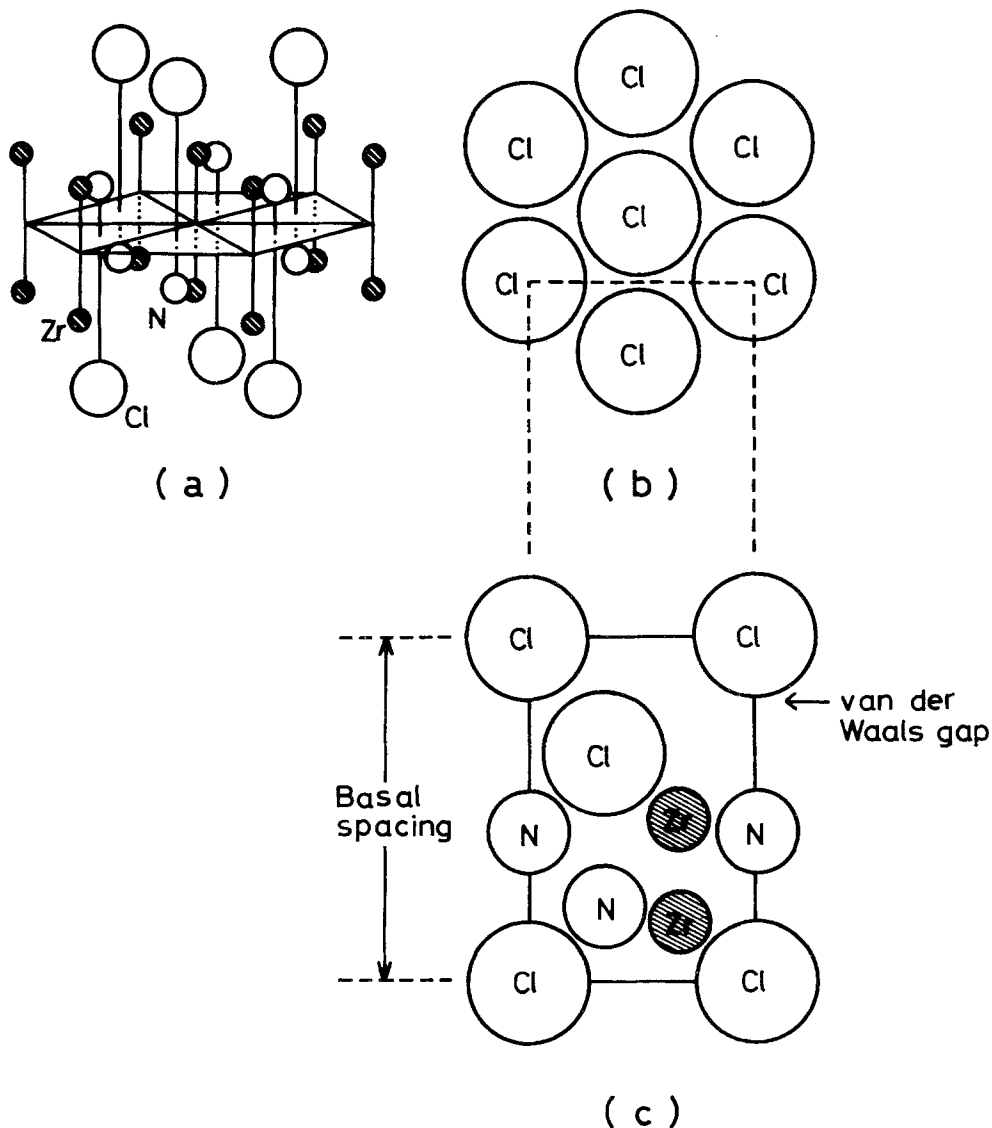


Figure 1. Schematic representation of the structure of  $\beta\text{-ZrNCl}$ . (a) perspective view, (b) viewed perpendicular to the close-packed chlorine layer, and (c) viewed parallel to the layers.

## 2. EXPERIMENTAL

### 2.1. Preparation of $\beta$ -ZrNCl

$\beta$ -Zirconium nitride chloride was prepared by the reaction of zirconium tetrachloride with ammonia at elevated temperatures according to a similar method reported by Juza and Hernalers.<sup>(3)</sup> The procedure was partly modified as follows; zirconium tetrachloride purified by sublimation was placed in a quartz tube installed horizontally in an electric furnace. A stream of dry ammonia was passed through the tube during the preparation. After the zirconium tetrachloride was left for an hour in the stream at room temperature, the temperature of the furnace was raised to 350°C and kept at this temperature for an hour to obtain  $\alpha$ -ZrNCl. Then, the temperature was raised again to 450°C and kept for an hour. Finally, the product was allowed to stand at 650°C for five hours in the ammonia stream in order to convert  $\alpha$ -ZrNCl to  $\beta$ -ZrNCl. Fine powder  $\beta$ -ZrNCl crystals of a pale yellow-green color were obtained.

### 2.2. Lithium Intercalation

The lithium intercalation compound of  $\beta$ -ZrNCl was prepared by the n-butyl lithium technique: the powder sample of  $\beta$ -ZrNCl was dispersed into a n-butyl lithium solution (15w/o in hexane) under a dry argon atmosphere. The sample was immediately colored black in the solution. After standing for 3 days, the colored sample was separated by filtration and washed with anhydrous hexane. The composition of the separated sample was determined to be  $\text{Li}_{0.29}\text{ZrNCl}$  by flame analysis.<sup>(2)</sup>

The electrochemical intercalation of lithium into  $\beta$ -ZrNCl was performed by constructing a cell with a pressed  $\beta$ -ZrNCl cathode and a lithium metal anode in 1 M  $\text{LiClO}_4$  solutions in tetrahydrofuran or propylene carbonate. Lithium perchlorate was vacuum-dried at 200°C for 20 h prior to the preparation of the electrolytes. The solvents used were purified by the procedure described in the following paragraph.

### 2.3. Swelling of the Lithium Intercalated $\beta$ -ZrNCl

Swelling of the lithium intercalated compound of  $\beta$ -ZrNCl in various nonaqueous solvents were studied. The compound used was prepared by the n-butyl lithium technique. Tetrahydrofuran (THF), acetonitrile (AN) and dimethyl sulfoxide (DMSO) were purified by refluxing with calcium hydride, followed by distillation. Propylene carbonate (PC), N,N-dimethylformamide (DMF) and pyridine (Py) were dried with molecular sieves (3A or 4A was used) and then distilled. Formamide (FA) was distilled under reduced pressure after neutralization with sodium hydroxide. The procedure was repeated until neutral distillate was obtained; the final distillation was carried out at temperatures below 80°C under a reduced pressure in the presence of sodium formate.

Since the lithium intercalation compound was very labile to water and oxygen, all the manipulations were done in a glove box filled with circulated and purified argon (< 20 ppm  $\text{O}_2$  and  $\text{H}_2\text{O}$  contaminations). Separate samples of the lithium intercalated  $\beta$ -ZrNCl were dispersed in

the above purified solvents for 24 h, and separated by filtration. The solvated samples were placed in a small compartment having thin polyethylene windows and filled with purified argon. X-ray investigations were performed by powder method in this compartment with nickel-filtered Cu K $\alpha$  radiation.

#### 2.4. Measurements of Electrical Conductivities

The electrical conductivities were measured by using a guard ring electrode on the  $\beta$ -ZrNCl samples pressed under a pressure of 100 MPa. Thin gold films were vacuum-evaporated onto the pressed sample as electrodes for the measurements. The lithium intercalated samples for the conductivity measurements were prepared by immersing another pressed  $\beta$ -ZrNCl into a n-butyl lithium solution (15w/o in hexane) for 3 days, followed by washing with anhydrous hexane. The conductivities of the intercalated samples were measured by the four-probe method.

### 3. RESULTS AND DISCUSSION

The electrochemical cell consisting of a pressed  $\beta$ -ZrNCl cathode coupled with a lithium anode was discharged at a constant current density of 200  $\mu\text{A}/\text{cm}^2$  in two kinds of electrolytes, 1 M LiClO $_4$ /THF and 1 M LiClO $_4$ /PC. Typical discharge curves are shown in Figure 2. Although the potentials are slightly different depending on the kind of electrolytes, the discharges proceed in two steps. In the first step in a range of the

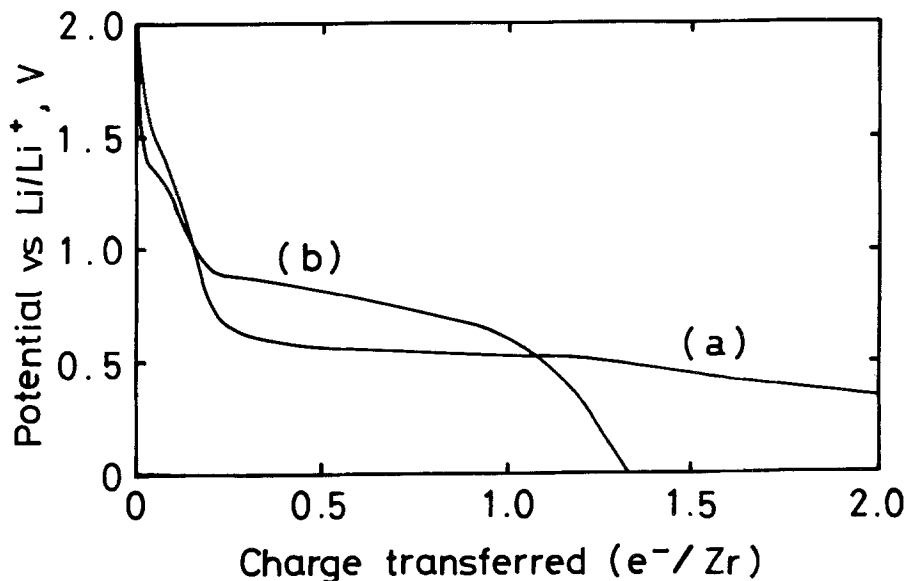
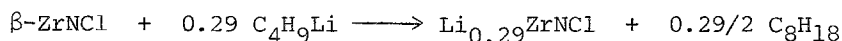


Figure 2. Typical discharge curves of the electrochemical cells at a current density of 200  $\mu\text{A}/\text{cm}^2$  in 1 M LiClO $_4$ /THF (a) and in 1 M LiClO $_4$ /PC (b).

charge transfer number  $x < 0.25$ , the potential decreases steeply from 2.0 to 0.8 ~ 0.6 V. In the second step in a range of  $0.25 < x < 1 \sim 1.25$ , the cells have low flat potentials at 0.6 ~ 0.8 V.

The upper limit for  $x$  of the lithium intercalated sample  $\text{Li}_x\text{ZrNCl}$  prepared by the reaction with *n*-butyl lithium was found to be 0.29:



This limit for  $x$  is almost comparable to the charge transferred by the first discharge step. *n*-Butyl lithium has a redox potential of about 1 V relative to  $\text{Li}/\text{Li}^+$ . This potential determines the upper limit of lithium intercalation by *n*-butyl lithium.<sup>(5)</sup> In the electrochemical process,  $\beta$ -ZrNCl can be further reduced and more than one equivalent of lithium can be intercalated in the interlayer spaces.

The basal spacing of  $\beta$ -ZrNCl is almost unchanged from the original 9.3 Å on lithium intercalation by the reaction with a *n*-butyl lithium solution in hexane. The lithium intercalated sample swells in various nonaqueous solvents, increasing the basal spacing as shown in TABLE I. Since the original  $\beta$ -ZrNCl does not swell in these solvents, the solvent molecules are presumably taken up by the solvation to the intercalated lithium. The samples solvated with FA, DMF and PC show particularly large increase in the basal spacing. These molecules seem to be accommodated in bilayers in the interlayer spaces.

It is well known that alkali metal intercalated transition metal chalcogenides and FeOCl form solvated phases even with water.<sup>(6) (7)</sup> On the contrary, when the lithium intercalated  $\beta$ -ZrNCl was placed in water, hydration did not occur, but the sample was bleached to the initial  $\beta$ -ZrNCl with the evolution of hydrogen, the intercalated lithium being released to the water.

Alkali intercalates can be classified into two groups<sup>(8)</sup>:

(i) alloy-like intercalates with very low free energies of formation such as the intercalates of graphite and (ii) salt-like intercalates

TABLE I. Basal spacings of the solvated lithium intercalates of  $\beta$ -ZrNCl.

Solvent	Basal spacing (Å)	Increase in basal spacing $\Delta d$ (Å)
( $\beta$ -ZrNCl )	9.3	
Tetrahydrofuran	13.5	4.2
Acetonitrile	12.9	3.6
Formamide	20.4	11.1
N,N-Dimethylformamide	19.7	10.4
Dimethyl sulfoxide	18.0	8.7
Propylene carbonate	23.3	14.0
Pyridine	15.7	6.4

with high free energies of formation such as the intercalates of transition metal dichalcogenides. In the intercalates of the latter group, the intercalated alkalis are almost completely ionized by donating the electrons to the host layers and behave like cations, whereas in the intercalates of the former group, the intercalated alkalis are partly ionized and retain the metallic activities to some extent. It should be noted that the discharge potentials shown in Figure 2 for  $\beta$ -ZrNCl are low compared with those ( $3 \sim 2$  V vs  $\text{Li}/\text{Li}^+$ ) for transition metal dichalcogenides and FeOCl, indicating that the intercalation compound is alloy-like. This is consistent with the above finding that the lithium intercalate of  $\beta$ -ZrNCl does not form hydrated phases.

Electrical conductivities were measured on  $\beta$ -ZrNCl and its lithium intercalate prepared by the n-butyl lithium technique. The typical values are shown in Figure 3 as a function of the reciprocal temperature. The original  $\beta$ -ZrNCl is an insulator having a conductivity of  $4 \times 10^{-7} \Omega^{-1}\text{cm}^{-1}$  at room temperature. The activation energy for the conduction is 0.28 eV. On intercalation, the pale yellow-green color of  $\beta$ -ZrNCl is changed to black; the conductivity increases by a factor of  $10^6$ . The temperature dependence of the conductivity becomes slightly negative. In a preliminary measurement on the lithium intercalate, we observed a smaller increase in the conductivity. (2)

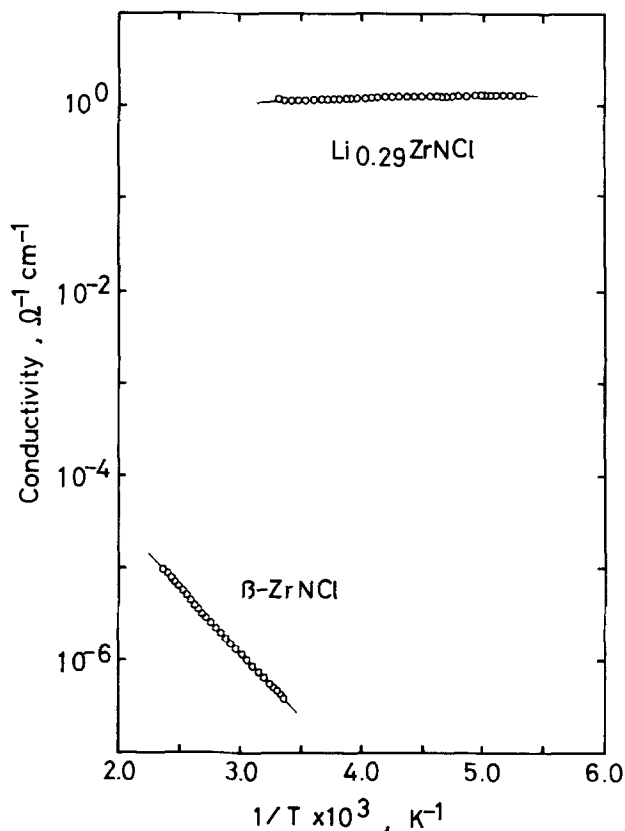


Figure 3. Electrical conductivities of the pressed  $\beta$ -ZrNCl and the lithium intercalated sample  $\text{Li}_{0.29}\text{ZrNCl}$  as a function of the reciprocal temperature.

Although the reason for the erroneous results is unknown, the smaller values would be caused by water contamination or inhomogeneous intercalation of lithium into the pressed  $\beta$ -ZrNCl.

It has been established that transition metal dichalcogenides and graphite show considerable changes in electrical and optical properties on intercalation of alkali metals and organic bases. The changes are attributed to the formation of the charge transfer complexes between the host layers and the interlayer electron donors. The large increase in the conductivity and the darkening in color observed for  $\beta$ -ZrNCl can be similarly interpreted in terms of a formation of conductive band by the electrons from the intercalated lithium donors.

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