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LITHIUM INTERCALATION AND ELECTROCHROMISM IN β-ZrNCl LAYERED CRYSTAL

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A layer structured crystal β-zirconium nitride chloride ZrNCl has been found to form a new lithium intercalate. The intercalation occurs either by the n-butyl lithium technique or by electrochemical redox reactions. The layer crystal exhibits electrochromic behavior on intercalation-deintercalation of the lithium.

Much attention has been paid to electrochromic materials because of potential application for display devices.[1)] A few kinds of transition-metal oxides have been investigated for such inorganic electrochromic materials. Among them, amorphous tungsten oxide is considered to be the most promissing candidate. Although attempts have been made to construct electrochromic display (ECD) cells by using tungsten oxide, new varieties of electrochromic materials are needed for the further development of this field. In the present study, a new type of layer structured crystal β-ZrNCl has been found to show electrochromic behavior on intercalation and deintercalation of lithium.

Zirconium nitride chloride has two polymorphs; low-temperature α form with a FeOCl type layer structure and high-temperature β form with a $CdBr_2$ type layer structure.[2,3)] The α form is very unstable to moisture in air, whereas the β form used in this study is stable even in water. A schematic structural model of β-ZrNCl is shown in Fig. 1. As seen from the figure, the zirconium nitride layer occupies the equivalent site of Cd^{2+} in the $CdBr_2$ structure and sandwiched between two hexagonal close-packed chloride layers. The stacking sequence of the ZrNCl layers are random like that of the bromide layers in the $CdBr_2$ structure.[3)]

β-Zirconium nitride chloride was prepared by the reaction of zirconium tetrachloride with a dry ammonia gas at elevated temperatures according to a similar method reported by Juza and Heners.[2)] The fine powder crystals obtained were of a pale yellow-green color. The apparent particle size was estimated from

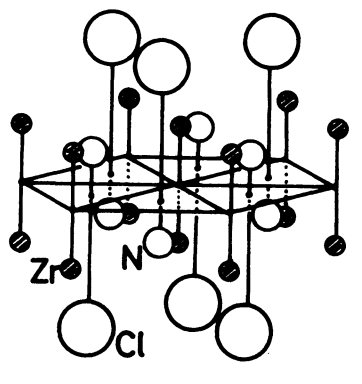

Fig. 1. Schematic structural model of β-ZrNCl.

the broadening of the X-ray powder pattern by using the Scherrer formula.[4] The dimensions were about 10 nm in thickness and about 30 nm in diameter. The composition of the product was determined by gravimetric analysis for zirconium content as ZrO_2, by the Kjeldahl and the Fajans' methods for nitrogen and chlorine contents, respectively. The chemical analyses gave a stoichiometric composition $Zr_1N_{0.96}Cl_{1.04}$ for the product.

The powder sample of β-ZrNCl was dispersed into a n-butyl lithium solution (15 w/o in hexane) under a dry argon atmosphere. The sample was immediately colored to black in the solution. The colored sample was separated by filtration and washed with anhydrous hexane. When water was added to the separated sample the color was bleached to the initial state with the evolution of hydrogen. The amount of lithium liberated to the water in the bleaching process was determined by flame analysis to be 0.29 equiv. on the ZrNCl formula basis. The X-ray powder pattern of the colored sample measured under a dry argon atmospher indicated that the basal spacing value was almost unchanged from 0.93 nm of the original β-ZrNCl. The sample bleached in water also showed the same spacing although a slight deterioration of the crystallization was observed. These results indicate that the lithium intercalation occurs according to the following equation;

$$\beta\text{-ZrNCl} + x\ n\text{-}C_4H_9Li \longrightarrow Li_xZrNCl + x/2\ C_8H_{18} \qquad (x = 0.29)$$

The intercalated lithium atoms seem to be accomodated in the interlayer octahedral vacant sites between the two adjacent close-packed chloride layers.

The electrical conductivities were measured on the β-ZrNCl sample compressed under a pressure of 100 MPa. The original β-ZrNCl has a conductivity of 4×10^{-7} $\Omega^{-1}cm^{-1}$ (measured by using a guard electrode). Another compressed sample was immersed into n-butyl lithium solution (15 w/o in hexane) and the conductivity was measured on the sample kept in the solution at room temperature by the four-probe technique. Figure 2 shows the change in conductivity as a function of the soaking time. The conductivity increases rapidly when the compressed sample is immersed in the solution, and with the prolonged soaking the value reaches a constant at about $1.5 \times 10^{-3}\ \Omega^{-1}\mathrm{cm}^{-1}$. It is interesting to note that the conductivity of the lithium intercalate is larger by a factor of $\approx 10^{4}$ than that of the original β-ZrNCl host layers. It is well known that layer structured compounds such as transition-metal dichalcogenides and graphite show considerable changes in electrical and optical properties on intercalation of alkali metals. The changes arise from 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 β-ZrNCl can also be interpreted in terms of the formation of a charge transfer complex between β-ZrNCl host layers and lithium electron donors.

In order to investigate the electrochemical intercalation of β-ZrNCl, the powder sample was supported on a platinum plate as follows: The powder was

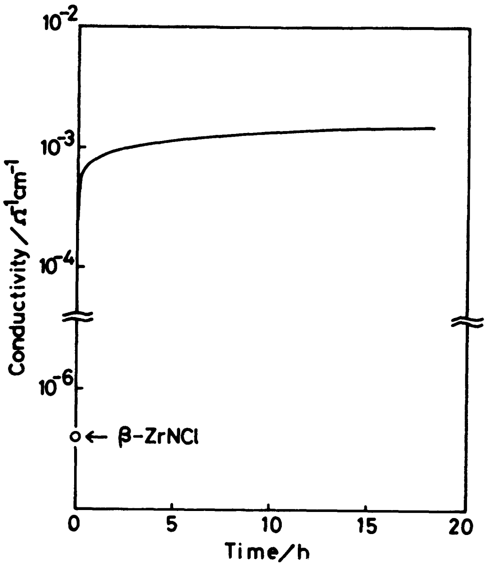

Fig. 2. Electrical conductivity of the compressed β-ZrNCl as a function of the soaking time in the n-butyl lithium solution.

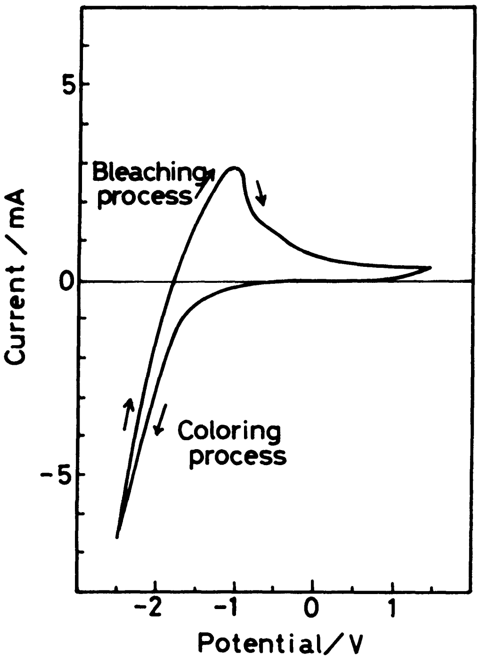

Fig. 3. Cyclic voltammogram of the β-ZrNCl thin film supported on a platinum plate in 1 $\mathrm{mol \cdot dm^{-3}}$ $LiClO_4$ tetrahydrofuran solution.

dispersed in a 1% polyvinyl alcohol aqueous solution and a platinum plate (2 x 1 cm^2) was covered with the dispersion in such a way that a uniform thin film was formed on evaporation of the water. The resulting thin film was heated at 110 °C for 15 h and used for a working electrode. The cyclic voltammetry of the film was performed by using a calomel reference electrode saturated with KCl and $KClO_4$ in 1 mol·dm^{-3} tetrahydrofuran, coupled with a platinum counter electrode in 1 mol·dm^{-3} $LiClO_4$ tetrahydrofuran electrolyte solution. Figure 3 shows the cyclic voltammogram measured for a sweep rate of 30 mV/s. The film on the platinum is colored to black during the reduction process starting at −2.0 V along with the increase in the reduction current. The color is bleached reversibly during the oxidation process starting at about −1.5 V. It is apparent that the reversible color change is brought about by the redox intercalation-deintercalation reactions:

$$\underset{\text{(pale yellow-green)}}{\beta\text{-ZrNCl}} + x\,Li^+ + x\,e^- \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} \underset{\text{(black)}}{Li_xZrNCl}$$

Detailed studies on the electrochromic characteristics of the film are now under way, and will be presented elsewhere.

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