ANODIC OXIDATION OF GRAPHITE IN $ZnCl_2$ - AQUEOUS SOLUTIONS

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INTRODUCTION

The mixing method [1] and the two-zone vapor method [2] are commonly used to synthesize $ZnCl_2$ - Graphite Intercalation Compounds (GICs) at elevated temperatures. Stumpp *et al.* synthesized $ZnCl_2$-GICs using an electrochemical method in a molten salt system of $ZnCl_2$-alkali metal chlorides [3]. Shioyama *et al.* investigated the synthesis of $FeCl_4^-$-GIC in an electrolyte in which $FeCl_3$ was dissolved in an aqueous solution of hydrochloric acid [4]. In this study, we synthesized $ZnCl_2$-GICs by the anodic oxidation of natural graphite using pure water as an electrolytic solvent. The electrochemical conditions for the GIC synthesis and corresponding GIC structure are investigated.

EXPERIMENTAL PROCEDURE

The host material used in the present work is natural graphite, with 99.9 wt.% carbon content. The graphite flakes have an average size of approximately 0.3mm in diameter . Zinc chloride with 98 wt.% purity was dissolved into distilled water as an electrolyte. The anodic oxidation process of graphite was performed in a three-electrodes cell which was maintained at 75°C by a water-bath. Natural graphite powder was surrounded by a platinum gauze and functioned as the host anode. Platinum sheet and the Saturated Calomel Electrode (SCE) were used as the counter and reference electrode, respectively. A Potentiostat / Galvanostat was used to perform chronoamperometry and chronopotentiometry. The initial concentration of $ZnCl_2$ in the electrolyte varied from 9 to 12 mole/liter. The potential and current density in the process ranged from 1.20 to 1.50V and from 15 to 50mA/cm^2, respectively. After reaction, the stage structures of products were characterized by powder X-ray diffraction and Raman spectrum.

RESULTS AND DISCUSSIONS

X-ray diffraction patterns and Raman spectra of the synthesized product indicate that the product is $ZnCl_2$-GIC. Figure 1 shows the typical patterns of stage 3 and 4. The c-axis repeat distance Ic of synthesized GICs and Raman frequency are listed in Table 1. Experimental results of synthesis are summarized in an electrochemical synthesis diagram in which domains of the GIC phase are plotted as a function of synthetic concentration and potential. In this diagram (Fig. 2), there are 4 domains: 1) Graphite zone in which no GIC was detected, 2) high stage (6 or 7) GIC and graphite co-exist zone; 3) the GIC zone in which low stage GIC is dominant; and 4) over potential zone in which the potential is high enough to cause side reactions dominating the electrochemical process. The boundary line between the graphite and GIC zones represents the thermodynamically conditions for GIC synthesis which are predicted by the modified Nernst' equation for electrochemical intercalation.

CONCLUSIONS

Stage 3 - 7 $ZnCl_2$-GICs were synthesized in the aqueous solutions by the anodic oxidation. The isothermal synthetic diagram as a function of electrolyte concentration and potential was determined experimentally.

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REFERENCES

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Table 1 Results of X-ray diffraction and Raman spectra

	Results of (oo*l*) X-ray diffraction				Frequencies of Raman	
Stage	$(00l)^{\#}$	$I_c / l(\mathring{A})$	FWHM$(^0)^*$	I_c Value $(\mathring{A})^@$	E^0_{2g2}	$\hat{E}_{2g2}$
3	005	3.2489	0.14	16.24(=9.54+2(3.35))	1588	1610
4	006	3.2641	0.18	19.58(=9.53+3(3.35))	1584	1606
5	007	3.2718	0.26	22.90(=9.50+4(3.35))	1582	1604
6	008	3.2765	0.16	26.21(=9.46+5(3.35))	1581.7	1600
7	009	3.2777	0.28	29.50(=9.40+6(3.35))	1581.3	1697

\# The Miller index of the strongest peak

* The full width at half maximum

@ I_c=ds+(n-1)C_0, C_0=3.35$\mathring{A}$

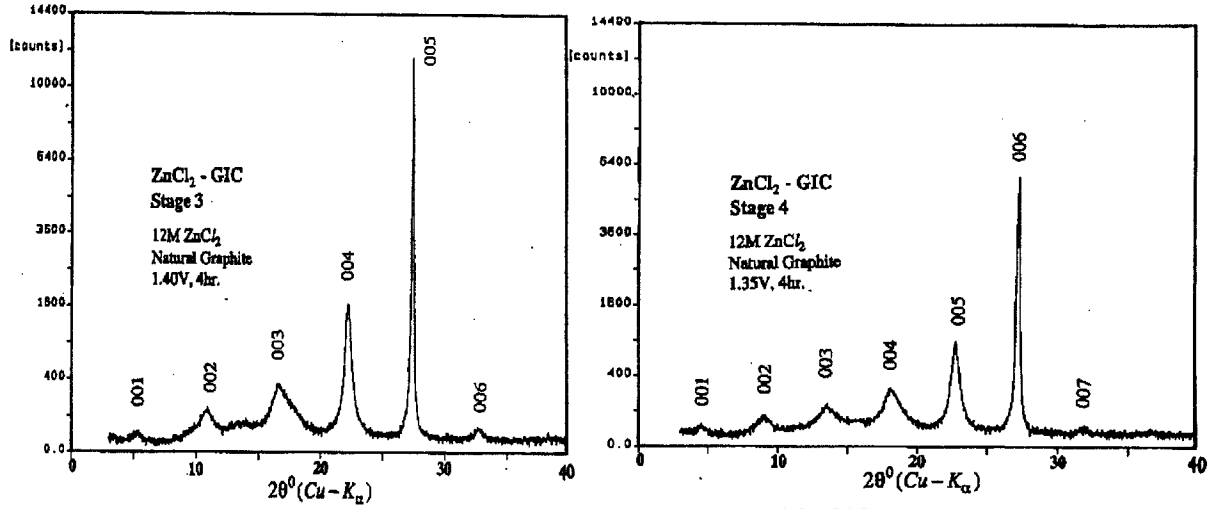

Fig.1 The X-ray diffraction patterns of stage 3 and 4 $ZnCl_2$-GICs

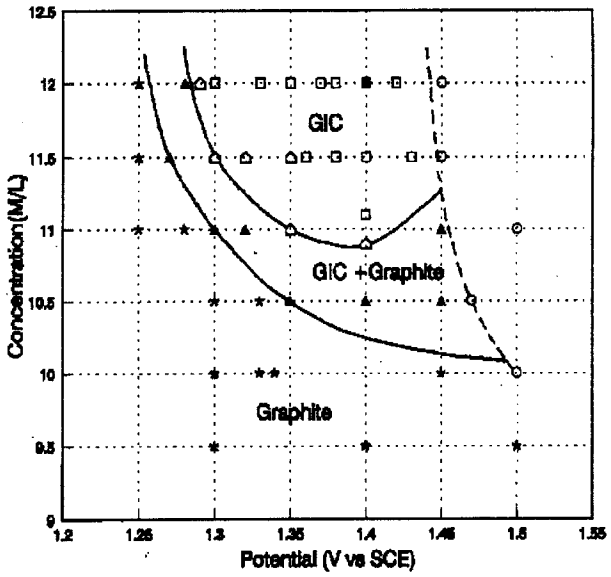

Fig.2 The concentration-potential diagram for electrochemical synthesis of $ZnCl_2$-GICs in aqueous solutions

■---Stage 3 GIC
□---Stage 4 GIC
⌂---Stage 5 GIC
▲---High stage GIC+G.
✱---Graphite (G.)
o---Oscillation