

# STABILITY OF GICs OF Cr<sup>VI</sup> COMPOUNDS

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## Introduction

Chromium ions with highest oxidation state of VI in CrO<sub>3</sub>-GICs have been found to be potentially useful in electrical and catalytical applications (1-3). There are many studies on the synthesis of the CrO<sub>3</sub>-GICs but no work has been reported on the stability of these GICs. In the recent study (4), stage-2 CrO<sub>3</sub>-GICs has been prepared by keeping CrO<sub>3</sub> and graphite in HCl at room temperature under atmospheric conditions. As knowledge on stability of these GICs is important information needed to develop their practical applications, present paper describes the chemical and thermal stability of these stage-2 CrO<sub>3</sub>-GICs.

## Experimental

Regent grade CrO<sub>3</sub> and HCl, and high purity natural graphite flakes of size 400 μm were mixed in the molar ratio of 1:2:1 in a flask and kept in open air at temperature for 15 days. The reaction products were washed with distilled water and then acetone to remove the unreacted CrO<sub>3</sub>. The stability of CrO<sub>3</sub>-GIC in solvents was evaluated by keeping the GICs in acetone, distilled water, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, for 15 days. Distilled water and acetone were selected in the present work because they are known to be good solvents for CrO<sub>3</sub>. Thermal stability of GICs was measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The stage structure of GICs and treated GICs were determined using X-ray diffraction.

## Results and Discussions

### Chemical stability

Fig.1 shows the XRD patterns of the prepared stage-2 CrO<sub>3</sub>-GIC having the I<sub>c</sub> value of 1.155 nm. Fig.1 also compares the change in XRD patterns of stage-2 CrO<sub>3</sub>-GIC after keeping GIC in liquids e.g. HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, acetone and distilled water for 15 days. GIC shows stability in acetone but slight change in position of XXRD peaks was observed ( Fig.1a). no appreciable deintercalation was shown by GIC after keeping in distilled water and nitric acid (Fig 1b and 1c) as

indicated by the appearance of very small and broad d<sub>002</sub> peak of graphite. However, GIC was fully deintercalated in presence of H<sub>2</sub>SO<sub>4</sub> as shown by the reappearance of sharp d<sub>002</sub> peak of graphite (Fig.1d) and disappearance of the peaks of CrO<sub>3</sub>-GICs.

Study shows that the GIC is highly stable in acetone, water and nitric acid in which CrO<sub>3</sub> itself is highly soluble. On the other hand, GIC is unstable in H<sub>2</sub>SO<sub>4</sub> which might be due to the penetration of H<sub>2</sub>SO<sub>4</sub> in the GIC layers, react with Cr<sup>VI</sup> and bring about deintercalation.

### Thermal stability

Stage-2 CrO<sub>3</sub>-GICs is found to be very stable in ambient air, as no change is observed in its I<sub>c</sub> value (1.155nm) even after storage for one year.

Fig. 2 shows the thermal degradation behaviour of stage-2 CrO<sub>3</sub>-GIC in presence of nitrogen and air using thermogravimetry. Similar behaviour of weight loss up to 600°C was shown by GIC in both the mediums. GIC shows high thermal stability up to 200 °C as only 4% weight was lost. This weight loss might be due to loss of water absorbed on the surface of the GIC. However, between 200°C and 300°C, a sharp weight loss of 17% is observed. Weight loss is similar in nitrogen and air. There is no heat flow or absorbed corresponding to the weight loss in TGA during this temperature range as shown by the DSC behaviour of GIC in Fig.3. The weight loss in this temperature range may be due to the loss of water, CO<sub>2</sub> and CO.

Weight loss is slowed down after 300°C and 12 % weight loss occurred up to 500°C in nitrogen and air atmosphere. High weight loss after 500°C in air may be due to oxidation of graphite.

A sharp exothermic peak of heat flow of 12KJ/gram is observed in DSC (Fig.3) in air atmosphere between 390°C and 500 °C. This peak is also observed in the presence of nitrogen but with much smaller heat flow of 90J/gram. Interestingly, this high heat flow is not associated with the any sudden weight loss in this temperature range in TGA (Fig.2). This suggests that the no major exfoliation occurred and this heat flow might be due to the change in oxidation state of chromium or change in stage structure of GIC. Further work on this is currently in progress.

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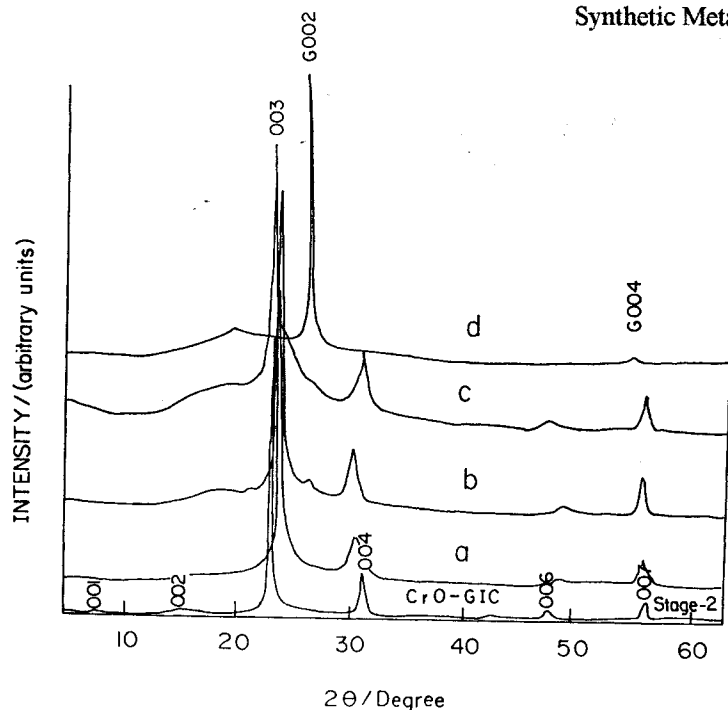


Fig.1 Changes in X-ray diffraction patterns of CrO<sub>3</sub>-GICs having stage-2 structure after keeping the GIC in various solvents for 15 days (a) acetone (b) HNO<sub>3</sub> (c) Water (d) H<sub>2</sub>SO<sub>4</sub>

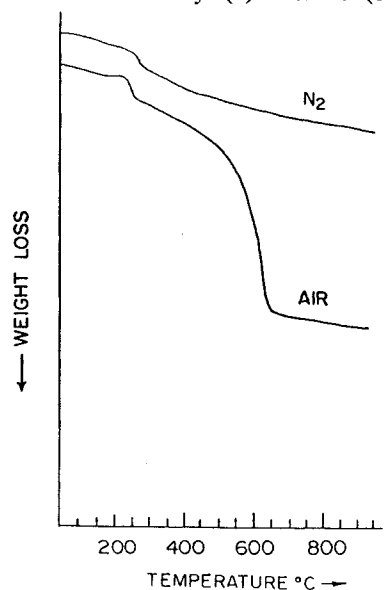


Fig.2 Thermal degradation behaviour of stage-2 CrO<sub>3</sub>-GIC in TGA under air and nitrogen atmosphere

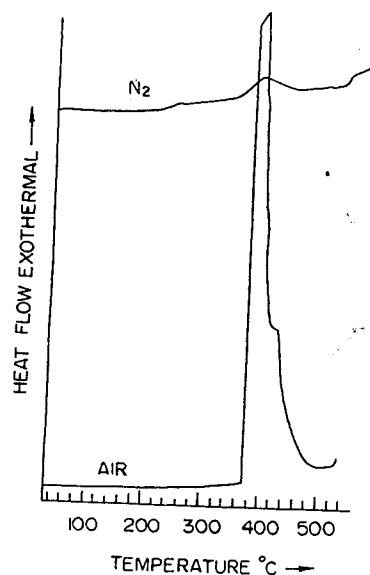


Fig.3 Heat flow behaviour of stage-2 CrO<sub>3</sub>-GIC during heating in DSC under air and nitrogen