PROCESSES AND PRODUCTS OF THE REACTIONS BETWEEN GRAPHITE FLUORIDE AND A FEW SELECTED METAL HALIDES

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INTRODUCTION

A recent study concluded that graphite fluoride reacted to $FeCl_3$ in the temperature range of 250-400°C. The products of this reaction may contain a large quantity of iron, with an iron to carbon ratio higher than that of any previously reported $FeCl_3$ intercalated graphite ($FeCl_3$-GIC) [1]. Reactions between graphite fluoride and metal halides (MX_n) other than $FeCl_3$ were subsequently investigated. It was hoped that similar reactions could be observed, and that the carbon products could contain metal with the highest possible concentration for applications typical for all GIC (e.g., manufacturing of batteries or catalysts).

Since intercalation is involved in these types of reactions [1], it was believed that the group of MX_n which can be intercalated with graphite and the group of MX_n which cannot, would react to CF_x differently.

The experiments described in this report are designed to investigate the hypothesis described above, and to study the role of intercalation in this type of reactions in general.

EXPERIMENTAL

Graphite fluoride was exposed to several different kinds of metal chlorides (MCl_n), which were chosen from the following 3 groups: the group which cannot be intercalated with graphite [2], the group which can be intercalated with graphite [2], and the group of pairs, each of which include one from the above two groups. Reactions of these three groups will be described separately and compared at the final part of this report.

The graphite fluoride used in this research was $CF_{0.68}$ made from graphitized carbon fibers P-100 [1,3]. The products of the reactions were analyzed by x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and weight analysis.

CF_x-MCl_n reactions where MCl_n cannot form GIC: $NiCl_2$, $PdCl_2$, and AgCl-AgI mixture

Exposing $CF_{0.68}$ fibers to these three samples at 350-400 °C in nitrogen did not cause any reaction to happen. The $CF_{0.68}$ simply defluorinated in the same way as it did in pure nitrogen at that temperature [3]. The AgCl-AgI used here was an equimolar mixture at 350°C. Even though it was in liquid phase under this condition, it did not wet the fibers and cannot form any chemical bonds to carbon during the defluorination of $CF_{0.68}$.

CF_x-MCl_n reactions where MCl_n can form GIC

In theory, the MCl_n-CF_x reaction is most spontaneous if the melting point (M.P.) and/or boiling point (B.P.) of the MCl_n are in 250-400°C range, above which CF_x decomposes explosively, below which the C-F bonding is strong. The $FeCl_3$-CF_x reaction described previously [1] meets this temperature criterion. For the following experiments, metal chlorides whose melting point and/or boiling point are not in this range are described separately.

1. $AlCl_3$ (sublimation point 178°C)

The $CF_{0.68}$ fibers were exposed to $AlCl_3$ vapors at 125°C for 10 hr, and then 190°C for 15 hr. The fiber product was coated by a heavy layer of salt, which was rinsed and dissolved easily in cold water. EDS shows a very large quantity of aluminum entered the fiber sample. The empirical formula was approximately $C_3AlF_{0.5}Cl_{0.5}$. XRD shows 3 low peaks, one for CF_x (9Å), one for either graphite or AlF_3 (3.55Å), and an unknown (2.97Å). This indicates incomplete defluorination and possibly some degree of intercalation.

This experimental result indicates that at low temperature (< 200°C), despite the strong C-F bonding, $AlCl_3$ can enter the CF_x molecular structure and force fluorine out. The strong affinity between $AlCl_3$ and the $CF_{0.68}$ fibers is further demonstrated when they reacted at 300°C. The fibers quickly packed with aluminum and, within 6 minutes, exfoliated. EDS data indicates the Al:C ratio for the exfoliated product is much higher than the 1:3 ratio described in the last paragraph.

2. $CuCl_2$ (M.P. 620°C, decomposed at 993°C)

$CuCl_2$ is selected for this study to test if it can react to CF_x at 250-400°C range. It is typically intercalated with graphitized carbon fibers at a high temperature: 480°C [4].

The $CF_{0.68}$ fibers were exposed to $CuCl_2$ in 310°C N_2 for 30 hr. The product contained CuF_2. In addition, it was partially intercalated with $CuCl_2$ (Stages 1 and 6, low XRD peaks). Its empirical formula was estimated to be $CF_{0.5}Cu_{0.2}Cl_{0.65}$. Again, a very high Cu:C ratio (1:5) was observed.

These results indicate that, comparing to graphite intercalation, MCl_n can be intercalated into the carbon structure in CF_x at a lower temperature.

3. $ZnCl_2$ (M.P. 283°C, B.P.732°C)
A $CF_{0.68}$ fiber sample was exposed to $ZnCl_2$ powder at 310°C in N_2 for 7 hr. The EDS data of the fiber product taken immediately after the reaction showed the fibers gained large quantity of $ZnCl_2$ but lost little fluorine. This fiber product was hygroscopic. After room temperture air exposure for 8 days, the moisture on the fiber surface was removed, and the sample was again examined. The EDS showed that the fibers lost most of its fluorine and some of its zinc and chlorine during the processes of air exposure and/or moisture removal. The XRD showed low and broad graphite peaks and very sharp ZnF_2 peaks, but no CF_x, $ZnCl_2$, or intercalation peaks. The low and broad graphite peaks suggest that some chemicals are located in the area between the graphite layers. These results are comparable to the results obtained from the CF_x-$FeCl_3$ reaction products [1].

For $ZnCl_2$, the boiling point is high, but the melting point is in the range where the C-F bonds in CF_x are weak. Therefore, the data described in the last paragraph suggest that molten metal chloride, if it can wet CF_x, may react to CF_x, regardless of the lacking of vaporous metal chloride.

<u>CF_x reactions to two metal chlorides, one ($CuCl_2$) can form GIC with graphite, the other ($PdCl_2$) cannot</u>
The $CF_{0.68}$ fibers were exposed to a mixture of $CuCl_2$ and $PdCl_2$ powder in N_2 at 310°C and 370°C for 40 hr and 10 hr, respectively. The product was examined after it was rinsed in cold water. It contained palladium (XRD data). The EDS showed the presence of copper and chlorine atoms, too. Subsequent heating in 1100°C for 1 hr resulted in $C_5PdCu_{0.15}Cl_{0.1}$. The XRD data show the palladium peaks and the two highest peaks for Cu_3Pd (Figure 1).

$CuCl_2$ apparently help $PdCl_2$ to enter the carbon fibers. It is possible that, similar to $PdCl_2$-Cl_2-graphite reaction [2], the actual element that activate $PdCl_2$ is chlorine gas generated during $CuCl_2$ decomposition.

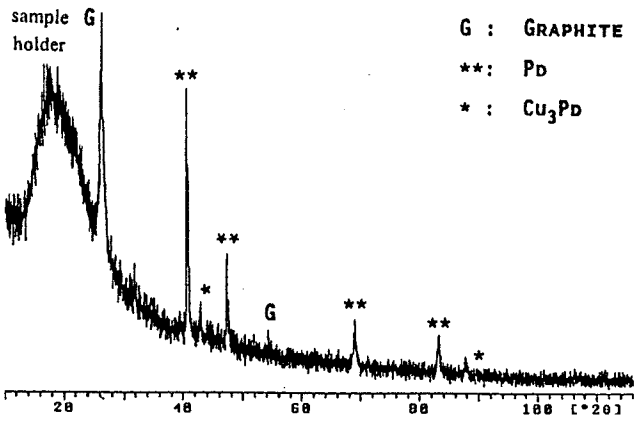

Figure 1. X-ray diffraction data from palladium-containing carbon fibers

CONCLUSIONS

All selected MCl_n which can form GIC with graphite reacted to CF_x, resulting in intercalated carbon-based products containing very high concentration of metal.

All selected MCl_n which cannot form GIC with graphite did not react to CF_x.

The MCl_n which is not reactive to CF_x may become reactive if additional metal chloride is also present in the environment. This is the case for $PdCl_2$ and $CuCl_2$, possibly due to the chlorine gas generated during $CuCl_2$ decomposition.

There may be exceptions of the above observations. However, at this time, these observations can be useful as guidelines to develop processes which produce carbon materials containing metal for the possible applications of battery or catalyst fabrications.

REFERENCE

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