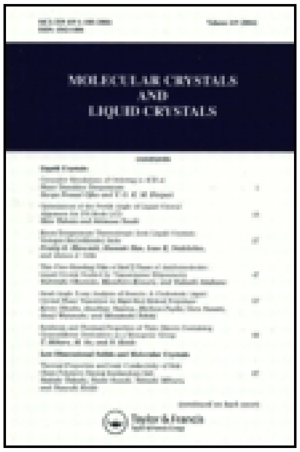

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Process of Intercalation of Manganese Chloride into Graphite Fibers and their Application in a Chemical Heat Pump

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Process of Intercalation of Manganese Chloride into Graphite Fibers and their Application in a Chemical Heat Pump

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First stage intercalation compounds of manganese chloride were obtained in graphite fibers owing to chemical vapor transport with gaseous heterocomplexes. These intercalated fibers used in a chemical heat pump for the reaction with ammonia gave better performance in energy and power.

Keywords: graphite fibers; intercalation; chemical heat pump; manganese chloride

INTRODUCTION

Carbon fibers are mainly used for the composite applications because of their high strength, low mass density, and also high electrical and thermal conductivities. Nevertheless, the intercalation of chemical species into fibers modifies the range of the properties of fibers, reducing the mechanical ones but increasing others. In particular, the chemical heat pump with ammonia systems are clearly enhanced by the use of metal chloride graphite fibers intercalation compounds (GFIC) instead of pure metal chloride, due to the improvement of the thermal and mass transfers[1].

The intercalation of chemical species into graphite fibers (GF) presents some difficulties and depends on different conditions :

• the degree of graphitization of the fiber : mesophase pitch based and vapor-grown carbon fibers are really better intercalated than the PAN ones. In the pitch based series, the well graphitized Amoco fibers are more easily intercalated.

• the nature of the intercalate : the obtaining of first stage GFIC has only been reached with alkali metals, though bromine intercalation has extensively been studied[2]. Acceptors as metal chlorides have been relatively less studied[2-8]. They generally give second stage GFIC except for vapor-grown fibers and in the case of arsenic pentafluoride acceptor.

• the method of intercalation : the two bulbs method is an excellent way in the case of the intercalation of alkali metals, but it does not give such good results with metal chlorides because of their low vapor pressures. It is known that the chemical vapor transport of metal chlorides can be strongly increased by the use of gaseous heterocomplexes[9,10]. This method has been used with success in several intercalations with graphite powders[11-15] and fibers[16,17] owing to Fe_2Cl_6, Al_2Cl_6 or possibly $CoCl_2$ as complexing gaseous species.

INTERCALATION INTO GRAPHITE FIBERS

Experimental

Carbon fibers were chosen between the pitch-based carbon fibers: Amoco P120, Amoco K1100 and Tonen FT700. Manganese, copper(II) and iron(II) chlorides were heated at 150°C for dehydration under vacuum before use. The fibers were placed in a Pyrex glass tube in presence of the mixed powders of manganese chloride and 10% iron(II) or copper(II) chloride. After a second dehydration which also allow the desizing of the fiber, the intercalation was performed under chlorine gas pressure (1 to 8 bars) at 500°C during about 5 days.

The $MnCl_2$-GFICs have been characterized by means of X ray diffractometry (CuKα), chemical analysis, diameter measurement, thermal conductivity and electrical resistivity

Reactions details

$MnCl_2$-$FeCl_3$ mixture

In the presence of chlorine, the iron(II) chloride is oxidized into iron(III) chloride. Then, the heterocomplexe is obtained according to[9] :

$$2\ FeCl_{3\,(S)} \Rightarrow Fe_2Cl_{6\,(G)} \qquad (1)$$

$$Fe_2Cl_{6\,(G)} + MnCl_{2\,(S)} \Rightarrow MnFe_2Cl_{8\,(G)} \qquad (2)$$

The thermodynamic values allow to calculate the vapor pressures of the different gases in equilibrium with the solid (Fig. 1). We can observe that for the selected intercalation temperature (500°C), the vapor pressure of $MnFe_2Cl_8$ complex is about 0.02 bar whereas pure $MnCl_2$ pressure is only 10^{-6} bar. Intercalation of the complex can already take place. Then, Fe_2Cl_6 being more volatile than $MnCl_2$, it can partially get out of the fiber so that the intercalated Mn/Fe ratio increases. In fact, Fe_2Cl_6 is used as a "taxi" in the chemical transport method.

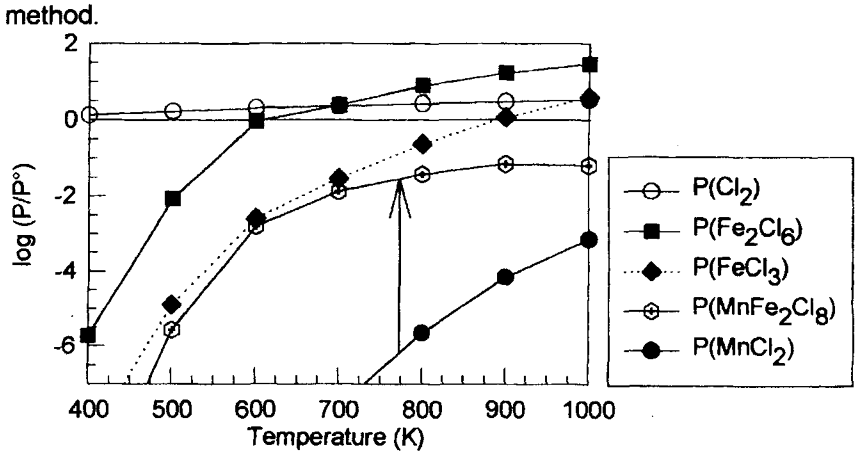

FIGURE 1 Calculated vapor pressure of $MnCl_2$ compared with its complex one in presence of an excess of $FeCl_{3\,(S)}$ under 1 bar of chlorine. The arrow indicates the $MnCl_2$ apparent volatility increasing.

$MnCl_2$-$CuCl_2$ mixture

In this mixture, several reactions can take place : .sublimations of $CuCl_{2\,(S)}$. into $CuCl_{2\,(G)}$ and of $MnCl_{2\,(S)}$ into $MnCl_{2\,(G)}$, decomposition of $CuCl_2$ into $CuCl_{(S)}$ and ½ $Cl_{2\,(G)}$. (this reaction is equilibrated at 480° under a chlorine pressure of 1 bar), trimerisation of $CuCl_{(S)}$ in Cu_3Cl_3 in the gas phase.

$CuCl_{2\,(G)}$ could form an heterocomplex with $MnCl_2$ as $MnCuCl_4$ (some $MCuCl_x$ complexes with M = Fe, Co, V... have been described).. Complexes of Cu_3Cl_3 with $MnCl_2$ can also be expected[10]. The intercalation mechanism should be chosen between a complex intercalation process, or a co-intercalation process ($CuCl_2$ being the first intercalated).

Results

The utilization of these gaseous complexes presents the following advantages for the manganese chloride intercalation : (i) a high reaction rate because of the high vapor pressure of the complexes, (ii) a good enrichment in the GFIC with $MnCl_2$ due to the enhancement of the mass transfer.

The progression of the reaction as a function of time was observed by the disappearance of the (002) graphite diffraction line. The (101) line completely disappeared which was usual for the GIC. But, the (100) line also disappeared which showed a high disorder increasing of the graphite planes orientation in the fibers. Stage 1 (with K1100) or a mixture of stages 1 and 2 (with P120) GFIC were obtained using the complexes method as we could see on the diffractometry results. Chemical analyses gave for example :

K1100:	P120:
$C_{5.2}Mn_{0.83}Fe_{0.17}Cl_{2.21}$	$C_{5.75}Mn_{0.76}Fe_{0.24}Cl_{2.19}$
$C_{2.97}Mn_{0.77}Cu_{0.23}Cl_{1.98}$	$C_{4.7}Mn_{0.75}Cu_{0.25}Cl_{2.31}$

The diameter increased from 10 µm for the pristine fiber to about 12.5 µm for the intercalated fiber. The thermal conductivity lost about 50% of the pristine graphite fibers ones (about 200 W/mK, value which was widely sufficient for the next application). The electrical resistivity decreased with a ratio of about 3.

APPLICATION TO CHEMICAL HEAT PUMP

The working[1,18] of the chemical heat pump is based on the reversible absorption solid-gas reaction placed in a reactor such as :

$$C_xMnCl_2(NH_3)_2 + 4\ NH_3 \Leftrightarrow C_xMnCl_2(NH_3)_6 \qquad (3)$$

The reaction is exothermic (~ -49 kJ/mol of NH_3 or 1590 kJ/kg of $MnCl_2$) and thus products heat. During this step, another reaction ($NH_{3\,(L)} \Leftrightarrow NH_{3\,(G)}$ takes place in the evaporator (connected to the reactor by a tube). This endothermic reaction (~ 20 kJ/NH_3 mol) supplies cold used for air conditioning, refrigeration...

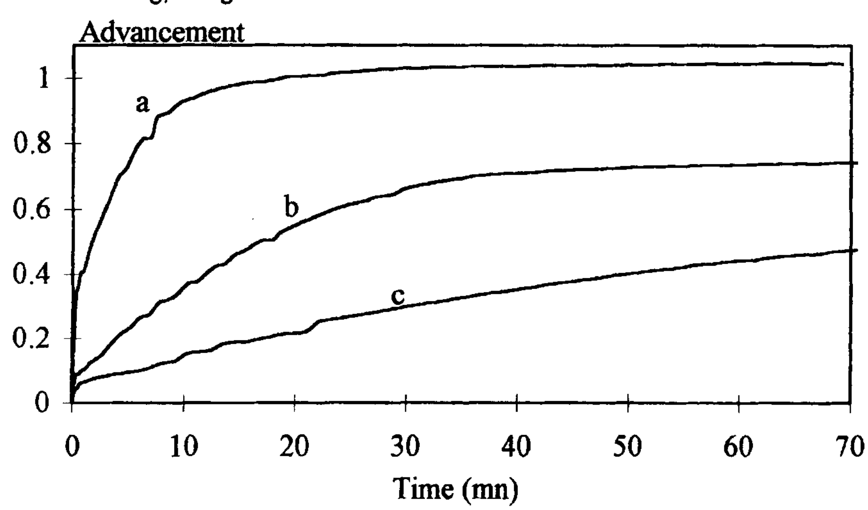

FIGURE 2 Advancement curves for the reaction (3) : a : (P120)GFIC ($C_{8.8}MnCl_2(FeCl_3)_x$); b: (FT700)GF and $MnCl_2$ powder ;c: pure $MnCl_2$.

The Fig. 2 presents the advancement curves as a function of time for different reagents. One can see the highest enhancement in kinetics with the use of (P120)GFIC due to the mass and thermal transfers. The energy yield is close to its maximum and the power very high.

CONCLUSION

Intercalation compounds of graphite fibers with manganese chloride gives promising applications of chemical heat pump systems for energetic production of heat and cold.

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