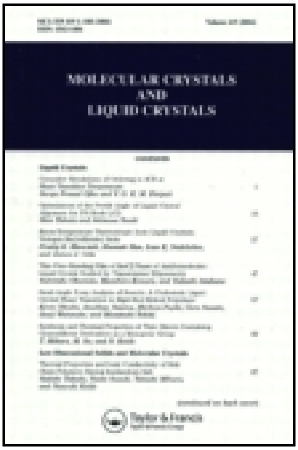

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Intercalation Reactions of Layered Manganese(III, IV) Oxides

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Intercalation Reactions of Layered Manganese(III,IV) Oxides

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Layered hydrated birnessite-type manganese oxides have been intercalated with *n*-alkylammonium ions by ion-exchange for interlayer sodium or potassium, and by acid-base reactions. The expanded phases have modified interlayer environments and can be used as precursors for intercalation of aniline, which is oxidised and polymerised between the layers.

Keywords: manganese oxide; birnessite; alkylammonium intercalates; polyaniline; nanocomposite electrode materials

INTRODUCTION

Ternary oxides A_xMnO_2 (A = Li, Na, K...) can adopt layered structures in which the alkali metal ions are located between sheets of edge-sharing [MnO_6] octahedra[1,2]. Owing to their open crystalline structure and the high redox potential of MnO_2 in relation to a lithium anode, these phases are highly attractive electrode materials for lithium batteries in which Li ions are reversibly intercalated between the layers[3-9].

Interleaving the layers of electro-active metal oxides with electronically conducting polymers can enhance the electronic conductivity of the host metal oxide and increase lithium mobility in the interlayer region, as well as introducing new properties such as hydrophobicity or additional redox capacity[10-12]. It would therefore be useful to prepare these kinds of composites with manganese oxides. Such hybrid materials with ordered nano-scale mixing of the polymer and metal oxide components may be prepared by exploiting the redox potential of the host to intercalate and polymerise *in situ*. An alternative approach is exfoliation of the metal oxide followed by re-stacking and encapsulation of a polymeric species. However both these methods require precursor host materials which can undergo expansion of the interlayer distance. Oxides such as MoO_3 and WO_3 can be pre-expanded by inserting lithium ions between the layers to give compounds which then absorb large amounts of water into the interlayer region[11]. $LiMO_2$ phases where M is a 3d element are typically non-hygroscopic[1], therefore an alternative approach is required for manganese oxide.

In this paper we describe the intercalation of layered MnO_2 compounds of the birnessite type with *n*-alkylammonium ions. This approach allows highly expanded phases to be obtained which have useful properties such as interlayer hydrophobicity and basicity. The compounds can then be exploited as precursors in the preparation of mixed polymer-oxide hybrid materials.

EXPERIMENTAL

Layered hydrated Na- and K-manganese oxides ("birnessites") were prepared by (i) slow addition of NaOH solution to a 1M solution of $MnCl_2$ to precipitate $Mn(OH)_2$, followed by oxidation with $NaMnO_4$[13], and (ii) hydrothermal decomposition of $NaMnO_4$ or $KMnO4$ in slightly acidified solution at 170 °C under autogeneous pressure[8,9]. H-birnessite was obtained by immersion of the Na compound in 1M HNO_3 for 5 days.

Intercalation compounds with *n*-alkylammonium ($3 \leq n \leq 10$) were obtained by equilibrating Na or K compounds in 0.5-1.0 M aqueous amine solutions acidified with HCl to pH7, or H-birnessite in 1 M acetone solutions, with an excess of amine/MnO_2. H-birnessite was also intercalated with propylamine by saturating with the vapour in a sealed dessicator at ambient temperature. Intercalation of (poly)aniline into decylammonium-expanded birnessite was achieved in 0.5-2 M solutions of aniline in acetonitrile.

Powder X-ray diffraction patterns were recorded on an automated Phillips diffractometer using Cu Kα radiation. Infrared data were obtained for samples dispersed in KBr using a Bomem DA8 FTIR spectrometer.

RESULTS AND DISCUSSION

Preparation of Alkylammonium Intercalates

The powder X-ray diffraction (XRD) patterns of the as-prepared A_xMnO_2 compounds (x = *ca.* 0.3, varying slightly for different preparations) were dominated in each case by two major peaks at *ca.* 7.2 Å and 3.6 Å, characteristic of synthetic birnessites containing alkali metal cations and a single sheet of water molecules between MnO_2 layers[2]. The XRD patterns of Na-birnessite prepared by method (i) and K-birnessite prepared by method (ii) are shown in Figure 1. The Na-birnessite prepared by the precipitation-oxidation method had a monoclinic structure, while the products of the autoclave method were hexagonal, in agreement with previously reported data[8,9].

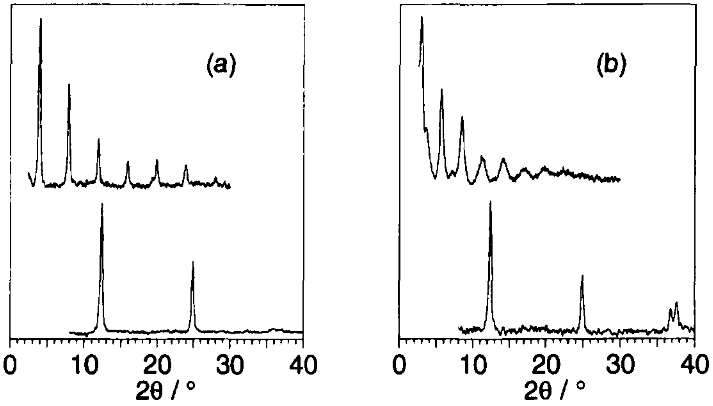

FIGURE 1 X-ray diffraction patterns of (a) Na-birnessite (precipitation-oxidation method), (b) K-birnessite (autoclave), and the respective decylammonium-exchanged products.

The 7 Å interlayer distance of birnessite phases may swell in aqueous solution to *ca.* 10 Å with insertion of a second layer of water molecules, facilitating exchange of the Na or K with alkylammonium ions[15]. After exchange the samples retained their crystallinity and peaks corresponding to an integral series of [001] interferences were observed, corresponding to expanded interlayer spacings. Spectrophotometric analysis for Na/K content and thermal analysis to determine the % organic content showed that stoichiometric exchange of alkylammonium ions for Na or K took place, giving intercalates of composition $(C_nH_{2n+1}NH_4)_xMnO_2$ in which $x = ca.$ 0.30. Infrared spectroscopy confirmed the presence of alkylammonium ions hydrogen-bonded to the MnO_2 sheets via the $-NH_3^+$ group and, particularly in the case of the longer-chain alkylammoniums, indicated that water had been mostly expelled from the interlayer regions.

The basal spacings of the alkylammonium intercalates, with the exception of the decylammonium-exchanged product of the monoclinic Na-birnessite obtained by method (i), increased linearly from propylammonium to decylammmonium by *ca.* 2.5 Å for each additional $-CH_2-$ group in the alkyl chain. This indicates the formation of well-organised layers of guest molecules.

Alkyl chain lengths increase by 1.27 Å per -CH_2-, therefore the increase in basal spacing for the MnO_2 compounds is consistent with a bilayer of guest molecules in extended conformation between the layers. The intercept at $n = 0$ is at *ca.* 6.2 Å. The layer thickness of ammonium-exchanged birnessite is 7.2 Å, therefore it is likely that the axes of the alkyl chains are inclined with respect to the MnO_2 sheets by an angle of *ca.* 60°, close to the value of 55° observed for some clays and for transition metal phosphates[14]. This conformation arises from the natural inclination of a trans-trans alkyl chain if the N-C bond is normal to the surface of the layers. A schematic representation of this structural model is shown in Figure 2 for propylamine.

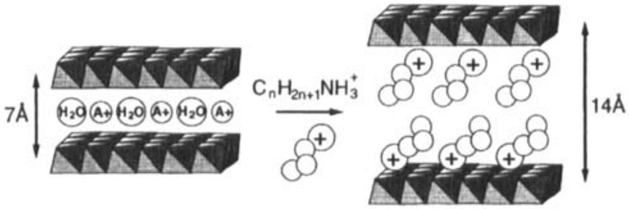

FIGURE 2 Proposed bilayer structure of alklammonium MnO_2 intercalate.

The decylammonium-exchanged products of Na-birnessite prepared by the precipitation-oxidation method (Figure 1(a)) had an interlayer spacing of only 22.2 Å, not correlating with the linear relation found for the other alkylammonium intercalates. The smaller basal spacing corresponds better to data for *n*-alkylammonium complexes with $n \geq 12$ reported by Golden *et al.*[15], who observed interlayer distances consistent with formation of interpenetrating monolayers of extended alkyl chains. The cross-sectional area of a trans-trans alkyl chain is *ca.* 20 Å^2, and packing densities of > 4 alkymines per 100 Å^2 are observed for α-$Zr(HPO_4)_2$ and some clays[14]. However the packing density of the bilayers of alkylamines in the MnO_2 compounds is lower, < 3 alkyl chains per 100 Å^2, comparable to that observed for alkylamines in γ-$Zr(HPO_4)_2$. Conformational changes in the alkyl chains and hence phase transitions in the structures of the bilayers might therefore be expected in the MnO_2 amine intercalates, particularly for the longer-chain species ($n \geq 10$).

However, although a small amount of 22 Å phase is visible in the XRD pattern of the intercalated K-birnessite autoclave product (Figure 1(b)), the autoclave birnessites consistently gave predominantly 31.5 Å phases with decylammonium, in contrast to the birnessites obtained by method (i). The amount of interlayer decylammonium in the two cases was found to be approximately the same, and constant despite variations in the saturating conditions. The difference in behaviour may be related to the different crystal symmetries of the birnessites, monoclinic and hexagonal, but it would be surprising that differences in the orientations of the layers before exchange should have such an effect on the structures of the expanded phases. An alternative explanation is that the charge densities may differ between the birnessites due to differences in the number of manganese vacancies and Mn^{4+}/Mn^{3+} ratios in the MnO_2 sheets. Large variations in these parameters are known to occur for birnessite-type compounds depending on the synthesis conditions[2]. Further investigations are under way with longer chain ($n > 10$) amines.

Intercalation of neutral alkylamines in vapour phase and non-protonating solvents was also achieved by acid-base reaction with H-birnessite. Infrared spectra showed formation of alkylammonium between the layers by reaction with the interlayer proton. The interlayer distances were identical to those obtained by ion-exchange correlating with the bilayer model. It is interesting to note that a 32 Å phase was obtained with decylamine in the H-birnessite prepared from the Na-birnessite of method (i). This suggests changes in charge density with the acid treatment, and may also be correlated with a phase change from monoclinic to hexagonal birnessite which is observed on removal of the interlayer sodium.

Intercalation of Polyaniline

The highly expanded decylammonium-MnO_2 intercalates are suitable precursors for preparation of polymer-MnO_2 hybrids. The modified interlayer environment may be exploited to induce exfoliation or for intercalative polymerisation reactions. We present here an example for *in situ* oxidative polymerisation-intercalation of aniline.

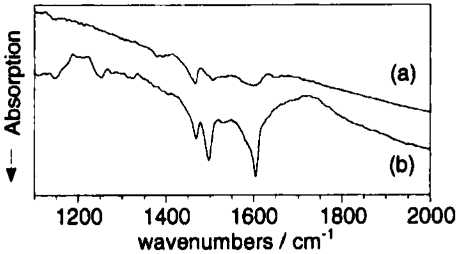

FIGURE 3 Infrared spectra of (a) decylammonium-MnO_2 and (b) the polyaniline-intercalated product.

Attempts to intercalate aniline into birnessite without a prior modification of the host lattice resulted in polymerisation of aniline at the oxide surface and gave amorphous products. However aniline was intercalated into decylammonium-expanded birnessite with preservation of a layered structure. The interlayer decylammonium in this case not only provides an open hydrophobic space but also creates a less acidic environment which prevents destructive hydrolysis of the MnO_2 host by the aniline. The infrared spectrum in the region 1200-1800 cm^{-1} is compared with that of the decylammonium-expanded precursor in Figure 3. The bands corresponding to polyaniline can be attributed to oligomers of the emeraldine base form[16], confirming that oxidation by the MnO_2 host occured during intercalation. Further chemical analysis and conductivity measurements are under way to characterise these polyaniline-MnO_2 hybrid materials; the results will be reported separately.

Acknowledgements

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