INFLUENCE OF TEMPERATURE AND HUMIDITY ON IONIC CONDUCTION OF MIXED METAL HYDROXIDES

P. PERNICE, O. MARINO and G. MASCOLO

Dipartimento di Ingegneria dei Materiali e della Produzione, Università di Napoli (Italia)

ABSTRACT

Results of conductivity (ac) measurements are reported for synthetic mixed metal hydroxides as a function of temperature, ranging from 323 to 353°K, and relative humidity, ranging from 50 to 80%.

The polycrystalline compacts of layered mixed hydroxides show protonic conductivities arising from the interlayer region.

The conductivity is strongly dependent on the temperature, relative humidity and composition of mixed metal hydroxides.

The conductivities are anisotropic with the direction of forming pressure owing to the preferential orientation of lamellar crystals, particularly evident with powders characterized by high crystal size.
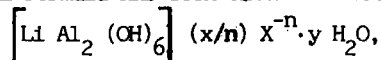
INTRODUCTION

Mixed metal hydroxides may be represented by the general formula:

$$\left[M(II)_{1-x}M(III)_x(OH)_2\right]^{+x} (x/n)\ X^{-n} \cdot yH_2O,$$
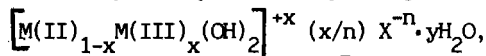
where M(II)=Mg, Zn, Ca...; M(III)=Al, Cr...; $X^{-n}=CO_3$, OH...; n=anionic charge. The M(II)/M(III) ratio changes between 1 to 5 with preferential values of 2 and 3. The above general formula has been extended including also:

$$\left[Li\ Al_2\ (OH)_6\right] (x/n)\ X^{-n} \cdot y\ H_2O,$$

a hydrocalcite-like compound with a monovalent cation (1).

The structure of such layered compounds has been reviewed by Allmann (2)

and Taylor (3). It consists of positively-charged layers:

$$\left[M(II)_{1-x} \ M(III) \ (OH)_2 \right]^{+x}$$
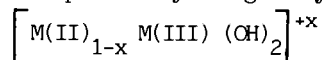
with or without ordered cations balanced by an equivalent negative charge $(x/n) \ X^{-n} \cdot yH_2O$ coming from interlayers anions; water molecules are also present.

Actually there is a high interest in these materials for use in the areas of catalysis, anionic exchange, ionic conduction, etc.

The high protonic conduction of Zr-Cr hydroxide (4) with $X^{-n}=OH^-$ has been explained by the presence of the OH^-/H_2O species of interlayer through which protons could move by Grotthus mechanism.

Anionic conduction with values ranging between 10^{-3} to $10^{-4} \Omega^{-1} \cdot cm^{-1}$ were also observed on compacts of $\left[Zn_2 \ Cr \ (OH)_6 \right]^+ \ X^- \cdot yH_2O$ with interleaved anions such as F^-, Cl^-, Br^- etc. (5).

Compounds belonging to Ca-Al hydroxide intercalated with different anions exibited conductivities depending on either the intercalated anion and/or the relative humidity (6). This behaviour closely resembles that of other layered materials (7-10).

In this paper the a.c. conductivity measurements carried out on double hydroxides belonging to Li-Al, Ca-Al and Mg-Al pairs are reported. Complex impedance as a function of temperature, ranging from 50 to 80°C, and relative humidity, ranging from 50 to 80%, were measured on polycrystalline compacts of such compounds.

EXPERIMENTAL

Mixed metal hydroxides of composition $\left[Li \ Al_2 \ (OH)_6 \right] OH \cdot 2H_2O$, $\left[Ca_2 \ Al \ (OH)_6 \right] OH \cdot 2H_2O$, $\left[Mg_2 \ Al \ (OH)_6 \right] OH \ 1.5H_2O$ and $\left[Mg_3 \ Al \ (OH)_8 \right] OH \cdot 2.25H_2O$ were prepared according to previous papers (11-13).

Samples for conductivity measurements were obtained by pressing the powder at 40MPa into pellets 6÷10mm thick, 16mm long and 8mm wide. For each mixed hydroxide two specimens were prepared: one obtained by coating with a silver paint the opposite faces parallel to the forming pressure, the other one by coating the faces perpendicular to the forming pressure. The a.c. conductivities were measured in the range $10^2 \div 6 \cdot 10^4$ Hz with a Solartron 1250FRA and a Solartron 1286 electrochemical interface connected to a HP 86B desktop computer. The silver-coated faces of the pellets were connected with copper

wires. This arrangement was sealed into an Erlenmeyer flask containing appropriate saturated solutions on which the samples were equilibrated at a constant value of relative humidity. The cells were thermostated in an oven with temperature regulation. Before each measurement in controlled hygrometry and temperature the samples were equilibrated for several days.

RESULTS AND DISCUSSION

Table 1 illustrates the crystal size and morphology of the mixed hydroxides as a function of the composition. All samples have been obtained through a hydrothermal treatment at $50^{\circ}C$ with the exception of Ca-Al hydroxide which forms at lower temperature ($25^{\circ}C$).

A characteristic of such hydroxides is the predominant growth of the crystals on the edges giving hexagonal-plate crystals having comparatively little thickness parallel to its principal axis (c-axis).

TABLE 1

Crystal size and morphology of mixed metal hydroxides

| Composition	Mg/Al=2	Mg/Al=3	Ca/Al=2	Li/Al=0.5
Temperature of the hydrothermal treatment ($^{\circ}C$)	50	50	25	50
Morphology	A	A	B	A
Size of platelets (μm)				
width	0.5	0.3	6	0.8
tickness	$<$ 0.1	$<$ 0.1	0.3	$<$ 0.1

A= Pisolitic aggregates of thin platelets
B= Hexagonal platelets

Ca-Al hydroxide resulted in well defined hexagonal crystals unlike the other mixed hydroxides that showed thin, poorly crystallized platelets.

The conductivities were measured from typical impedance plots in which an arc is present at high and medium frequencies, while an almost linear region is seen in the low frequency part of the plot, probably related to electrode

polarization. This trend does not change substantially with the various parameters considered such as composition of the samples, temperature and degree of humidity. The relative d.c. resistance of the bulk samples was obtained by the extrapolation of the arc on the real-impedance axis. The a.c. conductivity so measured on pellets gradually dropped to lower values due to the carbonation of the samples during the exposure to air. The interlayer OH groups of the samples are, in fact, easily converted into carbonate anions that, according to the following reaction, are held very tenaciously:

$$OH^- \cdot yH_2O + (1/2)CO_2 \text{ ------} \rightarrow (1/2)CO_3^{-2} \cdot (y-0.5)H_2O + 0.5H_2O.$$
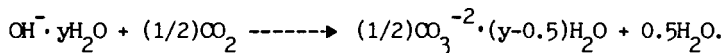
This reaction reduces the intercalated water molecules as was observed for Mg-Al hydroxide (14). This behaviour is confirmed for both Li-Al and Ca-Al hydroxides too. In fact in DTA curves of plain hydroxide, partly and fully carbonated forms of Li-Al hydroxides, the endothermic peak at lower temperature ($\simeq 200°C$), related to the loss of the intercalated H_2O molecules, gradually disappears with the degree of carbonation (fig.1).
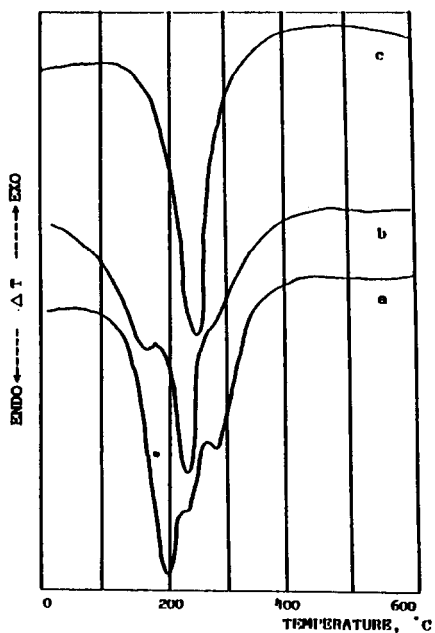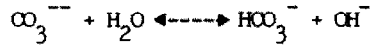

Fig. 1. DTA curves of Li-Al hydroxide at different degrees of carbonation; a,b and c: fully hydroxide, partly carbonated (20%) and fully carbonated forms.

A further reduction of the intercalated H_2O molecules may be related to the following chemical equilibrium, through a proton transfer, among the various anions of the interlayer:

$$CO_3^{--} + H_2O \longleftrightarrow HCO_3^- + OH^-$$

This hypothesis agrees with the contemporaneous presence of carbonate and bicarbonate ions observed from IR spectra of carbonate form of Li-Al hydroxide (15). The reduction of both H_2O molecules and/or concentration of the anionic species of the interlayer decreases the probability of protons jumping from H_2O to anions so reducing the conductivity as carbonation occurs. The a.c. conductivities, here reported, refer, consequently, to fully carbonated samples, the stablest form in air of mixed metal hydroxides.

Fig.2 summarizes the complex of the resulting a.c. conductivities of the samples as a function of composition, degree of humidity and temperature. It can be seen that the temperature dependences of the conductivities are of the Arrhenius type. The composition of the mixed hydroxides and relative humidity play an important role on the conductivity values.
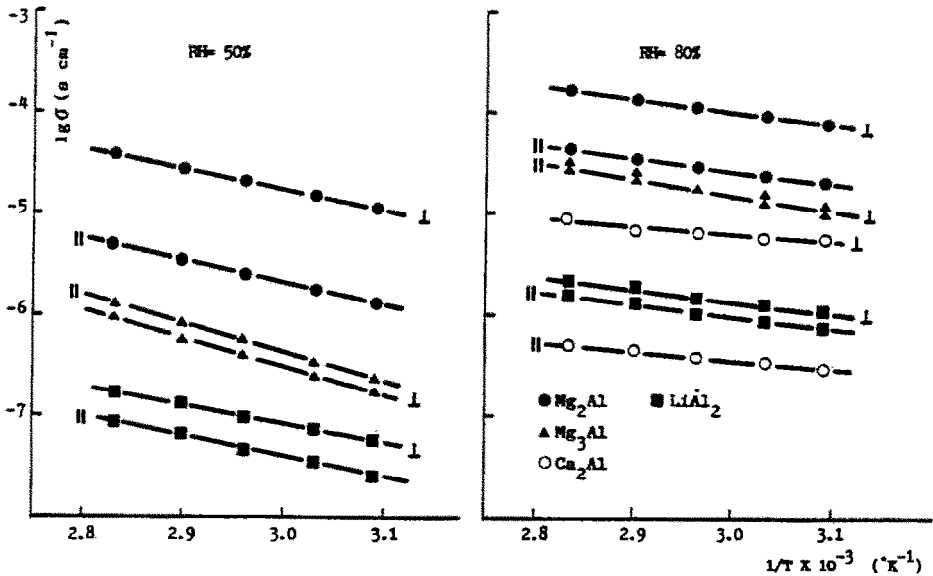

Fig. 2. Conductivity dependence on temperature, degree of humidity, composition and direction ($\perp$=perpendicular; $\parallel$=parallel) of forming pressure of mixed metal hydroxides.

Mg-Al hydroxide with low Mg content (Mg/Al=2) shows highest values of conductivity; Ca-Al hydroxide presents the strongest dependence of conductivity with the degree of humidity. In fact, it has been practically impossible to measure conductivity values at 50% of RH using equipments indicated in the experimental part. Besides this sample shows the strongest dependence of conductivity with the direction of forming pressure of the pellets. The values measured perpendicularly to the direction of forming pressure, in fact, are on average 18-20 times higher than those measured in parallel. These findings may be justified taking into account the relative large crystal size of Ca-Al hydroxide (Table 1). In this case the uniaxial forming pressure favours the preferential orientation of the hexagonal platelets of Ca-Al hydroxide.

REFERENCES

1 C.J. Serna, J.L. Rendon and J.E. Iglesias, Clay Minerals, 30 (1982) 180.

2 R. Allmann, Chimia, 24 (1970) 99.

3 H.F.W. Taylor, Min. Mag., 39 (1973) 377.

4 M. Lal and A.T. Howe, J. Chem. Soc. Chem. Comm., (1980) 737.

5 M. Lal and A.T. Howe, J. Solid State Chem., 39 (1981) 377.

6 G. Mascolo, P. Pernice and O. Marino, 8th International Congress on the Chemistry of Cement, Rio de Janeiro 1986, Vol. VI p.384.

7 G. Alberti, M. Casciola, U. Costantino, G. Levi and R. Ricciardi, J. Inorg. Nucl. Chem., 40 (1978) 533.

8 E. Krogh Andersen, I.G. Krogh Andersen, C. Knakkergard Moller, K.E. Simonsen, and E. Skon, Solid State Ionics, 7 (1982) 301.

9 S. Yde Andersen, J.S. Lundsgaard, J. Molling, and J. Jensen, Solid State Ionics, 13 (1984) 81.

10 M. Casciola, U. Costantino and S. D'Amico, Solid State Ionics, 22 (1986)127.

11 G. Mascolo, Miner. Petrog. Acta, 29-A (1985) 163.

12 G. Mascolo and O. Marino, Miner. Mag., 43 (1980) 619.

13 G. Mascolo and M. Marroccoli, Cement and Concrete Research, 16 (1986) 410.

14 G. Mascolo and O. Marino, Thermochimica Acta, 35 (1980) 93.

15 C.J. Serna, J.L. White and S.L. Hem, Clays Clay Miner., 25 (1977) 384.