

## CONDUCTIVITY STUDIES ON MODIFIED LAPONITES

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**Abstract**—Significant increase of the a.c. conductivity of Laponite is achieved when the sodium form is totally exchanged with potassium ions; however, the rheological properties alter, e.g. the clay will no longer form a gel with water. Exchange with  $\text{Li}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  or  $\text{Cu}^{2+}$  produces no increase in the a.c. conductivity over that of the sodium form. The synthesis of fluoro-laponites, with increased sodium contents, via a sol–gel method, gives materials of enhanced a.c. conductivity, which retain similar rheological properties to those of commercial Laponite. Some  $^{29}\text{Si}$  and  $^6\text{Li}$  MAS NMR data are reported for the new materials.

Laponite is a synthetic trioctahedral smectite clay with the ideal formula  $[\text{Si}_8(\text{Mg}_{5.34}\text{Li}_{0.66})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.66}$ . The material has many practical uses, including applications in the paper industry. Thus, specialist papers required in the electrographic printing process require a paper which has a mildly conductive layer and this is conveniently supplied by deposition of a thin film of the clay during the paper making process. Not only is Laponite colourless, but the rheological properties of clay–water mixes are ideal for deposition of thin films at the manufacturing stage. There is, however, a down side. Laponite, being a synthetic material, is more expensive than would be, say, a natural clay—but the natural clays have disadvantages which render them unsuitable. It may be that if some modification of the clay were achieved that an enhanced conductivity would result, with the consequence that less Laponite would be needed. It was shown recently that attempts to intercalate phenyltin compounds onto Laponite led to reaction of the organotin species on the clay surface and the formation of a tin oxide pillared clay.<sup>1</sup> This material has a significantly enhanced a.c. conductivity,<sup>2</sup> but only at the expense of a total loss of the desirable rheological properties in contact with water.

In this paper, experiments are described in which commercial Laponite is ion-exchanged with a range of monovalent ions other than sodium, and also,

in a further experiment, with copper(II) ions. In addition, advantage is taken of a recently reported sol–gel method to synthesize two synthetic Laponites with a higher proportion of exchangeable ions. A.c. conductivity measurements of all the materials are presented and discussed.

### EXPERIMENTAL

Laponite RD was obtained from Laporte Industries Ltd.; all other chemicals were obtained from Aldrich Ltd.

#### *Ion exchange of Laponite*

The classic method of Posner and Quirk<sup>3</sup> was used; an illustration is given for copper(II) exchange: Laponite RD (5 g) was washed with a 1 M solution of copper(II) chloride and separated by decantation. This procedure was repeated five times. The clay was then suspended in 1 M aqueous  $\text{CuCl}_2$  at pH 3 (adjusted with 1 M hydrochloric acid) and allowed to settle before decantation. This procedure was repeated three times. The clay was then resuspended in 1 M  $\text{CuCl}_2$ , pH 3, and stirred for 36 h. After setting aside, the clay was recovered and dialysed with deionized water until no chloride ions were detectable using the acidified silver nitrate test. Appropriate changes in the procedure afforded

lithium, potassium, rubidium and caesium exchanged Laponites (released sodium was monitored by Atomic Absorption Spectroscopy). The resulting clays were stored at a constant relative humidity of 52%.

#### *Synthesis of Laponites by a sol-gel process*

The method described by Luca *et al.*<sup>4</sup> was used precisely as reported to give a Laponite with a small degree of copper(II) substitution in the tri-octahedral layer of the clay; the process was then repeated as indicated to give a modified Laponite with no copper(II) substitution.

Tetraethylorthosilicate (41.66 g) was added to ethanol (100 cm<sup>3</sup>) and stirred at 60° C for 3 h. To this solution was added MgCl<sub>2</sub>·6H<sub>2</sub>O (21.40 g) dissolved in deionized water (200 cm<sup>3</sup>). This solution was stirred for 4 h, after which aqueous NaOH solution was added until a pH of 9.5 was achieved. The sol was stirred for 12 h, following which the Mg/Si precipitate was filtered and washed with deionized water. The solid was resuspended in deionized water, whereupon LiF (0.648 g) and NaF (~3 g) were added. The mixture was stirred for 12 h and then refluxed for 7 days. The suspension was filtered and dialysed to remove any excess cations. The material remaining was allowed to stand for 1 week in a beaker; if after this period no particulate matter had settled, the new clay was dried over silica gel.

#### *Physical measurements*

XRD and XRF data were obtained via the Department of Geology, University of Keele. The XRD data were obtained with a Philips APD 1700 instrument run at 40 kV and 40 MA over the range 3–30° 2θ. The XRF data were obtained with a Fisons (ARL) 8420 system with a double goniometer fitted. <sup>29</sup>Si and <sup>6</sup>Li MAS NMR data were obtained with a Bruker AC 300 instrument at 59.580 MHz (<sup>29</sup>Si) and 44.168 MHz (<sup>6</sup>Li) using rotor spinning speeds of ~5000 Hz.

#### *Conductivity measurements*

Approximately 2 g of the sample was pressed into a disc using a hydraulic press, a pressure of 10 tonnes being exerted for 3 min. The discs produced had diameter 13 mm and thickness approximately 1 mm. Accurate thickness measurements were made with a dial micrometer (±0.01 mm). Silver-loaded epoxy resin, obtained from RS components, was used to attach freshly stripped enamelled copper wire (0.7 mm diameter) to both surfaces of the

disc, taking care to avoid the edges. The resin was allowed to dry 1 week prior to measurement. All samples were measured in duplicate at least. The resistance and capacitance of the samples were measured using a Genrad impedance Digibridge. From the values of the capacitance (*C*), the capacitive reactance (*X<sub>c</sub>*) can be determined:

$$X_c = 1/2\pi fC,$$

where *f* = frequency (kHz) and *C* = capacitance. The total impedance, *Z*, may now be calculated:

$$Z = 1/[(1/X_c^2) + (1/R^2)]^{1/2},$$

where *R* is the measured resistance. Conductivity (*δ*) data were then calculated according to:

$$\delta = 1/Z\pi r^2.$$

The silver paste electrode system described above is dominated by the reactive component (see below) and hence a greater dependence on frequency is observed. However, this simple system is adequate to qualitatively place a series of materials in order of increase of a.c. conductivity.

## RESULTS AND DISCUSSION

### *Examination of new clays*

Some data for the new clays, the syntheses of which are described in the Experimental section, are gathered in Table 1. Comparison of <sup>29</sup>Si MAS NMR data for the materials designated **I** and **II** in Table 1 show quite conclusively that clay species have been formed. In particular, the *Q*<sup>3</sup> resonances are close to that observed for Laponite and the small particle size is also reflected in the observation of a clear *Q*<sup>2</sup> resonance, as is the case for Laponite.<sup>5</sup> In the <sup>29</sup>Si MAS NMR spectrum of **I**, a third resonance at -110.6 ppm vs TMS is noted. This may be attributed to a silica impurity, a fact reflected in the high SiO<sub>2</sub> percentage figure in Table 1 (by XRF), and also for the low magnesium figure. A more satisfactory SiO<sub>2</sub> figure is obtained for **II**, which shows no MAS NMR evidence of silica contamination (although here the magnesium figure is again low). The basal spacing [*d*(001)] figures of 13.55 (**I**) and 13.59 Å (**II**), obtained by XRD, for the two clays agree well with that reported for Laponite.<sup>6</sup> It has been noted previously<sup>7</sup> that the lower quadrupole moment of the less abundant <sup>6</sup>Li makes it a more attractive nucleus with which to study lithium-containing solids than <sup>7</sup>Li; indeed, <sup>6</sup>Li is sometimes referred to as a pseudo-spin 1/2 nucleus. During the lithium NMR experiments it was not possible to lock the spectrometer, hence

Table 1. Analytical and MAS NMR data for synthetic clays I and II

Ideal formula	% SiO <sub>2</sub>	% MgO	<sup>29</sup> Si <sup>a</sup>	<sup>6</sup> Li <sup>b,c</sup>
<b>I</b> [Si <sub>8</sub> (Mg <sub>4.98</sub> Cu <sub>0.02</sub> Li <sub>1.0</sub> )O <sub>20</sub> F <sub>4</sub> ]Na <sub>1.0</sub>	found 63.9 required 62.2	found 23.0 required 26.0	-85.4, -94.1 -110.6	0.71 <sup>d</sup>
<b>II</b> [Si <sub>8</sub> (Mg <sub>5</sub> Li)O <sub>20</sub> F <sub>4</sub> ]Na <sub>1.0</sub>	found 62.7 required 62.3	found 23.9 required 26.1	-86.2, -93.1	0.75
Laponite RD			-85.4, -94.4	0.65

<sup>a</sup> ppm vs TMS.<sup>b</sup> ppm vs aq. LiCl.<sup>c</sup> No lock.<sup>d</sup> Asymmetric to low field.

all lithium data were obtained sequentially under identical conditions. The data in Table 1 suggest similar environments for lithium in the three materials, but, interestingly, a shoulder is seen to low field on the <sup>6</sup>Li resonance of I. This may reflect the Mg/Mg and Mg/Cu nearest neighbour possibilities within the trioctahedral layer in this clay (see Fig. 1).

#### Conductivity data for new clays and alkali metal exchanged Laponite

A detailed study of the conductivity of Laponite has been carried out,<sup>8</sup> from which it was concluded that the major mechanism for conduction was ionic. The study also revealed that the detailed behaviour was a function of the particular electrode system

used; however, some success was achieved in modelling the various electrode behaviours. The experimentally most simple system, the silver-loaded epoxy contacts used here, was also the most complex to analyse. However, it was clearly established that measurements taken with this electrode system were a reliable way of ranking a series of materials in order of increasing conductivity. It is therefore appropriate to present the data in graphical form (Figs 2-4). The graphs give numerical values of the a.c. conductivity of the sample as a function of a.c. frequency, the a.c. resistance and capacitance being obtained from the Digibridge, which "sees" the sample as a perfect resistor and capacitor in parallel (see Experimental section); only the relative ordering of the curves is considered here.

Figure 2 considers the relative conductivities of Laponite when ion exchanged with monovalent ions Li<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> in comparison with that of the supplied sodium form. It is immediately apparent that the only real difference observed is with potassium, which induces a significantly higher conductivity. The mobility of the ions in the inter-

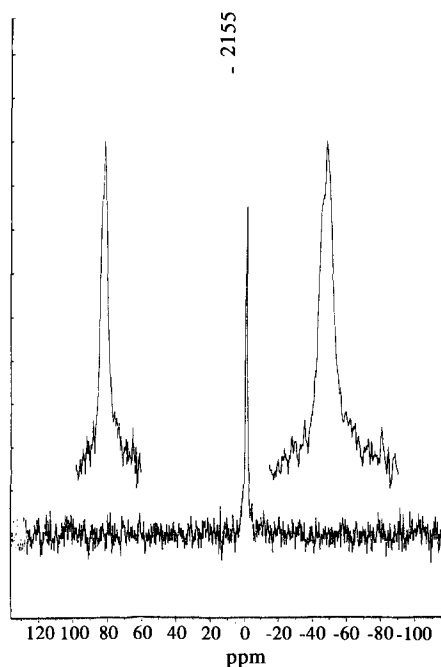
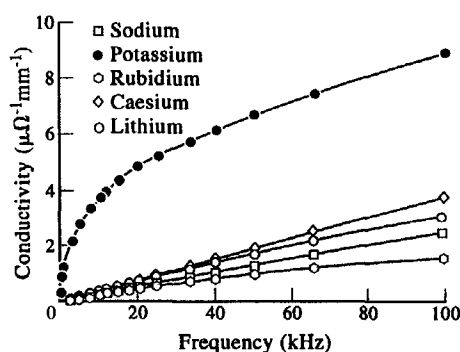
Fig. 1. <sup>6</sup>Li MAS NMR spectrum of clay I.

Fig. 2. Comparative a.c. conductivities of alkali metal ion-exchanged Laponites.

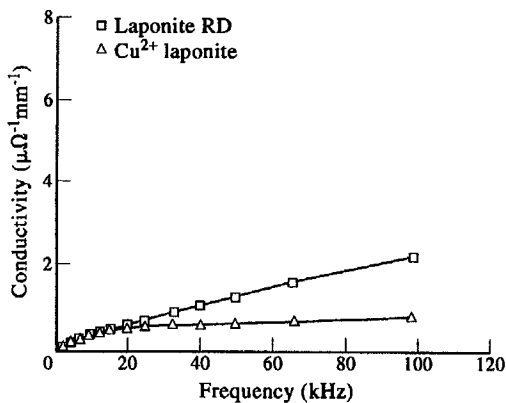


Fig. 3. Comparative a.c. conductivities of  $\text{Cu}^{2+}$ -exchanged Laponite and Laponite RD ( $\text{Na}^+$ ).

lamellar space is likely to be influenced both by the water content (at 52% relative humidity) and by the effective size of the solvated cation; within the present series of materials these factors appear to optimize at potassium. The rheology of the potassium-exchanged material is, however, very different to that of the sodium form; thus, whereas the sodium forms gels in water, the potassium form does not do so. It is possible to form a suspension of the potassium-exchanged clay in water following sonication. Figure 3 compares the a.c. conductivity behaviour of sodium Laponite and the copper(II)-exchanged material. The performance of the bivalent metal-exchanged material is, if anything, worse than that of the sodium form. This reflects stronger interaction between the  $\text{M}^{2+}$  and the silicate sheet, some evidence for which is derivable from the elegant ESR studies of copper(II)-exchanged hectorite by Mortland *et al.*,<sup>9</sup> which showed preferential orientation of the  $C_4$  axis of the Jahn–Teller distorted  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ions perpendicular to the silicate sheet.

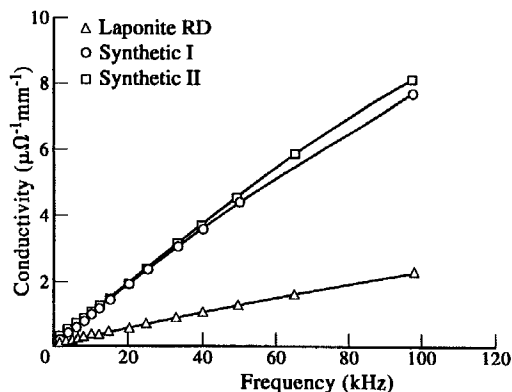


Fig. 4. Comparative a.c. conductivities of I, II and Laponite RD.

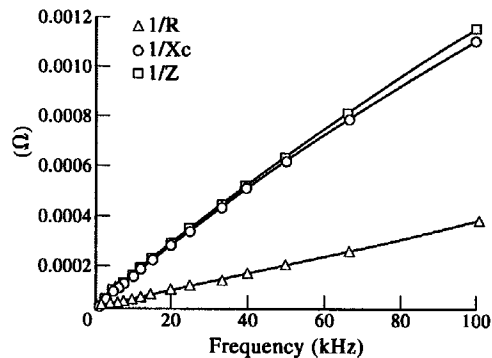


Fig. 5. Components of impedance for Laponite using the silver paste system.

Figure 4 shows the a.c. conductivities of the two clays prepared by the sol–gel method of Luca *et al.*<sup>4</sup> Not surprisingly, the data are similar for the two materials which should contain similar quantities of sodium ions, i.e. of charge carriers. Given the greater concentration of charge carriers than in commercial Laponite, the observed increase in conductivity is very satisfactory. Furthermore, the rheological properties are similar to those of Laponite; so, it would appear that from the applications viewpoint the best way to achieve an increase in conductivity is to revisit the initial formulation of the clay. It will not escape notice that the plots in Figs 2–4 show significant frequency dependence. This arises from the ohmic nature of the silver paste contacts, and hence to the fact that the reactive component accounts for the majority of the impedance. This is illustrated in Fig. 5, in which  $1/R$ ,  $1/X_c$  and  $1/Z$  are plotted separately as a function of frequency for Laponite examined with silver paste contacts. The method is reliable to rank materials in order of increasing a.c. conductivity, which is the objective of this paper.

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