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Studies of Zinc–Chromium Hydroxy Salts. II. Composite Anion Conductors of Pressed Disks of $[Zn_2Cr(OH)_6]X \cdot nH_2O$, Where $X^- =$ F^-, Cl^-, Br^-, I^-, NO_3^-, and $\frac{1}{2}CO_3^{2-}$

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We have found that pressed disks of the layered anion exchange compound $[Zn_2Cr(OH)_6]Cl \cdot 2H_2O$ exhibit reversible interparticle swelling to take up appreciable quantities of water, dependent on the relative humidity. This has a marked effect on the disk conductivity, enabling the chloride ions to easily pass through the channels so created to give a maximum conductivity of 10^{-3} ohm^{-1} cm^{-1} at 17°C. The transport number for Cl^- ions was found to be 1 ± 0.1, and there was estimated to be the equivalent of approximately eight water layers separating the particles in the disks. Such a large swelling probably has similar origins to the large swelling which can occur within the particles of the expandable clays, and probably arises because of the ease of donation of the Cl^- ions from the surfaces into the interparticle solution. The maximum conductivities of composites of the compounds with X^- = F^-, Br^-, I^-, NO_3^-, and $\frac{1}{2}CO_3^{2-}$ were in the range 10^{-3} to 10^{-4} ohm^{-1} cm^{-1}, which we also attribute to anion conduction.

Introduction

In general, high conductivity of anions within the lattices of inorganic crystals is inhibited by the large comparative size of most anions. Thus, although fluoride ion conductors, such as β-$PbSnF_4$, can have conductivities of 10^{-3} ohm^{-1} cm^{-1} at room temperature (*1*), which approach those of good cation conductors, the conductivity exhibited by other anions only reaches these values at elevated temperatures. For instance, chloride ion conductivity in $SrCl_2$ is only high at temperatures above a transition in the region of 730°C (*2*), and oxide ion conductors show conductivities, extrapolated to room temperature, of less than 10^{-6} ohm^{-1} cm^{-1} (*3*).

High anion conductivity, for a wide variety of anions, can, however, be attained in hydrated surface layers of both organic and inorganic anion exchange materials. Organic membranes, with interconnected networks of pores, have been produced which exhibit anion conductivities in the region of 10^{-2} ohm^{-1} cm^{-1} at room temperature (*4*) and have a high anion selectivity. Similarly, small particles of hydrous oxides such as SiO_2, SnO_2, TiO_2, and ThO_2 provide a hydrated surface for enhanced ionic conductivity (*5*, *6*). In acidic solution the hydrous oxide particles adopt a positive charge due to protonation, and are surrounded by a swarm of anions. Although the conduction properties of these systems have not been

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extensively studied, it is known that ThO_2 equilibrated in HCl solutions can be formed into a chloride-selective membrane with the aid of an organic binder. Even in the pressed membrane, the particles would appear to behave as particle hydrates, retaining sufficient surface hydrate water to provide an interconnected network for the chloride ions to move through, giving rise to the appreciable membrane conductivity observed of between 10^{-2} and 10^{-3} ohm^{-1} cm^{-1} at room temperature (*6*).

In view of the inherent difficulty in obtaining high bulk anion conduction in solids, we have explored further the phenomenon of high surface conductivity of hydrated particles of inorganic anion exchange materials, and in particular the high membrane conductivity that may result in pressed pellets.

In addition to the two known types of inorganic anion exchange materials, namely, the hydrous oxides referred to above, and the mercarbide salts $[C_2Hg_6O_2]X_2$ (*5*), the compounds $[Zn_2Cr(OH)_6]X \cdot nH_2O$, where X is an anion, have recently been shown to exhibit anion exchange properties (*7*). The X^- anions and the water molecules form negatively charged interlayers $[X \cdot 2H_2O]^-$ which lie between the positively charged brucite, $Mg(OH)_2$, type structural layers of $[Zn_2Cr(OH)_6]^+$, in which the Zn^{2+} and Cr^{3+} ions occupy, in an ordered fashion, the octahedral sites between two close-packed OH^- sheets.

We report here our study of the conduction properties of the anions in this class of compound. For the special case when $X^- = OH^-$, proton transport, independent of OH^- transport, is possible, and we have previously reported a conductivity of at least 6×10^{-4} ohm^{-1} cm^{-1} at 17°C for disks of $[Zn_2Cr(OH)_6]OH \cdot {\sim}2H_2O$ (*8*).

In part I of this study (*9*) we have reviewed the general field of hydroxy salts, and reported the analytical, X-ray, electron microscopic, and thermal characterization of the same compounds that we have used in the present study. The particles are crystalline, but less than a few hundred angstroms in size, and, under ambient conditions, can take up surface water amounting to up to $n = 1$ in the formula, in addition to the normal two intracrystalline waters of hydration ($n = 2$) (*9*). In the context of conductivity considerations, the surface water may be expected to play an important role.

Experimental

The samples were the same as those used for the study reported in part I (*9*). The X-ray patterns showed weak broad reflections due primarily to the small size of the particles (100–200 Å) (*9*), and the basal spacings agreed with those of Boehm (*7*). Water contents were determined by ignition to 1000°C in air using a Stanton Redcroft STA 780 microbalance.

Prior to conductivity measurements, the products were washed by repeatedly stirring with distilled water followed by centrifuging, or were boiled with a large quantity of distilled water which was then decanted and centrifuged off. In all cases the washings were continued until the conductivity of the wash solution was less than 5×10^{-4} ohm^{-1} cm^{-1}, so as not to interfere with the conductivity measurements. The final solution pH's were typically between 5 and 7.

For the conductivity measurements the samples were either squeezed between filter papers and the pastes pressed at 2 ton cm^{-2} (20 MPa), or they were completely dried in air before pressing. Ac conductances were measured *in situ* under pressure using stainless-steel plungers and a perspex die, as previously described (*10*), using either a Wayne Kerr B624 (1592 Hz) or B224 bridge (100 Hz–60 kHz using an external source and detector). The conductivities of selected samples showed no frequency anomalies over this range, and the conductances typically only increased by about 10 to 30% between 1592 Hz and 60 kHz for the wet or dry samples respectively, establishing that, within the general accuracy quoted, the given values at 1592 Hz represent the dc conductivities.

Results

Conductivities under Various Conditions

Our results for a variety of compounds are summarized in Table I. It can be seen that many of the conductivities are high, and approach those found in the known organic and inorganic ion exchange membranes. The highest conductivities were always found for pellets which had been pressed from wet pastes, from which the water was expelled during application of the pressure to leave a dense pellet. For the chloride, bromide and iodide samples the conductivity of pellets pressed from dried powders was very close to those obtained using pastes. However, dried powders gave appreciably lower conductivities for the fluoride, nitrate and carbonate forms.

TABLE I

PROPERTIES OF $[Zn_2Cr(OH)_6]X \cdot nH_2O$

X^-	n (± 0.1)	σ (ohm^{-1} cm^{-1}) Pressed powders	Pressed pastes
F^-	2.7	7×10^{-6}	6×10^{-5}–8×10^{-4}
Cl^-	2.9	3×10^{-4}	5×10^{-4}–1×10^{-3}
Br^-	1.7	1×10^{-4}	3×10^{-4}–1×10^{-3}
I^-	2.3	8×10^{-5}	7×10^{-5}–1×10^{-4}
NO_3^-	3.0	3×10^{-6}	3×10^{-4}–5×10^{-4}
$\frac{1}{2}CO_3^{2-}$	1.6	5×10^{-5}	1×10^{-4}–3×10^{-4}
OH^-		6×10^{-4}	

Note. The conductivities, σ, of disks pressed from pastes, and from powders equilibrated in air at 17°C are shown, together with the water contents, n, of the powders under the same conditions (from Ref. (*9*)). Variations in the disk densities can result in the range of conductivities shown for the pressed pastes. For $X^- = OH^-$ the conductivity is attributed mainly to proton transport (*8*).

Since the conductivities of the pressed pastes of several samples were actually higher than those of the parent solutions ($\leq 5 \times 10^{-4}$ ohm^{-1} cm^{-1}), and since for the chloride, bromide, and iodide the high conductivities existed for the dried powders, it is clear that the high conductivities of the pressed pastes were not caused by the presence of entrained electrolyte in the intergranular spaces or voids which may have existed within the pellets. The conductivities, although moisture dependent, are nevertheless true intrinsic properties of the materials.

The conductivities varied generally within a factor of about 3 between different preparations and treatments. Reproducible values could be obtained after about a 15-min application of the pressure on the die for both wet and dry disks. At this stage the pressure could be reduced to close to zero without a significant change in the conductivity, showing that the values were pressure independent. If the pressure was maintained, the conductivities dropped by a factor of up to 3 over 24 hr, due to slow final densification. The ranges of values given in Table I for the pressed pastes cover such variations, and also those observed between the two different preparations of each of the compounds perhaps caused by slight differences in particle sizes. However, in general, the conductivities measured in the initial plateau region achieved after about 15 min are reported, as in the case of the pressed powders described in Table I, and subsequently in the paper.

Disks pressed for 15 min from wet or dry powder at 2 ton cm^{-2} (20 MPa) were reasonably robust when removed from the die. After pressing overnight, however, they were much stronger and required considerable finger pressure to break. Such a chloride disk had a density of 2.68 ± 0.1 g cm^{-3}

at 23°C. An accurate calculation of the theoretical density is hindered by the observed broad X-ray peaks. However, taking $a = 5.36$ Å and $c = 7.76$ Å as reported by Boehm (7) for the chloride before drying at 110°C, the theoretical density for the dihydrate is calculated to be 3.19 ± 0.06 g cm^{-3}. The disk thus had a relative density of 82 ± 5%. Chloride disks pressed at 10 ton cm^{-2} (100 MPa) overnight had a relative density of 86 ± 5%. Such a reasonably high density achieved by cold pressing is probably achieved because of the presumed plate-like shape of the particles.

In view of the layer-like structure and possible conduction anisotropy, selected samples were measured in a special die, described elsewhere (*11*), which enabled the conductivities to be measured at right angles to the applied pressure, and therefore parallel to the anticipated lie of the platelet particles. The values were typically twice those normally obtained, which were for the direction perpendicular to the lie of the platelets. The overall conduction anisotropy of the pellets is therefore not pronounced. For comparison, in the layer compound $HUO_2PO_4 \cdot 4H_2O$, the anisotropy of proton conduction in pressed pellets was between a factor of 4 and 10 (*10*).

In view of the presence of OH^- groups in the compounds, the conductivities of samples in equilibrium with solutions of various pH's were measured to establish any possible effect of proton exchange with the solution. When 0.3 g of the chloride was added to 35 ml 0.001 *M* NaCl solutions of initial pH 2.3, 5.1, and 9.0, the pH values quickly changed, and after several hours the final pH's of the supernatant solutions remaining after centrifuging, under CO_2-free conditions, were all between 4 and 5, indicating partial reaction of the solids with the solutions. However, the conductivities of the pressed pastes taken directly from the solutions were all close to 1×10^{-3} ohm^{-1} cm^{-1}. Similar experiments, but adding 0.3 g of sample to a larger volume, 150 ml, of 0.001 *M* NaCl solutions of pH 2.3, 4.9, and 7.0 gave final pH's of 3.2, 5.2, and 5.5, and conductivities of 1.0×10^{-3}, 1.3×10^{-3}, and 1.3×10^{-3} ohm^{-1} cm^{-1}, respectively. The conductivities therefore show virtually no pH dependence. This contrasts markedly with the expected pH dependent proton conductivity of hydrous oxides such as $ZrO_2 \cdot nH_2O$ and $SnO_2 \cdot nH_2O$ (*12*), and would appear to reflect the fact that the ion exchange capacity of the zinc–chromium salts is constant as determined by the zinc/chromium ratio and not influenced by OH^--solution equilibria, as in the case of the hydrous oxides (*12*). The observed analytical ratio of Zn/Cr/Cl of 2.00/1.04/1.02 (9) clearly shows that all the exchange capacity is accounted for by Cl^-. Further evidence regarding the nature of the conducting species was obtained from transport number measurements, described below.

Transport Number Measurements

Transport number measurements were made using a cell with transference and cation reversible electrodes (*13*, *14*), of the following form

$$\overset{-}{\mathrm{Zn}}|\underset{(a_Z)_1,(a_-)_1,(a_H)_1}{\mathrm{ZnCl_2,HCl}}|\mathrm{S.E.}|\underset{(a_Z)_2,(a_-)_2,(a_H)_2}{\mathrm{ZnCl_2,HCl}}|\overset{+}{\mathrm{Zn}}$$

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2e \qquad \mathrm{Zn}^{2+} + 2e \rightarrow \mathrm{Zn}$$

$$2t_- \text{ moles of } \mathrm{Cl}^- \leftarrow$$

$$\rightarrow 2t_H \text{ moles of } \mathrm{H}^+$$

$$\rightarrow t_Z \text{ moles of } \mathrm{Zn}^{2+}$$

The two solutions were separated by the solid electrolyte (S.E.), which replaces the familiar plastic membranes used in similar cells to obtain the transport number of ions through membranes (*14*). The activities of zinc (a_Z), chloride (a_-) and hydrogen ions (a_H) are indicated. The processes which retain charge balance in either compartment concomitant with electrode reactions involving 1 mole of Zn, are expressed in terms of the appropriate transport numbers, where $1 = t_- + t_Z + t_H$.

The emf of the cell is given by the expression

$$E = \frac{RT}{2F} \ln \frac{(a_-)_2^{2t_-}(a_Z)_2}{(a_-)_1^{2t_-}(a_Z)_1} + \frac{RT}{2F} \ln \frac{(a_H)_1^{2t_H}(a_Z)_1^{t_Z}}{(a_H)_2^{2t_H}(a_Z)_2^{t_Z}}, \quad (1)$$

where the terms involving the reaction products appear in the denominators, and those from the reactants in the numerators. The expression has been broken into two parts for convenience of explanation. In our experiment $(a_H)_1 = (a_H)_2$ since the pH's of the solutions were the same, and $a_H \ll a_Z$ so that $(a_-)^2(a_Z) = (a_\pm)^3$ for $ZnCl_2$ solutions. Now, since the activity of the $ZnCl_2$ solution in compartment 2 is greater than that in compartment 1, the first term in Eq. (1) will be positive, whilst the second term will be negative. The maximum emf obtainable is thus when $t_Z = 0$ and $t_- = 1$, and is given by

$$E_{\max} = \frac{3RT}{2F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}. \quad (2)$$

The minimum emf of zero is obtained when $t_Z = 1$.

Several cells were made which contained disks of the chloride salt, pressed for several days at 10 ton cm^{-2} (100 MPa), and approximately 10 mm in diameter and 1 mm thick. Each was araldited over a hole drilled in the bottom of a glass beaker. This beaker was positioned inside a larger beaker to form a two-compartment cell. Reversible zinc electrodes were prepared by electrolytically depositing a thick layer of Zn on zinc plates. The emf between the two electrodes placed in the same $ZnCl_2$ solution was never more than a few millivolts, and measurements of the working cell were always made twice, with the electrodes interchanged, and the average value taken to overcome this small asymmetry. Concentrations of $ZnCl_2$ lower than 0.1 *M* gave more noticeable electrode asymmetry, and were therefore not used.

Solutions of 1 and 0.1 molal $ZnCl_2$, which had both been brought to a pH of 4.1 with HCl, were added to the inner and outer compartments. Reproducible emf's of between 73 and 74 mV were measured on a high-impedance voltmeter.

The value of $E_{\max}$ for our system can be theoretically evaluated from the known mean molal activity coefficients $\gamma_\pm$, where $(a_\pm)^3 = (\gamma_\pm)^3(m_-)^2(m_Z)$. For a 1 and 0.1 *m* $ZnCl_2$ solution $\gamma_\pm$ is 0.325 and 0.502, respectively (*15*). Substituting in Eq. 2 gives $E_{\max} = 71$ mV at 20°C.

It can be seen that the observed value of between 73 and 74 mV represents, to within the experimental accuracy, the maximum value obtainable, and therefore establishes that $t_- = 1 \pm 0.1$. The disks are therefore predominantly or completely Cl^- conductors, to the exclusion of a significant contribution from either H^+, formed by dissociation of the OH^- groups in the structure, or from Zn^{2+} from entrained external solution.

Nuclear Magnetic Resonance

The proton-free induction decay from the chloride powder sample at 22°C was obtained using a Bruker instrument, and showed an exponential decay characterized by one component having a width at half-height of approximately 20 μsec, indicating a value for T_2 of a similar order of time. This indicates a solid-like proton environment, which can be contrasted with values of T_2 of approximately 10 and 100 msec found for the good proton conductor $HUO_2PO_4 \cdot 4H_2O$ (*16*) and aqueous solutions, respectively.

The result for the zinc–chromium salt is inconsistent with motion of the ions, either Cl^- or possibly H^+, within an internal water network to produce conductivities in the range 10^{-5} to 10^{-3} ohm^{-1} cm^{-1} as observed, and suggests that the bulk conductivity of the materials is quite low. The water content n of the chloride at 22°C was 2.1, which would give insufficient surface water to be independently detected by the NMR experiment. The suggested slow bulk diffusion rates would be generally in keeping with the considerable time taken to exchange the anions in solution. Experiments which have been able to elucidate the role of surface versus bulk conduction will now be described.

Effect of Water Loss on the Disk Conductivities

It was found that the conductivities of all samples dropped upon drying in air at 17°C to the values given in Table 1. Drying at higher temperatures resulted in further marked reductions in the conductivity until all the values were in the region of 10^{-6} ohm^{-1} cm^{-1} at 50°C. Over these temperatures the TGA studies (9) showed a continued drop in water content of the powders.

The precise relationship between water content and conductivity is shown for the fluoride, chloride and iodide forms in Fig. 1. Since it was found that pressed disks had slightly higher water contents than the powders, the water content of each disk was determined. The conductivity of a disk was first measured, then the disk was punched out of the die, broken into about three parts, and one part was loaded directly into the TGA pan and the water content determined by ignition to 1000°C. For the wet disks care was taken not to have any water droplets or smears on the disks.

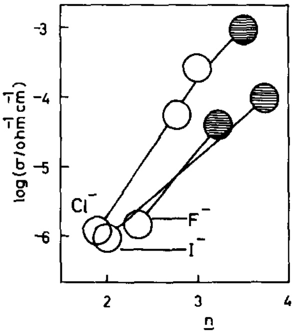

FIG. 1. The influence of water contents n on the conductivities σ of pressed disks of $[Zn_2Cr(OH)_6]X \cdot nH_2O$. The shaded circles represent water-saturated disks, while the remainder refer to disks equilibrated in air at 17, 22, or 50°C, the latter relating to those conductivity values near 10^{-6} ohm^{-1} cm^{-1}.

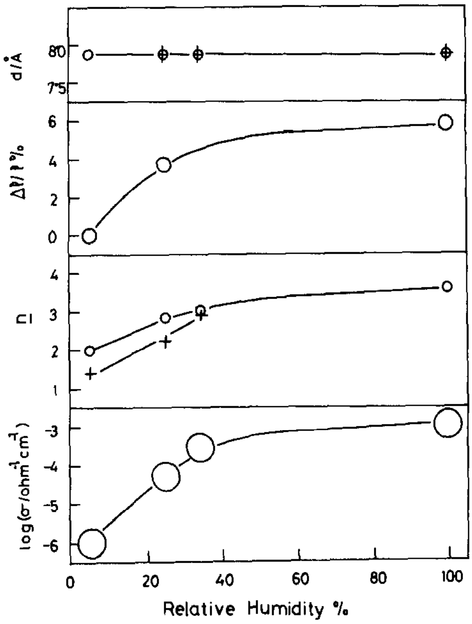

FIG. 2. Effect of relative humidity and temperature on the properties of $[Zn_2Cr(OH)_6]Cl \cdot nH_2O$ as both loose powder, crosses, and pressed disks, circles. The constancy of the basal spacing d contrasts with the changes in representative values of the diameters of disks $\Delta l/l$, water contents n, and conductivities σ.

The data in Fig. 1 clearly reveal that, despite the fact that the compounds were present as the dihydrates ($n = 2$), with very little excess water after being heated at 50°C, the conductivities were very low. This indicates that, in agreement with the NMR results, the conductivity within the crystals is very low, and that the enhanced conductivity at higher overall water contents is due to conduction within the surface layers. It has already been shown that water uptake beyond $n = 2$, for the halides at least, is not associated with lattice expansion but is attributed to uptake of surface water (9).

Interparticle Swelling

Figure 2 shows the correlation between several parameters measured both on powders and on disks, as a function of relative humidity. The disks were pressed at 10 ton cm^{-2} (100 MPa) overnight. The experiments were actually performed in air having approximately 5 mm Hg (0.7 kPa) water vapor pressure, at 17, 22, and 50°C, and also in wet conditions at 17°C, and the relative humidities were calculated from these conditions.

For both powders and pellets, the constancy, to within 1%, of the (001) *d* spacing (Fig. 2) shows that the crystals themselves do not expand upon wetting or drying. This contrasts with the large reversible increases in the measured diameters of the disks (Fig. 2), which increased by nearly 6% between 50°C in air, and in water. (We were unable to accurately measure the changes in the thicknesses of the disks.) The expansion is clearly not due to expansion of the crystallites themselves, and must be due to an expansion of the intercrystalline regions, the obvious cause of this being uptake of water to cause interparticle swelling. Figure 2 confirms that an appreciable uptake of water occurs for the disks. The powder also showed a similar, perhaps slightly smaller water uptake (Fig. 2). Finally, the disk conductivity is seen, in Fig. 2, to increase upon water uptake, as previously demonstrated, clearly indicating that the conductivity is enhanced because of conduction of the ions through the swollen interparticle regions.

The explanation in terms of interparticle conductivity was generally applicable to the behavior of all compounds, and we mention in support another observation. Although the conductivity and weight losses for the chloride were reversible between 17 and 22°C, upon cooling from 50 to 22°C the conductivity did not increase, and only about 30% of the weight loss was regained. This is explained by loss of interparticle water followed by sufficient dehydroxylation of the particle surface layers such that the Cl^- ions displace OH^- from the brucite-type structural layers, and thus become immobilized.

Discussion

In Fig. 3 we have illustrated the structural model of the disks indicated by the results for the chloride. The figure shows crystals separated by several layers of water molecules. Although individual crystals themselves may take up a certain amount of surface water, we have shown that pressed disks take up noticeably more water than the powders, which we attribute to the fact that water between adjacent crystal surfaces is stabilized by two positively charged brucite-type surfaces rather than one. Under the influence of such dual fields, the exchangeable X^- ions will tend to move away from the surfaces, aided as well by the increased extent of hydration possible, and will in turn further stabilize the interparticle water layers. As has been shown, considerable interparticle water is present under ambient atmospheric conditions.

We have estimated the thicknesses of the interparticle water regions upon the basis of

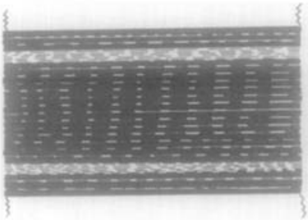

FIG. 3. Section of a pressed chloride disk, showing crystallites, 110 Å thick, and the conducting swollen interparticle regions, taken to be 6 Cl^-/H_2O layers (12 Å thick). Solid lines, $[Zn_2Cr(OH)_6]^+$ layers, dashed lines, $[Cl_x(3 - x)H_2O]^{x-}$ layers, where $x = 1$ for the interlayers within the crystals.

TABLE II

DISK SWELLING $\Delta l/l$ PERPENDICULAR TO THE LAYERS, WHICH WOULD RESULT FROM m SHEETS OF Cl^- AND H_2O, OF THICKNESS 2.0 Å EACH, SEPARATING EACH PARTICLE, SHOWN TO BE 110 Å IN THICKNESS (9). THE CORRESPONDING APPARENT WATER CONTENTS PER FORMULA n, ARE SHOWN

m	n	$\Delta l/l$ (%)
1	2.00	0
2	2.21	1.8
4	2.64	5.5
6	3.07	9.1
8	3.50	12.7
10	3.93	16.3

a simple model assuming parallel packing of adjacent platelets and ignoring edge effects. Table II gives the number of intercrystalline water layers which correspond to various values of n, and the calculated swellings, $\Delta l/l$ are also tabulated. For chloride disks in air at 17°C, for which $n \approx 3$, as shown in Fig. 2, each crystal would be separated from the next by six water layers, in which would be accommodated the Cl^- ions originating from both surfaces. This situation is depicted in Fig. 3. For pressed pastes, having $n = 3.5$ as given in Fig. 2, the particles would be separated by eight water layers.

The values of $\Delta l/l$ calculated from the uptake of the additional water are also shown. For disks in air at 17°C, a swelling of 9.1% is predicted. We could only measure accurately the increases in the disk diameters, rather than in the thicknesses, to which the figure of 9.1% relates. The observed swelling of about 4% at 17°C is therefore reasonable, given the further possibility that some of the swelling could be concealed by uptake in possible void regions of the disks, and given that swelling probably occurs between adjacent edges of particles in addition to adjacent faces, as just considered by the simple model.

In general, the swelling properties of the disks of the Zn–Cr hydroxy salts can be explained by comparison with the known swelling properties of clays (*5*), for which the interlayer intracrystalline swelling increases with decreasing counter-ion density in the interlayers. For instance, in the Na^+ forms, margarite, muscovite, and montmorillonite, which have a density of one Na^+ per 12, 24, and 75 $Å^2$, expand by 0, 1.9 Å, and ∞, respectively, when immersed in water (*5*). The Zn–Cr hydroxy salts have one counter-ion per 25 $Å^2$. By comparison with the clays, this would imply an expansion of one water layer. Now within the crystals of the Zn–Cr hydroxy salts we observe no swelling in water, but between the crystals we observe a swelling of about eight water layers, which, given the structural differences compared to the clays, is reasonable. As can be seen from the clay data, the extent of swelling is extremely sensitive to the counter-ion density. Small changes in the charge distribution at the crystal surfaces, plus the effect of structural mismatch resulting from the random stacking of the platelets on top of each other, and possibly also the effect of the turbostratically perturbed layers would all contribute to allow a finite interparticle swelling whilst having no intraparticle swelling. The powders were also observed to take up a noticeable quantity of water, and this may be because the submicron-sized crystallites have stacked one on top of each other during centrifuging, and the powder agglomerates consist of oriented platelets. This phenomenon is well known to occur for clay platelets (*17*).

The model of interparticle swelling naturally accounts for the observed conductivity behaviour. The water layers in the central portion of the interparticle region would be expected to be solution-like. Now the limiting molar conductivities in solution of Cl^-, Br^-, I^-, and NO_3^- are 76, 78, 77, and 71 ohm^{-1} cm^2 $mole^{-1}$, respectively (*18*), and their similarity and lack of dependence upon size would explain the comparable conductivities found in the hydroxy salts. The conduction model is thus one of a composite conductor consisting of the crystallites embedded in a second solution-like phase.

Finally, let us estimate the anion mobilities within the interparticle layers. Taking the example of the chloride, the minimum mobility is obtained by assuming that all the surface Cl^- ions are free and mobile. Taking the interparticle region cross section for $m = 6$ as 9.8% (12/(110 + 12)) gives a mobility of 1.1×10^{-5} cm^2 V^{-1} sec^{-1}. The maximum mobility that could be expected, that of Cl^- in aqueous solution of 8×10^{-4} cm^2 V^{-1} sec^{-1} (*18*), would correspond to only 1.4% of the surface Cl^- ions being mobile. Most likely, a significant proportion of the surface Cl^- ions are released from the brucite surface layers deeper into the interparticle layers, and conduct with a mobility slightly lower than that in aqueous solution. Due to problems of water loss at higher temperature we were not able to obtain an accurate activation energy. However an approximate value of 40 kJ $mole^{-1}$ was obtained for the chloride having $n = 2.9$, which would support the above conclusions of the presence of both a mobility and a trapping energy of the charge carriers in the activation energy expression.

In conclusion, the observed swelling properties would probably be found for pressed disks of many inorganic ion exchange materials, since the counter-ions are not strongly bound, and can move into and stabilise the interparticle regions. However, only for particles with dimensions around 100 Å, as in this case, would the swelling be easily measurable. As an example of this effect in other ion exchangers it was reported that hydronium β-alumina powder showed a small but definite uptake of physically and chemically adsorbed water (*19*). In contrast, however, TGA studies, capable of detecting less than a monolayer, revealed no uptake of surface water on powders of $HUO_2PO_4 \cdot 4H_2O$ (*20*), and pressed disks showed no signs of swelling (*21*) or of interparticle water uptake (*22*), indicating quite a different behaviour for this compound, for which the disk conductivity is the same as that of single crystals (*23*). This clearly represents a case for which uptake of water on the crystallite surfaces does not occur under ambient conditions.

One might be tempted to argue that a pressed paste of any inorganic material would exhibit appreciable conductivity due to surface migration of the ions. However, it is easily demonstrated that this is not the case. For instance, we found low conductivities of pressed pastes of such diverse materials as NaCl, silica gel, $KAl(SO_4)_2 \cdot 12H_2O$ and $Co(en)_3Cl_3 \cdot H_2O$ of 3×10^{-6}, 4×10^{-6}, 5×10^{-6} and 1×10^{-5} ohm^{-1} cm^{-1} respectively at 26°C. Such a comparison only serves to emphasize further the novel character of the conduction process in the Zn–Cr hydroxy salts composites.

The study has therefore highlighted an aspect of ionic conduction which has so far received little attention. We have shown that many of the constraints to solid-state ionic motion can be overcome in expanded interlayers contained within robust disks having good solid-state properties such as insolubility over a wide pH range, and chemical stability. The chloride ion conductivities of the compound approach those of organic ion-exchange membranes (*4*). In the case of Br^-, I^-, CO_3^{2-}, and NO_3^-, the Zn–Cr hydroxy salts show by far the highest conductivities reported for these ions in disks of inorganic materials, and the compounds may be useful where an anion transport number of unity is required, such as separators for metal-based redox batteries.

Acknowledgments

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References

1. J. M. Reau, J. Portier, A. Lenasseun, G. Villeneuve, and M. Pouchard, *Mater. Res. Bull.* **13**, 1415 (1978).
2. C. E. Derrington, A. Linder, and M. O'Keeffe, *J. Solid State Chem.* **15**, 171 (1975).
3. R. M. Dell and A. Hooper, *in* "Solid Electrolytes, General Principles, Characterization, Materials, Applications" (P. Hagenmuller and W. Van Gool, Eds.) p. 291. Academic Press, New York (1978).
4. E. Riande, *in* "Physics of Electrolytes" (J. Hladik, Ed.), Vol. 1. Academic Press, London (1972).
5. C. B. Amphlett, "Inorganic Ion Exchangers" Elsevier, London (1964).
6. J. I. Bregman and R. S. Braman, *J. Colloid Sci.* **20**, 913 (1956).
7. H.-P. Boehm, J. Steinle, and C. Vieweger, *Angew. Chem.* **89**, 259 (1977); *Angew. Chem. Int. Ed. Engl.* **16**, 265 (1977).
8. M. Lal and A. T. Howe, *J. Chem. Soc. Chem. Commun.*, 737 (1980).
9. M. Lal and A. T. Howe, *J. Solid State Chem.* **39**, 368 (1981).
10. P. E. Childs, A. T. Howe, and M. G. Shilton, *J. Solid State Chem.* **34**, 341 (1980).
11. C. M. Johnson, M. G. Shilton, and A. T. Howe, *J. Solid State Chem.* **37**, 37 (1981).
12. W. A. England, M. G. Cross, A. Hamnett, P. J. Wiseman, and J. B. Goodenough, *Solid State Ionics* **1**, 231 (1980).
13. S. Glasstone, "Treatise of Physical Chemistry," 2nd ed., p. 931. Macmillan, London (1956).
14. D. R. Crow, "Principles and Applications of Electrochemistry," 2nd ed., p. 113. Chapman & Hall, London (1979).
15. G. Scatchard and R. F. Tefft, *J. Amer. Chem. Soc.* **52**, 2272 (1930).
16. P. E. Childs, T. K. Halstead, A. T. Howe, and M. G. Shilton, *Mater. Res. Bull.* **13**, 609 (1978).
17. H. F. Shaw, *Clay Miner.* **9**, 349 (1972).
18. W. J. Moore, "Physical Chemistry," 3rd ed., p. 445. (1962).
19. M. W. Breiter, G. C. Farrington, W. L. Roth, and J. L. Duffy, *Mater. Res. Bull.* **12**, 895 (1977).
20. A. T. Howe and M. G. Shilton, *J. Solid State Chem.* **31**, 393 (1980).
21. A. T. Howe and M. G. Shilton, *J. Solid State Chem.* **28**, 345 (1979).
22. A. T. Howe and M. G. Shilton, unpublished work.
23. A. T. Howe and M. G. Shilton, *J. Solid State Chem.* **34**, 137, 149 (1981).