High Proton Conductivity in Pressed Pellets of Zinc–Chromium Hydroxide

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Summary Pressed pellets of the new layer compound $[Zn_2Cr(OH)_6]OH.nH_2O$ have a high proton conductivity, which is due to proton transfer between H_2O and OH^- species, in contrast with the usual involvement of H_3O^+ and H_2O in good solid-state proton conductors.

Good solid-state proton conductors are at present much sought after as possible solid electrolytes for a variety of electrochemical applications ranging from fuel cells[1] to electrochromic cells.[2] Those proton conductors which have conductivities in the useful range between 10^{-3} and 10^{-1} ohm^{-1} cm^{-1} at room temperature are all acid hydrates, namely $H_3PMo_{12}O_{40}.29H_2O$,[3] $H_3PW_{12}O_{40}.29H_2O$,[3] $HUO_2PO_4.4H_2O$,[4] $HUO_2AsO_4.4H_2O$,[4] $H_8UO_2(IO_6)_2.4H_2O$,[5] and H-montmorillonite clays.[6] We report here on the conduction in basic hydrates.

The compounds $[Zn_2Cr(OH)_6]X.nH_2O$, where $X^- =$ halides, NO_3^-, ClO_4^-, $\frac{1}{2}SO_4^{2-}$, $\frac{1}{2}HPO_4^{2-}$, and alkyl sulphates, were recently shown[7] to be one of the few known types of inorganic anion exchangers. The exchangeable anions, together with water molecules, are present as interlayers $[X.nH_2O]^-$ between the positively charged brucite-type, $Mg(OH)_2$, layers of $[Zn_2Cr(OH)_6]^+$, each layer consisting of two sheets of OH^- ions containing the ordered Zn^{2+} and Cr^{3+} ions. The compound with $X^- = OH^-$ has not been previously reported for the Zn–Cr system, but is found for the analogous cement component[8,9] $[Ca_2Al(OH)_6]OH.3H_2O$ and other related compounds.[10,11]

Samples were prepared in CO_2-free conditions by treating $[Zn_2Cr(OH)_6]Cl.2H_2O$[7] with 2 aliquots of an excess of 1 M NaOH for 2 h each at 330 K, followed by washing and centrifuging until the pH and conductivity of the supernatant solution were constant at 11·5 and 1×10^{-3} ohm^{-1} cm^{-1}, respectively.

The frequency-independent a.c. conductivity, measured *in situ*[12] on powders dried under nitrogen at 290 K and pressed at 20 MPa between stainless-steel plunger electrodes, was 6×10^{-4} ohm^{-1} cm^{-1} at 290 K. The essential independence of the conductivity between 1 and 50 kHz enables us to equate the value with the d.c. conductivity.

We were able to measure the conductivity after only a few minutes exposure to air. Over a period of a week in the press the value gradually dropped to a minimum of 5×10^{-5} ohm^{-1} cm^{-1} as carbonation occurred. A sample exposed to air for about 10 min prior to a C, H, N analysis showed the composition to be $[Zn_2Cr(OH)_6](OH)_{0 \cdot 78}(CO_3)_{0 \cdot 11}.nH_2O$. Water is easily lost from these compounds, but, by analogy with the halides,[7] *n* would be expected to be 2 at room temperature. The *X*-ray diffractograms of both partly and fully carbonated samples confirmed the characteristic cation-ordered layer structure,[7] having *a* 5·3 Å and *c ca.* 7·6 Å for both.

Upon the basis of the above, we ascribe a value of at least 6×10^{-4} ohm^{-1} cm^{-1} to the intrinsic conductivity of the layered compound $[Zn_2Cr(OH)_6]OH.ca.2H_2O$. Since the conductivity of the dense pellet was only marginally lower than that of the parent wash solution, it is clear that the pellet conductivity cannot be due to any extrinsic effects of residual solution in the voids or grain boundaries.

Pressed pellets of layered hydrates possess two kinds of potentially conducting interlayers: those within the crystallites and those constituted by the intercrystalline regions. Pellets of $HUO_2PO_4.4H_2O$ pressed from micron-sized platelets indicate only intracrystalline conductivity, equal to that measured on single crystals,[13] whereas pellets of the submicron-sized clay platelets probably possess both components.[6]

In Zn–Cr hydroxide, bulk conduction would be expected to contribute substantially because of the OH^-/H_2O interlayer network through which protons could pass *via* the Grotthus mechanism, without necessarily involving oxygen transport. The interlayer species are probably disordered, as was found for the Ca–Al hydroxide,[9] and may approach liquid-like behaviour as found in the clays,[6] and suggested by the ease of water loss upon heating. However, intercrystalline conductivity may also contribute because of the small platelet thickness, estimated to be 90 Å from the width of the (001) diffraction peak of the partly carbonated hydroxide. Some OH^- transport may also be possible this way.

The high conductivity of Zn–Cr hydroxide is explained by the presence of interlayers of what might be described as a semi-liquid or frozen 18 M hydroxide solution. The stability range, from pH 11 to 14, complements the aforementioned acidic and the following near-neutral proton conductors, $Sb_2O_5.4H_2O$, $SnO_2.3H_2O$, and $ZrO_2.2 \cdot 3H_2O$, which have conductivities between 3×10^{-4} and 3×10^{-5} ohm^{-1} cm^{-1} at 293 K, respectively.[14]

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