BATTERY AND OTHER APPLICATIONS OF A NEW PROTON CONDUCTOR: HYDROGEN URANYL PHOSPHATE TETRAHYDRATE, $HUO_2PO_4.4H_2O$*

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Summary

The recent discovery by Shilton and Howe that hydrogen uranyl phosphate tetrahydrate $HUO_2PO_4.4H_2O$ (HUP) is a rapid proton conductor, with a conductivity higher at room temperature than that of Na^+ ions in ceramic $Na\beta$-alumina, has opened up many prospects for its use in electrochemical devices. The material is insoluble, stable in air, and can be pressed into robust, transparent discs. The applicability of the material for various uses is compared with other solid proton conductors and with fluorocarbon polymers such as Nafion®**. For the first time, a hydrogen concentration cell which has a performance in the region of battery interest and is completely reversible has been constructed. The cell is a solid state secondary battery composed of an HUP disc sandwiched between two metal hydride electrodes. Preliminary polarization studies are reported, which indicate the absence of many of the problems previously experienced with solution-type hydrogen concentration cells. If CaH_2 and $TiFeH_2$ could compose the couple in a future cell, a voltage of 0.8 V and a theoretical energy density of 294 Wh/kg would be expected, and the advantages of such a cell are discussed. Other electrochemical applications of HUP are briefly described.

Introduction

Little mention is made of proton conductors in recent reviews of fast ion conduction in solids [1 - 3]. The best conductivity reported in the most recent reviews specifically on proton conduction [4, 5] is approximately
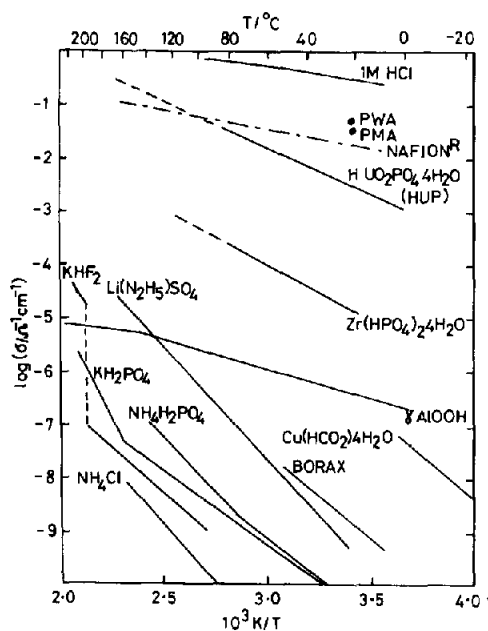

Fig. 1. Conductivities as a function of inverse temperature for some proton conductors.

10^{-6} ohm^{-1} cm^{-1} at room temperature, far below the conductivity of, for example, Na^{+} ions in β-alumina.

The increasing pressure for a hydrogen economy and for the utilization of metal hydrides for energy storage has emphasized the need for a fast proton conductor in the electrochemical utilization of hydrogen [6]. In addition to organic ion-exchangers in the acid form which can function as proton conducting membranes, e.g. Nafion$^{®}$, two new classes of rapid proton conductors have recently been reported. Kodama and coworkers [7] have reported room temperature conductivities of $\sim 2 \times 10^{-2}$ ohm^{-1} cm^{-1} in phosphomolybdic acid (PMA) and phosphotungstic acid (PWA) and their salts. Shilton and Howe [8] found a room temperature conductivity of 4×10^{-3} ohm^{-1} cm^{-1} in hydrogen uranyl phosphate tetrahydrate (HUP), and these results are discussed in the present paper. A recent study on copper(II) formate tetrahydrate [9] found an in-layer proton conductivity of 5×10^{-7} ohm^{-1} cm^{-1}, described as a "ready hydrate protonic conductor". Figure 1 compares some of the data available on proton conduction in solids with those of HUP, PMA and PWA. It can be clearly seen that these new materials represent a marked advance in our knowledge of proton conduction in solids. They can be described as *fast* proton conductors and their properties put them into the area of commercial interest. In this paper some of the properties of HUP are reviewed and its possible applications are described. In particular, we report for the first time the operation of a hydrogen concentration cell, using HUP, which has a performance in the region of battery interest.

Properties of HUP and its analogues

HUP belongs to a class of compounds whose general formula may be written as $M_{1/m}^{m+}(UO_2XO_4).nH_2O$ where M represents a mono- or di-valent cation and X may be P, As, V or mixtures of these. Minerals of this general formula exist naturally and the compounds may be synthesized from solution. They have been studied extensively over the last sixty years [10 - 19]. However, no reports of rapid ionic conductivity have been made until now [8]. HUP itself exists naturally but is extremely rare and often contains mixtures of other cations.

The crystal structures of compounds in this class have been studied by numerous workers [10, 12, 14] but no single crystal data have been published on pure H^+ analogues. Single crystal X-ray and neutron diffraction experiments are being carried out by MacDonald and Fender respectively to determine the details of the H_2O network in the compounds and to determine the positions of the protons. Figure 2 shows the structure of the related compound $K/H(UO_2AsO_4)4H_2O$ which is assumed to be very similar to HUP. The Figure shows puckered layers of $UO_2AsO_4^-$ which are held together by H bonding from the water network and by the charged cations. In HUP, protons replace the metal cations and are located on H_2O molecules which form a continuous, but unsaturated, H-bonded network. The proton vacancies [14] probably facilitate rapid proton migration. In $K/H(UO_2AsO_4).4H_2O$ all of the O—O bond lengths between water molecules
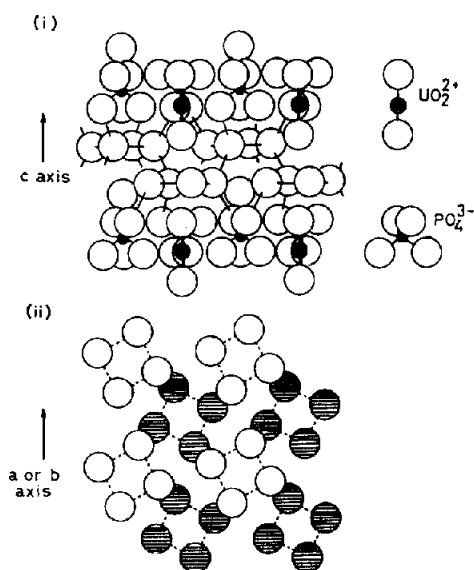

Fig. 2. The structure of the layered uranyl phosphates (after Ross and Evans [14a]). (i) The staggered water layers between $(UO_2PO_4)_n^{n-}$ layers; (ii) plan of the H-bonded water network. The unshaded water molecules are elevated with respect to the shaded ones.

are approximately equal and lie in the range 2.76 to 2.81 Å. N.m.r. experiments on the Na analogue [15] have shown that the water molecules are rotating at room temperature, and recent pulsed n.m.r. measurements on HUP [16] have shown that the proton hopping rate is in agreement with a.c. conductivity measurements [8].

HUP may be fabricated easily into compact, transparent, robust yellow discs which are indefinitely stable in air, and are suitable for solid electrolyte applications. Partial orientation of the crystallites occurs on pressing. A.c. and d.c. conductivity measurements were made on such discs and it has been demonstrated that proton conductivity is primarily through the bulk lattice rather than via grain boundaries or cracks. The activation energy is approximately 30 kJ/mol [8].

Comparison of HUP with other available proton conductors

Table 1 compares the properties of HUP with other available proton conductors of practical interest and in Fig. 1 the conductivity *versus* temperature for a HUP disc orientated in the preferred direction is compared with these, and other materials. From this information it may be seen that HUP has the best range of properties of all the available proton conducting solid inorganic electrolytes. At 100 °C it has a conductivity as good as Nafion[R]. The estimated costs for HUP are around $11 per m^2, compared to Nafion[R] of $450 per m^2.

Use of HUP in a solid-state hydrogen concentration cell

The principle of using two metallic hydrides with different hydrogen activities, separated by an electrolyte, to produce a secondary battery, has been recognized for some time [22]. The overall reaction can be represented by:

$$M'H_x + M'' \rightarrow M' + M''H_x$$
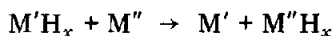
The cell voltage is given by the Nernst equation:

$$E_{cell} = -\frac{RT}{2F} \ln \frac{p_{H_2}''}{p_{H_2}'} \quad (p_{H_2}'' \ll p_{H_2}').$$

If the high vapour pressure hydride is, for example, the hydride of Pd, LaNi$_5$ or TiFe, and the low vapour pressure hydride is an alkaline earth hydride such as CaH$_2$, the e.m.f. of the cell will be of the order of 0.75 - 0.8 V.

The principles governing the use of solid solution electrodes have been discussed by Steele *et al.* [2]. The discharge characteristics of the above hydrogen cell will depend on the phase relationships of the hydrides. When the metal and the hydride phases are separated by a significant two-phase region, the voltage of the cell will be constant whilst the two two-phase

TABLE 1

Comparison of HUP with other available proton conductors

Compound	σ_{25} (ohm^{-1} cm^{-1})	σ_{100} (ohm^{-1} cm^{-1})	Operating range (°C)	Properties	Fabrication	Other comments
1 M HCl	4 × 10^{-1}	8 × 10^{-1}	0 - 100 (>100 under press.)	Liquid	Requires an adsorbent e.g. asbestos	Permeable to gases and other ions
PMA/PWA [7]	3 × 10^{-2}		10 - 40 (melt at 40)	Very soluble, melt at 40 °C, very corrosive to metals	May be cold pressed but attack metal dies	Tend to be easily reduced
Zr(HPO$_4$)$_2$.4H$_2$O [21]*	5 × 10^{-5}	3 × 10^{-4}	0 - 100 (H$_2$O loss at low VP)	Tends to form as a gel	Difficult to press, requires a binder	Requires hydrating before use. Swells on hydration
HUP [8]	4 × 10^{-3}	7 × 10^{-2}	<0 - >100 under press. (H$_2$O loss at low VP)	Insoluble Stable in air Non-corrosive	Presses well at RT Slightly brittle	Impermeable to gases
Nafion® [20]	~2 × 10^{-2}	~7 × 10^{-2}	0 - 150 (H$_2$O loss at low VP)	Polymeric, flexible, tough Chemically inert	Easily made into strong, thin sheets	Requires soaking in water or acid Swells in use

*Better properties are obtained (up to 150 °C) using admixtures with zeolites and can then be sintered into strong discs (C. Berger and M. P. Streer, in Regenerative EMF Cells, Advances in Chemistry Series 64, American Chemical Society, Washington D.C., 1967, Ch. 3, p. 17).
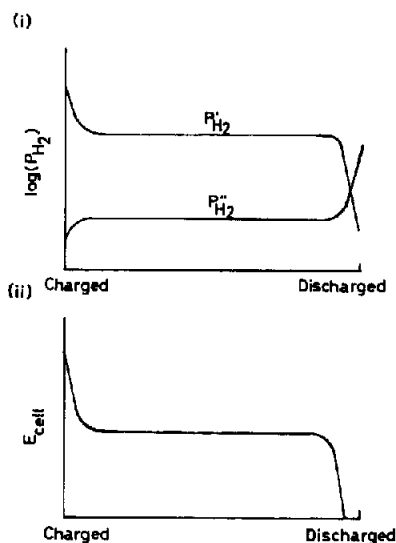
(i)

(ii)

Fig. 3. Changes in the hydrogen pressure (i) and in the cell voltage (ii) during discharge of a hydrogen concentration cell.

regions coexist during discharge. A more typical case is illustrated in Fig. 3(i), where a non-stoichiometric region existing at both extremities of the phase diagram results in the curves at the start and finish of discharge, which are reflected in the corresponding voltage variations shown in Fig. 3(ii).

Attempts to investigate hydrogen concentration cells have in the past been frustrated by the necessity to use an aqueous electrolyte, such as an acid or alkali [22], which would allow back diffusion of hydrogen from one electrode to the other. In addition, it has proved difficult to activate the surfaces of many metals such that hydride formation can occur reversibly. This is not a problem, however, for Pd, and concentration cells using Pd for both electrodes have given a cell voltage of about 50 mV [22].

The use of a solid hydrogen-conducting electrolyte offers a great advantage in restricting the back diffusion of hydrogen from one electrode to another, thereby enabling the charged state to be retained for longer periods than in a solution. Moreover, unlike the case for organic membranes, the transfer of protons through HUP does not appear to be accompanied by the transfer of water molecules. The selectivity of the proton conduction mechanism in HUP is evidenced by the comparatively low conductivity found when H^+ is replaced by alkali metal or alkali earth ions [20].

We have constructed a cell using HUP, and have realized for the first time some of the properties to be expected from a good hydrogen concentration cell. The cell, as shown in Fig. 4, consists of a zirconium hydride–palladium hydride couple, which can be written as Cu|Zr|HUP|PdH$_x$|Cu in the charged state. Assuming that the phases present are PdH$_{0.7}$–Pd and ZrH$_2$–Zr, we can calculate a pressure difference of 1.4×10^{-19} [23] corresponding to a voltage of 0.56 V. This value is obtained by extrapolating
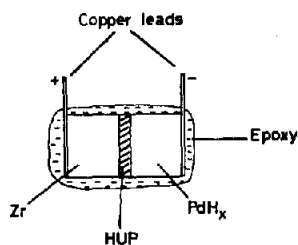
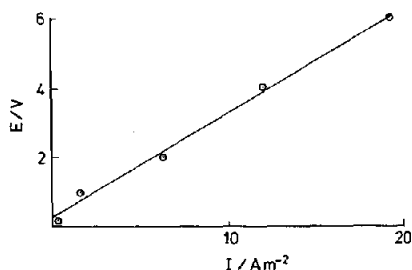Fig. 4. Construction of a solid state hydrogen concentration cell.

Fig. 5. Initial current following an applied voltage to the discharged cell. The linear response shows the absence of polarization effects.

high temperature thermodynamic data on ZrH_2 and $PdH_{0.7}$ to room temature.

The cell was assembled using a HUP disc produced as previously described [8] which was 0.1 cm thick and 1 cm^2 in area. Palladium foil and partially-hydrided zirconium foil were pressed on either side of the disc, between copper foil electrodes. The whole assembly was sealed in epoxy resin to minimize gas losses. The cell was thus assembled in a discharged form to avoid losses of hydrogen from hydrided palladium.

The cell was then charged at a constant voltage of 1 V, and passed an initial charging current of 1.3 mA, which dropped to 0.12 mA after charging for a further 20 minutes. Upon continued application of 1 V for several days a trickle current of 7 μA was observed. Maximum OCV's of 0.55 - 0.75 V were obtained, which extended above the theoretical value by up to 0.2 V. The discrepancy probably arises from uncertainties in the theoretical value derived from the vapour pressure data. Recycling the cell about 20 times over a period of 14 days resulted in a gradual loss of capacity, probably caused by a loss of hydrogen to the atmosphere. The initial capacity was approximately 0.5 C, which is less than the capacity expected on the basis of the weights of Pd and Zr (10 C), and is consistent with only a partial hydriding of the Zr.

Previous work [22] has reported difficulty in activating metals such as Zr, and it was of interest to explore any polarization effects which might be present due to an oxide film on the Zr. This was done in two ways. First, the a.c. conductivity of the partially discharged cell was measured at 1592 Hz, and was found to be only a factor of approximately two higher than the d.c. conductivity calculated from the discharge data. Such a difference reveals only a very small degree of polarization.

Secondly, the polarization during charging was investigated by applying a d.c. voltage to the fully discharged cell and noting the initial current which passed. The plot of current *versus* voltage is shown in Fig. 5, and it can be seen that an ohmic behaviour is found, with no evident polarization effects. The maximum current density was 20 A/m^2, but the cell was not designed

for optimum current density; quite thick discs were used which were oriented perpendicular to the preferred direction of proton motion.

The apparent absence of polarization effects even at appreciable current densities indicates the absence of any blocking oxide film. The activation process used for zirconium (to be the subject of a later paper) was therefore far more successful than previously published attempts [22]. Moreover, the absence of polarization effects also indicates that there is good physical contact between each electrode and HUP. The polarization tests were performed after the cell had been cycled about 20 times, so that any effects due to expansion and contraction of the electrodes with hydrogen absorption should have been apparent. Differential expansions are known to cause interfacial breakdown in ceramic solid state batteries having a β-alumina–β-ferrite interface [2]. The apparent absence of such effects in the solid state hydrogen cell is attributed firstly to the deformability of HUP on a microscopic scale, and secondly to the presence of water in the hydrogen uranyl phosphate tetrahydrate. At the interface with the electrode there will exist a layer of water, which will act as a proton-conducting filler able to retain the surface integrity during limited expansion and contraction of the electrodes.

We have demonstrated that many of the problems thought to be associated with hydrogen concentration cells can be overcome. We have not yet made any attempt to optimize the cells for use in secondary battery applications although present work may develop in this direction. It is worthwhile, though, to consider what the potential of a secondary hydrogen concentration battery might be.

One of the limitations of high energy density secondary batteries is their short shelf-life, in either the charged or discharged state. Since a HUP-based solid state battery does not have a reactive solution electrolyte, the prospect exists for extended storage lives in the discharged state. The hydrogen will then be bound in a stable state to the sink metal. In addition, the absence of catalysts or reactants which need to be kept in a state of high surface area (such as $NiO/NiOOH$ in the $Ni-H_2$ cell [24]) is a factor in favour of extended lifetimes.

In the charged state, the lifetime will depend on the ability of the system to retain the hydrogen against overall losses, and on the ability of both the solid HUP electrolyte and the seals to prevent back diffusion of hydrogen to the sink electrode. We have not yet performed experiments which will determine the relative contributions of these three effects. However, initial decay studies, using systems which could obviously be much improved, showed a fall in OCV of 40% over the first 24 h. Similar decays are observed in the $Ni-H_2$ system [25].

The highest performance may be achieved using the couple CaH_2 and $TiFeH_2$ with HUP, possibly using a protective metal screen such as Zr to separate CaH_2 from HUP. There is evidence [25] that even for very low concentrations of H in α-Zr an appreciable mobility of H is still retained. The theoretical voltage of 0.8 V and theoretical energy density of 294 Wh/kg

compare favourably, when taken together, with the achieved values of 1.3, 1.4 and 1.1 V and 30, 60 and 75–100 Wh/kg respectively for the Ni–Cd [26], Ni–H$_2$ [26] and Ag–H$_2$ [26] secondary batteries. Also an expected current density of 1000 A/m^2 for our cell compares favourably, for example, with that of 500 A/m^2 obtained in the Ag–H$_2$ cell [27]. Such a HUP-type cell would also be very compact. From the volumes of the reactants, a theoretical figure of 1100 Wh/dm^3 can be calculated. In addition to the hydrogen concentration cell, it is possible to use HUP in other types of solid state battery. These are currently being developed so that an evaluation of the various types of HUP-based solid state batteries can be made.

Other applications of HUP

Fuel cells, electrolysis cells and electrochromic cells utilizing HUP discs have been constructed and successfully operated [8, 20] and the use of HUP as a hydrogen–deuterium separator may be possible, and work is proceeding on these applications. The absence of a fast proton-conducting solid has seriously impeded progress in the following two areas:

(1) The study of mixed electronic and proton conductors. The hydrogen activity as a function of composition can be determined in compounds such as the metal hydrides and electronically conducting metal oxides which are also proton conductors, such as H_xWO_3, H_xMoO_3, by using a solid state hydrogen concentration cell as described above. In this case one electrode will be the standard. The proton conductivity in HUP is similar to that in the metal hydrides, and exceeds by far that in H_xWO_3. In addition to the above e.m.f. cells, a conductivity cell can be set up which will enable the ratio of proton to electronic conductivity to be determined in such materials. The cell

E|HUP|P|HUP|E

measures only the proton conductivity of the test sample P. E are the usual proton reversible electrodes. The electronic conductivity of HUP, measured using indium blocking electrodes at a potential of 1 V, is approximately 10^{-8} ohm^{-1} cm^{-1} at 295 K [20].

(2) The study of electronically insulating proton conductors. Transport numbers of protons with respect to other ions may be able to be determined using a similar cell to that above, since the conductivity of anions in HUP appears to be very low, giving a transport number close to unity [8].

Conclusions

The availability of HUP has opened up prospects for several solid state electrochemical devices. Using thin HUP membranes to decrease the cell resistance and mass, it should be possible to produce lightweight, high energy density batteries using metal hydrides as the hydrogen store. Such batteries

could be easily miniaturized and could be available in primary, secondary or chemically rechargeable configurations.

Acknowledgements

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