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ALUMINUM AND BORON PHOSPHATES AS POSSIBLE PROTON CONDUCTORS*

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ABSTRACT

The chemical stability and conductivity of boron and aluminum phosphates in steam are reported for P/B and P/Al atomic ratios greater than unity at temperatures from 100° to 280°C and steam pressures to 5 atmospheres. $Al(PO_3)_3$ and $H_2AlP_3O_{10}$ undergo the reactions

$$Al(PO_3)_3 + H_2O \rightleftharpoons H_2AlP_3O_{10}$$

and

$$H_2AlP_3O_{10} \longrightarrow AlPO_4 + H_2O \cdot P_2O_5 \uparrow$$

At 280°C and a steam pressure of 5 atmospheres gauge the product is mixture of $AlPO_4$ and $H_2AlP_3O_{10}$, while the conductivity of this solid is in the range of 10^{-2} ohm^{-1} cm^{-1}. The boron phosphates lose material and exhibit poor conductivity under similar conditions due to the instability of the BPO_4 phase as a result of the reaction

$$2BPO_4 + 6H_2O \longrightarrow B_2O_3 \cdot 3H_2O\uparrow + P_2O_5 \cdot 3H_2O\uparrow .$$

As a result of dehydration or hydrolytic reactions an increase in water vapor pressure does not always lead to increased conductivity even at higher temperature.

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INTRODUCTION

Some organic and inorganic solids exhibit proton conductivity at ambient temperatures and slightly above(1,2). Generally these materials are hydrated and at high temperatures lose water, or are not stable. There are a number of electrochemical applications where a proton conducting electrolyte, stable at temperatures above 200°C, would be of special value. For example, fuel cells for electricity production and high temperature vapor electrolysis of steam for hydrogen and oxygen production(3). Electrolyte conductivity for these applications must be in the range of 0.1 $\text{ohm}^{-1}\text{cm}^{-1}$ or better. Other applications such as electrochemical synthesis, novel batteries, electrochemical heat engines, etc. may be possible with such materials(4,5).

Phosphoric acid is a unique material in that it retains a relatively high conductivity even at temperatures up to 200°C, which is one property which makes it suitable as a practical fuel cell electrolyte(5). Thus, chemical modifications which produce proton conducting electrolytes able to operate above 200°C could be of practical significance. Work on alternative phosphate electrolytes is rather limited. Relevant to the above applications is the ability of metal phosphates to form basic, neutral and inorganic polymer compounds which are insoluble in water(6,7). Aluminum and boron phosphates are notable in this regard(8). Structural work on acid forms(9) has shown proton distributions such as in $[Al_2(H_{1+x}PO_4)_3]\ H_{3-3x}PO_4$ $(0 \leqq x \leqq 1)$ and suggests an examination of these materials as possible proton conductors.

This paper reports on our initial results obtained with boron and aluminum phosphate salts under conditions i.e., temperature and steam pressures where steam electrolysis for hydrogen and oxygen production is possible.

EXPERIMENTAL

A compressed powder sample of the material being studied was encapsulated in the cell shown in Figure 1(10). The basic cell is a set of stainless steel flanges which are sealed by means of a ceramic fiber paper seal such that the flanges are electrically isolated from each other. The electrolyte cake, which was 6 cm in diameter by 0.25 cm thick, was contained in a ring of insulating Saureisen cement obtained from Sargent Welch of Springfield, New Jersey, stock #S-14950 and S-14951-10. The cake of electrolyte was sandwiched between two conducting carbon felt pads which served as electrodes. A stainless steel screen grid was placed on top of each carbon felt and was in contact with the respective flanges. Each electrode was supplied with steam from an inlet fitting and could be exhausted from the cell via an outlet fitting. The cell could be pressurized with steam to 5 atmospheres gauge (=75 psig) and resistance measured as a function of steam pressure over the temperature range from 100° to 280°C.

The overall resistance of the cell was measured by means of an alternating current bridge at 1000 cycles/second (CPS) in which the capacitance component was balanced out in each measurement. In addition, some direct current polarization measurements were also made to check the correspondence in the level of alternating and direct current resistance. The alternating current conductivity χ in ohm^{-1} cm^{-1} was calculated from the measured cell resistance, R, according to the relation,

$$\frac{1}{\chi} = (R - Ro) \frac{S}{L} ,$$

where Ro is the resistance of the external circuit ($\approx 0.2\Omega$) and S and L are the geometric area of the electrolyte and thickness respectively. The direct current conductivity was calculated from the applied potentials Vo obtained by the current (I) interruptor technique such that

$$\chi = \frac{I}{(V-Vo)} \frac{L}{S} .$$

Schematic details of the steam supply system and the oven which contained the cell are shown in Figure 2. In all cases the cell was electrically isolated from the oven and steam supply system.

Aluminum metaphosphates, $Al(PO_3)_3$, i.e., types A and B were purchased from ICN Pharmaceuticals Incorporated as well as being synthesized(11). In the synthesis procedure an aqueous solution containing $AlCl_3/H_3PO_4$ in a 3 to 1 mole ratio is obtained by adding $AlCl_3 \cdot 6H_2O$ into 85% H_3PO_4. The solution is dried on a hot plate until solid and baked at 300°C overnight until no chloride ion is detected. $H_2AlP_3O_{10} \cdot 2H_2O$ was obtained by mixing 85% H_3PO_4 and $Al(OH)_3$ in H_2O in proportions to keep the P/Al atomic ratio equal to 3. The resulting suspension was heated on a hot plate while stirring until it turned into a transparent liquid. This liquid was baked at 300°C until solid. Chemical identities of the phosphates were checked by elemental analyses and x-ray powder diffraction patterns(11-13). In the case of $H_2AlP_3O_{10}$, the x-ray powder pattern of the product stored over P_2O_5 exhibited a main peak corresponding to d = 6.33Å. Upon exposure in air the powder diffraction pattern changed rapidly as the sample absorbed moisture to yield the pattern associated with the product $H_2AlP_3O_{10} \cdot 2H_2O$ (d = 7.91Å). Measurement of the infrared spectrum was consistent with this acid phosphate structure.

Boron phosphates were prepared by reacting 85% H_3PO_4 and H_3BO_3 in aqueous solutions containing the reagents to give compositions in the range of 1 to 3 P/B. The product was dried on a hot plate to powdery solids and then cured overnight at 80°C.

X-ray and iR spectra were recorded with Philips PW 1050 and P.E. 457 instruments.

Phosphorous and aluminum analyses were performed by dissolving the phosphates in alkali and determining aluminum by atomic absorption and phosphorous by precipitation as ammonium phosphomolybdate and weighing.

RESULTS

Figure 3 shows the alternating current conductivity, χ in ohm^{-1} cm^{-1}, as a function of temperature at 5 atmospheres gauge steam pressure. Data are shown for different starting materials e.g.,

a) $H_2AlP_3O_{10}$,

b) $Al(PO_3)_3$, type "B",

c) $Al(PO_3)_3$, type "A",

and

d) temperature recycled $Al(PO_3)_3$, type "A".

It is evident that the acid aluminum triphosphate $H_2ALP_3O_{10} \cdot 2H_2O$ and the type "B" aluminum metaphosphate $Al(PO_3)_3$ have conductivities (χ) in the range of 10^{-1} to 10^{-2} ohm^{-1} cm^{-1} at temperatures up to 280°C and 5 atmospheres gauge steam pressures, e.g. see "a" and "b" in Figure 3. As seen in "c" in Figure 3 the type A metaphosphate is unique. For example, at temperatures between 170° and 200°C χ decreases as for some other proton conducting materials(1,2), but above 200°C χ increases to 10^{-2} ohm^{-1} cm^{-1}. This level of conductivity is maintained when this material is recycled through the same temperature range, e.g., see "d" in Figure 3. In addition, Figure 4 shows the variation in conductivity as the steam pressure is varied from 0 to 5 atmospheres gauge pressure.

The direct current polarization curve, shown in Figure 5, for the type "A" metaphosphate, which was obtained after this electrolyte was cycled from 100° to 280° at 5 atmosphere gauge steam pressure, shows that most of the cell resistance is due to the electrolyte. This data is in essential agreement with the alternating current data ("d" in Figure 3), where the direct current value is in the range of 10^{-3} ohm^{-1} cm^{-1}.

In all cases the materials after cycling to the maximum temperature contain no appreciable quantities of the type "A" or "B" metaphosphates as shown by the absence of their characteristic peaks in the x-ray powder difraction pattern ($d = 4.36Å$ for "A" and $d = 5.46Å$ for "B") and in the infrared spectra ($\nu = 1310$ cm^{-1} for "A" and 1280 cm^{-1} for "B")(11,14). Rather, the recovered electrolytes were identified from the x-ray data as mixtures of $AlPO_4$ and the acid aluminum triphosphate, where the patterns of berlinite and $H_2AlP_3O_{10} \cdot 2\text{-}3H_2O$ were distinctly recognized(15,16) as well as from analysis for phosphorous and aluminum shown in Table 1.

Electrolyte phases were further substantiated by infrared spectroscopy. The essential features of the infrared spectra shown in Figure 6 were:

a) the double absorption at 3580 and 3510 cm^{-1}, indicating weakly hydrogen bonded water molecules(7),

b) two broad absorptions over the 3000-2600 cm^{-1} (ν max = 2910 cm^{-1}) and the 2500-2000 cm^{-1} (ν max = 2340 cm^{-1}) ranges arising from OH stretching vibrations in the acidic structure, ≡POH bonds(17),

c) the OH bending absorption at 1640 cm^{-1}(18),

d) the absorption maxima (ν max = 1240, 1210, 1170, 1125, 1050 and 980 cm^{-1}) which arise from the P-O stretching vibrations of hydrogen bonded $(H_xPO_4)^{x-3}$ anions(19), and

e) the weak medium intensity bands in the 780-360 cm^{-1} range where the rotary and translational vibration bands of water overlies the absorptions due to Al-O stretching and P-O bending vibrations(7).

These spectra are consistent with the presence of acid hydrated triphosphate species(13). The simpler $AlPO_4$ pattern cannot be easily recognized since the main P-O stretching vibrations fall between 1240 and 1100 cm^{-1} and contribute to broadening of the triphosphate species absorption pattern in that region(7). However, the band at 685 cm^{-1}, which is absent from the spectrum of neat $H_2AlP_3O_{10}$, is specific for $AlPO_4$ where Al-OP≡ bonds are strong enough to allow interaction between Al-O and P-O vibrations. The ratio of this band absorbance to that of the triphosphate species at 980 cm^{-1} shown in Table 1 correlates directly with the $AlPO_4/H_2AlP_3O_{10}$ mole ratio and supports the product identification based on the x-ray data and elemental analysis.

Solid boron phosphates containing P/B ratios $\geq$3.0 could not be prepared. Appropriate reagent mixtures were cured up to 900°C and the resulting product was always a viscous liquid. Solid materials with a P/B ratio between 1.0 and 2.5 were obtained. The infrared spectra in the 3000-2000 cm^{-1} range were similar to those of fresh $H_2AlP_3O_{10}$ and confirmed the presence of acidic structural ≡PO-H functions. However, these boron compounds were not stable and rapidly turned into viscous liquids upon standing in air at room temperature. BPO_4 did not exhibit any evidence of PO-H functions, but was a more stable solid material.

Conductivity data for BPO_4 were obtained in the test cell. At 280°C and 5 atmospheres gauge steam pressure values as low as 10^{-5} $ohm^{-1}cm^{-1}$ were measured, but the material was unstable i.e., no well defined solid cake was observed at the end of a run. Results suggest that the degradation, loss of the solid phase material, was related to the steam pressure and temperature. Even though the material was not stable, the cell conductivity data is shown in Figure 7 as it may be interpreted by the reader in terms of the chemical transformations going on during degradation of the BPO_4 material in the cell.

DISCUSSION

The results on $Al(PO_3)_3$ shown in Table 1 for temperatures between 100° and 280°C in steam can be interpreted as follows:

$$Al(PO_3)_3 + H_2O \rightleftarrows AlH_2P_3O_{10}, \quad (a)$$

and

$$AlH_2P_3O_{10} \longrightarrow AlPO_4 + H_2O{\cdot}P_2O_5,\uparrow, \quad (b).$$

The corresponding boron compounds are less stable and hydrolyze to products which may volatilize such as

$$2BPO_4 + 6H_2O \longrightarrow B_2O_3.3H_2O\uparrow + P_2O_5{\cdot}3H_2O\uparrow, \quad (c),$$

implying loss of H_3PO_4 from the material.

These phosphates, as shown in reactions "b" and "c", may have variable degrees of hydration depending on the temperature and steam pressure according to the generalized reaction(20),

$$M \cdot nH_2O \rightleftarrows M + nH_2O, \quad (d),$$

where M represents a phosphate salt. These materials contain OH functions either in the form of acidic structural functions (≡PO-H) and/or in the form of water of hydration and yield hydrogen bonded chains such as

$$-O - H - - - O -$$

of variable strength. In such systems proton conductivity is likely to be related to the strength and stability of hydrogen bonds(21).

Proton conductivity in hydrogen bonded systems is expected based on the transport of protons along such chains(22). Evidence for proton mobility is seen in the vibrational spectra(23). Increased splitting of OH vibrational levels and the appearance of double absorption bands between 3000 and 2000 cm^{-1} seen in Figure 6 occur as the energy barrier between the potential minima and O - - - O distance in the O - H - - - O bond system decrease. Considering Table 2, the OH stretching absorption frequencies (ν_{OH}) of representative samples of the phosphates appearing in reactions "a", "b" and "c", calculations23,24) from the absorption frequencies for the relative O - - - O distances R, the hydrogen bond energy V and energy barriers ΔV for the proton to overcome in order to transfer between positions of minimum potential energy show that proton transport in the strongest hydrogen-bonded compound $H_2AlP_3O_{10}$ is favored due to the highest bond energy and smallest energy barrier. Other treatments of OH frequency shifts yield different R, V and ΔV values, but do not change the relative order(21,25).

High temperature causes destruction of hydrogen bonds and results in reduced conductivity(21). The loss of acidic structural OH functions due to the condensation reaction,

$$\equiv PO - H + \equiv PO - H \rightleftharpoons \equiv P-O-P\equiv + H_2O, \quad (e)$$

is known to occur in phosphates at high temperature after loss of hydration water (see Alberti and Vesely in ref. 4 and Makatun in ref. 20). Thus, at increasing temperature, the acid aluminum triphosphate, in which conductivity is based on the presence of $\equiv PO-H$ functions, may exhibit higher conductivity than other hydrates shown in Table 2, where conductivity depends on the degree of hydration.

The experimental results seem to support these expectation, with the acid phosphate being the most conductive species. On the other hand $AlPO_4$ is clearly more stable. However the BPO_4 data suggest that the stability of neutral phosphates depends on the cation. As the intended application involves the use of these materials in steam environment at high pressures and temperatures where either dehydration or hydrolysis may occur, we plan to extend this investigation to the effects of the nature and concentration of metal cations and OH functions on the chemical behaviour and conductivity of phosphates.

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TABLE 1

The Starting Electrolyte and Recovered Product Compositions Along With the Ratio of Band Absorbance at 685 cm^{-1} for $AlPO_4$ and 980 cm^{-1} for $H_2AlP_3O_{10}$

	Recovered Product Composition[(a,b)]			
Starting Electrolyte	Mole % $H_2AlP_3O_{10}$	Mole % $AlPO_4$	Mole Ratio $AlPO_4/H_2AlP_3O_{10}$	A_{685}/A_{980} (c)
Type A $Al(PO_3)_3$	22	78	3.5	0.53
Type B $Al(PO_3)_3$	30	70	2.5	0.25
$H_2AlP_3O_{10}$	37	63	1.7	0.20

a)After cycling (see Figure 3) the starting material from 100° to 280°C at P_{H_2O} =5atm.

b)Calculated from analytical P/Al atomic ratios (R) by assuming that only mono- and triphosphate species are present and solving the equations $x + 3y = R$ and $x + y = 1$, where x and y are the mole fractions of mono- and triphosphates respectively.

c)Ratio of band absorbances at 685 ($AlPO_4$) and 980 ($H_2AlP_3O_{10}$) cm^{-1} in the IR spectra (Figure 6) of the recovered product.

TABLE 2

Infrared Absorption Data

Substance	$\nu_{OH}(cm^{-1})^{(a)}$	$R(Å)^{(c)}$	$V^{(d)}$ (Kcal/mole)	$\Delta V^{(e)}$ (Kcal/mole)
$Al(PO_3)_3$	3420	2.85	2.92	42
BPO_4	3210	2.77	4.37	28.5
$AlPO_4$	3130	2.74	4.92	23
$H_2AlP_3O_{10}$	$2625^{(b)}$	2.62	8.40	5

a)OH stretching absorption frequency.

b)Average frequency from the two PO-H band in Figure 6.

c) +O-----O distance in the O-H------O bond.

d) H-bond energy.

e)Energy barrier height for the hydrogen bond system in the hydrates of fresh metal phosphates.

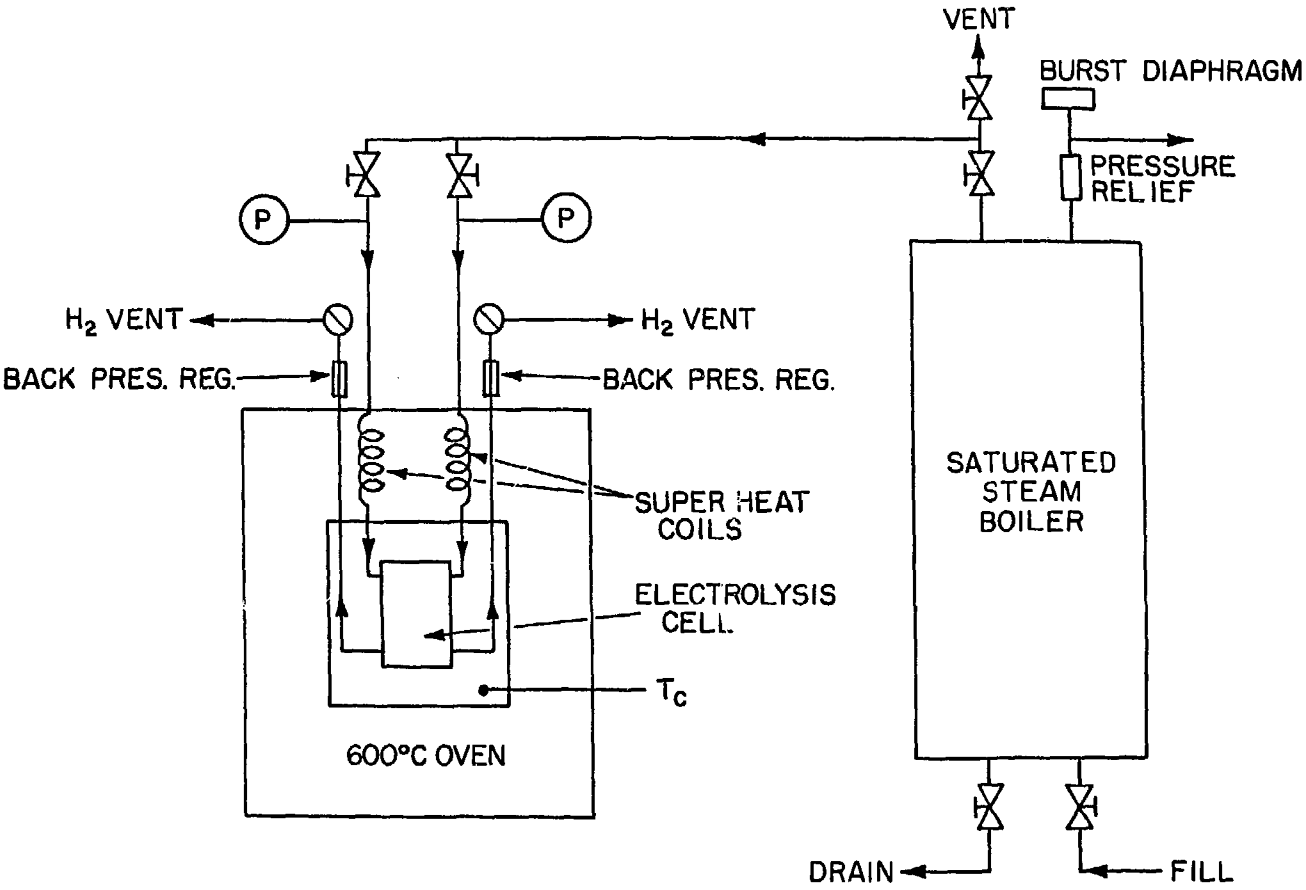

Fig. 1. Schematic layout of the test system.

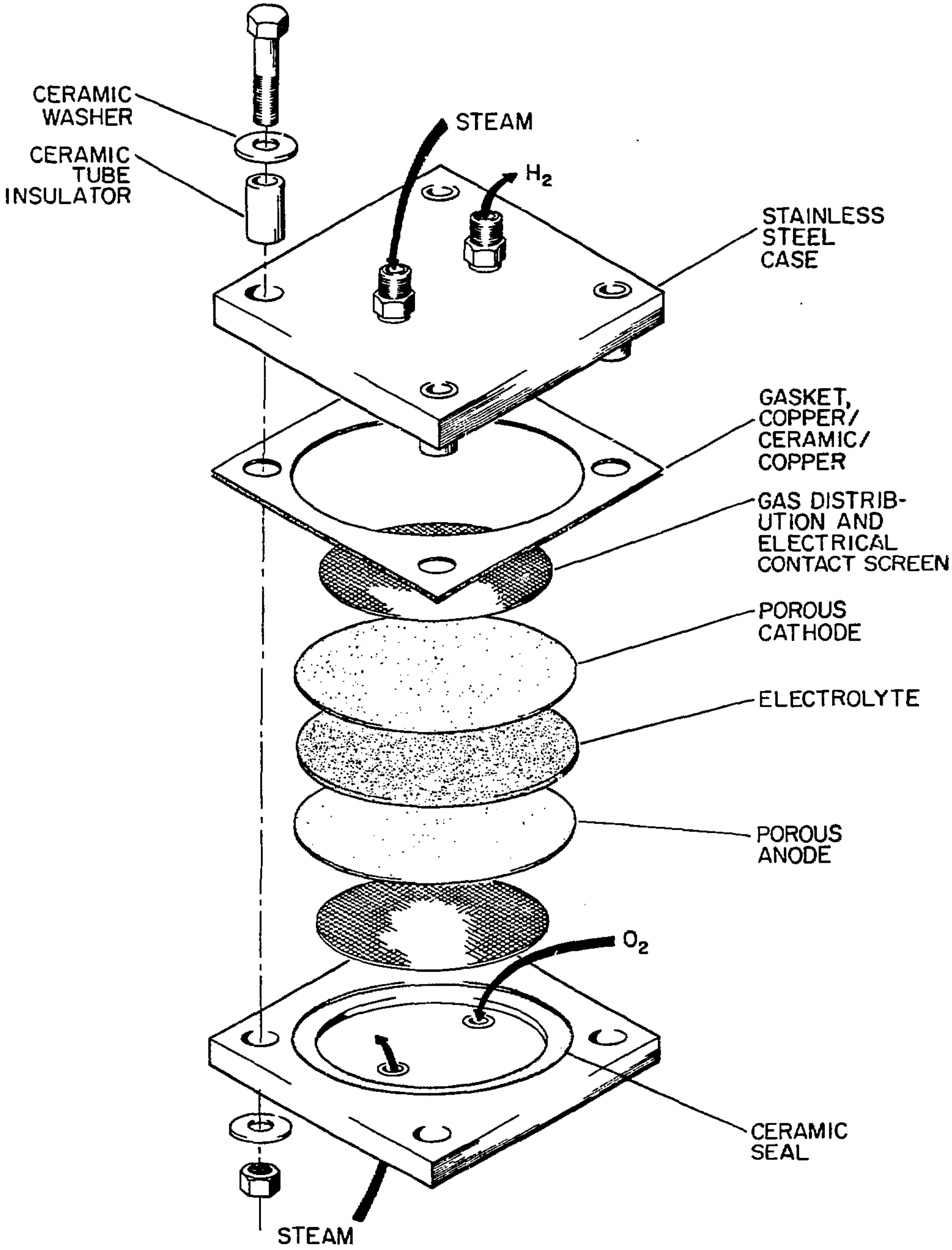

Fig. 2. Exploded view of the test cell.

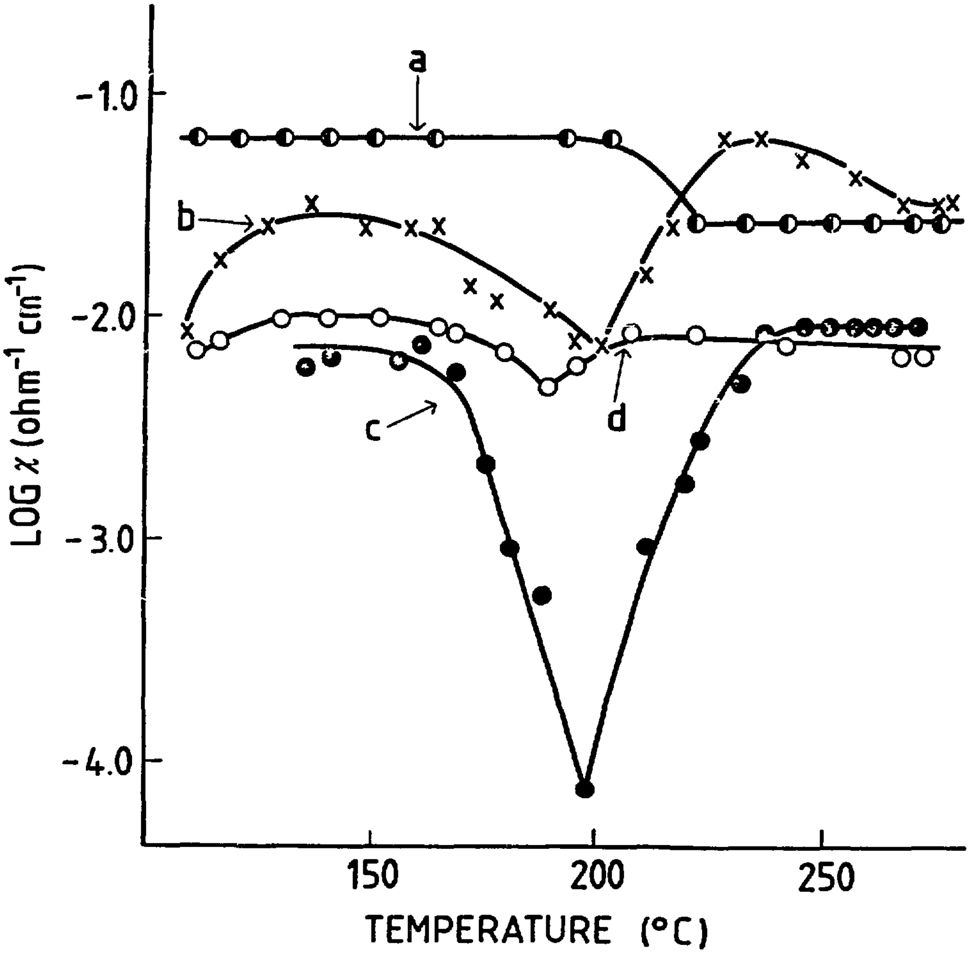

Fig. 3. Alternating current (1000 cps) conductivity, χ in ohm^{-1} cm^{-1}, as a function of temperature at a steam pressure of 5 atmospheres gauge.

The starting materials are:
a) $H_2AlP_3O_{10}$
b) $Al(PO_3)_3$, type "B"
c) $Al(PO_3)_3$, type "A"
d) $Al(PO_3)_3$, type "A" recycled.

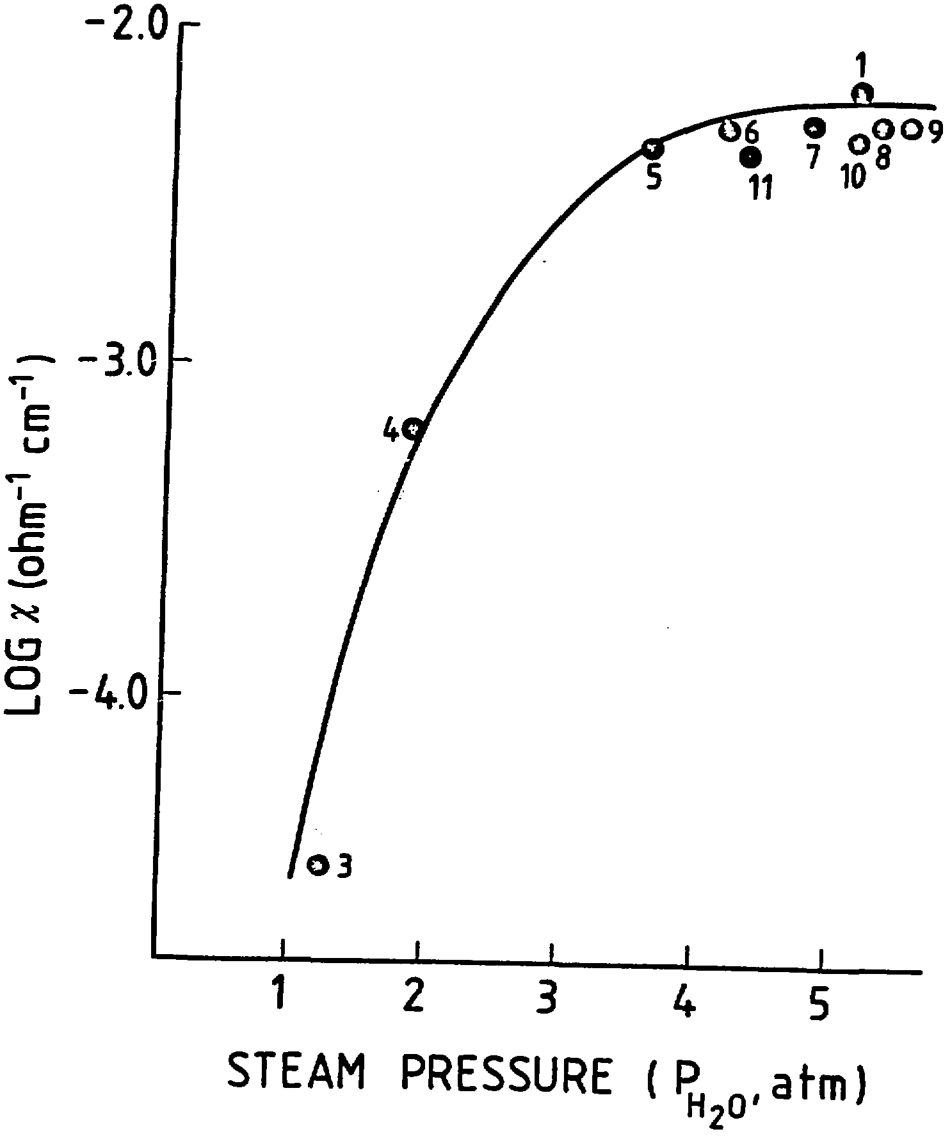

Fig. 4. Alternating current (1000 cps) conductivity, χ in ohm^{-1} cm^{-1}, as a function of steam pressure in atmospheres gauge at 280°C for $Al(PO_3)_3$ type "A", which was previously cycled twice from 100° to 280°C to 5 atmosphere gauge steam pressure. The sequence of measurements is indicated by the numbers by each data point.

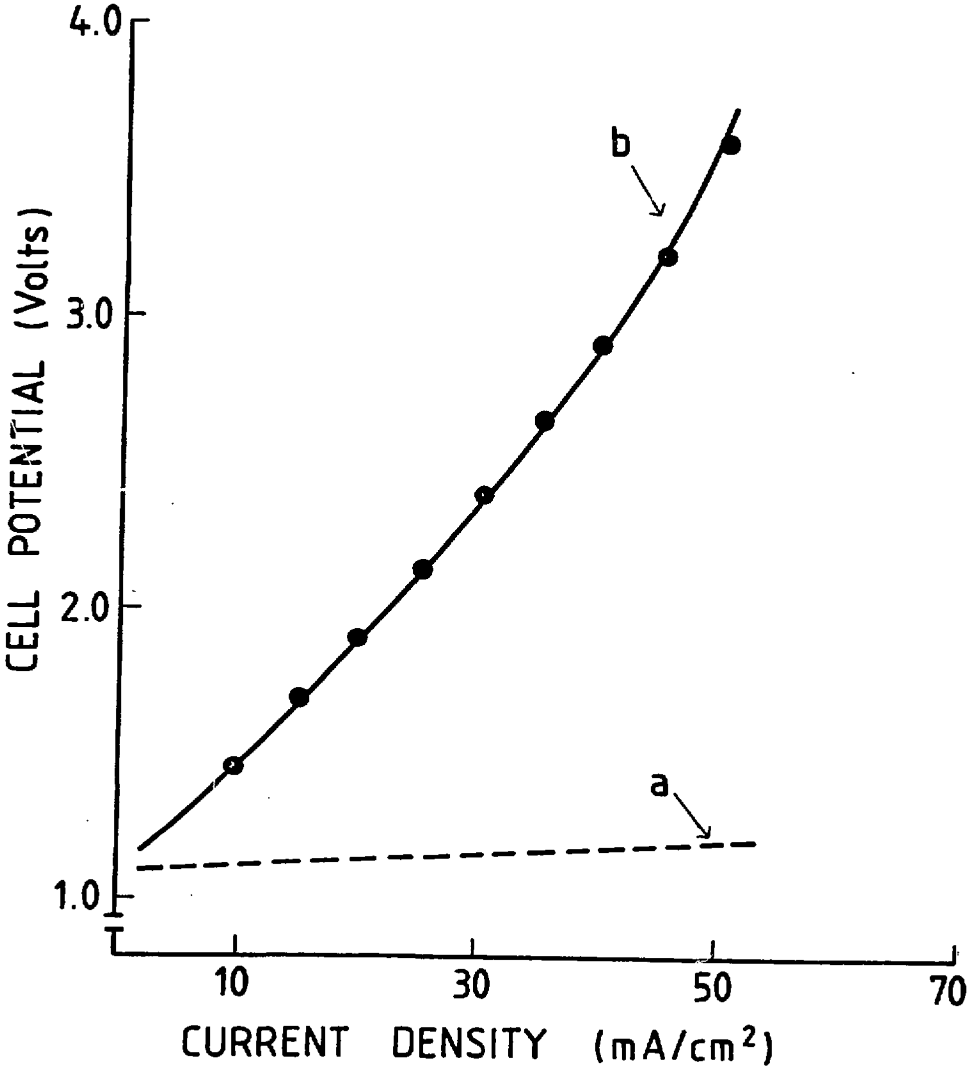

Fig. 5. Direct current polarization curve of $Al(PO_3)_3$ type A in the cell at 280°C and 5 atmospheres gauge steam pressure. Curve "a" is corrected for ohmic loss, while "b" is uncorrected. This material was previously cycled from 100° to 280°C to the above steam pressure.

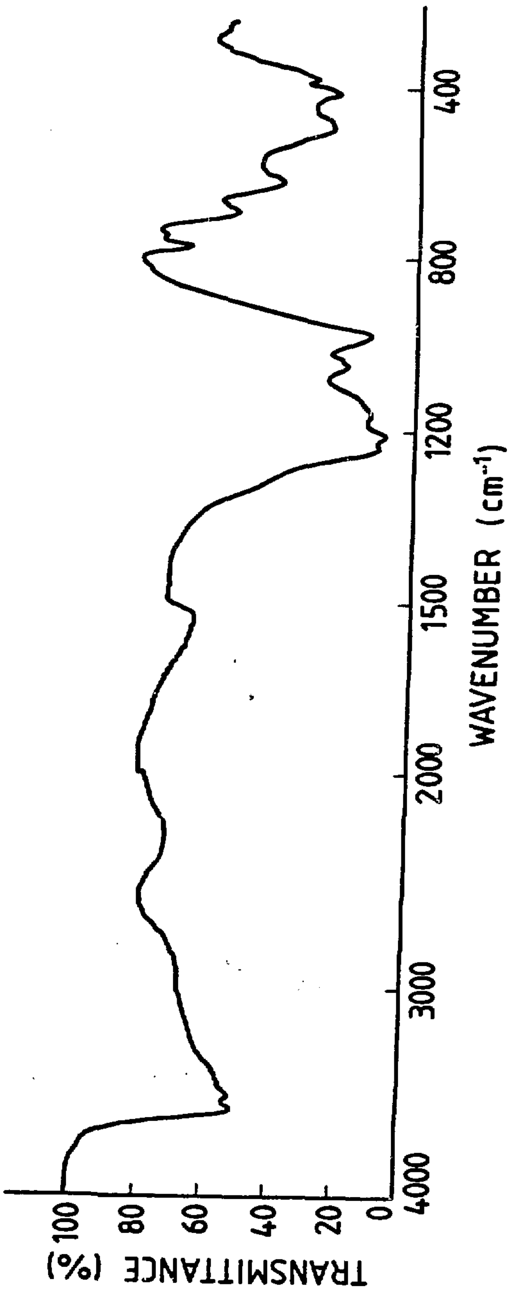

Fig. 6. Infrared spectrum of the material recovered from cycling $H_2AlP_3O_{10} \cdot 2H_2O$ from 100° to 280°C to the maximum steam pressure.

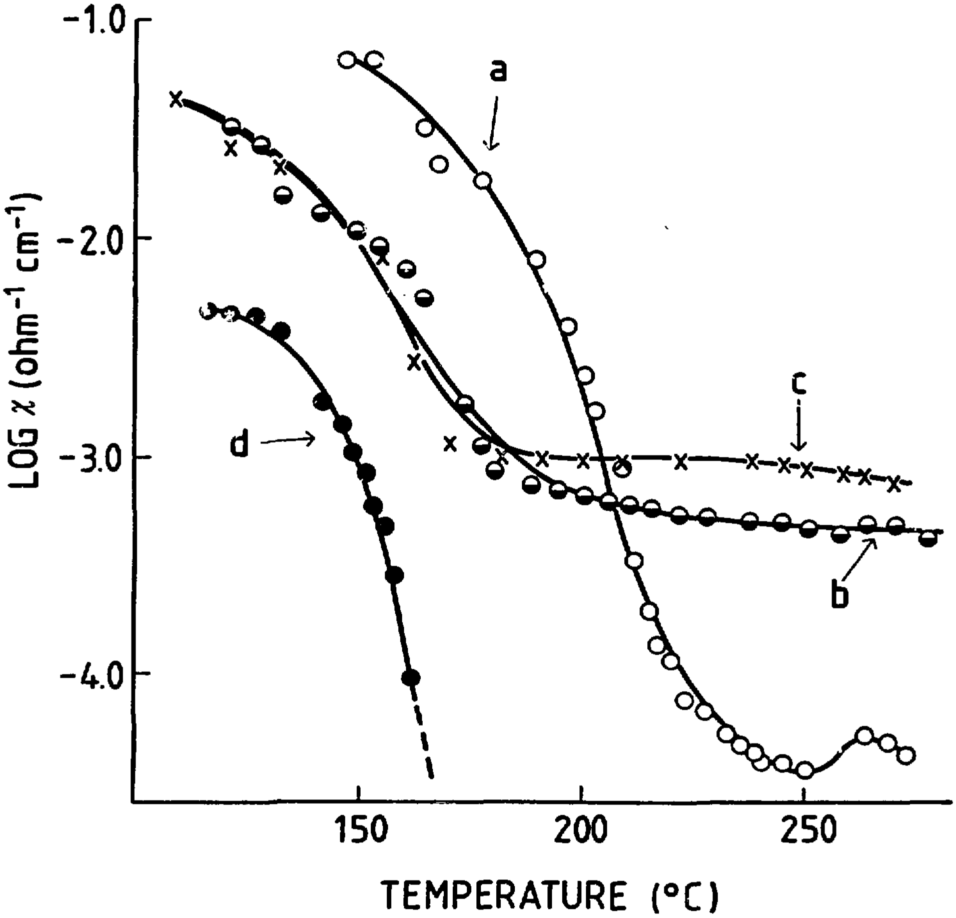

Fig. 7. Alternating current (1000 cps) conductivity, χ in ohm^{-1} cm^{-1}, of BPO_4 as a function of temperature at various steam pressures.

a) 5 atmosphere gauge pressure in flowing steam.
b) 1.5 atmosphere gauge pressure in flowing steam.
c) In flowing steam at ambient pressure.
d) In air.