Electrical-Transport Properties of Hydrated and Anhydrous Vanadyl Phosphate in the Temperature Range 20−200 °C

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The ac/dc conductivity of hydrated and anhydrous vanadyl phosphate has been measured in the range 20−200 °C in wet and dry nitrogen. Emf and thermoelectric power measurements have also been carried out at room temperature and 180 °C, respectively. At 20 °C and 58% relative humidity, the ac conductivity of a pellet of $VOPO_4 \cdot 2H_2O$ is of the order 10^{-5} S cm^{-1}. Both conductivity and emf measurements indicate that at room temperature $VOPO_4 \cdot 2H_2O$ is a mixed protonic−electronic conductor with dominant protonic component ($t_{H^+} \approx 0.9$). The presence of mixed conduction has allowed to use $VOPO_4 \cdot 2H_2O$ as an electrode able to exchange reversibly protons with a solid-state protonic conductor. Proton conduction in hydrated vanadyl phosphate decreases with increasing temperature, due to the loss of intercalated water, and vanishes at 70 °C concomitantly with the formation of $VOPO_4 \cdot H_2O$. The activation energy for electronic conduction of anhydrous $VOPO_4$ in a dry nitrogen atmosphere is 11.9 kcal/mol between 100 and 200 °C. In this temperature range the electronic conductivity is enhanced by the presence of water chemisorbed on surface sites. Possible mechanisms accounting for this effect are suggested.

Introduction

Vanadyl phosphate is a compound closely related to the catalysts used industrially for the production of maleic anhydride from butane or butene.[1] Anhydrous α-vanadyl phosphate has a layered structure[2] with an interlayer distance of 4.11 Å. The layers consist of distorted VO_6 octahedra sharing all their equatorial oxygens with four PO_4 tetrahedra; the double-bonded vanadyl oxygen (bond length 1.58 Å) occupies one of the two axial sites, the other one being filled by the oxygen of a vanadyl group of an adjacent layer which forms a weak V−O bond (2.85 Å). In monohydrated $VOPO_4$, the structure of the $(VOPO_4)_n$ layers is conserved but the interlayer distance increases to 6.3 Å,[3] the weakly bonded axial oxygen being replaced by a water molecule (coordinated water). In $VOPO_4 \cdot 2H_2O$ (interlayer distance 7.41 Å[4]) the second water molecule is inserted into the space between PO_4 tetrahedra of adjacent layers. All water molecules are presumed to be linked together by hydrogen bonds making a double layer between $VOPO_4$ sheets.[4-6] The strong acidic character of vanadyl phosphate layers leads to the formation of H_3O^+ ions in the interlayer region.[6]

Vanadyl phosphate is interesting for its ability to undergo intercalation reactions with Lewis bases (such as alcohols,[7,8] amines,[9] carboxylic acids,[10] pyridine[11]) which replace the coordinated water. In addition, mono- and divalent cations can be intercalated[12] with simultaneous reduction of V^V to V^{IV} by a proper reducing agent.

While various articles have appeared concerning the electrical properties of intercalated $VOPO_4$,[13-18] very little work has been devoted to the electrical properties of $VOPO_4$ in its anhydrous and hydrated form. In the range 400−500 °C, anhydrous $VOPO_4$ phases were

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found to be extrinsic n-type semiconductors.[19] On the other hand, the low-temperature features of the dielectric loss of dihydrated $VOPO_4$ seem to indicate the presence of mobile protons jumping between the phosphate oxygens and the interlayer water.[20] The presence of dominant positive charge carriers in hydrated $VOPO_4$ and negative carriers in the anhydrous material was also demonstrated by means of Seebeck effect measurements.[21]

On the basis of these results, it seemed of interest to investigate the evolution of the electrical transport properties of vanadyl phosphate in the range of temperature where the dominant charge carriers change from protons to electrons. The conductivity of vanadyl phosphate was measured in the range 20−200 °C by means of combined ac/dc measurements in order to estimate protonic and electronic transport as a function of temperature and water content. Emf measurements at room temperature and thermoelectric power measurements at 180 °C were also carried out to give independent experimental support to the results of conductivity measurements.

Experimental Section

Dihydrated vanadyl phosphate was prepared by refluxing vanadium pentoxide (48 g) in 28% mass phosphoric acid (1430 mL) for 2 days.[21] The reaction mixture was bubbled with oxygen during refluxing. After filtration the solid was washed several times with cold water to remove phosphoric acid. The content of V^{IV}, determined by magnetic susceptibility and EPR mesurements, was in the range 0.5−1% of the total vanadium content.

Thermogravimetric determinations were carried out by a Stanton Redcroft STA 780 thermal analyzer at a heating rate of 1 °C min^{-1}.

Pellets, 10 mm in diameter and 1−1.5 mm thick, were prepared by pressing ≈200 mg of material at 40 kN/cm². The two flat surfaces of the pellet were coated by composite electrodes consisting of a mixture of the sample material with graphite (Carlo Erba) in the ratio 1:3.

The ac conductivity of the pellets was determined by an HP 4192A impedance analyzer in the frequency range 10 Hz to 10 MHz with a signal level ≤100 mV. Measurements at 20 °C were carried out by a sealed-off stainless steel cell containing in the lower part a saturated NaBr solution (58% relative humidity). Measurements in the range 40−200 °C were performed by means of a flow cell purged with wet nitrogen (≈10 mL/min); relative humidity was controlled by bubbling the purging gas in water heated at a suitable temperature between 20 and 80 °C. The tube connecting the humidifier to the cell was kept at a temperature higher than that of the humidifier to avoid vapor condensation.

Two kinds of electrochemical cells were tested by emf measurements. One cell consisted of a pellet of $VOPO_4·2H_2O$ sandwiched between a graphite disk and a sputtered platinum electrode. In the other cell, a pellet of $VOPO_4·2H_2O$ was put in contact with a graphite disk, on one side, and with a sheet of pellicular α-zirconium phosphate, on the other side. The free surface of the sheet was coated with sputtered platinum. Pellicular zirconium phosphate was prepared as described in ref 22. Emf measurements were carried out by an HP44701A integrating voltmeter. The measuring cell was purged with
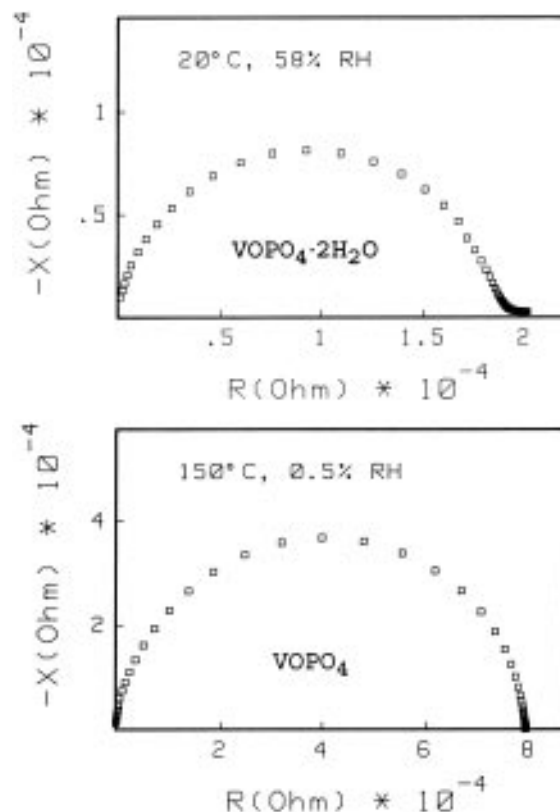
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Figure 1. Impedance plots for dihydrated and anhydrous vanadyl phosphate at the indicated temperatures and relative humidities. The impedance plot referring to 150 °C was recorded during the heating cycle in wet nitrogen.

mixtures of nitrogen and hydrogen humidified at 20 °C through a saturated NaBr solution (58% relative humidity).

For thermoelectric power measurements, the opposite sides of a vanadyl phosphate pellet were sputtered with carbon. The sample was mounted between two metal blocks provided with platinum contacts. One of the metal blocks was heated by a resistance heating to produce a temperature gradient across the sample. The gradient (2 K mm^{-1}) was monitored by nickelchromium−nickel thermocouples. The measurements were carried out at 180 °C in dry air, in dry nitrogen, and wet nitrogen which was humidified by bubbling through water at room temperature.

Water Influence on Proton Conductivity

The ac conductivity of hydrated and anhydrous vanadyl phosphate was determined with composite graphite electrodes by the impedance technique. At room temperature, the impedance plot of a pellet of $VOPO_4·2H_2O$ consists of a single semicircle ending with a low-frequency tail (Figure 1) which is likely to be associated with the presence of the protonic carriers which are not discharged at the electrodes. The ac conductivity was calculated by semicircle extrapolation to the real axis on the low-frequency side.

The ac conductivity dependence on temperature and hydration was investigated in the range 40−200 °C in a flow of wet nitrogen humidified at 20 °C. A pellet of $VOPO_4·2H_2O$ was first heated up to 200 °C and then cooled to 100 °C; the cell was finally purged with dry nitrogen and the conductivity determined from 200 to 100 °C. The pellet was held at each temperature until the conductivity reached a constant value; the steady-state ac conductivities are shown in Figure 2. Changes in the shape of the impedance plots were observed
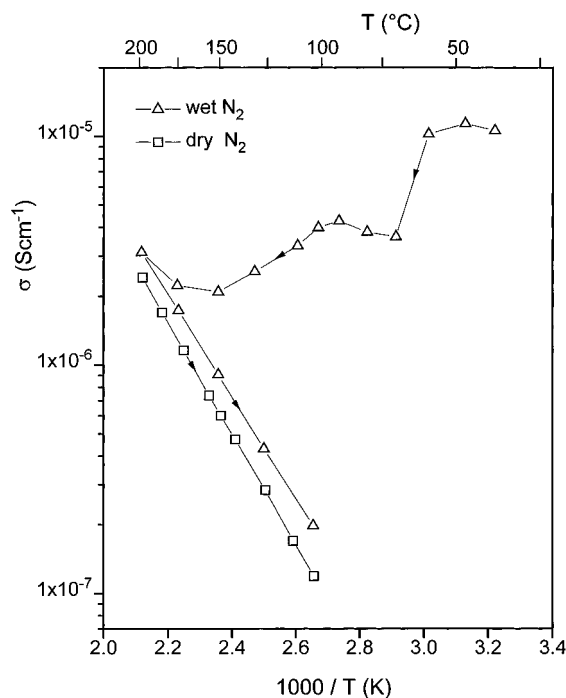
Figure 2. Ac conductivity of a pellet of vanadyl phosphate, initially in the dihydrated form, during subsequent heating and cooling cycles (arrows show the direction of temperature changes).

Table 1. Results of Combined Ac/Dc Measurements on Pellets of Vanadyl Phosphate at Different Temperatures[a]

T (°C)	$n(H_2O)$	$\sigma(0)_{ac}$	$\sigma(0)_{ac}/\sigma(\infty)_{ac}$	$\sigma(\infty)_{ac}/\sigma(\infty)_{dc}$
20.0	2.00	9.7×10^{-6}	1.7	9.3
40.9	1.97	1.3×10^{-5}	2.1	4.0
58.0	1.55	1.2×10^{-5}	2.8	2.1
70.4	1.03	3.6×10^{-6}	1	1.1
151	0.08	2.1×10^{-6}	1	1.0

[a] $\sigma(\infty)_{ac}$, $\sigma(\infty)_{dc}$: steady-state ac and dc conductivities. $\sigma(0)_{ac}$: ac conductivity before starting the dc experiment. $n(H_2O)$: number of water molecules per unit formula.

during the heating in wet nitrogen: the low-frequency tail shrinks with increasing temperature and disappears starting from 70 °C (Figure 1) thus suggesting that, above this temperature, the main carriers are electronic.

To estimate the protonic and the electronic components of the ac conductivity, combined ac/dc measurements were carried out with graphite proton-blocking electrodes.[23] The steady-state dc conductivity arises from the diffusion of the electronic carriers only while the ac conductivity gives the sum of both components.

Combined ac/dc measurements were performed at constant temperature by applying to the pellet a dc load of 0.2 V with composite graphite electrodes; at regular time intervals, the dc load was removed and the ac conductivity was measured. The ac conductivities at time zero ($\sigma(0)_{ac}$), the ratio between $\sigma(0)_{ac}$ and the steady state ac conductivity ($\sigma(\infty)_{ac}$), as well as the ratio between $\sigma(\infty)_{ac}$ and the steady state dc conductivity ($\sigma(\infty)_{dc}$), are reported in Table 1 for different temperatures. Two different trends are seen for the two conductivity ratios: (i) $\sigma(\infty)_{ac}/\sigma(\infty)_{dc}$ decreases with increasing temperature in the range 20−60 °C and is equal to 1 at

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temperatures higher than 70 °C, within the precision of the measurement; (ii) $\sigma(0)_{ac}/\sigma(\infty)_{ac}$ increases in the range 20−58 °C and is 1 above 70 °C.

Let us discuss the data of Table 1 on the basis of the processes occurring in the $VOPO_4 \cdot nH_2O$ pellet when a dc current is passed with proton-blocking electrodes. When electrons are released by the cathode to vanadyl phosphate, two limit situations can occur: (i) the electrons migrate toward the anode or (ii) the excess of negative charge is compensated by the insertion of protons in the interlayer region:

$$V^VOPO_4 \cdot nH_2O + e^- + H^+ \rightarrow HV^{IV}OPO_4 \cdot nH_2O \quad (1)$$
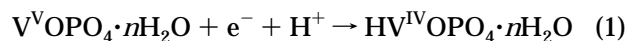
Similarly, when electrons are transferred from substitutional V^{IV} to the anode, the resulting positive charge can be compensated (i) by electrons coming from the cathode region or (ii) by expelling protons from the interlayer region:

$$HV^{IV}OPO_4 \cdot nH_2O \rightarrow V^VOPO_4 \cdot nH_2O + e^- + H^+ \quad (2)$$

If reactions 1 and 2 occur to some extent, at the steady state the concentration of V^{IV} and interlayer protons in the cathodic region will be higher than that in the anodic region. Depending on the relative weight of the protonic and the electronic component, three different situations can occur. If the protonic conductivity (σ_p) is much higher than the electronic conductivity (σ_e), then the charge compensation reactions 1 and 2 do not alter σ_p, so that

$$\sigma_{ac} = \sigma_p + \sigma_e \cong \sigma_p$$

$$\sigma(0)_{ac}/\sigma(\infty)_{ac} \cong 1$$

$$\sigma(\infty)_{ac}/\sigma(\infty)_{dc} \gg 1$$

This situation is never observed in the investigated temperature range; therefore σ_e is not negligible in comparison with σ_p even at 20 °C. In this case σ_p and σ_e are affected by the composition changes due to reactions 1 and 2 and σ_{ac} is expected to be time dependent as observed between 20 and 58 °C; the increase of $\sigma(0)_{ac}/\sigma(\infty)_{ac}$ and the decrease of $\sigma(\infty)_{ac}/\sigma(\infty)_{dc}$ in the range 20−58 °C is consistent with the progressive increase of σ_e and the concomitant decrease of σ_p. Finally if $\sigma_e \gg \sigma_p$, then σ_{ac} is independent of time and $\sigma_{ac} \cong \sigma_e \cong \sigma_{dc}$, as found for temperatures higher than 70 °C.

To understand to what extent the ac conductivity is affected by the presence of interlayer and coordinated water, the water content of vanadyl phosphate was determined on pellets heated under the same conditions used in the conductivity measurements and, in particular, for the same time needed to reach a constant conductivity. Comparison of the conductivity data of Figure 2 with the water content data of Table 1 shows that the sharp drop of σ_{ac} between 60 and 70 °C is associated with the loss of 0.5 water molecule (interlayer water[6]) leading to the formation of monohydrated vanadyl phosphate. Since at 70 °C $\sigma_{ac} \cong \sigma_e$, it is inferred that water molecules in excess of one per formula unit are necessary to the proton transport through the interlayer region. This is consistent with the depen-
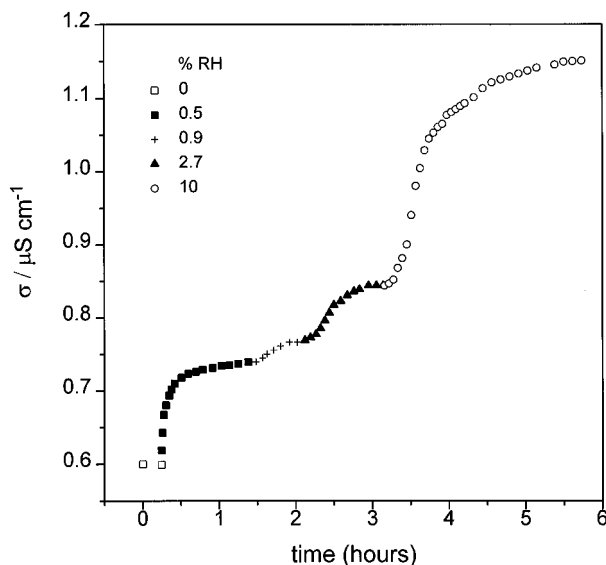
Figure 3. Electronic conductivity as a function of time, at 150 °C, for anhydrous vanadyl phosphate exposed to a flow of wet nitrogen at the indicated relative humidities (RH).

dence of the thermoelectric coefficient on temperature reported in ref 21.

The conductivity decrease in the range 100–150 °C is concomitant with the loss of the coordinated water. Once water is completely lost, the conductivity increases with increasing temperature. During the cooling cycle from 200 to 100 °C the conductivity shows an Arrhenius type behaviour with an activation energy of 11.0 kcal/mol. In dry nitrogen, the conductivity turns out to be lower and the activation energy higher (11.9 kcal/mol) than those correspondingly measured in wet nitrogen.

Water Influence on Electronic Conductivity

To understand how the loss of water could influence the pellet conductivity in the range 100–150 °C, it can be observed that the associated particle contraction (due to the shortening of the interlayer distance from 6.3 to 4.11 Å) should increase the resistance of the interparticle contacts thus reducing to some extent the pellet conductivity. This argument, however, cannot account for the different conductivities measured during the cooling cycles in dry and wet nitrogen. Thermogravimetric experiments showed that water is completely lost at 200 °C and that, when anhydrous $VOPO_4$ is held at 100 °C in a flow of nitrogen humidified at 20 °C, the water uptake is too low ($\Delta w/w < 10^{-3}$) to determine changes in the interlayer distance. This excludes any particle contraction when the pellet is heated to 200 °C in dry nitrogen after the cooling cycle in wet nitrogen. On the basis of these considerations it must be concluded that electronic conductivity is influenced to some extent by water chemisorbed on the surface of $VOPO_4$ particles. To give direct experimental evidence to this expectation, ac conductivity measurements were carried out at 150 °C on a pellet of anhydrous $VOPO_4$ exposed to a flow of nitrogen humidified at different temperatures (from 20 to 80 °C) so as to have relative humidities in the range 0–10%. The dependence of conductivity on relative humidity is shown in Figure 3. Combined ac/dc measurements, carried out at the highest relative humidity, proved the conductivity to be fully electronic. Preliminary investigations revealed that conductivity

enhancements also occur with a number of gaseous Lewis bases such as ammonia, ethanol, diethyl ether, and acetone.

On the basis of the above results, it was thought of interest to carry out thermoelectric power measurements in dry/wet nitrogen or in dry air. At 180 °C, the sign of the thermoelectric coefficient S of anhydrous vanadyl phosphate was found to be negative regardless of the gas environment, thus indicating that in any case electrons are the prevailing charge carriers. S values are -580 μV K^{-1} in dry air, -550 μV K^{-1} in dry nitrogen, and -530 μV K^{-1} in wet nitrogen. Taking into account the conductivity data reported in the present work and that the conductivity of anhydrous $VOPO_4$ decreases with increasing oxygen pressure,[19] it can be observed that, in comparison with dry nitrogen, wet nitrogen and dry air influence both conductivity and thermoelectric power in opposite directions. The conductivity decrease in oxygen was ascribed to chemisorption of oxygen on single-ionized oxygen vacant sites ($V^{\bullet}_O$):

$$V^{\bullet}_O + {}^1/_2 O_2 + e' \rightarrow O_O$$
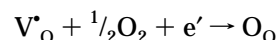
While the decrease of S in dry air must be associated with the reduction of the number of free electrons according to the above reaction, its increase in wet nitrogen (as well as the corresponding conductivity enhancement) seems to indicate that chemisorbed water (or more generally a chemisorbed Lewis base) increases the number of free electrons. This can be accounted for by assuming the presence of surface electron-acceptor sites which are able either to accommodate the base lone pair or to trap free electrons of the conduction band. The chemisorption of a Lewis base is therefore expected to reduce the number of trapped electrons and to enhance the electronic conductivity.

Two types of acceptor site are expected to be present on the surface of vanadyl phosphate. According to ref 19, the conductivity of vanadyl phosphate is partly due to surface oxygen vacancies (V_O) containing two electrons, one of which can easily be lost:

$$V_O \rightarrow V^{\bullet}_O + e'$$

The number of free electrons could be further increased if a Lewis base (B) is chemisorbed on $V^{\bullet}_O$

$$V^{\bullet}_O + B \rightarrow + B^{\bullet\bullet}_O + e'$$
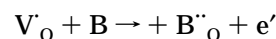
On the other hand, it can be pointed out that the loss of the coordinated water molecule in monohydrated $VOPO_4$ makes an octahedral coordination site vacant (V_{H_2O}) around V^V: in the bulk, this site is filled by the double-bonded axial oxygen of an adjacent layer, while on the surface it could act as an acceptor site for free electrons of conduction:

$$V_{H_2O} + e' \rightarrow V'_{H_2O}$$
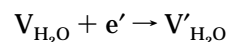
The number of trapped electrons can be reduced if a Lewis base is chemisorbed on V'_{H_2O}:

$$V'_{H_2O} + B \rightarrow B_{H_2O} + e'$$
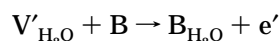
Emf Measurements

Although protons are the dominant charge carriers at 20 °C, the results of ac/dc measurements show that
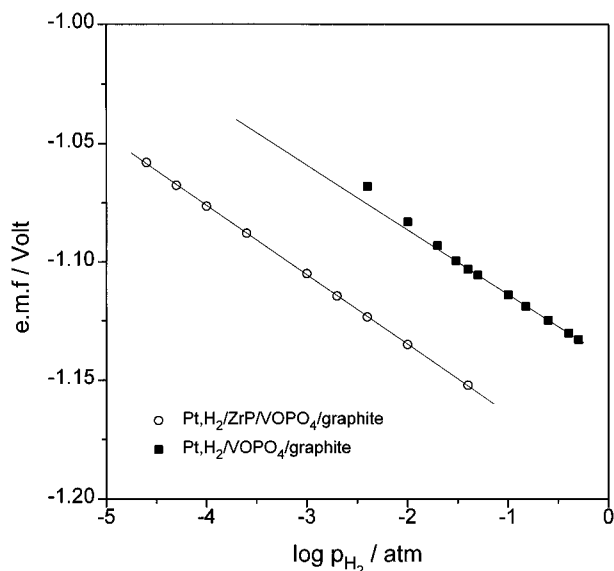
**Figure 4.** Emf of the indicated cells as a function of hydrogen pressure at 20 °C and 58% relative humidity.

the electronic conductivity is not negligible. Due to the presence of mixed conduction, $VOPO_4 \cdot 2H_2O$ could be used as a reference electrode in electrochemical cells based on solid-state proton conductors (SSPC), such as the following:

$$graphite/VOPO_4 \cdot 2H_2O/SSPC/Pt, H_2 \qquad (3)$$
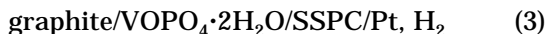
The potential of the platinum electrode (E) against the graphite electrode was measured at 20 °C by using pellicular α-zirconium phosphate (ZrP) as a proton conductor. Figure 4 shows that E depends linearly on the logarithm of hydrogen pressure. The equation of the least-squares straight line is

$$E(V) = -0.0293 \log p(H_2) - 1.1936$$

The slope of the straight line is that expected from the Nernst equation (i.e., -0.0291 V) for a reaction occurring at 20 °C and involving two electrons, as is the case of the reduction of V^V to V^{IV} by hydrogen and the concomitant proton insertion in the interlayer space of $VOPO_4$:

$$2V^VOPO_4 \cdot 2H_2O + H_2 \rightarrow 2HV^{IV}OPO_4 \cdot 2H_2O \quad (4)$$
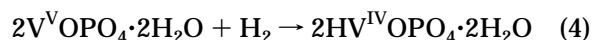
Measurements were also carried out on an electrochemical cell where the platinum electrode was in direct contact with the pellet of vanadyl phosphate:

$$graphite/VOPO_4 \cdot 2H_2O/Pt, H_2 \qquad (5)$$
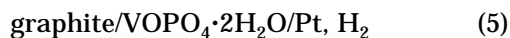
The potential of the platinum electrode against the graphite electrode depends linearly on $\log p(H_2)$ for hydrogen pressures higher than 3×10^{-2} atm (Figure 4). The equation of the least-squares straight line is

$$E'(V) = -0.0273 \log p(H_2) - 1.1411 \qquad (6)$$

It can be observed that the same electrochemical process (i.e., reaction 4) occurs when current is passed through

cells 3 and 5, except for the fact that in cell 5 a fraction of current t_e is carried by electrons. The following relation is therefore expected between E and E':[24]

$$E' = (1 - t_e)E$$

which implies that the ratio between the slopes of the two straight lines of Figure 4 must be equal to the ratio between their intercepts. From the equations of E' and E, the ratio of the intercepts is 0.95 while that of the slopes is 0.93 so that, on average, $t_e = 0.06$. This value is not far from that which can be calculated from the steady-state ac and dc conductivities at 20 °C:

$$t_e = \sigma_e/(\sigma_e + \sigma_p) = \sigma(\infty)_{dc}/\sigma(\infty)_{ac} = 0.11$$

At low hydrogen pressures, the deviation of the potential of cell 5 toward more positive values than those predicted by eq 6 can be explained on the basis of kinetic considerations. The following processes can occur at the platinum electrode:

$$V^V + e^- = V^{IV} \qquad (7)$$

$${}^1\!/_2 H_2 + e^- = H^+ \qquad (8)$$

When the hydrogen pressure is high enough as to make reaction 8 much faster than reaction 7, the potential of the platinum electrode is determined by the couple H^+/H_2 and the overall cell potential by reaction 4. However, when reaction 8 is much slower than reaction 7 because of low hydrogen pressure, the same couple (V^V/V^{IV}) is responsible for electron exchange both at the platinum and at the graphite electrode so that the cell potential is zero. As a consequence, with decreasing hydrogen pressure, the cell potential is expected to tend toward zero more rapidly than expected for process 4.

Conclusion

Hydrated $VOPO_4$ was proved to be a mixed protonic−electronic conductor in the range 20−60 °C. It was shown that $VOPO_4 \cdot 2H_2O$ can be used as a proton-reversible electrode which could find application in electrochemical devices based on a solid proton electrolyte. As a consequence of water loss, the protonic component decreases with increasing temperature so that at 70 °C monohydrated $VOPO_4$ turns out to be an electronic conductor. The electronic conductivity of anhydrous $VOPO_4$ is enhanced by water and more generally by Lewis bases chemisorbed on surface sites.

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