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Intercalation Compounds of Vanadyl Phosphate Dihydrate with Rubidium Ion and Their Electrical Properties

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Intercalation compounds of vanadyl phosphate with rubidium ($Rb_xVOPO_4 \cdot yH_2O$) were prepared by reacting $VOPO_4$ with rubidium iodide solutions in acetone/water (volume ratio 9:1) at temperatures between 18 and 40 °C. Two phases with interlayer distance of 0.703 and 0.644 nm were formed during the intercalation; their composition is $0.20 \leq x \leq 0.28$ and $x \geq 0.48$, respectively. The water content of the intercalates increases with decreasing the rubidium content and goes from $y = 1.4$ for $x = 0.557$ up to $y = 2.2$ for $x = 0.110$, at 58% relative humidity. Samples with $x = 0.18$, 0.28, and 0.48 were investigated by ac and dc conductivity measurements which were carried out on pellets at 20 °C as a function of relative humidity (RH). In all cases the conductivity is fully electronic up to 30% RH. The electronic conductivity of the 0.703 nm phase is $\sim 10^{-7}$ S cm^{-1} at 0% RH and reaches a maximum ($\sim 10^{-5}$ S cm^{-1}) at around 5% RH. No appreciable change is correspondingly observed in the electronic conductivity of $Rb_{0.48}VOPO_4 \cdot yH_2O$. In all cases, at relative humidity higher than 30% the conductivity starts being mixed, ionic−electronic, as a consequence of the increasing surface hydration of the microcrystals. Electromotive force measurements showed that the diffusion of Rb^+ gives a significant contribution to the ionic conductivity.

Introduction

Vanadyl phosphate serves as a precursor in catalytic systems used for the selective oxidation of hydrocarbons.[1] In the tetragonal structure of $VOPO_4 \cdot 2H_2O$, two types of water molecules bonding to the host layer were found.[2] One of them is coordinated to the vanadium atom by its oxygen, complementing the coordination number of vanadium to six. The other water molecule is bonded by weak H-bridges to the oxygen atoms of the vanadium phosphate layers.

Layered vanadyl phosphate dihydrate undergoes oxidoreduction reactions with cations in the presence of a proper reducing agent.[3] In this process, pentavalent vanadium atoms are reduced to V(IV). The negative charge formed in the $(VOPO_4)_\infty$ layers is compensated by cations that are anchored in the interlayer space. As cations are inserted between the layers, the reaction is often denoted as a redox intercalation. This reaction has been studied for cations of alkali metals such as lithium, sodium, and potassium and for hydronium cation.[4−6] The redox intercalation of cations leads to lowering of the interlayer distance, owing to stronger interactions between intercalated cations and negatively charged layers. In $VOPO_4 \cdot 2H_2O$ intercalated with lithium[5] and sodium,[4] a staging effect was observed as inferred from X-ray powder patterns.

The host material, $VOPO_4 \cdot 2H_2O$, is a mixed protonic−electronic conductor.[7] The protons formed by the dissociation of the interlayer water molecules are responsible for the prevailing part of the conductivity at ambient temperature. Redox intercalation causes a decrease of the total conductivity. It is presumed that the intercalated cations are strongly anchored to the negatively charged layers so that they cannot serve as charge carriers. The reduced $(VOPO_4)_\infty$ layers are less acidic[8] than the original host so that the conditions for the dissociation of the water molecules to form protons as the charge carriers are less favorable. As inferred from these considerations, the conductivity depends also on the amount of water in the interlayer space of the intercalate. As layered materials based on $VOPO_4$ can

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easily uptake water from a surrounding gas, the relative humidity of the atmosphere influences the conductivity.

The present paper complements the series of papers dealing with redox intercalations of alkali metals into $VOPO_4 \cdot 2H_2O$.[4-6] In contrast to the previous studies, this work is enlarged upon a study of conductivity as a function of relative humidity.

Experimental Section

Vanadyl phosphate dihydrate was prepared by the method proposed by Ladwig.[9] The product was sieve analyzed, and the fraction with the particle size of 0.125−0.25 mm was used.

Commercially available rubidium iodide was used both as a source of rubidium cations and the reducing agent. The redox intercalations were simply accomplished by contacting solid $VOPO_4 \cdot 2H_2O$ with a 0.26 M solution of rubidium iodide in a mixture of acetone and water (volume ratio 9:1). A total of 2 g of $VOPO_4 \cdot 2H_2O$ were suspended in 100 mL of the RbI solution (Rb:V molar ratio roughly 4:1) and the reaction mixture was intensively shaken. The reactions were carried out at 18, 21, and 40 °C. Rubidium intercalates with various cation contents were obtained by changing the reaction time from several minutes to several days. After a proper time, the reaction mixture was filtered and the solid was washed with acetone two times and dried in air. The content of rubidium in the intercalates was determined by amperometric titration of the released iodine in the filtrate with thiosulfate. The product was used for powder XRD measurements and the study of the electrical properties.

α-Zirconium phosphate ($\alpha\text{-}ZrH_2(PO_4)_2 \cdot H_2O$) and its half-loaded rubidium form ($\alpha\text{-}ZrHRb(PO_4)_2 \cdot H_2O$) were prepared as described in ref 10.

The powder XRD data of the intercalates were obtained with an X-ray diffractometer (HZG-4, Germany) using the Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5405$ Å) with discrimination of the Cu K_β by a Ni filter. The Cu $K_{\alpha 2}$ intensities were removed from the original data. Silicium ($a = 5.43055$ Å) was used as an external standard. Diffraction angles were measured from 10° to 50° (2θ). The relative contents w_i of the phases in the reaction products were calculated from the equation:[4]

$$w_i = I_i / \sum_n I_i \qquad (1)$$

where I_i is the intensity of the basal diffraction line (in the region from 11 to 15° 2θ) of the ith phase and n is the number of present phases. The content of the guest in phases x_i was calculated by multidimensional linear regression of the equation:

$$x = \sum_n x_i w_i \qquad (2)$$

where x is the total content of rubidium in the samples.

DT and TG analyses were performed using a Derivatograph MOM (Hungary). The measurements were carried out in air between 20 and 600 °C at a heating rate of 5 °C min^{-1}. The weight of the sample was 100 mg.

Pellets, 10 mm in diameter and 1−1.5 mm thick, were prepared by pressing ∼200 mg of material at 40 kN/cm^2. The two flat surfaces of the pellet were coated with composite electrodes consisting of a mixture of the sample material with graphite (Carlo Erba) in the ratio 1:3. Impedance measurements were carried out by a Solartron Sl 1260 Impedance/Gain Phase Analyser in the frequency range 0.1 Hz to 10 MHz with a signal level ≤ 100mV. Measurements at 20 °C were carried out at controlled relative humidity (RH) by a stainless steel sealed-off cell containing in the lower part a saturated salt solution for RH in the range 11 to 90%, or a 69.4 wt % sulfuric acid solution for RH = 5%, or P_4O_{10} for RH = 0%. Direct current (dc) conductivity was determined by an Amel 554 potentiostat with a dc load of 0.1 V.

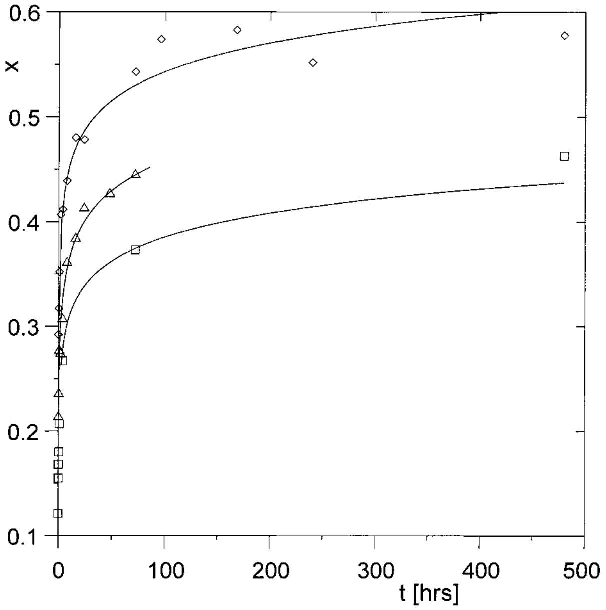

Figure 1. Amount of rubidium x intercalated in $VOPO_4 \cdot 2H_2O$ as a function of the time t of the reaction at 40 (diamonds), 20 (triangles), and 18 °C (squares).

The cell used for electromotive force measurements consisted of a $Rb_xVOPO_4 \cdot yH_2O$ pellet sandwiched between two pellets made of $\alpha\text{-}ZrH_2(PO_4)_2 \cdot H_2O$ and $\alpha\text{-}ZrHRb(PO_4)_2 \cdot H_2O$. The free surfaces of the external pellets were coated with sputtered platinum. The cell was purged with nitrogen containing 4% v/v hydrogen humidified at 20 °C through a saturated $BaCl_2$ solution (90% RH). Electromotive force (emf) measurements were carried out by an HP44701A integrating voltmeter.

Results and Discussion

Rubidium Intercalation. The content of rubidium in the products with a general formula $Rb_xV^{V}_{1-x}V^{IV}_{x}OPO_4 \cdot yH_2O$ depends on the reaction time. The amount of rubidium (x) in the intercalate as a function of the reaction time shows an exponential character (Figure 1). The reaction is distinctly slower compared with the intercalation of other alkali metal ions.[4-6] From Figure 1, it is seen that the highest content of rubidium is apparently reached at 40 °C with a reaction time longer than 96 h. This rubidium content ($x = 0.58$) is however much lower than that theoretically expected ($x = 1$). To find the maximum amount of rubidium which can be intercalated by this reaction, a long-term intercalation at 40 °C was carried out for 100 days in a RbI solution with a molar excess of rubidium to vanadium 16:1. The rubidium iodide solution was renewed twice during the reaction to retain the excess of rubidium. The amount of rubidium intercalated was $x = 0.918$. With increasing the rubidium loading, and consequently the concentration of V^{IV}, the yellow-green color of $VOPO_4 \cdot 2H_2O$ becomes progressively darker and verges on black.

As observed in X-ray powder diffraction patterns (Figure 2), two well-defined phases with different interlayer distance are formed consecutively during the intercalation. The interlayer distance in these phases together with their relative amount is given in Figure

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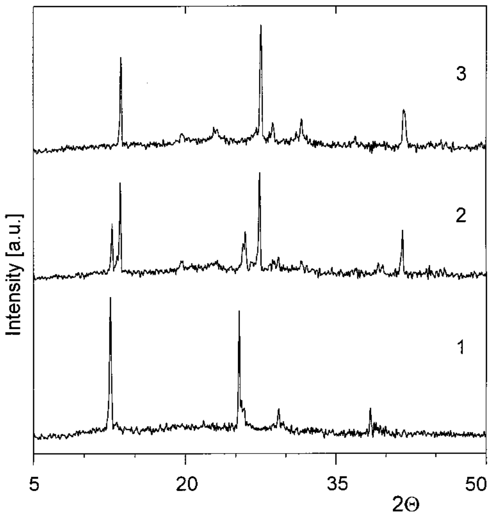

Figure 2. X-ray powder diffraction patterns of the $VOPO_4$ intercalates with various content of rubidium: (1) $Rb_{0.275}VOPO_4 \cdot 2.00H_2O$, (2) $Rb_{0.407}VOPO_4 \cdot 1.63H_2O$, (3) $Rb_{0.480}VOPO_4 \cdot 1.60H_2O$.

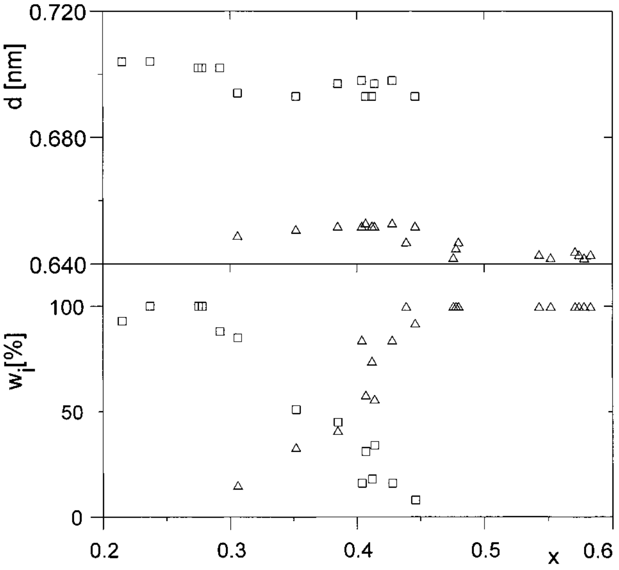

Figure 3. Interlayer distance *d* (upper part of the figure) and phase relative amount w_i (lower part) as a function of stoichiometric coefficient *x* in $Rb_xVOPO_4 \bullet yH_2O$.

3 as a function of the content of the intercalated cation *x*. Single phases are formed for *x* between 0.20 and 0.28 ($d = 0.703$ nm) and $x \geq 0.48$ ($d = 0.644$ nm).

The amount of intercalated rubidium *x* influences the amount of water molecules in the interlayer space *y*. The content of water, determined by TGA for samples kept in an atmosphere with 58% relative humidity for 10 days, decreases from $y = 2.2$ for $x = 0.110$ to $y = 1.4$ for $x = 0.557$. The sample with the highest content of Rb ($x = 0.918$) has $y = 1.3$. This decrease can be ascribed to the fact that the voluminous Rb^+ ions replace the weakly bonded water molecules in the interlayer space. The influence of relative humidity on the water content (*y*) was studied for intercalates with $x = 0.18$, 0.28, and 0.48. In all cases (Table 1) the maximum amount of water is achieved at relative humidity as low as 50%.

Table 1. Water Content (*y*) for $Rb_xVOPO_4 \cdot yH_2O$ Compounds as a Function of Composition (*x*) and Relative Humidity

	y		
% RH	$x = 0.18$	$x = 0.28$	$x = 0.48$
0	0.9	0.8	0.9
11	1.6	1.8	1.4
53	2.0	2.2	1.4
90	2.1	2.2	1.4

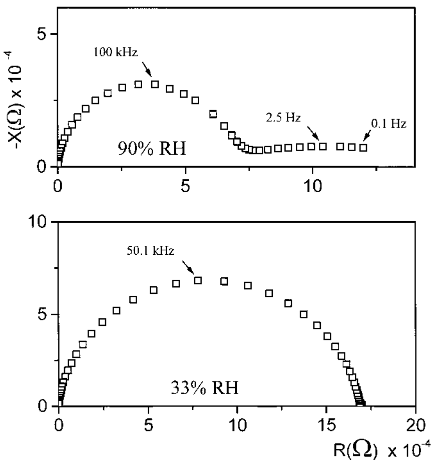

Figure 4. Impedance plots for $Rb_{0.18}VOPO_4.yH_2O$ at 20 °C after equilibration at 33 and 90% RH.

Electrical Conductivity. As the parent vanadyl phosphate, its rubidium intercalation compounds are also expected to be mixed ionic–electronic conductors. The ionic conduction could be associated with the diffusion of rubidium ions and/or of mobile protons coming from the dissociation of the intercalated water. A preliminary electrochemical investigation was carried out by impedance measurements on $Rb_xVOPO_4.yH_2O$ pellets ($x = 0.18$, 0.28, 0.48) at 20 °C as a function of relative humidity (RH) by using composite graphite electrodes. For relative humidities up to 33% the impedance plots consist of a single semicircle going through the origin of the complex plane and touching the resistance axis at the low frequency side (Figure 4). This type of diagram is characteristic of an electrolyte containing one mobile charged species and placed between completely nonblocking electrodes.[11] Since the graphite electrodes are blocking to any ionic species, it is inferred that at low relative humidity the ionic species are not mobile and that the rubidium intercalates are fully electronic conductors. With increasing relative humidity above 50%, a tail appears at the low-frequency side of the semicircle until it takes the shape of a flat arc at 90% RH (Figure 4). These diagrams are similar to those observed for $VOPO_4 \cdot 2H_2O$[7] and suggest the presence of mixed conduction where, with increasing relative humidity, an ionic component grows beside the electronic component. The conductivity calculated from the extrapolation to the resistance axis of the semicircle going through the origin of the complex plane will hereafter be indicated as ac conductivity (σ_{ac}). In the case of mixed conduction, σ_{ac} is the overall electrolyte conductivity, i.e., the sum of the ionic and electronic conductivities.

Information about the nature of the charge carriers can also be obtained by comparing the ac conductivity

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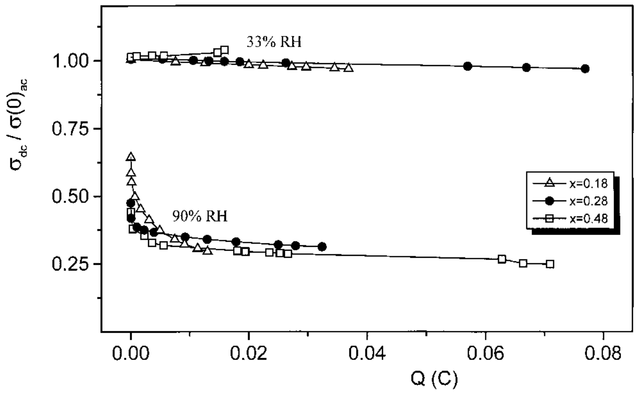

Figure 5. Direct current conductivity at 20 °C (σ_{dc}) as a function of the passed charge (Q) for the indicated compounds after equilibration at 33 and 90% RH; $\sigma(0)_{ac}$ is the initial ac conductivity.

(σ_{ac}) with the dc conductivity (σ_{dc}), measured with ionically blocking electrodes. As discussed in a previous paper,[7] if the conduction is fully electronic, then σ_{dc} is independent of the amount of passed charge (Q) and equal to σ_{ac}. In the case of mixed conduction, the dc conductivity is lower than the ac conductivity and may depend on Q due to the composition changes occurring at the anodic and cathodic regions. In particular, since the charge associated with the transfer of the electronic carriers between the electrodes and the electrolyte is compensated to some extent by the migration of ionic species, the cathodic region becomes progressively richer than the anodic region in V^{IV} and in the ionic species.

Direct current conductivity measurements were carried out with ionically blocking graphite electrodes on pellets which had been equilibrated at 33 and 90% RH. Figure 5 shows the ratio of the dc conductivity (σ_{dc}) to the initial ac conductivity ($\sigma(0)_{ac}$) as a function of the charge passed. This ratio is nearly independent of Q and close to 1 at 33% RH while decreases with increasing Q at 90% RH, thus confirming the hypotheses formulated on the basis of the impedance plots. Direct current measurements could in principle be used to estimate the H^+/Rb^+ contribution to the ionic conductivity if the measurements were carried out with platinum electrodes in a wet hydrogen atmosphere.[12] In this case the electrodes are blocking toward rubidium ions and nonblocking toward protons so that the decay of the dc conductivity should provide information on Rb^+ mobility. Attempts to carry out these measurements failed because some vanadium turned out to be reduced by hydrogen at the platinum electrodes.

Qualitative information about H^+/Rb^+ contributions to the ionic conduction can however be obtained from the electromotive force (emf) of the following electrochemical cell:

$$H_2(p_1),Pt/\alpha\text{-}ZrH_2(PO_4)_2 \cdot H_2O/\\ Rb_xVOPO_4 \cdot yH_2O/\alpha\text{-}ZrHRb(PO_4)_2 \cdot H_2O/Pt,H_2(p_2)$$

where the material under test ($Rb_xVOPO_4.yH_2O$) is in contact with two ionic conductors (α-zirconium phosphate, $\alpha\text{-}ZrH_2(PO_4)_2 \cdot H_2O$, and its half-loaded rubidium form, $\alpha\text{-}ZrHRb(PO_4)_2 \cdot H_2O$) containing different concentrations of H^+ and Rb^+ ions. Since both zirconium phosphates are electronically insulating, the emf of the cell is not affected by the electronic conduction of $Rb_xVOPO_4 \cdot yH_2O$. Electromotive force measurements were carried out with $p_1 = p_2 = 0.04$ atm, at 20 °C and 90% RH. Under these conditions, according to ref 13, the emf of the cell is zero only if the transport number of the rubidium ion is negligible in comparison with that of the proton. Otherwise, an emf will appear across the cell with the positive pole on the side of $\alpha\text{-}ZrH_2(PO_4)_2 \cdot H_2O$, due to Rb^+ diffusion from $\alpha\text{-}ZrHRb(PO_4)_2 \cdot H_2O$ to $\alpha\text{-}ZrH_2(PO_4)_2 \cdot H_2O$. Electromotive force values of 245, 267, and 276 mV were found for $x = 0.18$, 0.28, and 0.48, respectively, with the positive pole on the expected side, thus showing that Rb^+ transport is not negligible in comparison with H^+ transport and increases with Rb^+ content.

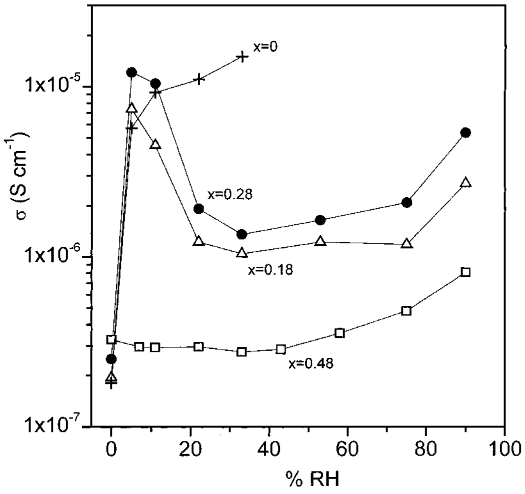

Figure 6. Alternating current conductivity at 20 °C as a function of relative humidity for $Rb_xVOPO_4 \cdot yH_2O$.

Figure 6 shows the ac conductivity (σ_{ac}) of $Rb_xVOPO_4 \cdot yH_2O$ pellets as a function of relative humidity. As already pointed out, σ_{ac} results from the sum of the electronic and ionic conductivity (when present). In all cases σ_{ac} increases with relative humidity for RH > 50% in concomitance with the appearance and the growth of ionic conduction. Since the content of bulk water of the samples is constant in the RH range 50−90% (see Table 1), it can be concluded that the ionic conduction occurs mainly on the surface of the microcrystals, the surface hydration being expected to change with relative humidity. A completely different situation is observed in the RH range 0−33% where the conductivity is fully electronic. While the conductivity of the sample richest in rubidium is nearly constant, that of $Rb_{0.18}VOPO_4$ and $Rb_{0.28}VOPO_4$ first increases from $\sim 10^{-7}$ S cm^{-1} to $\sim 10^{-5}$ S cm^{-1} for relative humidity up to 5% and then decreases by an order of magnitude in the relative humidity range 5−33%. Reproducible conductivity values were found on increasing and decreasing relative humidity between 0 and 33%. It must therefore be excluded that the conductivity changes are associated with irreversible changes of the interparticle resistance eventually caused by microcrystal contraction/expansion concomitant with water loss/uptake. The dependence of

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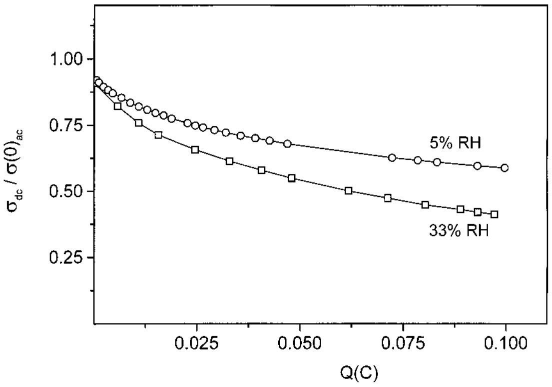

Figure 7. Direct current conductivity at 20 °C (σ_{dc}) as a function of the passed charge (Q) for $VOPO_4 \cdot yH_2O$ after equilibration at 5 and 33% RH; $\sigma(0)_{ac}$ is the initial ac conductivity.

the electronic conductivity on the content of bulk water is not surprising because it was already observed[7] that the electronic conductivity of $VOPO_4$ is enhanced by the coordination of water (and more generally of a Lewis base) to the vanadium atom.

The presence of a maximum in the electronic conductivity of $Rb_{0.18}VOPO_4$ and $Rb_{0.28}VOPO_4$ indicates rather a complex modification of the band structure reflecting changes in the coordination sphere of vanadium. These changes are expected to depend on the amount of intercalated water and on the ratio water molecules/rubidium ions, since the interaction H_2O-Rb^+ should hinder to some extent the coordination of water to the vanadium site. In agreement with these considerations the weakest influence of relative humidity on the electronic conductivity is observed for the compound with the highest rubidium loading and the lowest water content.

In ref 7 it was shown that at 58% RH, $VOPO_4 \cdot 2H_2O$ is a mixed protonic–electronic conductor with dominant protonic component, while the anhydrous material is an electronic conductor. On the basis of the results of the present work it was thought of interest to compare the rubidium intercalates with the parent material under the same experimental conditions. Samples of vanadyl phosphate were equilibrated at relative humidities in the range 0–33% and their water content and conductivity were correspondingly determined. As for the intercalates with low rubidium content ($x = 0.18$ and 0.28), the ac conductivity of $VOPO_4 \cdot yH_2O$ increases sharply between 0 and 5% RH in concomitance with the uptake of 1.5 water molecules. However, differently from the above intercalates, σ_{ac} continues increasing with relative humidity in the range 5–33% and σ_{dc} starts being dependent on the amount of charge passed at relative humidity as low as 5% (Figure 7). These results show that the protonic component of the conductivity appears in vanadyl phosphate at lower relative humidity than the ionic component in its rubidium intercalated forms. It is therefore inferred that proton conduction (if any) is hindered to a large extent by the presence of intercalated rubidium ions. This is likely due to the H_2O-Rb^+ interaction which is expected to reduce the rotational and/or diffusional mobility of the interlayer water and, consequently, proton diffusion by the Grotthuss or vehicle mechanisms.

Conclusion

The conduction properties of vanadyl phosphate are modified to a great extent by the intercalation of rubidium even at concentrations as low as 18% of the maximum allowed loading. At fixed rubidium content, the bulk and surface hydration of the microcrystals influences the nature of the conductivity which, in all cases, is fully electronic up to at least 30% relative humidity and ionic–electronic at higher relative humidity. The electronic conductivity of the phase with low rubidium content ($x \leq 0.28$) is dramatically affected by changes in the content of bulk water and shows a maximum at 5% relative humidity. On the other hand, the increasing surface hydration is responsible for the appearance and the growth of the ionic conductivity which is significantly affected by Rb^+ diffusion.

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