Water-Triggered Conduction Mediated by Proton Exchange in a Hygroscopic Fulleride and its Hydrate

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ABSTRACT: Impedance spectroscopy is employed to probe the impact of water on the dc conductivity and ac dielectric response of the polycrystalline $C_{60}(ONa)_{24}$ fulleride, both in its bulk-hydrate form, stable only below 370 K, and in the pure form, obtained by heating to high temperature. Exposure of the pure material to ambient air results in the condensation of water vapor on the crystallites' surface, which in turn leads to an enhancement of the room-temperature conductivity by four orders of magnitude due to charge transport through the hydration layer. Electrical conduction in the hydrate between 320 and 380 K is dominated by a non-equilibrium contribution associated with the structural water, which leads to a value of the dc conductivity that is higher than that of the pure material by almost two decades at 360 K. Both conductivity enhancements are most likely due to a proton exchange mechanism. All impedance spectra exhibit, in the radiofrequency range, a dielectric loss feature related to the accumulation of free charges at grain boundaries, whose strength is strongly affected by the presence of hydration water.

1. Introduction

The presence of water has in general a strong impact on the conduction properties of inhomogeneous and porous materials, both in the case of ionic and electronic charge transport.¹ Exposure to humid air and the ensuing condensation of water vapor onto a material's surface introduces new mechanisms for charge generation and transport, which in semiconducting and insulating materials may result in an increase of the overall conductivity by several orders of magnitude.²⁻⁶ This well-known effect is exploited in many kinds of humidity sensors based on inorganic materials such as ceramics or organic materials such as polymers.^{7,8} The presence of water can also have an important effect on the dielectric response of materials, e.g. leading to an increase of the dielectric constant due to the high orientational polarizability of the H₂O molecules. Given that many organic materials are hydrophilic and/or hygroscopic, determining the impact of H₂O adsorption or uptake on their charge transport properties is not only interesting from a fundamental point of view but is also crucial for their implementation in electronic or sensing devices.

Most organic materials are insulating or behave as disordered semiconductors in which the main conduction mechanism is electron, hole, or ion hopping.⁹ The dc conductivity of organic and inhomogeneous inorganic semiconductors in their pure form is quite low, so that the introduction of new charge carriers or conduction paths upon adsorption of water leads in many instances to an increase in the material's conductivity, for some cases even by several orders of magnitude.²⁻⁶ The exact mechanism underlying such effect both in organic and inorganic systems is a matter of debate,² and it may not be unique nor the same for all materials.

Given the complexity of the issue, to achieve a microscopic understanding of water-induced conduction in organic materials it is necessary to identify and probe model solids with low disorder and as simple a structure as possible, so as to be able to discriminate between (and possibly rule out) distinct mechanisms for the water-triggered conductivity enhancement. To this aim, we investigate here the impact of water on the charge transport in a relatively simple organic system, namely the ordered solid phases of a highly symmetric fullerene derivative salt (of chemical formula C₆₀(ONa)₂₄), which is

synthesized as polycrystalline powder and which forms a polycrystalline hydrate (of chemical formula $C_{60}(ONa)_{24} \cdot 16 H_2O$) upon prolonged exposure to air.¹⁰ The existence of two well-defined solid phases based on the same organic molecule (pure material and hydrate) allows investigation of the impact on the electric conduction of two distinct types of water molecules, characterized by different interactions with the organic matrix: namely, structural water – which is an integral part of the hydrate’s crystal structure – and surface hydration water – which is present at the external surface of crystalline domains.

The $C_{60}(ONa)_{24}$ molecule is closely related to another better known fullerene derivative, namely fullerol ($C_{60}(OH)_{24}$), from which it is in fact obtained by substitution of the hydrogens of the hydroxyl groups.¹⁰ Although fullerols have been suggested to act as proton conductors both in powder form, inside membranes and in aqueous solution,¹¹⁻¹³ no evidence for proton conductivity was reported in a recent studies on the pure $C_{60}(OH)_{24}$ and $C_{60}(ONa)_{24}$ materials.^{10,14} In fact, pure $C_{60}(ONa)_{24}$ exhibits low intrinsic conductivity stemming from the hopping of electronic charge carriers, and no evidence of ionic conductivity at least up to 575 K.¹⁴ We show here that exposure of pure $C_{60}(ONa)_{24}$ to ambient air leads to a dc conductivity increase by four orders of magnitude, which arises from the charge transport through the hydration water layers at the grains’ surface. In the hydrate, the dc conductivity is strongly temperature-dependent, and it is found to be higher than that of the pure material by almost two orders of magnitude around 350 K. We argue that both conductivity enhancements are due to a hydrogen-bond exchange (proton shuttling) mechanism. This suggests that only the hydrated forms of the derivatives $C_{60}(OX)_{24}$ ($X = H, Na$), and not the pure materials, behave as proton conductors. Moreover, our findings help shed light on two well-known and yet controversial water-induced conductivity effects, namely the surface conductivity enhancement and the worsening of electrical insulation in a humid environment,²⁻⁶ and the conductivity changes associated with structural dehydration.¹⁵

2. Materials and Methods

Sodium oxofulleride ($C_{60}(ONa)_{24}$) was synthesized in the last step of a synthetic route starting from Buckminster fullerene C_{60} as detailed in refs 10, 16 and 17. The product was a hygroscopic polycrystalline brown powder, soluble in water, which was stored in air prior to measurements. The

material was characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier-transform infrared (FTIR) spectroscopy, x-ray powder diffraction, and broadband dielectric spectroscopy¹⁸ (also known as impedance spectroscopy). For both infrared and dielectric spectroscopy the powders were mechanically pressed into pellets of submillimeter thickness.

For the FTIR measurements it was necessary to add KBr powder to the organic material to achieve free standing pellets, and the spectrum of a pure KBr pellet was used as baseline. FTIR spectra were measured in the mid-infrared range ($4000 - 400 \text{ cm}^{-1}$) using a Nicolet 6700 spectrophotometer equipped with a He/Ne laser source and DTGS-CsI detector. Each spectrum was the average of 32 scans collected with 1 cm^{-1} resolution. TGA scans were acquired while heating the sample under N_2 flow between room temperature (300 K) and 600 K at a rate of 2 K min^{-1} , by means of a Q50 thermobalance from TA-Instruments. DSC measurements were carried out in an open vessel between 300 K and 600 K at a rate of 2 K min^{-1} , using a Q100 calorimeter from TA-Instruments.

High-resolution x-ray powder diffraction (XRPD) profiles were recorded with a vertically mounted INEL cylindrical position-sensitive detector (CPS120). The generator voltage and current were set to 35 kV and 35 mA, and monochromatic Cu $\text{K}\alpha_1$ radiation was selected with an asymmetric-focus curved quartz monochromator. The detector was used in the Debye-Scherrer geometry (transmission mode), yielding diffraction profiles over a 2θ range between 4° and 120° with an angular step of 0.029° (2θ). The powder sample was placed into a Lindemann capillary tube (0.5 mm diameter), which was maintained open during the measurement so as to reproduce the pressure conditions of the other experiments. During data collection the capillary tube was rotated perpendicularly to the x-ray beam direction to minimize possible effects of preferred orientations. Temperature control was achieved with a liquid-nitrogen 700 series Cryostream Cooler from Oxford Cryosystems. The peak positions were determined by fits with pseudo-Voigt functions using the DIFFRACTINEL software.

Dielectric measurements were carried out in the frequency (f) range from 10^{-2} to 10^6 Hz with a Novocontrol Alpha analyzer, using stainless steel electrodes in a parallel-plate capacitor configuration. Isothermal frequency scans were acquired in the temperature range between 200 and 550 K (with a

temperature stability of 0.3 K) in a N₂ flow Quatro cryostat. The isothermal dielectric spectra are displayed in two representations, namely as real part of the ac conductivity $\sigma'(f)$, and as imaginary part of the relative permittivity $\varepsilon''(f)$, which is known as dielectric loss spectrum. The two functions are related as $\sigma'(f) = 2\pi f \varepsilon_0 \varepsilon''(f)$. The value of the dc conductivity (σ_{dc}) at each measuring temperature was taken to be the low-frequency plateau value of the logarithmic plot of $\sigma'(f)$. In the spectra exhibiting a spectral bending at the lowest frequencies due to electrode polarization, the magnitude of σ_{dc} was taken to be the value of σ' at the point of inflection, that is, at the frequency for which $d\sigma'/df$ was minimum (zero of $d^2\sigma'/df^2$). When they could be applied simultaneously, the two methods gave consistent results.

Each loss spectrum was fitted as the sum of a conductivity background proportional to reciprocal frequency and a Havriliak-Negami function representing each dielectric loss feature, whose analytic expression¹⁸ is:

$$\varepsilon_{HN}(f) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{(1 + (if/f_{HN})^{\alpha})^{\beta}}$$

Here $\Delta\varepsilon = \varepsilon_s - \varepsilon_{\infty}$ is the dielectric strength, ε_{∞} and ε_s are the high-frequency and static low-frequency limits of the real permittivity, α and β are shape parameters in the range from 0 to 1, and f_{HN} is a fitting parameter from which the frequency f_{max} at which the dielectric loss is maximum is obtained¹⁸ as:

$$f_{max} = f_{HN} \left(\sin \frac{\alpha\pi}{2 + 2\beta} \right)^{1/\alpha} \left(\sin \frac{\alpha\beta\pi}{2 + 2\beta} \right)^{-1/\alpha}$$

From the dielectric strength $\Delta\varepsilon$ and the dc conductivity σ_{dc} another characteristic frequency f_{σ} can be obtained, defined as $f_{\sigma} = \sigma_{dc}/(2\pi\varepsilon_0\Delta\varepsilon)$, which represents the characteristic relaxation frequency of spatial charge fluctuations in a conducting medium.¹⁹ The temperature evolution of σ_{dc} , f_{max} and f_{σ} is visualized by means of logarithmic plots versus inverse temperature (Arrhenius plots), from whose slope the activation energy of the conductivity or of the corresponding loss process is obtained.

3. Results and Discussion

3.a. Preliminary Characterization

As mentioned in the introduction, $C_{60}(ONa)_{24}$ is a hygroscopic salt that forms a polycrystalline hydrate upon storage in air. Figure 1a displays the room temperature FTIR spectra of the as-stored hydrated powder and of the powder heated to 423 K, which no longer contains the structural water.¹⁴ The spectra are normalized to the height of the most intense band at 1458 cm^{-1} , which corresponds to the bending mode of the covalent C–O bonds of the $C_{60}O_{24}$ anion. Such normalization is equivalent to rescaling the spectra to the relative fullerene content.¹⁰ The presence of water in the as-stored powder is confirmed by the observation of intense bands (indicated by arrows in Figure 1a) at 3465 cm^{-1} (stretching vibration of the O–H bonds of water) and 1690 cm^{-1} (bending mode), whose intensity is significantly reduced after heating to 423 K.

The crystalline nature of both the as-stored and pure materials is revealed by the XRPD patterns of Figure 1b. The observation of well-defined diffraction peaks indicates that the as-stored material is in fact a crystalline hydrate, whose stoichiometry was shown to be $C_{60}(ONa)_{24} \cdot 16\text{ H}_2\text{O}$ in a previous study.¹⁰ We will hereafter refer to this phase as the hydrate salt. The diffraction pattern of the pure material, obtained by heating the hydrate, exhibits a much higher scattering background and significantly broader peaks, suggesting only partial ordered and smaller grain size in the pure material than in the hydrate. The average grain size was estimated in both phases from the angular width of non-overlapping diffraction peaks using the Scherrer equation,^{20,21} and found to be $32 \pm 4\text{ nm}$ for the pure material and $50 \pm 10\text{ nm}$ for the hydrate. A smaller linear dimension of the pure grains may be expected considering both the loss of water volume and the possible formation of defects upon the structural change. The structure obtained after heating to 500 K exhibits no clear peaks below $2\theta = 20^\circ$ and displays main peaks at much higher scattering angles than the hydrate. This indicates that the pure material is characterized by a smaller first-neighbor distance, as expected due to the loss of structural water.

Figure 1. Room-temperature FTIR spectra (a) and XRPD patterns (b) of the as-stored hydrate and of the pure material (after heating to 423 K). The XRPD patterns are normalized to acquisition time and displayed with an offset for clarity. Inset to panel b: close-up of the XRPD pattern in the 2θ range between 37 and 41 degrees. TGA (c) and DSC (d) curves measured on the as-stored hydrate powder. Three different processes associated with the loss of water may be identified: P1 - desorption of surface water; P2 - dehydration of structural water accompanied by phase change; P3 - desorption of migrated water.

Panel c displays the TGA scan acquired while heating the hydrate. The curve displays an initially slow decrease of mass (marked in the Figure as P1) starting at room temperature up to approximately 350 K, the temperature that marks the onset of the main water loss (marked as P2). The overall loss of 25% of the initial mass indicates that the amount of water in the as-stored powder is quite large; this can only occur if the water molecules are present also as interstitial, structural moieties, as already pointed

out in ref 10. The temperature of maximum mass loss (obtained by taking the first derivative of the TGA curve) is approximately 370 K, i.e. roughly the boiling point of pure water at standard pressure, in agreement with a previous study,¹⁰ and coincides with the crystallographic transition between the hydrate and pure material (see below). We assign the initial mass loss between room temperature and 350 K to desorption of H₂O molecules adsorbed onto the outer surface of the crystalline grains, which are less tightly bound than the structural (interstitial) ones. The main loss corresponds instead to the decomposition of the hydrate. Both assignments will be further corroborated in Section 3.b.

It may be observed that the TGA graph (panel c) does not exhibit the same slope throughout the main water loss. Similarly, the DSC curve (panel d) exhibits a structured peak with weak shoulders on both sides. All observed DSC features correspond to endothermic processes. Such multiple-component spectra are reminiscent of those of other C₆₀-derived systems,²² and result from the different processes accompanying the loss of water, namely the breaking of hydrogen bonds between water and fullerene units, the re-crystallization into a new lattice structure, the migration of water to the outer surface and its final desorption, which is the last process that takes place (we label it as P3 in Figure 1c). The temperature range of each process and the corresponding mass loss are highlighted with dashed lines in panel c (see caption of Figure 1c). The main (intermediate) mass loss is consistent with the stoichiometry of the hydrate reported in ref 10.

The powder diffraction spectra measured near the transition temperature of 370 K (not shown) reveal a single structural change between a crystalline hydrate and a partially ordered pure phase which is obtained irreversibly by heating to high temperature. The structural change therefore occurs simultaneously with the main water loss. The XRPD pattern of the hydrated phase could be indexed by pattern-matching as a monoclinic P2/m phase (see Supporting Information file).

Figure 2 shows the frequency-dependent dielectric spectra acquired on the as-stored material (hydrate) during heating from room temperature to 433 K. The data are shown both in the dielectric loss (left-hand panels) and ac conductivity (right-hand panels) representations, and displayed in separate temperature ranges to highlight the observed changes in line shape. The high-temperature spectra shown

in d (and partially in c) exhibit basically the same line shape and temperature dependence as those of the pure $C_{60}(ONa)_{24}$ salt that were published in a recent work.¹⁴ This confirms that the pure material is obtained by heating the hydrate to 370 K, in agreement with our TGA and XRPD results.

Figure 2. Dielectric loss (left panels, 1) and ac conductivity (right panels, 2) spectra acquired on heating the as-stored hydrate, in separate temperature ranges: (a) 298 to 333 K; (b) 338 to 363 K; (c) 368 to 393 K; (d) 398 to 433 K.

The dielectric loss (ϵ'') is characterized, both in the hydrate and in the pure material, and at almost all investigated temperatures, by a conductivity background proportional to reciprocal frequency at low frequency¹⁸ and a loss feature at radiofrequency, visible both in the as-stored material (hydrate, a1) and in the pure material (d1). The conductivity spectra exhibit an almost constant value at low frequency, corresponding to σ_{dc} (see Section 2); at high temperature (c2 and d2) they display a characteristic low-frequency “bending” due to the electrode polarization effect (also visible, although less pronounced, in the corresponding dielectric loss spectra).¹⁸

The dielectric response of the hydrate exhibits a complex dependence on temperature. Below approximately 315 K (a), both the frequency of the relaxation maximum and the dc conductivity are temperature-activated, as seen from the quasi-rigid shifts (in logarithmic frequency scale) of both the permittivity and conductivity spectra. Between 315 and 333 K, the shift of the relaxation frequency slows down, until it appears to stop at 333 K (a1). Between 338 and 363 K (b), both the relaxation frequency and σ_{dc} are observed to shift much faster with temperature than they do at lower temperatures. Finally, in the range between 368 and 393 K, that is, in the temperature interval of the main mass loss and structural change, a dramatic change of spectral profile is observed in the dielectric loss spectrum (c1), accompanied by a decrease of the dc conductivity by almost one order of magnitude (c2).

The loss peak exhibits a sudden jump to lower frequency around 370 K. We may take this temperature, which corresponds to the maximum mass loss (Figure 1c), to mark the structural change from hydrate to pure material. As all water has left the sample above 380 K (Figure 1b), the loss peak observed at higher temperatures (d1) cannot be associated with a dipolar relaxation of H₂O molecules. This confirms the identification of the dielectric loss in the pure material as a conductivity-related feature associated with the accumulation of charge at spatial heterogeneities in the sample.¹⁴

The non-monotonic temperature-dependence of σ_{dc} and of the frequency of the loss maximum observable in Figure 2 may be at first surprising, as one expects both the conductivity and the characteristic loss frequency to increase with temperature.¹⁸ However, such behavior is not uncommon in water containing porous systems near the water desorption temperature,^{1,2,10,23-26} as will be discussed

in Section 3.b. Given the complexity of the results and the presence of two modalities of hydration in the as-stored powder (Figure 1c), we have probed separately the effect of the structural and surface hydration water. This was achieved by subjecting the as-stored material to different temperature treatments prior to measuring, as discussed in the following.

3.b. Dielectric Spectroscopy Study and Discussion

The rest of the paper is organized in two separate sections, each focusing on a different aspect of the impact of water on conduction properties. In Section 3.b.1 we focus on the effect of surface hydration water on the pristine material (the properties of the pure $C_{60}(ONa)_{24}$ compound, as obtained by annealing to high temperature under nitrogen atmosphere, were investigated in a previous work¹⁴). In Section 3.b.2 we present the conduction and relaxation properties of the $C_{60}(ONa)_{24} \cdot 16 H_2O$ hydrate, and analyze the effect of the loss of structural water.

3.b.1. Effect of the Surface Hydration Water on Pure $C_{60}(ONa)_{24}$

Given that the transition from the hydrate to the pure material is accompanied by a significant mass loss and a change of structure and unit cell volume, heating a pellet made with the hydrate powder (as in Figure 2) likely results in a sample with pronounced inhomogeneity due to the loss of the water volume. Therefore, in order to probe the pure material by dielectric spectroscopy, we preheated the as-stored powder to 430 K prior to pressing it into the pellet form necessary for dielectric characterization. Between the preheating and the measurements the sample was exposed to ambient air.

The spectra acquired on one such quasi-pure pellet, which are displayed in panels a and b of Figure 3, did not exhibit the changes observed in the hydrate upon heating (Figure 2), but rather a single, non-reversible spectral modification as the temperature was raised from room temperature to 360 K. The dc conductivity (Figure 3c) was initially much higher than that of the dehydrated material, and only dropped to a value comparable with the latter upon heating to 325 K. Above this temperature, the temperature-dependence of the conductivity was the same as in pristine $C_{60}(ONa)_{24}$,¹⁴ and the spectra obtained in subsequent heating-cooling cycles under constant nitrogen flow overlapped with the first cool-down data, confirming that all surface water leaves the sample in the first heating to 325 K.

A single, broad permittivity feature was observed in all dielectric spectra (a). The Arrhenius plot of the characteristic frequency $f_{\max}$ (resp., strength $\Delta\epsilon$) of such feature is shown in the main panel of Figure 3d (resp., in the inset). In the same temperature range of the conductivity change, the loss feature undergoes a non-monotonous frequency shift and a significant decrease in strength (by a factor of three).

Figure 3. Dielectric loss (a) and ac conductivity (b) spectra acquired on a pellet made with powder preheated to 430 K and then exposed to ambient air, in the temperature range between 293 and 373 K. (c) Arrhenius plot of σ_{dc} for the same data. For comparison, the σ_{dc} values extracted from measurements performed cooling down from 500 K are also shown (after ref 14). (d) Arrhenius plot of the relaxation frequency, compared with that of σ_{dc} . Inset: dielectric strength $\Delta\epsilon$ as a function of the reciprocal temperature.

The observed decrease of σ_{dc} upon desorption of water is reminiscent of the behavior of many insulating and semiconducting porous inorganic materials²⁻⁵ in which a conductivity enhancement is observed after exposure to humidity. It may be gathered from panel c that the conductivity variation is approximately of four orders of magnitude, a dramatic effect which is in line with reported conductivity enhancements in inorganic systems.²⁻⁵ The recovery of the conductivity value of the pristine material at relatively low temperatures and the absence of the other changes visible in the hydrate (Figure 2) together indicate that, in the short exposure to air prior to measurement, the material did not have time to form a stable hydrate phase containing structural water. We thus conclude that air exposure led to condensation of (loosely bound) hydration water onto the surface of pure $C_{60}(ONa)_{24}$ grains. In what follows, we will refer to this water contribution as “surface hydration water” to distinguish it from the structural water. Pure $C_{60}(ONa)_{24}$ is a polycrystalline powder with rather low conductivity (10^{-11} S/cm at room temperature)¹⁴ and relatively large surface area, considering the size of the crystalline grains (~ 30 nm). The large surface area rationalizes the observed dramatic (surface) conductivity increase upon air exposure. The conductivity enhancement is responsible also for the more prominent electrode polarization effect visible in the room-temperature spectra (panel b).

Water-induced conductivity enhancements are known to occur in inorganic metals and oxides, and it is generally accepted that they arise from small-ion transport through chemisorbed and physisorbed water layers.^{5,6,27} In fact, the conductivity enhancement is purely a surface effect, as water cannot penetrate inside their tight lattice structure of inorganic materials. The exact nature of the underlying conduction mechanism is debated,² but the most likely candidates are ion diffusion and proton exchange, the latter being a “shuttle” mechanism by which O-H bonds are interchanged between adjacent water molecules. The proton exchange mechanism is responsible for the electrical conductivity of a wide range of systems such as pure water, ice, phosphoric acid, pharmaceutical phosphate salts, as well as some hydrated organic compounds.²⁸⁻³² This mechanism, known in water as “Grotthuss shuttling,” is sometimes accompanied by rearrangements of the molecular orientations and of the solvation shells.²⁸ Contrary to what has been proposed for some inorganic materials, where the protons

responsible for the surface conductivity enhancement have been suggested to stem from the chemisorption of water onto activation sites,⁵ the surface effect reported here is unlikely to arise from a chemisorption process, as the extra surface-conductivity contribution vanishes upon heating to moderate temperatures (lower than 350 K), indicating that the surface water molecules maintain their integrity (the desorption of chemisorbed water from e.g. metal oxide surfaces takes instead place at 473 K).³⁹ Similarly, we can exclude that the surface conductivity is due to the motion of the sodium species, as it has been shown that the sodium atoms remain tightly bound to the fullerene molecules up to at least 575 K.¹⁴ A more likely explanation is that the surface-enhanced conductivity is due to charge propagation by hydrogen-bond exchange (proton-shuttling) between intact, physisorbed water molecules in higher hydration layers.

As visible in Figure 3a, the loss feature is initially visible at room temperature above 10^5 Hz, that is, at a significantly higher frequency than the relaxation feature of the bulk hydrate (see Figure 2a). As visible in panels a and d of Figure 3, upon raising the temperature the loss feature is observed to shift to lower frequencies while the conductivity decreases. Such temperature dependence of the loss feature is anomalous (the characteristic frequency should increase with temperature due to the higher thermal energy), and resembles that observed in other hydrated systems such as organic¹⁰ and inorganic^{2,23-25} porous materials. The origin of this effect has been the object of controversy, and has been related either to a reduction of the available free volume per defect in the hydrogen-bond network of interstitial water upon heating,^{10,23,24,33} or to a Maxwell-Wagner-Sillars polarization effect due to the strong increase of the static permittivity of a porous sample when water adsorbs onto inner surfaces.²⁶ The data of Figure 3 reveal that a different mechanism is responsible for the anomalous shift of the loss feature in $C_{60}(ONa)_{24}$. In fact, as seen in panel d, the variation with temperature of the loss frequency is identical to that of the conductivity (both vertical scales in panel d span the same number of decades). This situation, analogous to that reported for the pure material,¹⁴ indicates that the origin of the loss feature is the accumulation of charge carriers at the sample's heterogeneities such as grain boundaries. Our results demonstrate that the strong decrease in the sample's conductivity upon desorption of hydration water

can lead to a non-monotonic temperature dependence of the loss feature, although by itself it is not sufficient to explain the simultaneous observation of anomalous temperature dependencies of distinct loss features reported in some samples.^{10,23}

Below 348 K the loss spectrum does not exhibit any change in line shape but rather undergoes a rigid shift to lower frequency as the temperature is raised with no loss of spectral intensity. The line shape variation and the decrease in strength of the loss feature (by a factor of three) occur only above 348 K (inset to panel d). Notice that the dielectric strength does not go to zero, but to a constant value corresponding to that of the pure material.¹⁴ Because in the case of the preheated powder no structural changes occur during the measurements, the observed three-fold enhancement of the dielectric strength is due solely to the presence of physisorbed water. The fact that a decrease in dielectric strength in the loss feature occurs only after the conductivity has dropped to its value in the pure material is worth noticing. Water adsorbed onto hygroscopic or hydrophilic surfaces is organized in different hydration layers, the first (interfacial) hydration layer being the most strongly bound and the last to desorb upon heating. The dielectric strength is observed to decrease only at the highest temperatures (i.e., at the very last stages) of the desorption, indicating that the intensity of the loss feature is determined by the first (interfacial) hydration layer. This may be expected for a loss originating from charge-carrier accumulation at crystalline grain boundaries, as the presence of interfacial water molecules with their large orientational polarizability is likely to affect the overall dipolar character of such charge accumulations. At the same time, the fact that the σ_{dc} value starts dropping already at the initial stages of H₂O desorption indicates that the conductivity enhancement is due to conduction through higher hydration layers, in agreement with previous studies.^{2,5,6,27}

To summarize, while pure C₆₀(ONa)₂₄ exhibits low conductivity due to hopping of electronic charge carriers between crystalline grains, physisorption of water on the surface of C₆₀(ONa)₂₄ grains leads to a four-decade enhancement of the overall conductivity due to the introduction of new charge carriers and new conduction paths through the hydration layers. It is the water in higher hydration layers that is responsible for the conductivity enhancement and for the frequency shift of the (conductivity-induced)

dielectric loss feature; instead, the shape and intensity of the loss feature are determined by the interfacial water molecules that are directly adsorbed onto the organic matrix (first hydration layer). Indeed, the dielectric strength of the permittivity feature does not vary with the conductivity (which is strongly temperature-dependent), but rather only depends on whether water is present (or absent) at the very surface of the crystalline grains. The higher dielectric strength of the loss feature in the presence of an interfacial hydration layer reflects a partial contribution to the loss feature from interfacial water dipoles.

3.b.2. The $C_{60}(ONa)_{24} \cdot 16H_2O$ Hydrate

Given that pellets made from the as-stored powder (Section 3.a) contain both structural and surface hydration water, and since the latter affects not only the shape of the loss spectrum but also the magnitude of the dc conductivity (Section 3.b.1), in order to obtain a more reliable characterization of the bulk hydrate we preheated the pellets to 323 K in nitrogen atmosphere, so as to minimize the amount of surface hydration water.

The results of the characterization of the hydrate preheated to 323 K are displayed in Figure 4 (the data are plotted in separate temperature intervals to highlight the spectral changes). The sample's conductivity and main (lower-frequency) loss feature display initially weak temperature dependency up to 323 K (a). Above 323 K the temperature dependence becomes steeper, as evidenced by the larger spacing between consecutive spectra in panel b. Between 368 and 383 K, in the temperature interval of the structural dehydration, the conductivity is observed to decrease while the main dielectric loss feature undergoes a shift to lower frequency (arrows in panel c). Above 388 K, after all structural water has left the sample, the spectra resume their initial weak temperature dependence (d). Neither the pronounced slowing-down observed around 333 K in Figure 2a nor the anomalous behavior below 350 K reported in Figure 3 are observed, which indicates that the anomalous relaxation behavior below 350 K in the as-stored material is due exclusively to the surface hydration water.

Figure 4. Dielectric loss (left panels, 1) and ac conductivity (right panels, 2) spectra acquired on heating the hydrate preheated under nitrogen atmosphere to 323 K, in different temperature intervals: (a) 293 to 323 K; (b) 328 to 363 K; (c) 368 to 383 K; (d) 388 to 423 K.

It may be gathered from Figure 4a that, prior to the loss of structural water, the permittivity spectra are characterized (besides the conductivity background) by two loss features, one in the same frequency range of the conduction-related feature of the pure material, and a second one at higher frequency, visible only below room temperature in our experimental frequency range. Both relaxation features exhibit simply activated behavior. While the lower-frequency (slower) feature, which has activation energy of approximately 1 eV, is associated with charge accumulation at grain boundaries (see below), the low-temperature feature visible at high frequency, which displays activation energy of 0.9 eV (not

shown), likely has a dipolar origin. As this faster feature is observed only in the hydrate and has no analog in the pure material, we associate it with the dipolar relaxation of structural H₂O molecules or clusters, which, given the crystalline nature of the hydrate, may only exhibit reorientational motions (e.g., as in a plastic phase). The activation energy is significantly higher (by almost a factor of two) than that observed in supercooled or confined water,¹⁰ which may be ascribed to the much stronger interactions and orientational correlations between the structural H₂O molecules in the crystal lattice of the hydrate.

Figure 5a displays the Arrhenius plots up to 320 K of the conductivity and of the maximum loss frequency of the lower-frequency relaxation. The dc conductivity follows a linear Arrhenius temperature dependence between 285 and 320 K. This contrasts with the case of the pure compound, where a power-law dependence of the dc conductivity on temperature is reported,¹⁴ of the form $\text{Log}(\sigma_{\text{dc}}) = A - B/T^n$ with n close to 1/2. The latter is typical of hopping electronic conduction^{34,35} and is observed in a wide variety of systems ranging from metal-cluster compounds to ceramic metals or to doped or amorphous semiconductors in which hopping is determined by a Coulomb-type electron-electron correlation.³⁵⁻³⁷ The simply activated behavior observed in the hydrate suggests instead that conduction is not purely electronic, as might be expected due to the massive presence of structural water, which may result in partially protonic or ionic conductivity mechanism (see also below). The activation energy of the dc conductivity of the bulk hydrate is slightly above 1 eV, and it is higher than the effective activation energy observed in the pure material, which in this temperature range varies between 0.7 and 0.8 eV.¹⁴ This may be rationalized considering that the electronic contribution to the conductivity is hindered in the hydrate by the larger intermolecular spacing (Section 3.a).

Figure 5. (a) Arrhenius plots of σ_{dc} between 285 and 320 K (filled markers) and f_{max} between 273 and 320 K (open markers), as measured on the hydrate preheated to 323 K, and respective linear fits (continuous lines). The two temperature ranges are different as no reliable estimate of σ_{dc} could be obtained from the dielectric data down to 10^{-2} Hz. (b) Plot of σ_{dc} versus $2\pi\epsilon_0\Delta\epsilon f_{\text{max}}$ between 285 and 320 K to test the validity of the BNN relation (see text).

The Arrhenius plot of the frequency f_{max} of the slower relaxation feature (Figure 5a) similarly exhibits a simply activated behavior. It may be gathered from the figure that the activation energy of f_{max} is very similar to that of the dc conductivity, which would suggest a correlation between the slower dielectric feature and the long-range charge transport. In Figure 5b we have plotted σ_{dc} versus the quantity $2\pi\epsilon_0\Delta\epsilon f_{\text{max}}$ to test the validity of the so-called Barton-Nakajima-Namikawa³⁸ (BNN) condition. Although the ratio of these two quantities is always of the order of unity (in fact, between 0.4 and 0.5), the linear correlation predicted by the BNN theory (according to which $\sigma_{\text{dc}} \sim 2\pi\epsilon_0\Delta\epsilon f_{\text{max}}$) is far from being perfect, especially at high temperature. This implies that the loss feature is not a pure space-charge effect, contrary to the case of the pure material.¹⁴

Figure 6 shows the Arrhenius plots of the main (slower) relaxation (a) and of the conductivity (b) in the whole temperature range of the spectra of Figure 4. In panel a, together with the maximum loss frequency f_{max} we show another characteristic frequency defined as $f_{\sigma} = \sigma_{\text{dc}}/(2\pi\epsilon_0\Delta\epsilon)$ (see Section 2),

introduced in analogy to the BNN relation and which represents the characteristic relaxation frequency of spatial charge fluctuations in the medium.¹⁹ For comparison purposes, in (b) we show plotted σ_{dc} for the pure material, measured upon cooling after full dehydration. The correspondence between the line shapes of all three Arrhenius plots (σ_{dc} , f_{max} and f_{σ}) upon heating is remarkable. Both f_{max} and σ_{dc} display a crossover to steeper temperature dependence above 323 K. This more pronounced variation with temperature slows down at 350 K, until its trend is reversed at around 370 K (the temperature of the structural transition), with both σ_{dc} and f_{max} decreasing with increasing temperature. The non-monotonic behavior of the dc conductivity is simultaneous with that of the loss feature, and both exhibit a maximum at 365 K. The Arrhenius plot of f_{σ} displays a similar behavior. All these similarities and the continuous evolution of the main loss feature in the hydrate into that of the pure material (which is known to arise from a space-charge accumulation effect¹⁴) are all strong indications that the main loss feature in the bulk hydrate is in fact correlated with the dc conductivity.

Figure 6. Arrhenius plots of a hydrate sample preheated to 323 K: (a) frequency f_{max} of the loss feature and f_{σ} (see text for details); (b) dc conductivity upon heating (red open markers) and cooling (blue filled markers). Inset to panel a: dielectric strength $\Delta\epsilon$ of the data acquired upon heating, as a function of reciprocal temperature. The data upon heating correspond to the spectra of Figure 4.

As shown in the inset to panel a, the dielectric strength of the loss feature decreases with increasing temperature in line with the results presented in Figure 2 in Section 3.a. As it can be inferred from a visual comparison between the permittivity spectra of panels a1 and d1 of Figure 2 or 4, and as clearly visible in the insets to Figure 3d and Figure 6a, the strength $\Delta\epsilon$ of the loss feature is always higher in the (even partially) hydrated samples than in the pure material. In particular, upon heating the structural hydrate the dielectric strength shows two abrupt changes to lower values, the first around 323 K, in coincidence with the crossover to steeper Arrhenius dependence, and the second one at 370 K, in correspondence with the structural transition. There is an overall decrease of strength by a factor of 7 between the hydrate and pure material. The higher value of $\Delta\epsilon$ in the presence of water and the fact that at low temperature the Arrhenius plots for $f_{\max}$ and of f_{σ} do not overlap (Figure 6a), as well as the only approximate validity of the BNN condition and the slight difference between the activation energies of the dc conductivity and of the permittivity feature (Figure 5), are all clear indications that, while the loss feature and the conductivity are correlated, the origin of the loss cannot be a pure space-charge effect as in the pure material. In particular, it appears evident that the structural/interfacial water molecules contribute directly to the strength of the permittivity feature. To rationalize our findings, we suggest that the fundamental origin of the main loss feature in the hydrate is accumulation of charge at the sample's heterogeneities, as in the pure material; however, such dielectric feature also contains in the hydrate a partial dipolar contribution associated with the reorientational motions of the structural H₂O dipoles which accompany the oscillation of the interfacial dipole associated with the accumulation of charge carriers.

We finally analyze the effect of the structural dehydration on conduction. The observation of a local maximum of conductivity close to the maximum water loss (Figure 6b) indicates that σ_{dc} is dominated in this temperature range by a charge transport mechanism associated with water. This is confirmed by the fact that the higher value of the conductivity is not recovered upon cooling through the same temperatures. The charge carriers associated with the hydrogen-bonded network of structural water molecules are probably protons, which as mentioned in Section 3.b.1 are known to contribute by

hydrogen-bond exchange to the conductivity of several hydrogen-bonded and hydrated systems.²⁸⁻³² The abrupt change in the value of the dielectric strength at 323 K, where the temperature dependence becomes steeper, could then be associated to a more active role of the water molecules, which above this temperature become directly involved in the charge conduction process. Notice that this temperature is well below the onset of the loss of structural water, which takes place at 350 K (Figure 1c); hence, the conductivity enhancement cannot be ascribed to the formation of internal voids in the hydrate, which makes it unlikely that it can be explained by means of a vehicle mechanism.

The observation of a conductivity maximum entails that the density of charge carriers is not constant. In fact, in a series of spectra taken at a fixed temperature of 350 K under constant N₂ gas flow (in a different experimental run than that of Figure 6) the conductivity was observed to decrease with time. These data, displayed in Figure 7, clearly show that, in the temperature window where water starts leaving the sample, the measured σ_{dc} value is not an equilibrium value. The non-equilibrium value of the conductivity enhancement entails that its activation energy cannot be extracted from Figure 6b.

The fact that the conductivity drops in time proves that the conductivity enhancement cannot be due to sodium, hydronium or hydroxyl ions that start diffusing through the voids left in the lattice by the departing water, for in such case one would expect the conductivity to increase (or, at least, to remain constant) as more water leaves the sample (moreover, no ionic conductivity is reported for the pure material¹⁴). Having ruled out a vehicle or Na⁺ ion mechanisms, and given that the surface conductivity enhancement (section 3.b.1) is due to proton shuttling, we propose that the proton-exchange scenario applies also for the enhancement preceding the dehydration process. Proton shuttling in the bulk hydrate might be enabled by the reorientational motions of the structural water molecules. In fact, the conductivity crossover to steeper Arrhenius dependence occurs above 323 K, i.e. at higher temperature than that of the surface conductivity enhancement. Since the structural water is more tightly bound than the surface hydration water, this would be consistent with the fact that the onset of the long-range hydrogen-bond fluctuations and molecular reorientations necessary for proton exchange requires higher thermal energy in the bulk than in surface hydration layers.

Figure 7. Series of conductivity spectra acquired at 348 K every 5 minutes, after heating for the first time a hydrate pellet to this temperature.

To summarize, the $C_{60}(ONa)_{24} \cdot 16 H_2O$ hydrate exhibits two dielectric relaxations. The fastest one at higher frequency is assigned to reorientational motions of the structural H_2O molecules. The slowest one at lower frequency (“main relaxation”) is observed to evolve, upon dehydration, into the conductivity-induced relaxation feature of the pure $C_{60}(ONa)_{24}$ salt. While this suggests a common origin associated to charge-carrier accumulation at the sample’s heterogeneities, the dielectric strength and temperature-dependence of the main relaxation indicate that it involves also the reorientational motion of water dipoles at the same heterogeneities. Before and across the structural dehydration several conductivity anomalies are reported. A decrease of conductivity is observed at the structural transition, obviously related to the phase change. At temperatures well below such transition we observe a cross-over of the conductivity to a more pronounced temperature dependence, which we ascribe to the onset of a water-induced conduction mechanism likely involving hydrogen-bond exchange. The effects of water on conduction and dielectric properties appear to be closely intercorrelated: on one hand, water reorientations accompany the space-charge relaxation of carriers at heterogeneities; on the other, the

onset of proton exchange is likely accompanied by the onset of reorientational motions of the water molecules.

4. Conclusions

We have employed impedance spectroscopy to probe the impact of water on the frequency-dependent conductivity of the polycrystalline $C_{60}(ONa)_{24}$ fullerene derivative and of its hydrate, of chemical formula $C_{60}(ONa)_{24} \cdot 16 H_2O$. While the pure material exhibits low conductivity due to hopping of electronic charge carriers, exposing it to humid atmosphere leads to a four-decade conductivity enhancement below 325 K, which is due to charge transport through the hydration layers present on the surface of crystalline grains. In the hydrate, the dc conductivity is strongly temperature-dependent, and it is higher than that of the pure material by almost two orders of magnitude around 350 K. We showed that both conductivity enhancements arise most likely from a proton exchange mechanism. A dielectric loss associated with charge accumulation at grain boundaries is observed in all spectra. Its dielectric strength is strongly affected by the presence of water at the grains' surface: it drops by a factor of approximately three upon desorption of the surface hydration water, and by a slightly lower factor upon loss of the structural water. Our results indicate that interfacial water has a strong impact not only on the long-range charge transport but also on energy dissipation processes that accompany the accumulation of charge at crystalline grain boundaries. A second loss mechanism is observed below room-temperature in the hydrate, possibly related to reorientational motions of structural H_2O molecules or clusters in the crystalline hydrate phase.

Our study sheds light on two well known but not fully understood phenomena, namely the surface conductivity enhancement in porous materials upon adsorption of water vapor, and the change in conductivity across the structural dehydration of crystalline hydrates.¹⁵ In particular, we have shown that the extra surface conduction takes place through secondary hydration layers and involves proton hopping between whole water molecules; and that the conductivity change may actually already occur at lower temperature than the structural decomposition of a hydrate. Our results also imply that the anomalous non-monotonic behavior of relaxations observed in porous water-containing systems may

arise simply as a result of the change of conductivity induced by the desorption of water. Finally, we have shown that it is the presence of water around the fullerene derivatives which results in proton drift, while the water-free material does not exhibit protonic conduction, a result which rationalizes earlier findings.¹¹⁻¹⁴ As a final remark, we reported in a recent dielectric spectroscopy study on hydrated organic systems¹⁰ that the strength and frequency of the dielectric loss in hydrated phases varied slightly from sample to sample. In light of the results shown here, this is hardly surprising as both the value of σ_{dc} and that of the dielectric strength $\Delta\epsilon$ depend on the amount of water, which is likely to vary according to e.g. humidity conditions or sample preparation.

ASSOCIATED CONTENT

Supporting Information. Indexing and pattern matching analysis of the XRPD pattern of the hydrate; room-temperature crystal symmetry and lattice parameters of this material. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors.

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ABBREVIATIONS

TGA, thermogravimetry analysis; DSC, differential scanning calorimetry; FTIR, Fourier-transform infrared spectroscopy; XRPD x-ray powder diffraction; BNN, Barton-Nakajima-Namikawa.

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