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Proton Conductivity (1)

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Limits of Proton Conductivity

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In this journal, Ji and co-workers recently reported on the "highest proton-conductive material to date".[1] Indeed, the room-temperature proton conductivity of a hydrated, highly ordered nanoassembly of trimesic acid and melamine in the shape of whiskers is reported to be 5.5 $\mathrm{S\,cm^{-1}}$, which is more than one order of magnitude higher than the ionic conductivity of 1 M HCl.[2,3]

In an attempt to explain this extraordinary finding, the authors refer to "the highly ordered helical water chains" which "efficiently transfer the numerous available protons of the acid–base complex along the axis of the nanowire".

On the group's website, the term "proton ultraconductivity" was used for this putative phenomenon, and the *Nachrichten aus der Chemie* recently highlighted the paper.[4]

In view of the relevance of this apparent finding, the fact that such a high proton conductivity challenges our current understanding of proton-conduction phenomena in general and doubts the way the conductivity had been determined, we decided to have a careful look at the conductivity of hydrated trimesic acid/melamine whiskers.

In the following, we would like to briefly

1) explain why the reported conductivity is beyond the limit expected from basic physico chemical considerations,
2) present conductivity data on the same materials obtained in a different way, and
3) comment on the problems of determining the conductivity of small objects.

Until the mid 90s, it was still common textbook understanding that the unique mobility of protonic charge carriers (especially in aqueous media) is indeed the consequence of "concerted proton transfer along ordered hydrogen-bonded chains". But this simple mechanistic view completely ignored the corresponding energetics: the energy increase associated with the polarization of a water chain involving several hydrogen bonds in an unrelaxed highly dielectric ($\varepsilon = 81$) environment such as water is of the order of 1 eV. The corresponding dipolar moment is just too large for the typical hydrogen-bond strength within aqueous structures, and the dielectric response of the aqueous environment is too slow to follow a fast polarization process (the dielectric constant of water severely decays in the frequency range 10^9–10^{10} $\mathrm{s^{-1}}$,[5] which is very slow compared to the rate of intermolecular proton transfer involved in proton-conduction processes (typically 10^{12} $\mathrm{s^{-1}}$ with activation enthalpies not much higher than 0.1 eV)). Therefore, the elementary reactions that mobilize protonic charge carriers must be local processes, and in the case of water, details were first described by Tuckerman et al.[6a,b] and Agmon[7] and later revisited by Kreuer.[8] The mechanism is essentially a structural diffusion process, in which the protonic charge is following the "diffusing" center of symmetry of the hydrogen-bond pattern. Similar to the "presolvation" process in the Marcus theory of electron transfer,[9] this is brought about by solvent reorganization, which, in the case of water, comprises processes of breaking and forming hydrogen bonds. It goes without saying that such processes cannot occur at a high rate within "ordered hydrogen-bond chains", as suggested by Ji and co-workers. There rather must be a delicate balance between order and disorder, allowing both high rates of intermolecular proton transfer and the breaking and forming of hydrogen bonds.[8] It is interesting to note that for aqueous solutions this balance is optimal under pressure, as indicated by the fact that the mobility of protonic charges is passing through a maximum around $p = 0.8$ GPa.[3,10a–c]

The other important aspect is symmetry: as in the case of concentrated acids or bases, the high concentration of charged sites of the trimesic acid/melamine complex is expected to structurally bias the hydrogen bonds of the water structure. This induces local anisotropy, which tends to suppress intermolecular proton-transfer reactions. Therefore, proton conductivity, which is proportional to concentration and mobility of protonic charge carriers, also tends to level off or even passes through a maximum with concentration. At best, the total ionic conductivity of an aqueous solution may reach a value of approximately 1 $\mathrm{S\,cm^{-1}}$ at room temperature,[11] again, for a liquid with the optimal concentration of ions and the proper degree of disorder of its hydrogen-bond network.

One may also argue that the low dimensionality of the "helical water chains" may favor unusually fast proton transport. In fact, there is some truth to this reasoning, considering the fact that proton transport in aqueous bulk media is controlled by a significant coupling to the aqueous solvent. Indeed, there is increased proton cooperativity within strands of water confined in carbon nanotubes, but the effective rate of protonic charge transport is found to be low as a consequence of slow rates of hydrogen-bond reorganization within the water chains.[12] But while water is virtually not

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interacting with the walls of carbon structures, in the present case, there is strong acid–base interaction, which rather resembles the situation of hydrazinium chains in $LiN_2H_5SO_4$[13,14] or the water strands within transmembrane proteins, such as bacteriorhodopsine,[15] both showing moderate proton-transport rates only.

It should be noted that different limits apply to other types of hydrogen-bond networks. As shown recently, the compound with the highest intrinsic proton conductivity, molten phosphoric acid, shows a high degree of self-dissociation through polarization of extended hydrogen-bonded chains with subsequent separation of the charged species through a fast depolarization mechanism.[16] Compared to the situation in water, the essential differences are the very strong hydrogen bonds, which favor the long-range polarization process, and the network frustration, which leads to fast chain depolarization, thus preventing reversal of the charge separation process. But even this mechanism leads to a proton conductivity of only approximately 0.1 $\mathrm{S\,cm^{-1}}$ just above the melting point, which actually increases through the addition of water to a maximum of about 0.3–0.5 $\mathrm{S\,cm^{-1}}$.[17]

The discussion of the conduction mechanism in the nanoassembly of trimesic acid and melamine by Ji and co-workers is by far not meeting today's understanding of proton-conduction phenomena, which is just adumbrated here. But since we did not want to exclude the possibility of an unexpected discovery, we prepared whiskers in the same way that Ji and co-workers did and measured the conductivity in humidified atmosphere. In addition, we took a few measurements on samples provided by Ji and co-workers (we thank Prof. Ji for his cooperation).

In contrast to the procedure used by Ji and co-workers (we thank Prof. Ji for providing details of the preparation procedure), we washed the whiskers with water in a separate Petri dish and placed a single whisker (diameter ≈25 μm) on a PVC plate before contacting it with two "point" contacts formed from silver–epoxy resin. The set-up (Figure 1) responded almost like an ideal capacitor with no significant conductivity. For the impedance in humidified air, a lower limit of several GΩ is estimated, corresponding to an upper limit of the specific conductivity of approximately $10^{-6}\,\mathrm{S\,cm^{-1}}$, calculated with 25 μm as the whisker diameter and 265 μm for the separation of the point contact.

Since we could not detect any significant conductivity, the very high conductivity reported by Ji and co-workers seems to be the consequence of the way the samples were prepared and the conductivity was measured. We could actually not identify a single effect that fully explains the reported conductivity, but we made several observations about factors that may have contributed to the reported result:

In contrast to what is reported in the paper, whiskers were obviously placed on the glass plate together with the solution before odd whiskers were removed and electrodes deposited. We therefore put some solution, in which whiskers had been grown, into the gap formed by two platinum electrodes deposited on a glass plate. Some material precipitated from this solution (especially at the edges, see picture in Figure 2). This configuration actually showed some conductivity under wet condition. If one had assumed that the corresponding current (2.7 nA at a voltage of 0.1 V) was flowing through a whisker of 250 nm diameter (length of ≈60 μm) the corresponding specific conductivity would have been 0.34 $\mathrm{S\,cm^{-1}}$. This is still lower than 5.5 $\mathrm{S\,cm^{-1}}$ reported by Ji and co-workers, but there may be other effects stemming from the high dc voltage (10 V) applied in the experiments by Ji and co-workers. Indeed, there is an effect of voltage on the ac impedance (Figure 1), which may have different reasons (e.g., electronic conductivity as a result of decomposition).

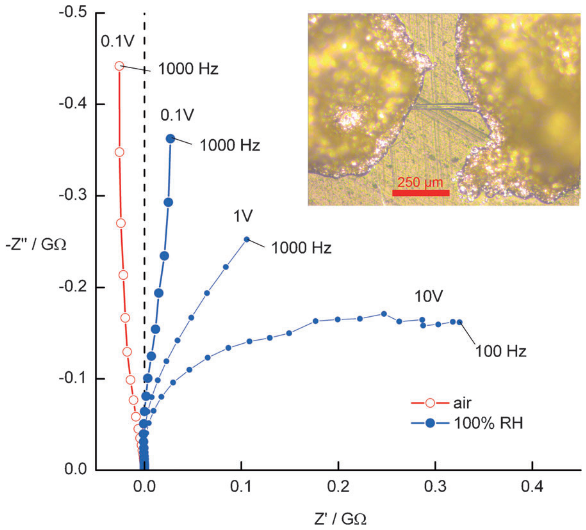

Figure 1. Complex ac-impedance of a trimesic acid/melamine whisker in air and under humid (RH = 100%) conditions (see text). The whisker is placed on a flat PVC support and contacted with silver–epoxy resin (see insert).

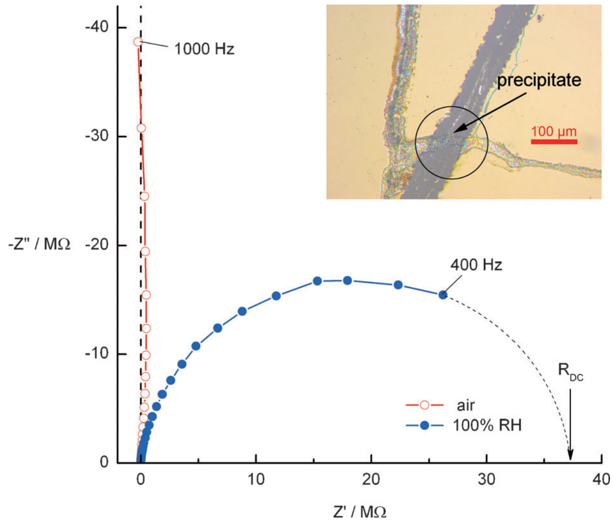

Figure 2. Complex ac impedance of a glass gap (width ≈60 μm) between two platinum electrodes contaminated with a precipitate from a solution, in which trimesic acid/melamine whisker had been grown. Under humid conditions (RH = 100%), the dc resistance amounts to about 37 MΩ.

We have also measured the ac impedance of a contacted sample from Ji and co-workers. This obviously was not the original sample (the dimensions were different and, apart from some undefined solid contaminations, several whiskers were bridging the two electrodes). In fact, there was some

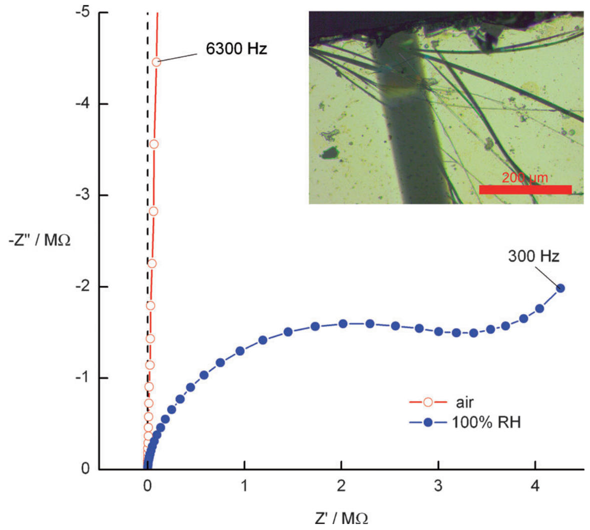

Figure 3. Complex ac impedance of a sample provided by Ji and co-workers in air and humid conditions (RH = 100%). Apart from several whiskers bridging the gap between the electrodes, some solid undefined contaminations are visible.

humidity-dependent conductivity for this sample (Figure 3), but even this did not amount to the reported value using estimated dimensions for the whiskers ($\approx 8\times10^{-3}\,\mathrm{S\,cm^{-1}}$). The group also provided a mesh of whiskers on a plastic slide, and the fact that this showed a similar resistance under humidified conditions suggests that it is the precipitate rather than the glass surface that conducts the electrical current.

Since the effects described above cannot completely explain the published results, we would also like to point out a few apparent inconsistencies within the paper and for the dimensions of the sample we received from the group and the published pictures. In short: within the main text, evaporated gold electrodes structured with a photolithographic process are reported while in the supporting information platinum electrodes sputtered using a copper-wire mask are described. The dimensions of the gap between the electrodes in Figures 3 and 5 are different. The diameter of the whisker shown in Figure 3 (≈ 250 nm) is substantially smaller than the diameter of the whiskers of the device we obtained from the group (≈ 2 µm). We have actually used whiskers with a larger diameter of 25 µm, which reduces the effect of parasitic currents.

It is therefore very likely that the group measured a small parasitic current along the glass surface contaminated with precipitates from the solution. Assuming by mistake, that all of that current was flowing through an extremely small whisker may then have resulted in the faulty specific conductivity published by Ji and co-workers. This is actually pointing toward a general problem in measuring the transport properties of very small objects. In fact, there have been several reports on surprisingly high ionic (also protonic) conductivity and ionic diffusion in, for example, thin films and narrow channels in high impact journals. Without specifying the corresponding publications, these results should be received very carefully. The small fluxes (e.g., currents or mass flows) make the results very vulnerable: as in the present case, there may be parasitic fluxes parallel to the sample or residual driving forces (e.g., small gradients in pressure, temperature, chemical potential) producing fluxes which are not considered in the evaluation (e.g., chemical diffusion, hydrodynamic flow).

Unfortunately, an increasing fraction of publications has to be withdrawn especially from high impact journals,[18] which is pointing toward an increasing deficit in the way we are doing and disseminating science. The more, we would like to thank Prof. Ji for his cooperation and his open way in dealing with our concerns.

Experimental Section

We used IMI E-Solder 3021 as silver–epoxy resin for forming point contacts. These contacts were connected to an impedance analyzer (novocontrol technologies alpha A mainframe, POT/GAL 15V-10A electrochemical interface), and the sample holder was placed in a closed chamber equipped with micro contacts,[19] which was flushed with either dry or humidified (close to 100% relative humidity (RH)) air. Impedance spectra were recorded in the frequency range of 10^2–5×10^6 Hz with an applied voltage of 0.1 V (measurements with 1 V and 10 V were obtained for comparison).

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