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Proton Conductivity (2)

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Reply: High Proton Conductivity of Water Channels in a Highly Ordered Nanowire

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Our group recently published a Communication in this journal, in which we discussed our finding of a trimesic acid/melamine nano/microwire with a proton conductivity of 5.5 $S\,cm^{-1}$.[1] It has since been questioned how much of this measured conductivity can be attributed to the nano/microwire complex. Recently, we sent several old devices to Kreuer and Wohlfarth for impedance testing.[2] Since Dr. Wang, who had performed the original experiments, had left the group, we picked several devices out of a number of devices prepared by him. However, we could not identify the one that was used for the experiments reported in the above-mentioned publication. These old devices, along with devices prepared from Kreuer and Wohlfahrt, did not show the high conductivity we had demonstrated in our Communication and the results are shown in Kreuer's Correspondence in this issue.

The difference may be due to the unique difficulty of measuring the conductivity of this system. The nature of our supramolecular crystal means that the wires are held together by π–π interactions and hydrogen bonds; there are no covalent bonds keeping the system intact. This makes the wires very fragile, and attempts to move them from their original substrate will very likely fracture the crystal, resulting in a null conductivity measurement. On the other hand, as we have discovered, measuring on their original substrate can result in undesired parallel current flow, which will exaggerate the measured conductivity. We undertook conductivity measurements to attempt to correct this issue. The goal was to compare the conductivity change of a substrate against our measurement area (Figure 1). While some parasitic current was expected, we were attempting to determine whether it was significant. Under atmospheric conditions, the conductivity of the clean polyethylene substrate was found to be below the noise limit of our instrument, measuring less than 1 nA of current between −5 and 5 V. While the wire showed some small conductivity, it was still very minor. Comparing the same two areas in 100% saturated air showed a change in conductivity for both (Figure 2). However, while the current through the substrate rose by two orders of magnitude, the current through the wire increased by more than six orders of magnitude. From this we can conclude that while there is indeed a parallel current which is inflating the calculated conductivity, the sample on its own is still proton conductive.

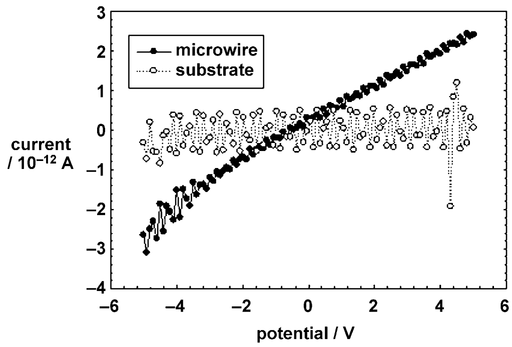

Figure 1. Comparison of conductivity of a clean polyethylene substrate to a microwire sample under atmospheric conditions.

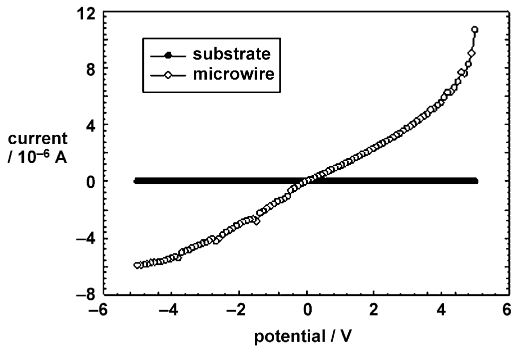

Figure 2. Comparison of conductivity of a clean polyethylene substrate to a microwire sample under 100% relative humidity (RH).

However, the performance of the the single wire devices still varies from device to device, depending on the quality of the nanowires. Furthermore, the heat of thermal evaporation or sputtering can potentially damage the wires, while single wire samples tend to fracture in transport, giving complex or null results.

For this reason, we prepared a network of nanostructures to introduce redundancy into the system. The two new devices were made of a network of nano/microwires on a plastic surface and were sent to Kreuer and Wohlfarth, who did impedance measurements. Contrary to the expectation on

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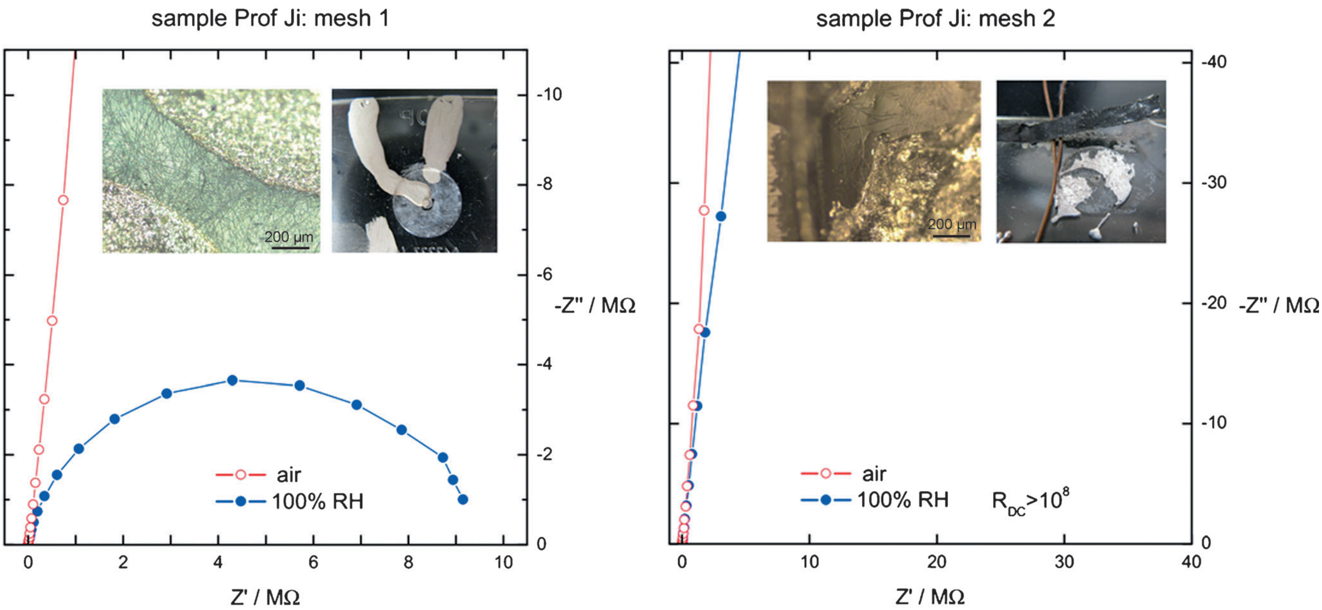

Figure 3. Impedance measurement of a trimesic acid/melamine nanostructured network. Insets show magnified view of the connection (left) with a macroscale view of the device (right).

a consistent conductivity of the nanowire network, the two samples also showed significantly different results (Figure 3 from Kreuer and Wohlfahrt): one showed 10000 fold conductivity enhancement from dry to 100 % RH conditions, another only showed less than 10 fold enhancement. Their results on our new samples confirmed that the system is conductive, however, the exact magnitude of the conductivity is difficult to determine. It is noteworthy that the conductivity is not occurring through the surface of the plastic, as the plastic is neither proton nor electron conductive.

In summary, we would like to amend our statement that the trimesic acid/melamine nanowires have the highest proton conductivity to date, with a measured conductivity of 5.5 $S\,cm^{-1}$. Based on all the experiments Kreuer and Wohlfahrt, and our group have conducted, we conclude that the quality of the nanowire is crucial for its high proton conductivity. While the complexities of the measurement make exact determination difficult, the nanowires are capable of transporting protons. The nanowires seem to be prone to defects, with conductivities drastically changing depending on nanowire quality, sample preparation, and measurement conditions. Our future goal is to solve the problems related to the stability/fragility of the system in order to obtain a reproducible result for practical use of this new family of proton-conductive material.

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[1] H. Wang, X. Xu, N. M. Johnson, N. K. R. Dandala, H.-F. Ji, *Angew. Chem.* **2011**, *123*, 12746–12749; *Angew. Chem. Int. Ed.* **2011**, *50*, 12538–12541.
[2] K.-D. Kreuer, A. Wohlfarth, *Angew. Chem.* **2012**, DOI: 10.1002/ange.201203887; *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.201203887