Experimental report

30/10/2020

Proposal: 6-07-55 **Council:** 10/2019

Title: Water and Polymer Dynamics in Nanoporous Polypyrrole-Silicon Membranes

Research area: Soft condensed matter

This proposal is a resubmission of 6-07-53

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Samples: Nanoporous Silicon
Polypyrrole/Silicon
Polypyrrole/Nanoporous Silicon

Instrument	Requested days	Allocated days	From	To
IN16B	5	3	21/08/2020	24/08/2020
IN5	3	0		
IN6-SHARP	4	0		

Abstract:

We could recently show that by a combination of self-organized nanoporosity in silicon (npSi) with polymerization of an artificial muscle material (polypyrrole, PPy) inside pore space a material can be synthesized that shows macroscopic electrostrain; i.e. immersed in an aqueous electrolyte the material expands and contracts reversibly under electrical potential control. The voltage-strain coupling parameter is 3 orders of magnitude larger than the best-performing, all solid-state piezoelectric material (PZT). The exceptionally small operation voltages (0.3-0.8 V) along with the biocompatibility and the simple synthesis of the material could pave the way for silicon-based (bio-)actuorics. For obtaining a mechanistic understanding of the electroactuation dynamics of the PPy filled npSi membranes and for a comparison with ongoing Molecular Dynamics simulations studies, it would be important to determine the self-diffusion dynamics of water inside the PPy as well as the polymer dynamics inside the silicon pore space. Therefore, we are going to perform comprehensive quasi-elastic studies of dry and fully hydrated PPy-npSi hybrids as well as dry and hydrated bulk films of PPy on Si.

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Measurements on dry polypyrrole films have shown no perceptible quasi-elastic line broadening within the resolution of the IN16B neutron backscattering instrument. Polypyrrole films have been wetted with water over the vapour phase with a relative humidity of around 84 %. In a first step elastic fixed window scans in cooling (uncontrolled cooling rate) and heating have been conducted (see fig. 1 left) in conjunction with an inelastic fixed window scan on heating with energy transfers of ±2.5 µeV and ±6.0 µeV (see fig. 1 right). The elastic fixed window scan shows a clear hysteresis in

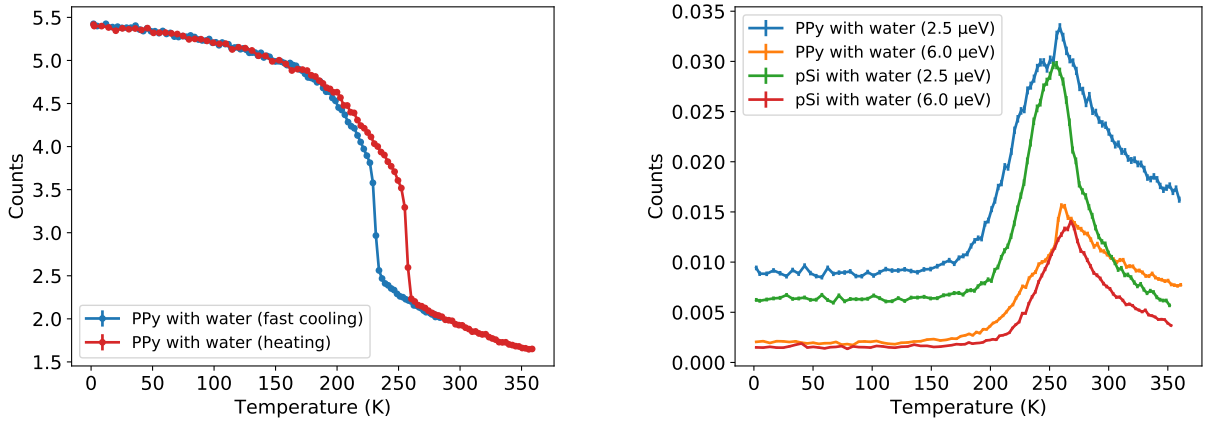

Figure 1: *(left)* Elastic fixed window scans for wet polypyrrole, *(right)* inelastic fixed window scans with a fixed energy transfer of ±2.5 µeV and ±6.0 µeV for wet polypyrrole and water in porous silicon. All datasets shown in the graphs are averaged over all wave vector transfers Q.

the temperature dependence of the water dynamics within the polypyrrole films between heating and cooling. Furthermore the phase transition is distributed over a large temperature range compared to the bulk water (see e.g. fig. 2) and shifted to considerably lower temperatures.

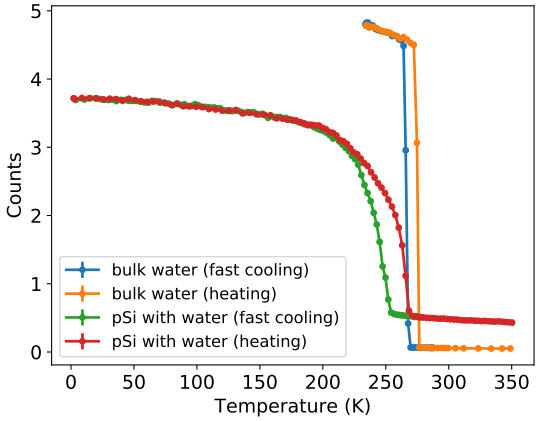

Figure 2: Elastic fixed window scan for water in porous silicon nanopores (averaged over all Q).

Full energy transfer spectra have been measured at four different temperatures for the wet polypyrrole films. The corresponding, over Q averaged, data are plotted in figure 3 and are showing the temperature dependence of the water dynamics within the polypyrrole films.

The original aim of the experiment was to investigate the water dynamics in polypyrrole within porous silicon nanopores. However, due to an unforeseen spontaneous reaction the samples have been destroyed just on arrival at the ILL. Therefore, as an alternative, preliminary experiments on the water dynamics within porous silicon membranes have been conducted.

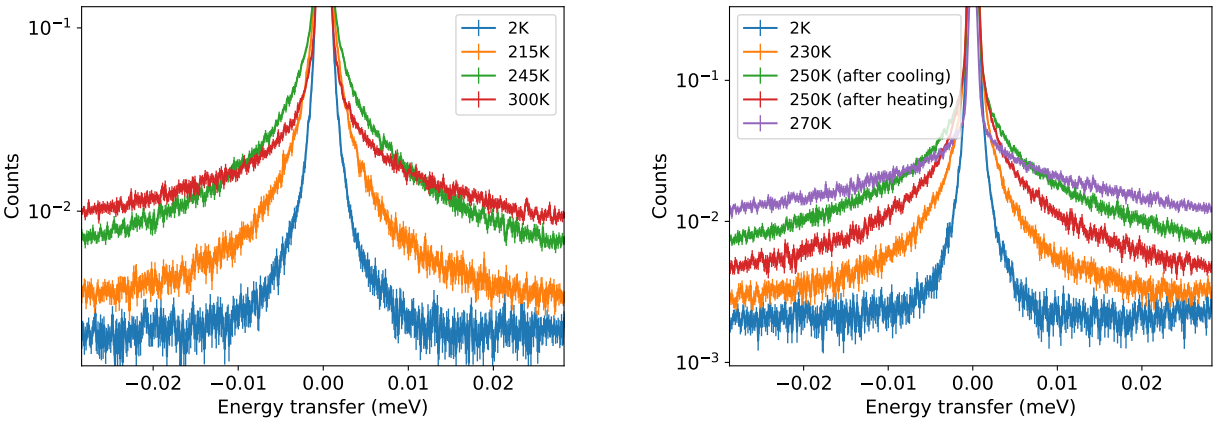

Figure 3: QENS spectra *(left)* of wet polypyrrole at different temperatures and *(right)* of water confined in porous silicon membranes (Q-averaged spectra).

Figure 2 shows an elastic fixed window scan in heating and cooling of the confined water in comparison to bulk water. In contrast to the bulk the phase transition temperatures in confinement are shifted to lower temperatures and show a distinct hysteresis. In addition there is no first order but a gradual phase transition over a wide temperature range observable. This can be also seen from the corresponding inelastic fixed window scan with a fixed energy transfer of $\pm 2.5\,\mu$eV and $\pm 6.0\,\mu$eV (see fig. 1 right).
Full energy transfer spectra were acquired at four different temperatures below the bulk melting temperature. Alike the hysteresis in the elastic fixed window scan, a remarkable difference between the dynamics (see fig. 3) is found when measuring the spectra on heating and on cooling, respectively. It is planned to investigate this in more detail during a further beamtime.