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# Proton dynamics of phosphoric acid in HT-PEFCs: towards “operando” experiments

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**Abstract.** High Temperature Polymer Electrolyte Fuel Cells (HT-PEFCs) have been studied with quasielastic neutron scattering, which gives access to the proton diffusion in the fuel cell on local length- and timescales. So far, the different components such as the proton conducting membrane and the electrode layers have been studied separately. Here we show that also operating fuel cells can be investigated and the proton diffusion can be measured under real working conditions. The proton diffusion during power production is compared to that “at rest” but at elevated temperatures.

## INTRODUCTION

High Temperature Polymer Electrolyte Fuel Cells (HT-PEFCs) are promising candidates for the conversion of chemical energy to electrical power in the medium power range (~5kW), e.g. for small stationary applications [1]. Phosphoric acid embedded in a polymer matrix is the proton conductor in these fuel cells. The advantages of this type of proton exchange fuel cells include high proton conductivity, low sensitivity to CO contamination and no need of complicated water management due to the operation at elevated temperatures (~160°C). The conductivity of such fuel cells is proportional to the amount of the phosphoric acid, which has the highest intrinsic proton conductivity of any known substance.

The central part of the fuel cell is a membrane-electrode assembly (MEA), which consists of two catalytic layers separated by a proton exchange membrane. In a HT-PEFC the proton conducting membrane is typically a polybenzimidazole-type (PBI) polymer doped with phosphoric acid [2, 3]. The catalyst layer is a composite material containing nanoporous carbon, poly(tetrafluoroethylene) (PTFE) and platinum nanoparticles.

So far, we investigated parts of the fuel cell with neutron scattering separately and not under real working conditions. For example the diffusion in the proton conducting membrane has been investigated in [1]. The proton diffusion relates well to the macroscopic conductivity of the membrane. To the best of our knowledge, observation of the local proton diffusion with quasi-elastic neutron scattering technique in an operating high temperature polyelectrolyte fuel cell has not been investigated so far.

## EXPERIMENTAL SETUP

For “operando” fuel cell studies, two possible strategies can be envisaged. Either a fuel cell is optimized for the conditions of neutron scattering to avoid as much as possible scattering from parts of the fuel cell, which have no function concerning the proton diffusion (i.e. all parts except of the MEA). Or one compromises on the background situation in neutron scattering and operates a “real world” fuel cell, where the electrochemistry and gas flow is not altered due to larger edge-effects for example for a redesigned fuel cell. We followed the second path and investigated a fuel cell built for test stand operation and not altered in any way, in order to maintain realistic conditions. A fuel cell test stand has been built and operated already in neutron and synchrotron radiography applications [4,5].

SANS experiments at KWS-2 (MLZ, Garching) [6] have been conducted in order to judge the amount of scattering coming from the different components. The full cell (not in operation) and different parts of it (cell without end plates, MEA only) have been measured (Fig. 2). The experiment showed that the large amount of materials not under investigation, such as the Aluminum end plates and the gas flow channels, contribute to the small angle scattering signal, but still a large amount of the scattering comes from the MEA with a typical power law decay of  $I(q)$  of a fractal structure. The experiment has been done without operation in order to demonstrate the potential possibility to observe the structural changes due to temperature effects or gas flow and changes over time of the micro- and nanostructure in an operating fuel cell. Care has to be taken of course to separate the different scattering contributions from the electrode layer and the proton conducting membrane.

Backscattering experiments have been conducted at SPHERES (MLZ, Garching)[7]. The high energy resolution of the backscattering experiment allows one to look at the rather slow proton diffusion processes in the operating fuel cell. The huge incoherent scattering cross section of H for neutrons makes this technique an excellent tool for diffusion studies. The proton diffusion is also related to the conductivity of the proton conducting membrane and electrode layers. Therefore the neutron scattering results can help understanding macroscopic properties of the fuel cell. Figure 1 shows the fuel cell mounted at the sample position of the backscattering spectrometer SPHERES. The fuel cell consists of two aluminum end plates with thickness of 0.5 cm at the neutron beam position. The next layer is the gas flow field produced from carbon composite with thickness of 5 mm. The MEA is placed between two flow fields. The overall thickness of the fuel cell at the beam position is more than 3 cm. The fuel cell has been heated to 430 K with an external heater which would be also the typical operating temperature in a test stand. H<sub>2</sub>-gas and normal air is provided by a gas handling system which provides a gas flow of 140 ml/min H<sub>2</sub> at max. 2 bar.

In the backscattering experiment [7], due to the massive construction very large angle analyzers and detectors were shadowed by the cell in transmission geometry. Thus, the experiment has to be performed at transmission as well as at reflection positions (fuel cell rotated by 90° between the two configurations).

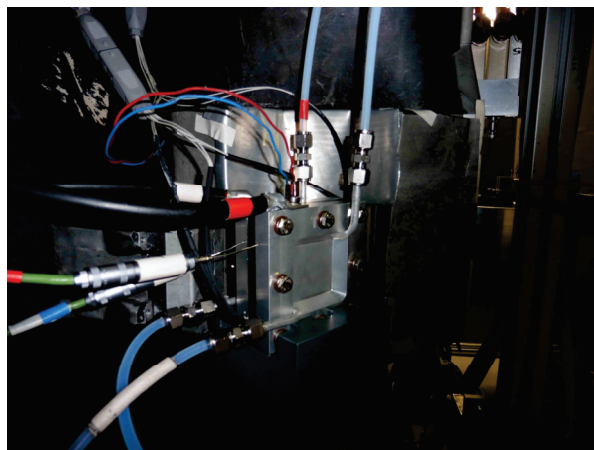
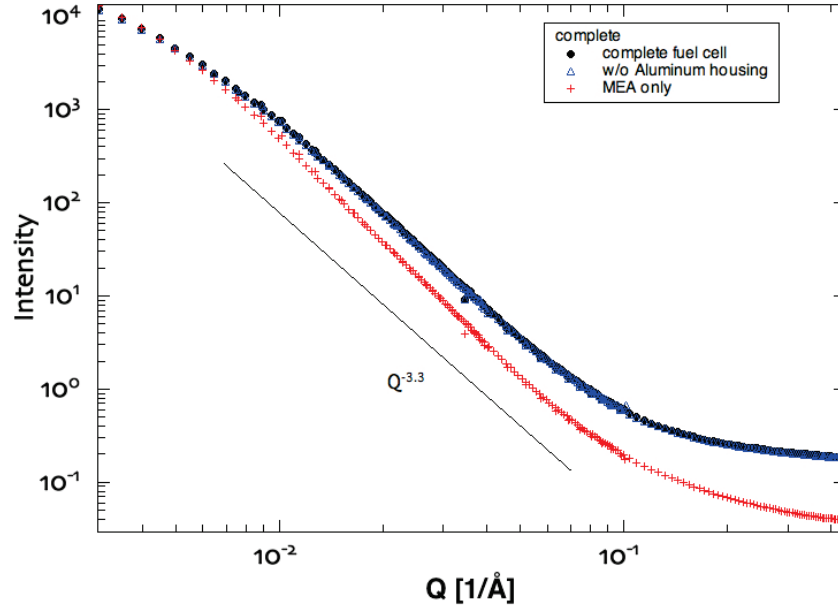


FIGURE 1. Fuel cell at the sample position of the backscattering spectrometer.



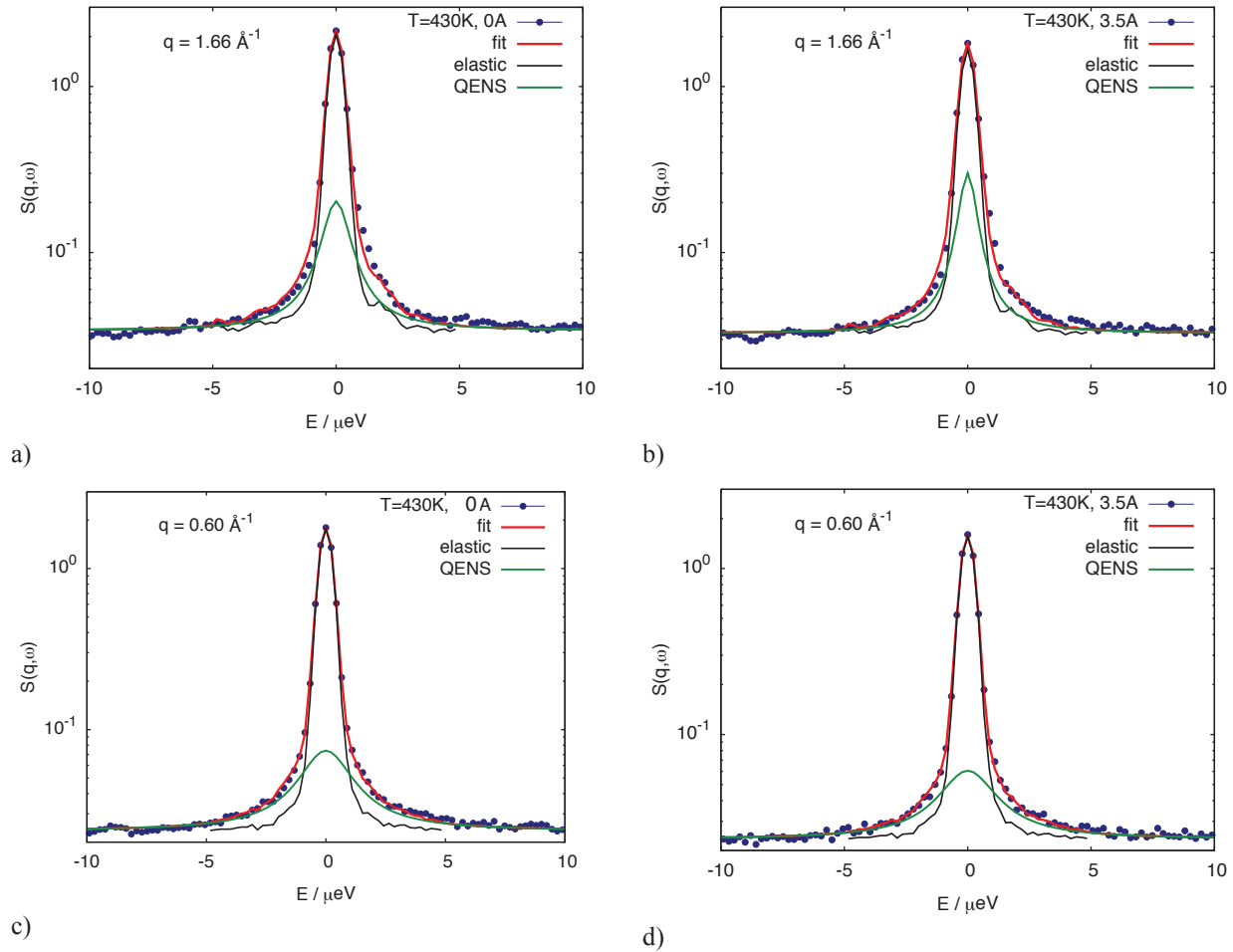
**FIGURE 2.** SANS measurements of the complete fuel cell and parts of it, showing that the major contribution comes from the MEA stack despite of the large amount of material in the end plates, gas flow channels etc.

## RESULTS AND DISCUSSION

The two main components, the proton conducting membrane (PBI doped with phosphoric acid) and the electrode layer, have been studied with quasielastic neutron scattering, small angle X-ray and neutron scattering and electron microscopy [8,9]. The SANS experiments, although with a fuel cell not in operation, showed that the major scattering contribution of this rather thick sample comes from the MEA itself (Fig. 2). This makes us believe that also structural changes can be observed under load, which might help to relate e.g. structural changes and ageing behavior of the fuel cell.

Backscattering spectroscopy allows one to study the proton diffusion in the MEA during different operation conditions. Figure 3 shows different operating conditions (cell heated up to operating temperature of 430 K, but at 0 Amps, vs cell operating at 3.5 Amps). Two different scattering geometries have been chosen, one in reflection geometry, where the scattering vector  $q$  is in the plane of the MEA, and a second one with a rotated cell with the  $q$  vector perpendicular to the MEA and in the direction of the current flow. QENS spectra from the fuel cell have been resolution corrected with a standard resolution measurement of a Vanadium sample as an elastic scatterer. In both cases, a quasielastic broadening could be observed despite the large amount of material in the beam that is not subject to the backscattering investigation. Background subtraction is rather difficult again due to the large amount of material in the beam, therefore only the same geometry under different conditions is compared here and no background measurement has been subtracted. Due to the large scattering contribution from the fuel cell “infrastructure” we want to ensure not to introduce additional artifacts with a different “empty” fuel cell for this first experiment. In transmission geometry the proton diffusion is measured along the current flow (Fig 3 c) and d)), where no significant difference in the quasielastic broadening is observed at this first evaluation. Reflection geometry (Fig 3 a) and b)) showed a slight change in the QENS signal, with a slightly larger broadening for the non-operating cell. The scattering vector was  $q=1.66 \text{ \AA}^{-1}$  in reflection geometry and  $q=0.6 \text{ \AA}^{-1}$  in transmission geometry, corresponding to length scales of  $d=2\pi/q=3.79$  and  $10.5 \text{ \AA}$  respectively. Differences in diffusion between the two orientations might occur on the one hand due the current flow perpendicular to the membrane (the macroscopic diffusion being approximately one order of magnitude lower than the proton mobility on local scales). The line width (FWHM) of the QENS signal of the order of  $E \sim 2 \text{ \mu eV}$  is linked to the Stokes-Einstein Diffusion constant  $D =$

$1/(t q^2)$  by the relaxation time  $t$  [ns] =  $1.317 / E$  [ $\mu\text{eV}$ ] [10]. The experiments show the feasibility of QENS studies on operating fuel cells, with resulting diffusion constants of the order of  $10^{-11} \text{ m}^2/\text{s}$ , similar as reported in [1] for a phosphoric acid doped PBI membrane measured with neutron spin echo spectroscopy. The uncertainties due to background scattering of the fuel cell however make us believe that a more detailed discussion of the differences needs further experiments with a better knowledge of the background situation. Future work needs to allow assess the fuel cell effects properly, and the results of operando fuel cell measurements have to be related to corresponding measurements of the proton conducting membrane alone with QENS [1,11] and NMR [12] and NMR measurements of phosphoric acid alone [13] and measurements of the electrode layer [8]. Here we only want to focus on relative changes under the same conditions, i.e. under different currents, but with exactly the same geometry.



**FIGURE 3.** QENS spectra from SPHERES at different operating conditions with zero amps (left) and 3.5 Amps (right). a) and b) in reflection geometry (i.e. the scattering vector  $q$  is in the plane of the MEA stack). c) and d) in transmission geometry (i.e. the scattering vector  $q$  is perpendicular to the MEA stack and in the direction of the current flow).

## CONCLUSION

Proton diffusion and also structural investigations are possible in operating high temperature fuel cells. Fuel cell designs for test stand applications but with a minimization of background producing material in the beam will be studied in the future, where still realistic conditions in terms of electrochemistry are present, but the background is reduced for the neutron scattering experiment. However, even in the fuel cell optimized for the performance the proton diffusion is visible as a line broadening of the heated and operating fuel cell. Rotating the cell is a way of

measuring the proton diffusion along different directions, parallel to the current flow and perpendicular to it. We see indications that perpendicular to the current flow, the proton diffusion is altered in the operating fuel cell (Fig. 3a vs Fig. 3b), while the diffusion along the current direction seems to be unaffected by operation. A detailed separation of different contributions from the different parts of the MEA is ongoing work. We believe that in the future, QENS measurements on the proton diffusion can be linked to the macroscopic conductivity and will help in this way identifying the parts of the fuel cell which have potential for optimization.

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