Experimental report

14/09/2023

Proposal: **9-12-672**

Council: 10/2022

Title: Nanostructure of ionomer in fuel cell catalyst ink by SANS

Research area: Engineering

This proposal is a resubmission of 9-12-654

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Samples: Mixture: Pt, Carbon, Nafion, Water, Alcohol

Instrument	Requested days	Allocated days	From	To
D22	1	1	14/06/2023	15/06/2023

Abstract:

Zero emission automotive using hydrogen as a fuel and powered by a proton exchange membrane (PEM) fuel cell is now commercially available. However, large-scale commercialization of fuel cell vehicles requires progress in performance, cost and durability, for which the electrode is the most limiting component. It is made of a random assembly of platinum and carbon based nanoparticles within a proton conducting polymer network. The electrode is obtained from a slurry after evaporating the solvents. Currently, research and development to improve the performance and reduce the manufacturing cost rely on a trial and error basis, because information is lacking. Indeed, little is known on the structure of the slurry, especially regarding the ionomer dispersion, whereas it is now established that it plays a crucial role. The proposed experiment aims at using SANS with contrast variation to characterize the ink structure, and more precisely the dispersion of the ionomer, to estimate its degree of agglomeration and its coverage on the catalyst support. Thisis a preliminary study, as a prerequisite for the PhD project that has been funded in the frame of the InnovaXN program.

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Experiment details

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Title: Nanostructure of ionomer in fuel cell catalyst ink by SANS

Instrument: D22

Date of experiment: 14/06/23 – 15/06/23

Aim of experiment

Fuel cells are used in hydrogen-powered electric vehicles, where developments in performance and durability are crucial for further commercialization, which the final structure of the electrode (catalyst layer) strongly influences. Composed of Pt nanoparticles supported on a carbon composite, embedded in a proton conductive polymer (also known as ionomer), the catalyst layer structure is known to be directly connected to that of the catalyst ink, where the components are dispersed in solvent, which is then dried to give highly heterogeneous structures. These are currently not well understood, leaving new developments reliant on a trial and error approach. This is especially the case for the ionomer component, although it is known to have a crucial impact on the ink structure. The aim of this experiment is to develop our understanding of component interactions in catalyst inks, specifically related to the few nanometer thick ionomer layer on the carbon aggregates. Contrast-variation small angle neutron scattering is used to extract information on specific components from the initially complex, multi-component dispersion. The developed understanding of catalyst ink structures will then be linked to the final catalyst layer structure and further to the electrode performance.

Experiment report

Throughout the 24 hour period, approximately 70 different samples were measured, each at two different configurations: with the back detector at 17.6 m and 4 m, both using a $6\dot{A}$ neutron wavelength. This was in order to obtain improved statistics in a higher Q range, where we expect to see a peak related to the ionomer at Q = 0.03 $\dot{A}^{-1}$, while maintaining a large Q range to obtain information on the carbon aggregates. Additionally, four ink compositions have been measured with the back detector at 17.6 m using a neutron wavelength of a $11.5\dot{A}$, in order to achieve Q values as low as 0.0014 $\dot{A}^{-1}$, and verify whether it is possible to obtain further information on the structure of the carbon aggregates. For each ink composition, 6 samples of different contrasts were measured. This was achieved by replacing the usual isopropanol/water solvent with isopropanol-d8 and D_2O in determined fractions. For the 17.6 m configuration, each ink sample was measured for 5 minutes, with the exception of inks with a fully deuterated solvent which were measured for 10 minutes. For the 4 m configuration, each ink sample was measured for 2 minutes, with the exception of inks with a fully deuterated solvent which were measured for 5 minutes. In the case when a neutron wavelength of $11.5\dot{A}$ was used with the back detector at 17.6 m, each ink sample was measured for 15 minutes, with the exception of the inks with fully deuterated solvents which were measured for 20 minutes.

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Reference solvents for each proportion of solvent deuteration were measured in all configurations for the same time interval as the inks.

The obtained data has been reduced using the grasp software, and corresponding data measured at 17.6 m and 4 m has been stitched together for each ink and reference solvent. The background for each ink has been removed by subtracting the data of corresponding reference solvents. The data is then cut at Q = 0.5 $\dot{A}^{-1}$. Figure 1. Shows the fully cleaned stitched CV-SANS data for one ink composition:

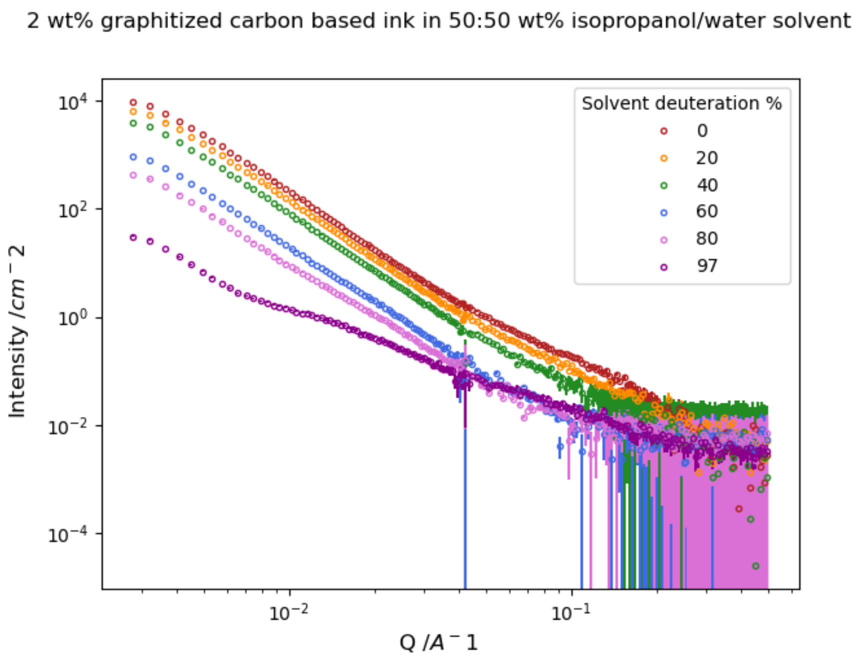

Figure 1. CV-SANS data for an ink based on graphitized carbon, using nafion ionomer with an I/C ratio of 0.8, in a 50:50 wt% isopropanol/water solvent, with deuteration content ranging from 0 (red) to 100 % (dark purple).

Figure 2. shows an ink series measured using the neutron wavelength of 11.5$\dot{A}$.

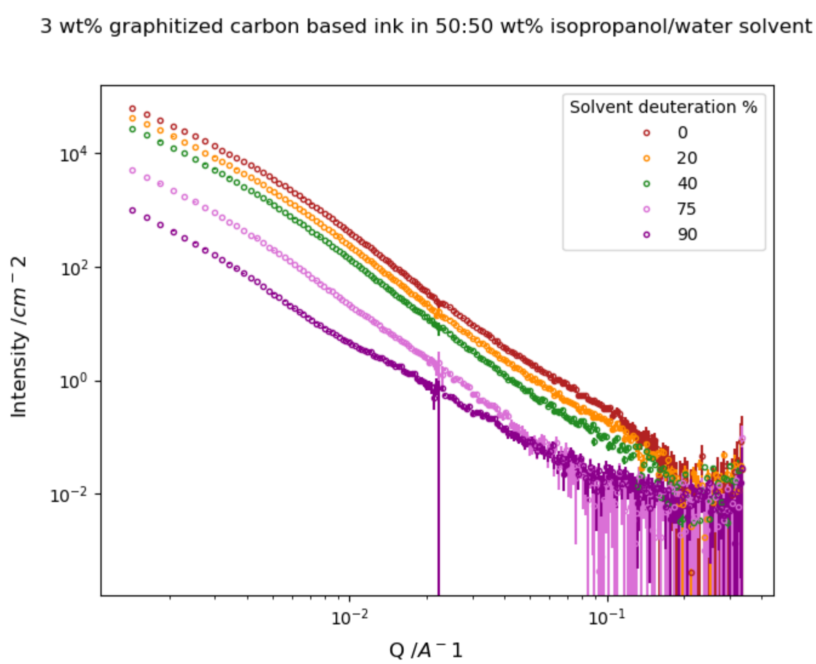

Figure 2. CV-SANS data for an ink based on graphitized carbon, using nafion ionomer with an I/C ratio of 0.8, in a 50:50 wt% isopropanol/water solvent, with deuteration content ranging from 0 (red) to 90 % (dark purple).

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The contrast variation series will be processed using singular value decomposition in order to obtain partial scattering functions for the carbon-carbon and polymer-polymer interactions, as well as to obtain a carbon-polymer correlation function (figure 3). These will then be fit using corresponding models to obtain quantified results for parameters such as the ionomer shell thickness and density, the volume fraction of ionomer adsorbed onto the carbon aggregates, or the surface roughness of the carbon. This is specifically crucial in the case of inks based on 3 wt% carbon, the closest composition to industry standards, as maximum deuteration of the solvent cannot be achieved, and therefore the SLD of the solvent is further away from that of carbon. This is due to the nature of the commercial ionomer dispersion used in sample preparation.

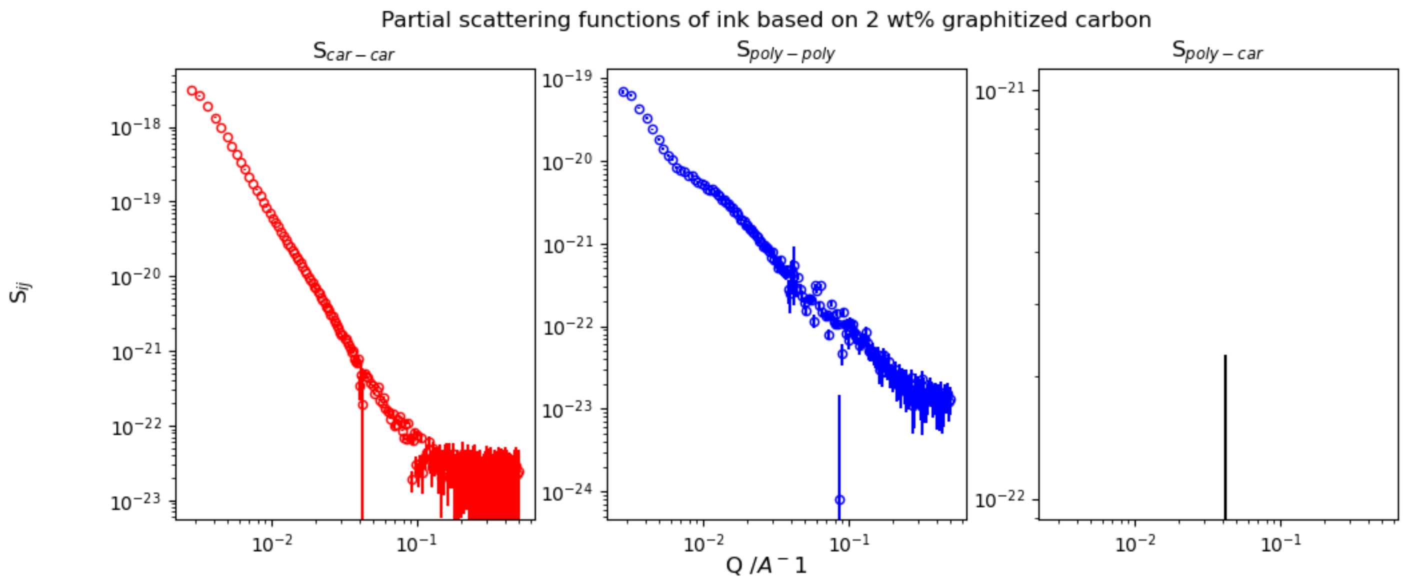

Figure 3. Partial scattering functions of 2 wt% graphitized carbon based ink (see figure 1.): carbon-carbon function (red), polymer-polymer function (blue), carbon-polymer function (black).

The experiment went smoothly with no issues encountered, leading to a large number of samples that could be measured. Data analysis is currently underway. The data from the experiment will be used in the thesis of the InnovaXN PhD project: 'Investigation of manufacturing process related structure and performance of fuel cell electrode thanks to neutron small angle scattering', and the data will potentially be used in a future publication.