Experimental report

12/02/2020

Proposal:	**9-12-542**	**Council:**	4/2018

Title: SANS study of bio-mimicking catalytic layers for Proton Exchange Membranes Fuel Cells

Research area: Materials

This proposal is a new proposal

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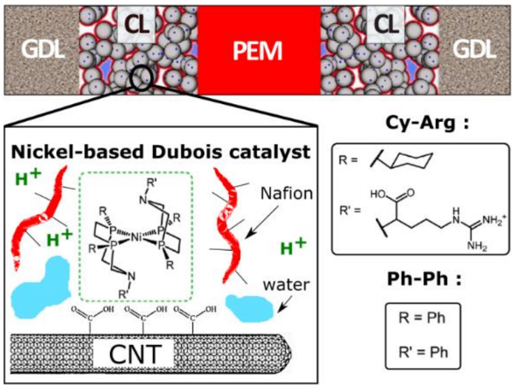
Samples: carbone nanotubes , nafion, nickel diphosphine complex

Instrument	Requested days	Allocated days	From	To
D33	0	0		
D22	2	1	01/10/2018	02/10/2018

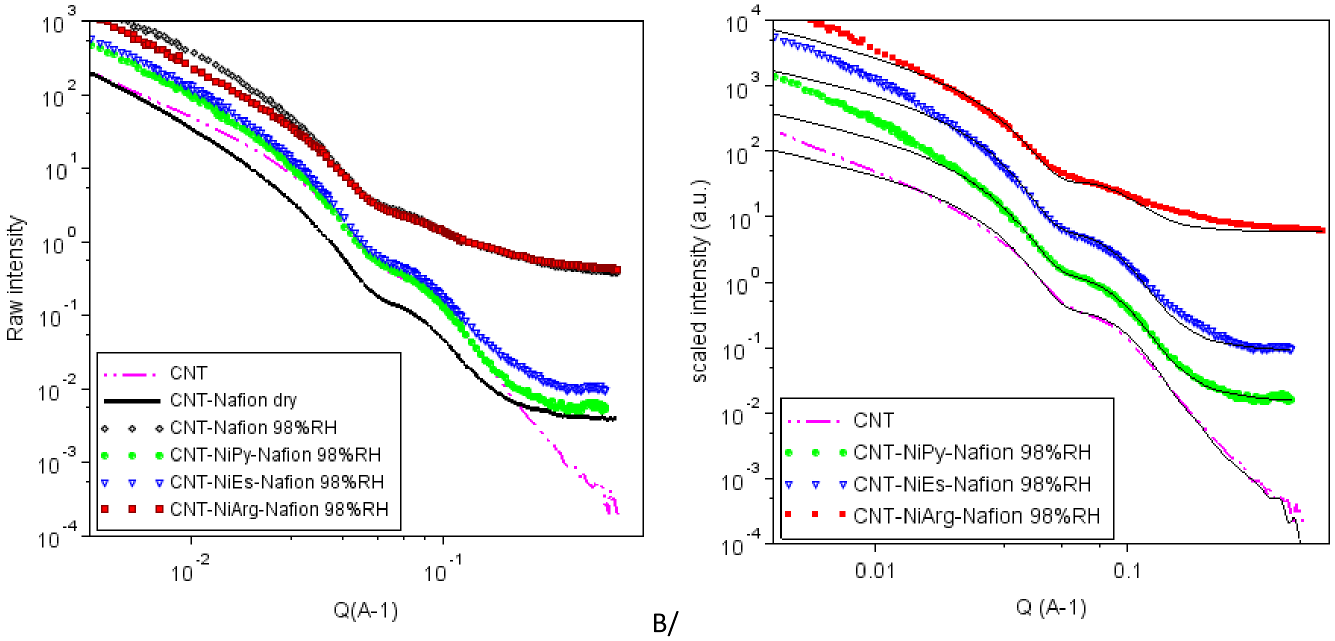
Abstract:

Commercial proton exchange membrane fuel cells (PEMFCs) use Pt as catalyst in the electrodes, but the high price and scarcity of Pt make this technology unsustainable for worldwide energy supply. Pt-free fuel cell catalysts are thus the subject of intense research efforts. We develop new bio-mimicking catalysts supported on a conductive carbon nanotubes network and a state-of-the art ionomer (Nafion). The bio-inspired catalysts are nickel diphosphine complexes mimicking the active site of hydrogenases. Our team has reported high catalytic activity and assembled the first fully Pt-free PEMFC. The electrode microstructure is supposed to be critical to the system performance, but very little is known on the catalyst morphology. Therefore we propose to study catalytic solutions and powders as a function of composition by SANS. We expect to establish the relation between material architecture, ink preparation, electrode processing and final performance of the electrode. The knowledge gained by SANS, taking advantage of the uniqueness of contrast variation to disentangle the various contributions, will help in developing the practical use of a bio-mimicking electrode for fuel cell.



The system is composed of two catalytic layers (CLs) supported on porous gas diffusion layers (GDL) and separated by a polymer electrolyte membrane (PEM) (Fig. 1). The bio-inspired nickel diphosphine, present in CLs, was initially developed in organic solvent in the DuBois group (*Liu et al., Nature Chemistry 2013, 5, 228*). We immobilized catalysts of this family onto CNTs (*Le Goff et al., Science 2009, 326, 1384*) and obtained the first PEMFC compatible CLs with bidirectional activity (*Coutard et al., Chem Comm 2016, 52, 13728*). The current densities of single anodes in hydrogen production and oxidation already compete with those of state-of-the art low Pt loading CLs. However, power densities in full PEMFC remain below expectations. In electrochemical tests, it appears that Nafion, massively added in PEMFC, has a tremendous positive or negative effect on catalytic currents depending on catalyst-to-CNT grafting chemistry. Electron microscopy images show differences in nano/microstructure of the CNT-catalyst-Nafion composite that we suppose due to specific interactions between Nafion and CNTs that we plan to investigate in detail.

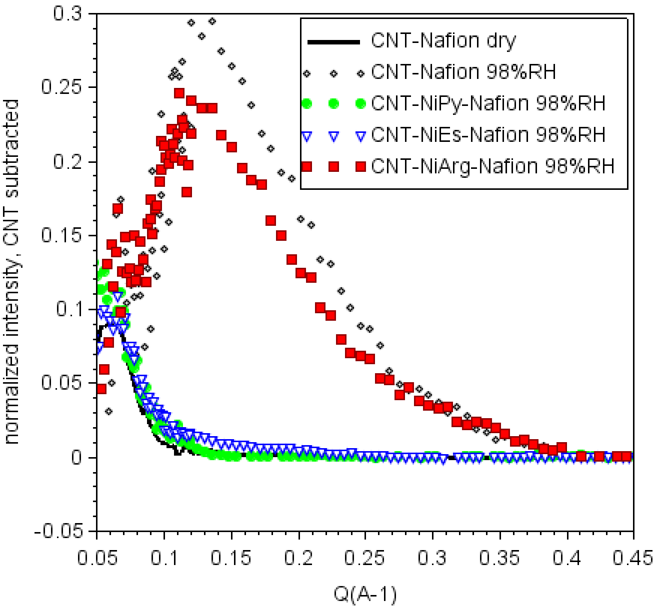
Comparison of carbon nanotube (CNT)-catalyst-Nafion hydrated samples for catalysts NiPy, NiEster, NiArg. Samples were hydrated under 98% relative humidity at room temperature for 3 days. A/ raw SANS spectra, compared to the control CNT spectrum and the control CNT-Nafion dry and hydrated samples. B/ Scaled spectra with best fit of a model of core-shell cylinder (using SASFit free software). C/ Evidencing the ionomer peak by subtracting the CNT control spectrum. D/ For comparison, same ubtraction on CNT-NiArg without Nafion, CNT-NiArg-Nafion dry and hydrated.



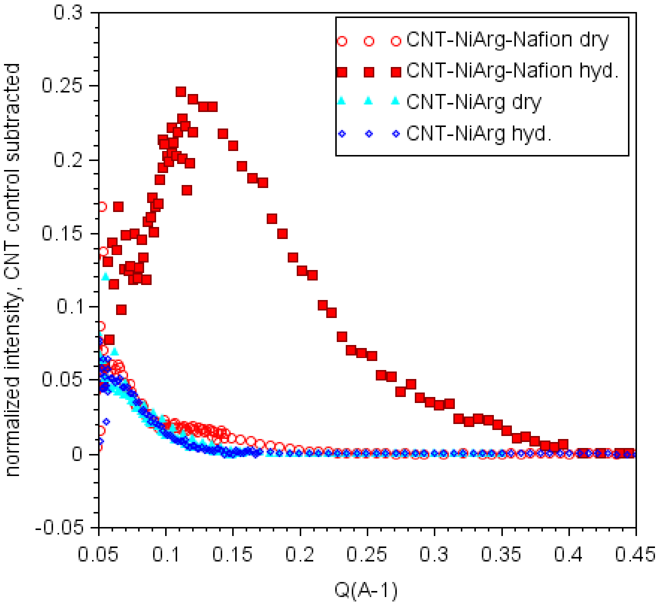
A/ B/

In figure A/, SANS profiles show mainly CNT diffusion with a form factor with 2 waves, typical of cylinder shape, and a constant absorption at high Q due to hydration, visible on all spectra except for control CNTs. Figure B/ shows best fits (black lines) of a model of core-shell cylinder with solvent absorption. Fit is excellent in the Q=0.02-0.5 $Å^{-1}$ range. Intensity at very low Q does not fit with the model but fits rather as Q^{-2}, which might be due to aggregation of CNTs as a 2D mat when drying the sample on the quartz window. Samples NiEs and NiArg also show excess intensity around 0.12 $Å^{-1}$. For a closer look at this position, the CNT control spectrum is subtracted on Figure C/, revealing a peak typical of ionomer[1] organisation at Q=0.12 $Å^{-1}$. The CNT spectrum was normalized at Q=0.04 $Å^{-1}$ before subtraction, an a constant signal normalized at Q=0.4 $Å^{-1}$ was simultaneously subtracted to take into account the solvent diffusion. The hydrated CNT-catalyst-Nafion system containing catalyst NiArg shows a ionomer peak similar to that of the hydrated

CNT-Nafion without catalyst. As a contrary, the systems based on the other types of catalysts NiEs and NiPy show no (NiPy) or very little (NiEster) such ionomer peak. Figure D/ shows in more detail the ionomer peak observed in the dry and hydrated state for CNT-NiArg-Nafion and the control CNT-NiArg samples.



C/



D/

These SANS data show a critical difference in behaviour between the three compared catalytic systems. Without catalyst, the hydrated CNT-Nafion system shows ionomer self-organization in hydrophobic ionomer backbone ropes and hydrophilic pockets (yielding the peak at 0.12 Å^{-1}). The ionomer self-organisation has been well described in the literature: the fluorinated backbones associate in 40 Å wide fibers, surrounded by sulfonated acid functions. These moieties capture ambiant water producing hydrated pockets, the size of which (2-10 Å) depends on the hydration level (ref 1). At full hydration a caracteristic SANS peak is observed at 0.12 Å^{-1}. In our CNT-Nafion system, the peak becomes more intense when Nafion is added in excess (data not shown).

In the catalytic system CNTCOOH-NiArg-Nafion, Nafion seems to make the same structure. In the other systems CNT-NiPy-Nafion et CNTNH2-NiEster-Nafion, no ionomer peak is observed and we can see that the capacity of the material to capture ambient water is strongly reduced (lower intensity at high Q). It thus appears that Nafion is unable to selforganise in these systems. We propose that the strong affinity of the Nafion hydrophobic backbone for the CNT hydrophobic surface when non functionalized leads to Nafion immobilization in CNT-NiPy-Nafion. In the CNTNH2-NiEster-Nafion, the sulfonate moieties of Nafion have a probable affinity for the ammoniums at the surface of the functionalized CNT (CNTNH2), leading to the same result.

Fitting parameters

Fit parameter core-shell cylinder	CNTCOOH	CNT-NiPy-Nafion hyd.	CNT-NiEs-Nafion hyd.	CNT-NiArg-Nafion hyd.
Core radius	2.11 nm ^{a}	2.1 nm ^{b}	2.1 nm ^{b}	2.1 nm ^{b}
Shell thickness ^{a}	2.4 nm ^{a}	2.9 nm ^{a}	2.7 nm ^{a}	2.2 nm ^{a}
SLD core/shell/solv. 10^{-6} Å^{-2}	0^{c}/ 10^{a}/ 0^{c}	0^{c}/ 6.2^{a}/-0.1^{a}	0^{c}/ 7.4^{a}/-0.2^{a}	0^{c}/ 9.3^{a}/1.6^{a}
Vol. frac.	0.0021	0.0058	0.0058	0.021
^{a} best fit on Q range [0.04 0.15] Å^{-1}, ^{b} fixed from reference CNTCOOH, ^{c} based on SLD calculation. Fixed param. : length 100nm, hard sphere form factor, 40% polydispersity on radius/shell/length (9 points)				

These data will be published in a coming paper.

1 L. Rubatat, G. Gebel and O. Diat, *Macromolecules*, 2004, **37**, 7772–7783.