Neutron nanomediators for non-invasive temperature mapping of fuel cells

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1 Introduction

Electrochemistry is at the heart of many systems essential to the energy transition towards renewable sources. While devices such as fuel cells (for hydrogen powered cars) and electrolysers (for electricity storage as hydrogen) have demonstrated their technical readiness, cost issues still prevent their large scale commercial deployment in energy related applications. The cost issue can be addressed not only by reducing the material costs (e.g. using less or no precious metals in the catalysts), but also by improving the power density – which finally translates into a smaller amount of materials for a given desired power output. This second approach requires a deep understanding of the internal limitations, and advanced characterization techniques are of high interest. Neutron imaging has readily proved its ability to give insight into one of the major challenges of the polymer electrolyte fuel cell (PEFC) technology, the water management, as neutrons are directly interacting with water. But the high penetration of neutrons through the structural materials of electrochemical devices can be further exploited using indirect sensing techniques.

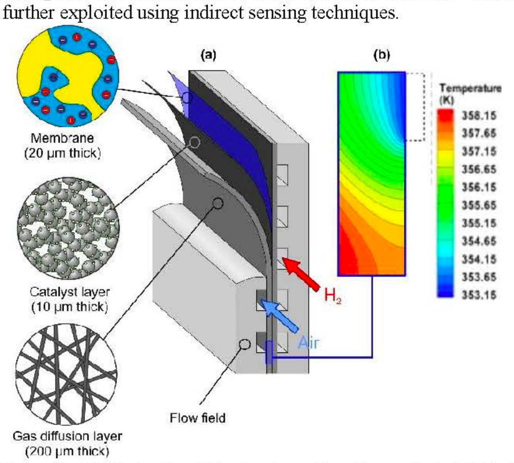

Figure 1 – (a) Illustration of the structure of a polymer electrolyte fuel cell (PEFC). (b) Simulation (reported in (1)) of the temperature gradients over the gas diffusion layer, assuming anisotropic or isotropic thermal conductivity.

Measuring the temperature distribution at the very heart of fuel cells is of utmost importance to understand both water transport and degradation. To date, such measurements were reported using micro-thermocouples (2) inserted between the gas diffusion layer and catalyst layer. Although providing interesting insights, the highly invasive character of such an approach has to be emphasized, as illustrated in Figure 2. Similarly, the reported use of optical phosphor is invasive due to the need to gain optical access, and is limited to the material surface.

Here, we propose the introduction of neutron *nanomediators* in combination with neutron depolarization imaging to sense the temperature distribution in a fully non-invasive way. These nanomediators are ferromagnetic nanoparticles with their size and composition tuned to obtain a Curie temperature in the range of interest (e.g. 70°C – 100°C). Below this temperature, the randomly oriented magnetic fields generated by the ferromagnetic nanoparticles will depolarize the neutron beam. Above this temperature, the particles will be paramagnetic and will not affect the beam polarization. The use of particles in the nanometer size range as well as the carefully considered integration routes (see below) will allow us, for the first time, to perform such measurement in a completely non-invasive way. While the present project will be focused on application to fuel cells, the developed methodology has a much broader field of applications, in electrochemistry and beyond.

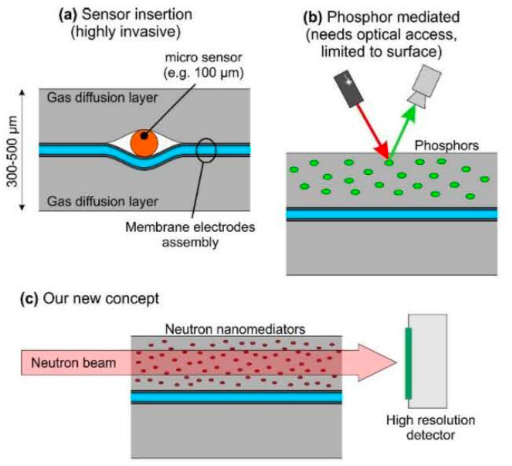

Figure 2 – Measurement concepts reported in the literature using sensor insertion (a) or optical phosphors (b) and our newly proposed concept with neutron nanomediators.

2 Research plan

2.1 Nanomediator selection

As previously mentioned, the general concept is to use nanoparticles of ferromagnetic materials having a Curie temperature sufficiently low (e.g. 70°C – 100°C). Two principal routes will be considered for the adjustment of the Curie temperature: size variation and alloying. In the nanometer size range, the Curie temperature of nanoparticles is lowered compared to the corresponding bulk material (3). It was also shown that the Curie temperature of ferromagnetic metals could be lowered by alloying them (4). Using both nanometer sized particles and alloying Ni with Cu, Curie temperature as low as 43°C were reported (5) – to be compared to the Curie temperature of 354°C for bulk Ni. In the proposed work, the preferred route will be the use of nanoparticles made of ferromagnetic transition metals (Ni, Fe, Co) with the primary focus on Ni as it has the lowest bulk Curie temperature of the three. The main route for alloying will be the inclusion of other transition metals (in particular Cu), but alloying with noble metals (Pt, Pd, Au) will also be explored. It is important to note that, for the considered sizes (a few nm), materials such as Nickel exhibit superparamagnetic behavior (6). However, the time scale probed by neutron depolarization is short enough such that superparamagnetic particles will have the same effect as ferromagnetic ones.

2.2 Nanomediator synthesis

The main considered synthesis route will by the polyol process. As discussed in the comprehensive review by Fievet *et al.* (7), it allows an important variety of nanometer sized metallic particles to be synthesized. According to them, the synthesis of small nanoparticles (e.g. < 10 nm) is more challenging than for noble metals, but can be realized with the help of strong reducing agents (8). It has been shown that a reasonably narrow particle size distribution (e.g. a range of 3-5 nm) can be obtained (9). It must be emphasized that our proposed method does not *a priori* require a very narrow size distribution, as the quantitative nature of neutron imaging should allow us to estimate the temperature even if the depolarization occurs progressively over a broader temperature range. The polyol process was also shown to be suitable for the synthesis of some alloy nanoparticles, such as the Ni/Cu particles mentioned above (5). For some application cases (see below), protection from the fuel cell acidic environment will be required. In this case, our preferred synthesis route will be the adsorption of an organic layer (e.g. using surfactant molecules) and its subsequent graphitization.

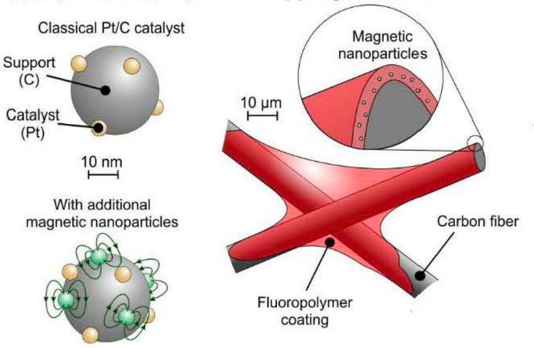

Figure 3 – Integration of the nanomediators in the catalyst layer (a) and in the gas diffusion layer (b).

2.3 Integration in electrochemical materials

Different routes will be considered for the integration in electrochemical materials, depending on the layer of interest (see Figure 3). For the catalyst layer, the nanoparticles will be supported on carbon, similarly to the classical Pt/C catalysts (Figure 3a). In this case, a protective coating as described above will be required. For the integration in the gas diffusion layer, the nanomediators will be mixed into the fluoropolymer dispersion used to apply the hyodrophobic coating. In that case, we expect that at a least of fraction of the nanoparticles will be covered by the fluoropolymer and will not require further protection. These integration methods are designed for being minimally invasive with respect to the operation of the electrochemical cell. This aspect will be verified by *ex situ* testing of the electrochemical materials characteristics, as well as by *in situ* performance testing in real electrochemical devices.

2.4 Detection with neutrons

Due to the strong interaction of neutrons with magnetic fields, the change of nanomediator state (e.g. from ferromagnetic to paramagnetic) can be detected by ***depolarization neutron imaging***. This method uses a polarized neutron beam as available at the BOA beam line of PSI. The spin orientation of the neutrons will be affected by the changing magnetic field orientations in the material, resulting in depolarization. A comprehensive review of the possibilities of polarization measurements is given in the recent topical review by Strobl et al. (10). Among these, white beam depolarization imaging was already demonstrated to be suitable for the measurement of the Curie temperature. A critical point is the realization of depolarization imaging with high spatial resolution, due to the sample-detector distance induced by the spin analyzer. However, for the limited field of view (< 1mm) required by our application, a single polarizing super-mirror plate with limited dimensions (~30 mm) can be used. While the further development of the neutron imaging instrumentation is not an intrinsic part of the present project, it will benefit from recent developments in other projects in the neutron imaging and applied materials group (NIAG) of the LNS laboratory.

3 Project organisation

This ***nanotechnology based multi-disciplinary project*** will be conducted as a collaboration between PSI experts in various fields, as detailed below. The hired PhD student will have a shared appointment between the Laboratory for Neutron Scattering and Imaging (LNS) and the Electrochemistry Laboratory (LEC).

- **Michel Kenzelmann** (LNS, expert in magnetism and superconductivity), will be the PhD thesis advisor („Doktorvater“).
- **Pierre Boillat** (LEC/LNS, expert in *operando* imaging of electrochemical systems), will be the direct supervisor.
- **Markus Strobl** (LNS, expert in neutron imaging and scattering methods), will be co-supervisor.

Besides the supervisors, we will be advised by the following PSI specialists:

- **Emiliana Fabbri** and **Alexandra Patru** (LEC) are experts in electrocatalysis and experienced in the synthesis of nanoparticles and of catalyst layers.
- **Armin Kleibert** from the Microscopy & Magnetism Group of the Condensed Matter Laboratory (LSC) is an expert in the magnetic properties of nanoparticles.

The project will be supported by the availability of the following competences and equipment at PSI:

- Within the LNS laboratory: Spin analyser for use at the BOA beam line. Corresponding competences in data processing.
- Within the LEC laboratory: Synthesis of nanoparticles, deposition of catalyst layers, MPL and GDL, assembling and testing of electrochemical devices.
- As a long term (>15 years) collaboration between the two laboratories: *operando* neutron imaging of electrochemical devices.

The project will be divided into 3 work packages as follow:

- **WP1**: Identification of promising materials and *ex situ* testing of relevant characteristic (Curie temperature).
- **WP2**: Integration into electrochemical materials (catalyst layers, GDL) and *ex situ* measurements.
- **WP3**: Integration into a fuel cell and *operando* measurements

	Year 1				Year 2				Year 3				Year 4	
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2
Work package 1														
Work package 2														
Work package 3														
Publications & Thesis														

Table 1 – Time planning of the different tasks.

4 References

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