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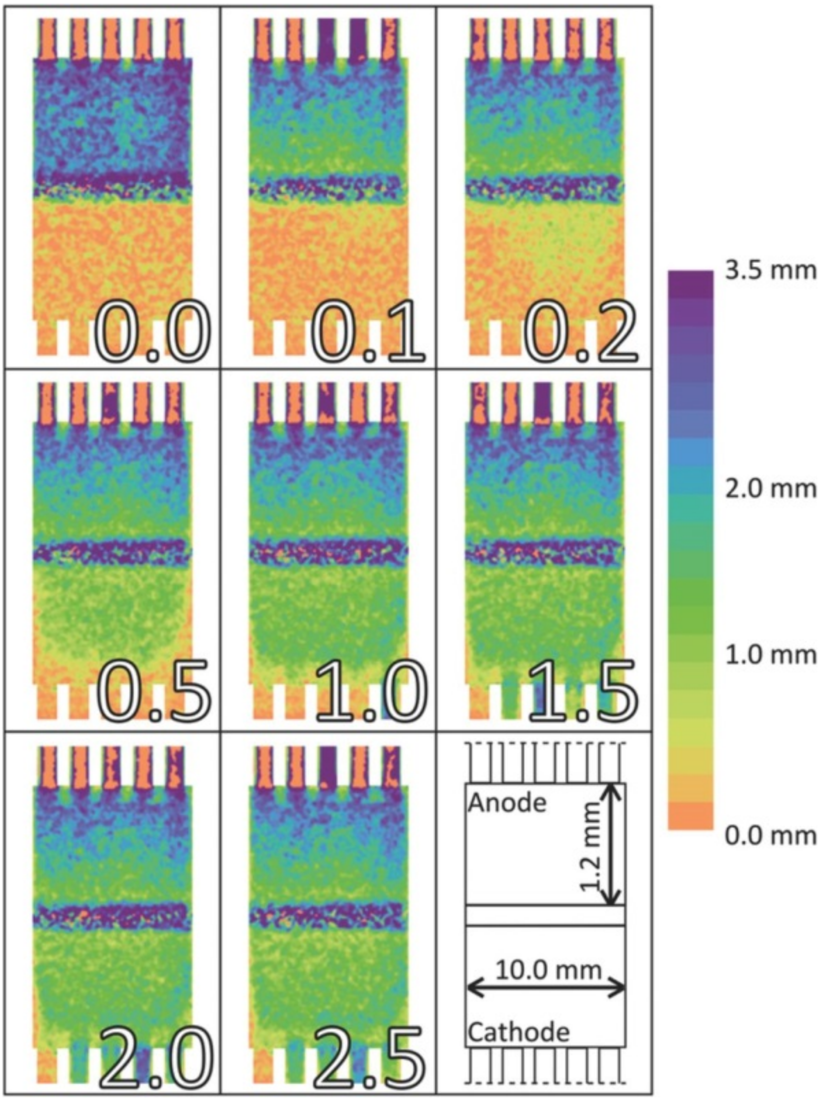
Final report

PEEC-NR

In situ study of water transport processes in polymer electrolyte electrolysers with neutron imaging



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Zusammenfassung

Elektrolyseure sind Apparate, die mit Hilfe von elektrischem Strom Wasserstoff produzieren. Mit einem stetig wachsenden Anteil von neuen erneuerbaren Energien wie Sonnen- und Windkraft, und deren stark fluktuierenden Aspekt, kann Wasserstoff eine wichtige Rolle spielen in der Lösung des Speicherungsproblems, da dieses Gas sich ökonomisch speichern lässt. Obwohl Elektrolyseure bereits kommerzielle Produkte sind, sind sie bis jetzt nur in gewissen Anwendungen in Einsatz, die eine hohe Wasserstoffreinheit erforden. Solche Anwendungen sind nicht auf einen maximalen Wirkungsgrad ausgerichtet, und die Details der internen Prozesse in Elektrolyseuren sind entsprechend nicht intensiv erforscht worden. Die Anwendung für Energiespeicherung braucht dagegen den bestmöglichen Wirkungsgrad, und Verlustquellen, die früher als vernachlässigbar betrachtet worden sind, können bedeutend werden. In diesem Projekt zielten wir auf ein besseres Verständnis der Prozesse, die die Wasser- und Gasverteilung in Elektrolyseuren im Betrieb bestimmen. Wir haben dafür Neutronenradiographie benutzt, eine ähnliche Methode zu der aus dem medizinischen Feld bekannten Röntgenradiographie, aber mit besondere Eigenschaften: Während Röntgenstrahlen von schweren Materialien abgeschwächt werden, können Neutronen solche Materialien (und insbesondere das Titan der porösen Strukturen in Elektrolyseuren) sehr gut durchleuchten, und stellen dagegen einen hohen Kontrast für leichtere Materien wie Wasser dar. Dank dieser Eigenschaften konnten wir die Menge Gas, die sich im Betrieb in den porösen Strukturen sammelt, direkt beobachten. Diese Ergebnisse bilden eine Basis für ein besseres Verständnis von Transportprozessen in Elektrolyseuren, mit der Ziel, unnötige Effizienzverluste zu vermeiden.

Résumé

Un électrolyseur est un appareil permettant de produire de l'hydrogène à partir d'électricité. Les nouvelles énergies renouvelables telles que solaire et éolienne occupant un part toujours plus importante de la production d'électricité sont intermittentes. L'utilisation de l'hydrogène produit par electrolyse peut jouer un rôle important dans la résolution du problème posé par le stockage de grande quantités d'énergie électriques, étant donné que le stockage d'hydrogène peut être réalisé facilement et à moindre coût. Bien que l'électrolyse soit déjà utilisée à l'echelle industrielle pour certaines application nécessitant de l'hydrogène très pur, ces applications ne sont pas tributaire d'un très haut rendement de conversion. En conséquence, le detail des processus internes aux électrolyseurs n'a que peu été étudié par le passé. En revanche, l'utilisation pour le stockage d'énergie requiert le meilleur rendement possible et des sources de pertes considérées comme négligeable par le passé peuvent devenir importantes. Dans ce projet, nous avons visé une meilleure compréhension des procédés déterminant la distribution de l'eau et des gas dans les électrolyseurs. Nous avons pour cela utilisé l'imagerie neutronique, similaire à l'imagerie aux rayons X utilisée par example en médecine, mais possédant des charactéristiques particulières : alors que les rayon X sont atténués par les matériaux denses, les neutrons peuvent très bien pénétrer au travers de ceux-ci (et en particulier au travers du Titane des structures poreuses des electrolyseurs) tout en ayant une très haute sensibilité à certains matériaux légers comme l'eau. Grâce à cela, nous avons pu observer la quantité de gaz s'accumulant dans les structures poreuses d'électrolyseurs lors de leur fonctionnement. Les résultats obtenus consistuent un base pour une meilleure compréhension des procéssus de transport internes aux electrolyseurs, dans l'optique d'éviter l'apparition de pertes de rendement non nécessaires.

Summary

Water electrolysers are devices which can use electricity to produce hydrogen. With an increasing share of intermittent renewable sources such as solar and wind power in the electricity production, they may play an important role in solving the issue of large scale energy storage, hydrogen being very easy to store in inexpensive ways. Although water electrolysers are established devices for certain markets requiring high purity hydrogen, such current applications do not usually depend on a very high efficiency. As a consequence, the internal processes such as the detailed distribution of water and gas in operating electrolysers were not extensively studied in the past. The application as large scale energy storage, however, sets higher requirements on efficiency and loss processes which were considered negligible can become relevant. The present project aimed at a better understanding of the water and gas distribution in operating electrolysers. To this purpose, we used neutron imaging, a method which is similar to the well-known X-ray imaging used for example in medical application, but with very different characteristics: while X-rays are mostly attenuated by dense materials, neutrons can easily penetrate them (including the Titanium used in the porous structures of electrolysers), while keeping a high sensitivity to lighter materials such as water. As a result, we could observe the quantity of gas accumulating in the porous structures of operating electrolysers. The obtained results will be used as a basis for constructing a better understanding on the transport processes in electrolysers, with the aim of avoiding unnecessary losses of efficiency.

Contents

List of abbreviations

EIS	Electrochemical Impedance Spectroscopy – A measurement method consisting in applying small sinusoidal current variations of different frequencies around a fixed operating point, to analyse the response of the system at different time scales.
MEA	Membrane Electrodes Assembly – A three layer assembly including the proton conducting polymer electrolyte membrane and a catalyst layer on each side.
PTL	Porous Transport Layer – A porous layer responsible for multiple transport processes: supply of water, removal of produced gases, electrical and heat conduction. Usually made of titanium sinter.

1 Introduction

The present report summarizes both the methodological developments and the measurement results obtained under the project “In situ study of water transport processes in polymer electrolyte electrolysers with neutron imaging” funded by the Swiss Federal Office of Energy. The project aimed at obtaining a better understanding of the water and gas transport in operating electrolysers, as well as at creating the necessary infrastructure and methods to establish this topic as a new line of research at PSI.

2 Infrastructure and methodological development

2.1 Mobile electrolysis test bench

Experiments at large scale research facilities such as the neutron imaging beam lines require specific test hardware able to fit within the limited available space and to be mounted and dismounted in a reasonable time. Although the existing fuel cell test infrastructure was not directly adapted to operate electrolysers, given components could be recovered from decommissioned test benches.

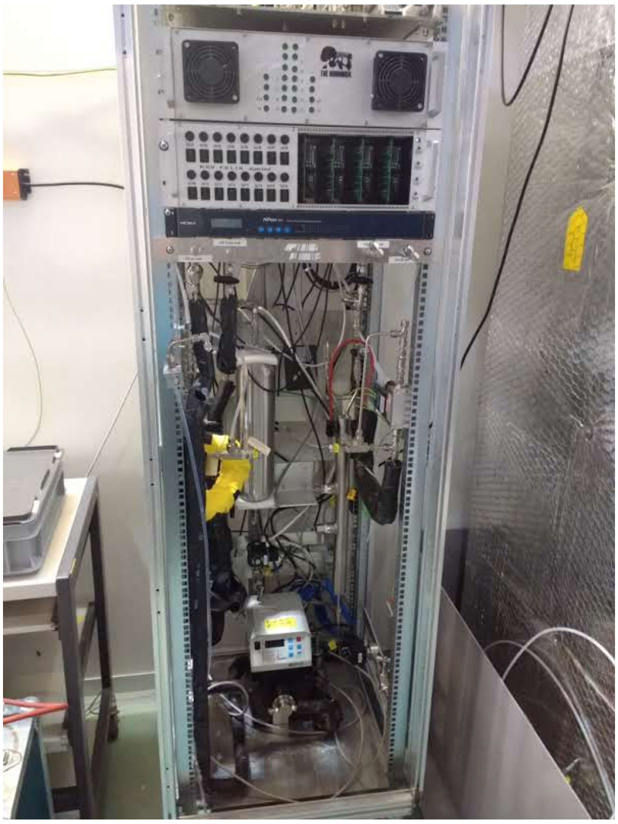

Figure 1 – The mobile electrolysis test bench realized in the frame of this project.

Owing to the long standing experience in the field of neutron imaging of fuel cells, the setup of a new test bench did not represent significant difficulties. Most of the equipment necessary to operate the electrolysers was integrated in a single rack as illustrated in Figure 1.

2.2 Electrolysis test cells

It was decided to focus in a first time on the local aspects of water transport in electrolysers, namely the transport characteristics of porous materials. This is in line with the other electrolysis projects which were and are still conducted in the PSI Electrochemistry Laboratory. In this view, we first evaluated whether the cells used in other project would be suitable for neutron imaging, but finally considered that dedicated cells optimized for imaging would be more suitable. Two generation of cells were designed, manufactured and used in the frame of this project, with a further optimization of the second generation for the last measurements.

2.2.1 First generation cell

The first generation cell was configured so that it could be imaged from any orthogonal direction and in particular in the configuration where the beam is parallel to the flow channels (see Figure 2), allowing a distinction not only from the different layers of the cell but also from the land and channel areas.

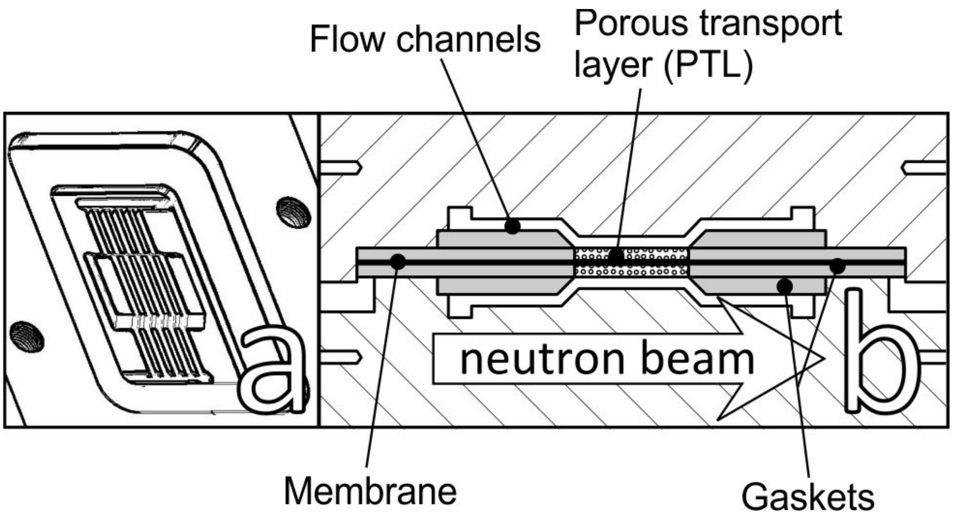

Figure 2 – First generation cell design. (a) 3-dimensional view of one flow field with an elevated active area. (b) Configuration of the cell relative to the neutron beam.

The cell active area was set to be conservatively small (1 cm^2) with a dimension of 10 mm along the beam direction. To avoid interference in the image from the flow channels before and after the active area, a complex shape with an elevation of the active area was used for the flow field (see Figure 2a). This configuration was ideal for imaging purposes, but had some drawbacks in terms of the complexity of cell manufacturing and mounting (in particular due to the complex gasket system).

2.2.2 Second generation cells

From the results from the measurements with the first generation cell (see §3.1), we observed that the distribution of water/gas in the porous layers did not feature a strong channel-land distribution (such as is often seen in fuel cells, in particular in partly humidified conditions). Therefore, we developed a second generation of test cells with a simplified flow field design, which does not allow the imaging in the configuration described in Figure 2 but provides other significant advantages: besides the easier mounting, the “sandwich” comprising the fuel cell, gaskets, porous transport layers (PTLs) and membrane electrodes assembly (MEAs) can be relatively easily interchanged, allowing measurement with several cells in the same imaging campaign.

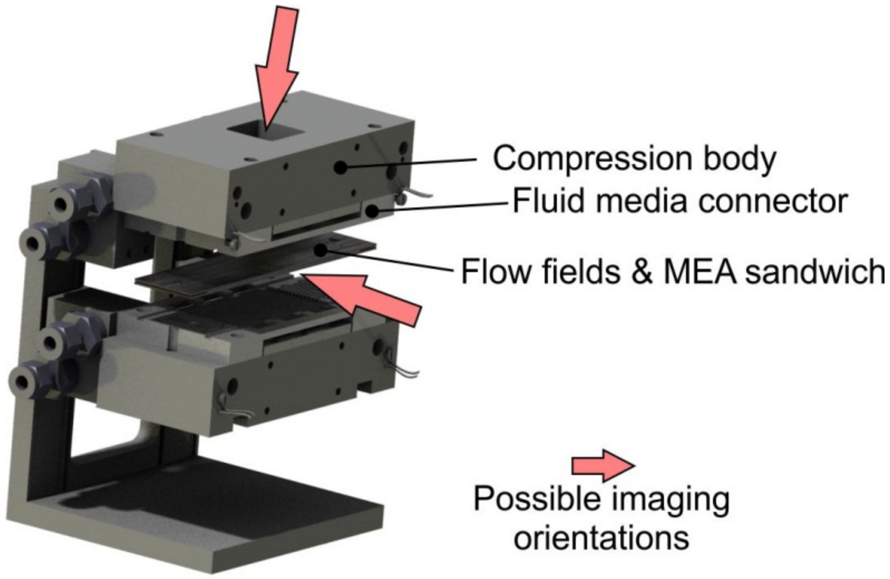

Figure 3 – Second generation cell design. The flow channels are along the longest direction of the flow fields.

The size of the active area was kept to 1 cm^2 after the good imaging experience with the 1st generation cell, though the test cell design would also allow but larger active areas, up to 12 cm^2 (20 mm x 60 mm).

2.2.3 Latest optimizations

With the 2nd generation cell, we had a remaining issue of concerns about the experimental repeatability, in particular in relation with the difficulty of compressing the cell to ensure both gas/water tightness and a good electrical contact. We identified as a potential source for this issue the too large stiffness of the PTFE gasket, in relation with its important area (approximately 30 cm^2). While in fuel cells the gasket stiffness is not an issue due to the highly flexible porous layers, electrolyser PTLs are made of Titanium sinter and are very stiff. We evaluated different options for the gasket improvement such as the use of elastomer based gaskets, but we considered as the best option a structured gasket having a protruding “rib”. The base gasket thickness was set to be slightly lower than the PTL thickness, so that it mostly acts as a mechanical spacer and filler, and the rib area (~1.6 cm^2) was alone responsible for the water/gas tightness.

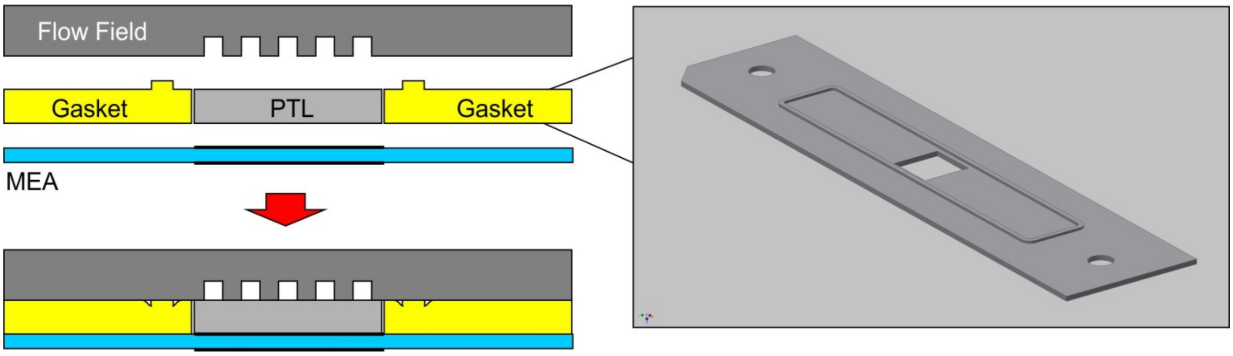

Figure 4 – Optimized gasket concept, strongly lowering the area of the region used for gas/water tightness. Only half of the Flow-field/PTL/MEA „sandwich“ is shown for the sake of simplicity.

2.3 Neutron imaging

2.3.1 Test of imaging configurations

During the first imaging campaign (in 2014), two different imaging configuration were tested:

- The “through plane” configuration with the neutron beam perpendicular to the membrane. This configuration allows to measure the total water content for each point of the cell area, but does not allow to resolve the water distribution across the cell structure.

- The “in plane” configuration with the neutron beam parallel to the membrane. The cell was placed with the flow channels parallel to the beam axis. This configuration allows resolving the water distribution across the cell structure, as well as across the land/channel structure.

For the through plane measurements, a standard neutron imaging setup was used. For the in plane measurements, having different resolution requirements in the direction along and across the membrane, an anisotropic setup was used as developed and used in the past 10 years for fuel cell applications [1, 2].

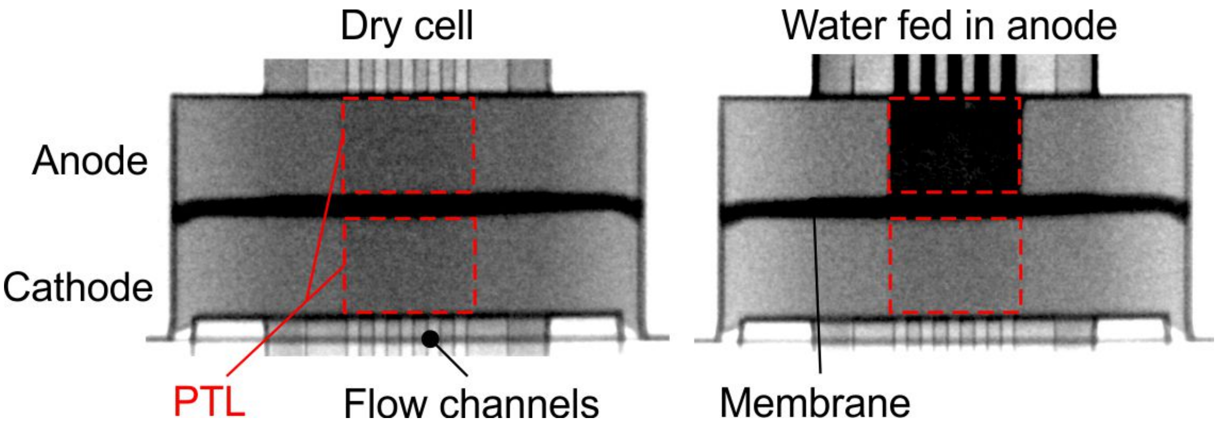

Figure 5 – Neutron imaging of the 1st generation cell in two reference states: dry (left) and with water flowing in the anode flow field (right).

The though plane configuration was a classical neutron imaging case with no expected transparency issues. For the in plane measurement, the large thickness of Titanium (10 mm of PTL with less than 50% porosity) to be transmitted through was also expected to be suitable for neutron imaging, which was confirmed in the first imaging campaign as illustrated in Figure 5. The transparency is clearly sufficient to visualize the difference between a dry and water saturated PTL, as shown by the difference between the two reference states. On the other hand, we could not measure any meaningful value for the membrane in this configuration. During the further neutron imaging campaigns (in 2015 and 2017), the 2nd generation cell was used exclusively in in plane configuration, because we evaluated that the through plane imaging mode had a limited interest for the study of water in the PTLs (see §3.1.1). As shown from the images of the last imaging campaign, and as expected, water in the PTL can perfectly be imaged with this cell as well. The intensity measured in the membrane region is also clearly higher than zero, as can be seen by comparing to the intensity measured behind a block of neutron shielding.

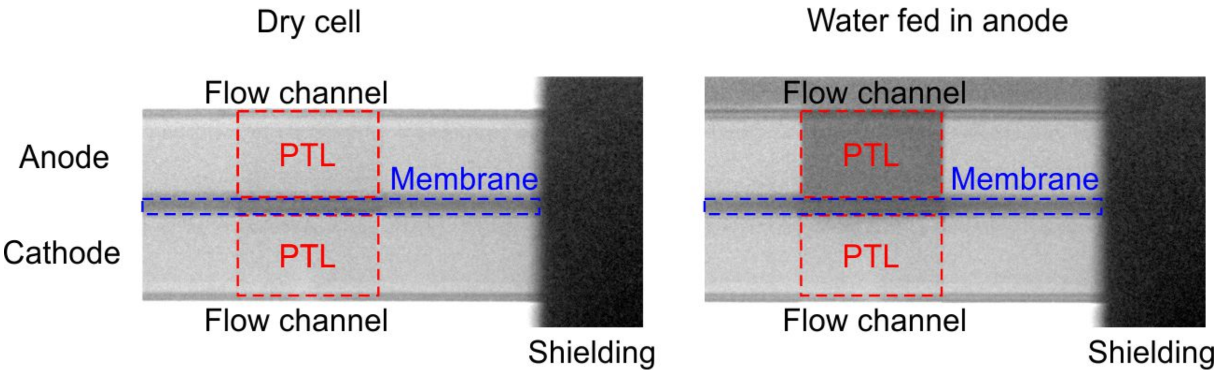

Figure 6 – Neutron imaging of the 2nd generation cell in two reference states: dry (left) and with water flowing in the anode flow field (right).

This means that the 2nd generation cell potentially allows measurements in the membrane region. However, the transmission is still rather low (in the range of 7%) for a wet membrane. Moreover, the measurements can be biased by water diffusing to the regions of the membrane situated outside of the active area. In summary, measurement in the membrane area must be taken with care, at least when absolute numbers are considered.

2.3.2 Visualization of cation contamination using Gadolinium as a proxy

Cation contamination can degrade the performance of electrolysers over time. A better understanding of the cation mobility in electrolysers bears the promise of understanding which operating strategies can mitigate this contamination, and whether *in situ* regeneration strategies can be used. We decided to use Gadolinium as a model element having the property of an extremely high cross section for neutrons, allowing the visualization of very low amounts of cations. The most common oxidation state of this element is Gd^{3+}, making it an interesting compound to mimic usual electrolyser cation contaminants such as Fe^{3+}, at least in a qualitative way. The setup used for this specific experiment is shown in Figure 7. This setup allowed switching the anode water feed from pure water to a diluted solution of Gadolinium salt as a source of Gd^{3+}, and opposite.

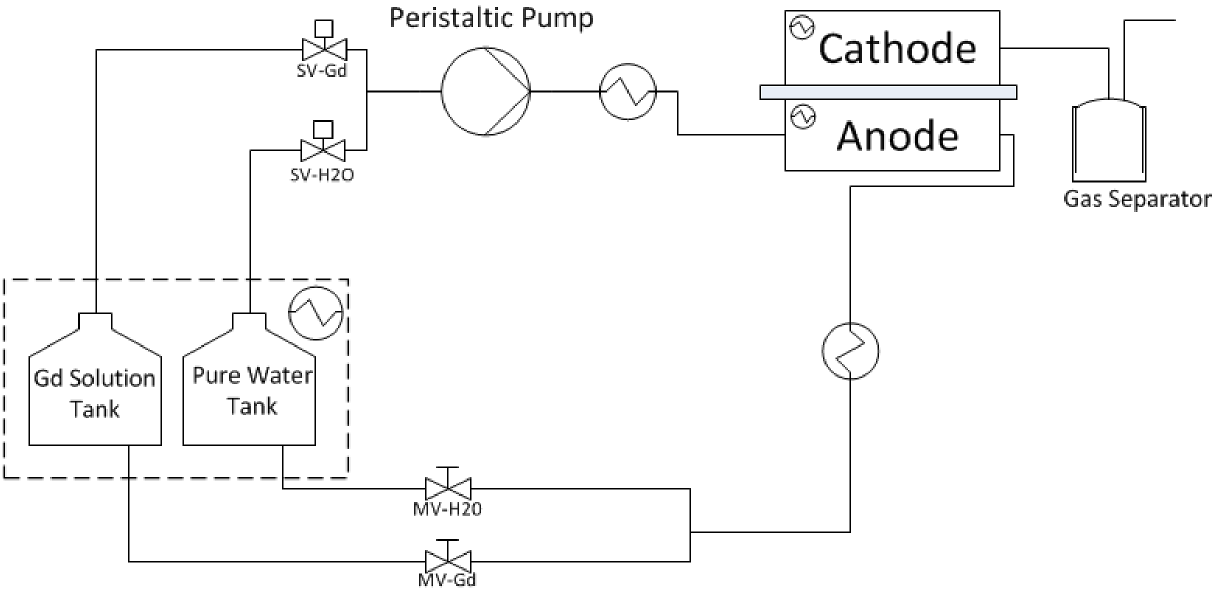

Figure 7 – Special setup (simplified schematic) for the Gadolinium contamination experiments

3 Results and dissemination

3.1 Water transport in electrolyser porous transport layers

3.1.1 Through plane imaging

The results of measurements performed in through plane orientation with the 1st generation cell are presented in Figure 8, comparing the situation with no current (but water fed on the anode side) and with a current of 2.5 A/cm^2. Remaining that our main interest is the study of water gas in the porous transport layer, we emphasized the water thickness in this region on the images in the left part of the figure. As can be observed, the total amount of water increases when drawing current. If we assume that the anode PTL is initially flooded with water (which is consistent with the thickness of 0.3 mm) and the cathode PTL is initially dry, we can conclude that the filling of the cathode PTL is dominating the change between the initial situation without current and the operation of the electrolyser. This will be further discussed in the light of the in plane results.

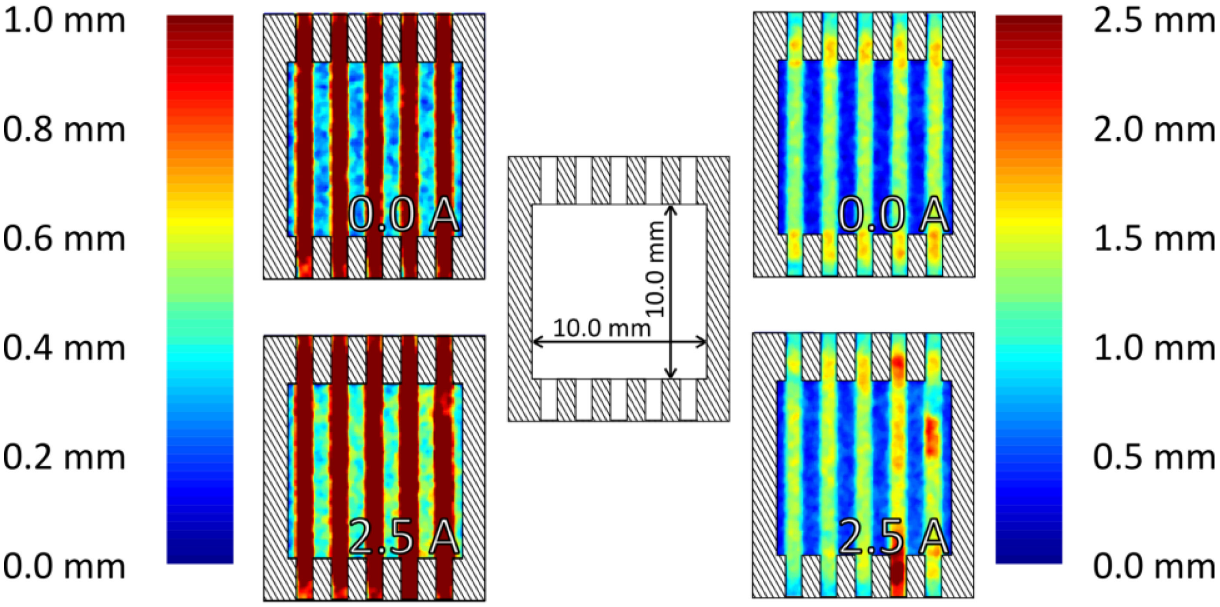

Figure 8 – Through plane imaging results. The left and right images represent the same data with different color scales.

This result indicates that the through plane imaging mode is of limited interest for the study of water/gas distribution in the PTL, because the most interesting point is to know how much gas accumulates in the anode side. On this basis, we conducted all subsequent experiments in in plane mode.

3.1.2 In plane imaging

With the same cell, measurements were performed in in plane orientation, with the flow channels parallel to the beam axis so as to observe the difference between land an channel regions. The corresponding images are presented in Figure 9. The first observation is that, as expected and discussed in the previous paragraph, the anode side PTL is filled when water is circulated in the anode channels. The cathode PTL remains dry when no current is drawn. As soon as a current even as small as 0.1 A/cm^2 is applied, a pattern of water gas distribution appears in the anode PTL. This pattern features a strong gradient in the direction across the PTL, with no significant land/channel differences. Increasing the current up to 2.5 A/cm^2 (25 times higher than the smallest value applied) does not result in any change of the water/gas distribution in the anode. On the contrary, the cathode starts to be saturated with liquid water.

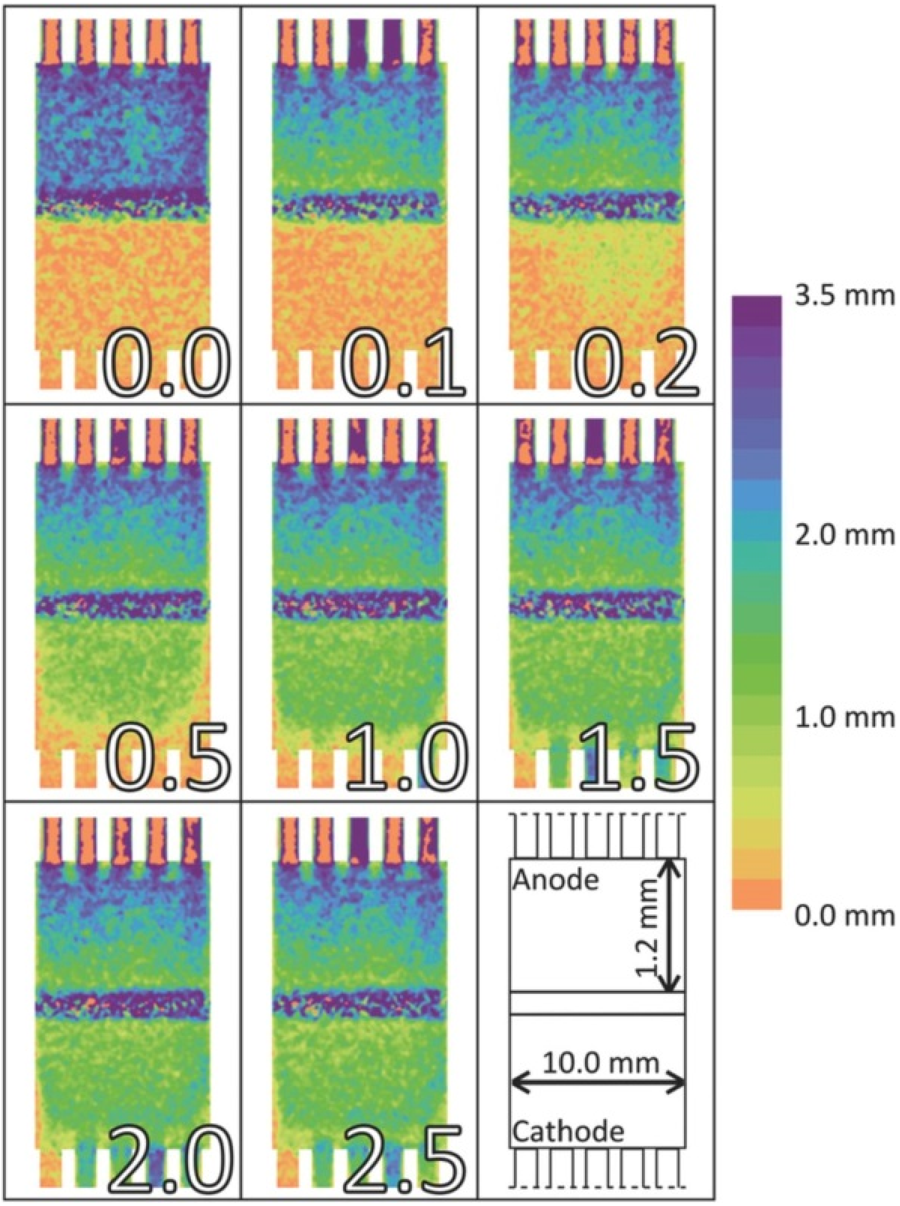

Figure 9 – Water distribution across the structure of an operating electrolysis cell (reproduced from [3], Copyright 2016, the Authors, published by ECS).

These observations are displayed in a quantitative manner in Figure 10. As suggested by the images of the previous figure, the established profile of water/gas distribution is not affected by the magnitude of the current. On the cathode side, the PTL starts to fill at 0.5 A/ cm^2 and reaches a stable pattern at 1 A/ cm^2.

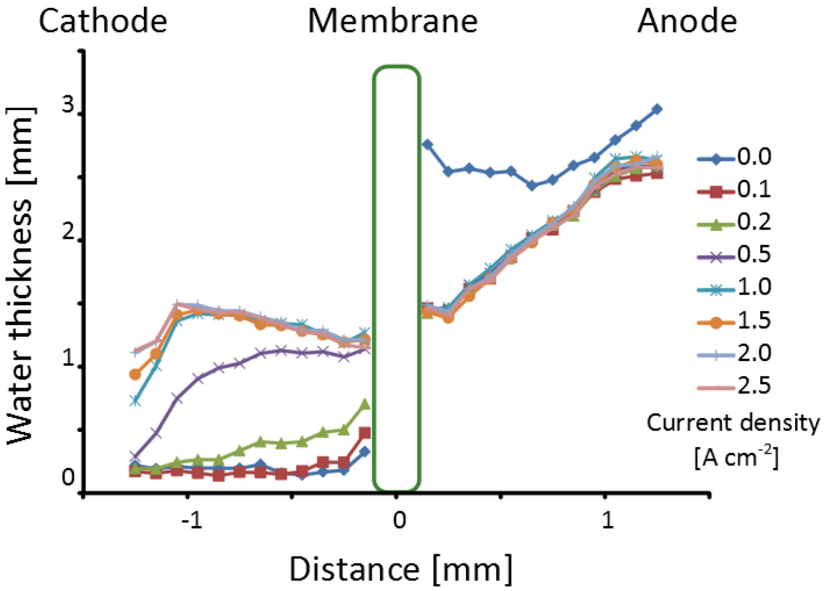

Figure 10 – Measured water thickness in the cathode and anode PTLs of an operating electrolysis cell.

The anode gradient is explainable by the process of capillary fingering in porous media. Because the electrochemical reaction occurs over the whole area, a large number of gas pathways are necessary. These pathways merge together in their way towards the anode flow channels, resulting in less space occupied by the gas for the positions far away from the catalyst layer. It is worth noting that such gradients are not observed in the porous media of fuel cells. The major difference to explain these different behaviors is that fuel cell porous media are highly heterogeneous and only slightly hydrophobic, resulting in important hysteresis in the capillary pressure – saturation relation. Thus, the pores which have been invaded by the liquid in the process of crossing the porous media are not emptied after the break through, even if they are dead ends. In the case of the electrolyser, the PTL is made of titanium only, and is significantly hydrophilic as shown by its fast filling as soon as water is fed to the anode flow channels. Thus, after the initial capillary pressure necessary for the gas to break through the material has been released, the dead end pathways are likely to be filled back by water. In the light of the results obtained with in plane imaging, the difficulty of observing the anode PTL filling with gas in through plane mode is easily understood, as the amount of water filling the cathode PTL largely offsets the amount of water removed from the anode PTL.

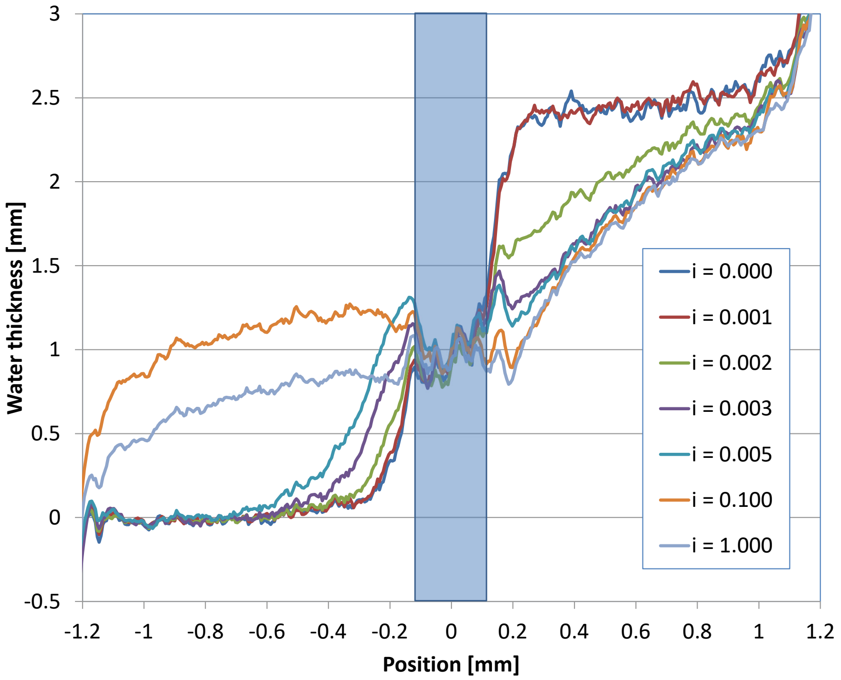

Figure 11 – Measured water thickness in the cathode and anode PTLs of an operating electrolysis cell including very low current densities (using 2nd generation cell).

Further measurements conducted with the 2nd generation cell included operation at very low current densities (down to 1 mA/cm²). The trend observed previously is generally confirmed. Only the lowest current density does not result in any gas evolution. The anode PTL fills significantly with gas already at 2 mA/cm² and starting from 3 mA/cm², nearly the same profile as for the higher current densities is established. This result confirms even more clearly than the initial measurements that the viscous forces play a negligible role (as there is no dependency on the produced gas velocity) in determining the amount of gas accumulating in the PTL. It is worth mentioning that, while our results on water/gas transport in PTLs can be considered as being in line with the expectations from the known theories of two phase flow in porous media (in particular from soil research), they nevertheless constitute the first direct observation of two phase flow in the porous media of electrolysers. Moreover, some authors suggest that capillary fingering is not the only transport mode [4] and we expect our results to trigger further scientific discussion on the topic. The quantitative analysis of the water gas distribution may be used in the future for the validation of transport models in PTLs and as a support for the design of advanced PTL materials, e.g. with porosity or pore sized gradients across their thickness.

3.2 Transport of cationic contaminants

In a first experiment, the evolution of Gd accumulation over time was visualized by operating the electrolysis cell at a constant current density (1 A/cm²) and, at a time defined as t=0, switching for the pure water feed to the Gd solution feed.

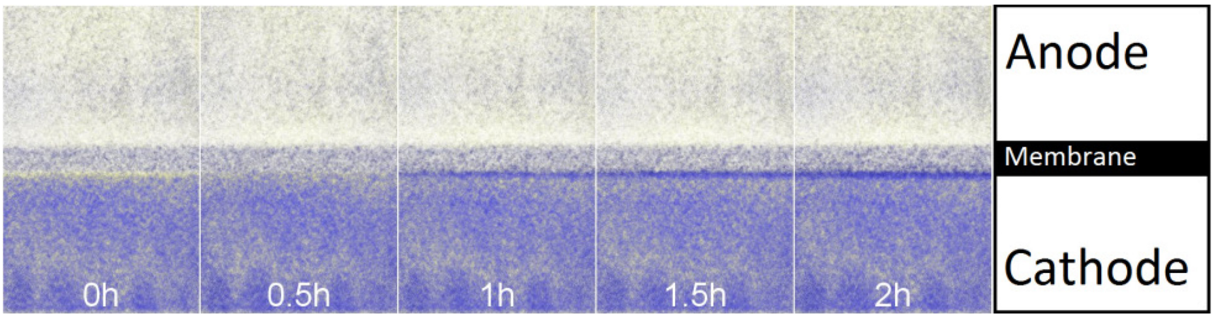

Figure 12 – Contamination by Gd cations with steady cell operation (1 A/cm^2). Anode is on the top side and cathode on the bottom side.

As seen in Figure 12, the accumulation of Gd is clearly visible, appearing as a darker line at the cathode side border of the membrane. This can be explained by the fact that the positively charged Gd cations tend to flow in the same direction as the electrical current (from the anode to the cathode). The cations thus are pushed towards the cathode side catalyst layer, where they cannot leave the MEA because of the absence of negative counter-ions. To demonstrate the effect of the electrical current, a further experiment was conducted where the current was successively stopped and restarted. The disruption of the current results in the disappearance of the observed Gd accumulation on the cathode side. The ions probably diffuse back to the membrane, as restarting the current results in the reappearance of this accumulation.

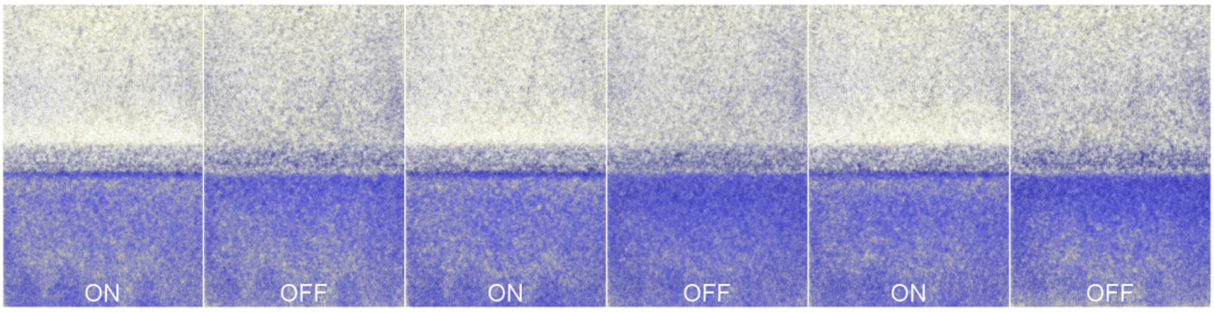

Figure 13 – Movement of cations during stop and restart cycles.

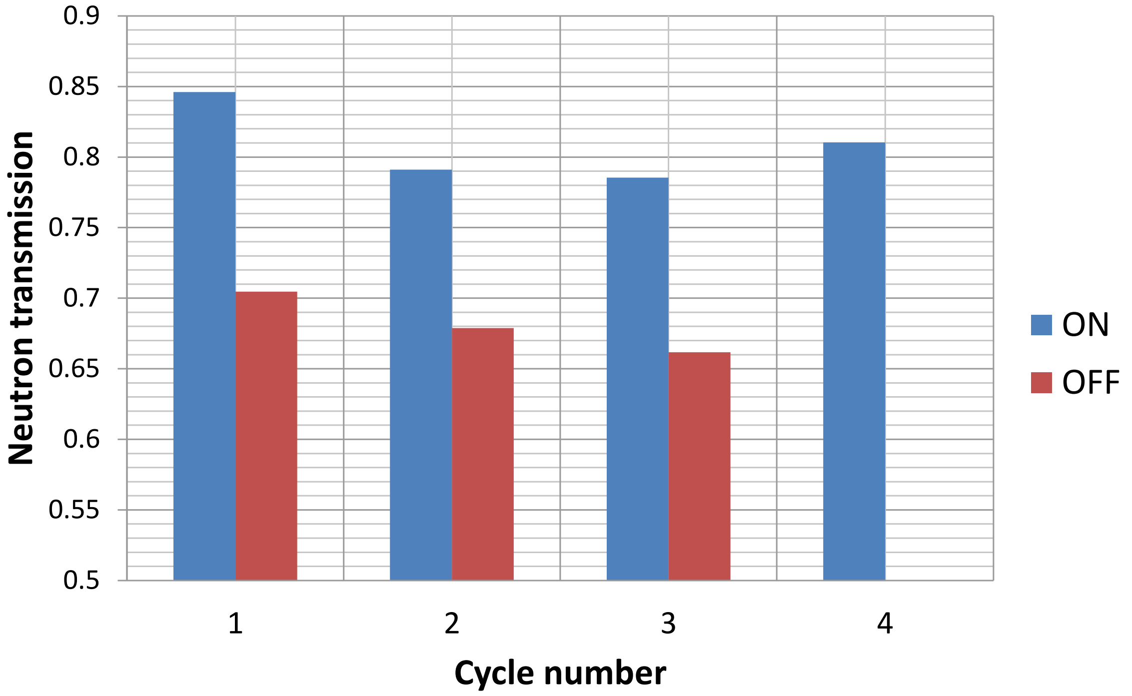

Figure 14 – Neutron transmission in the membrane area as a function during ON/OFF cycles. A lower transmission represents a higher amount of Gd.

This assumption is also corroborated by the values of the neutron transmission in the membrane region, presented in Figure 14. This transmission is significantly reduced when the electrolyser operation is stopped, as expected from a higher concentration of Gd in the membrane.

These results have different implications. The first one is that cation mobility has to be taken into account when analyzing the impact of cation contamination on the ionic conductivity of the membrane and of the catalyst layers. A known method of measuring the ionic conductivity of the catalyst layer is the used of electrode impedance spectroscopy (EIS) in a special, non-operating configuration where the electrode of interest is exposed to nitrogen and the counter electrode to hydrogen. Our results indicate that such a method cannot be applied for cation contamination, because the concentration of cations in the catalyst layers in a non-operating mode is not representative of the concentration during operation.

Secondly, our observations could be used to inspire *in situ* regeneration strategies. The fact that the current displaces the cations on the cathode side could be used to promote the regeneration by flowing a low concentration acid in the cathode while operating the electrolyser. Another approach could be to flow CO_2 gas in the cathode, which would generate carbonic acid by mixing with the water present in the cathode PTL (as seen in §3.1.2).

3.3 Dissemination of the results

The initial results (water/gas distribution obtained with the 1st generation cell) were presented as a poster at the ECS Electrochemical Energy Conversion & Storage Conference (Glasgow, July 2015) and subsequently published in the peer-reviewed Journal of the Electrochemical Society [3], as part of a focus issue ("JES Focus Issue on Electrolysis for Increased Renewable Energy Penetration"). No further peer-review publications were submitted yet. We however expect to publish two more peer-reviewed articles out of the latest results, one on the water/gas distribution (§ 3.1.2) and one on the movement of cationic contaminants (§ 3.2).

4 Conclusions

In the frame of this project, we could set-up the infrastructure (test bench and cells) necessary for establishing the neutron imaging of electrolysers as a new topic in the PSI research portfolio. Moreover, we could obtain significant results summarized as follows:

- On the topic of water/gas distribution in electrolysers, our work constitutes the ***first reported direct observation of the water/gas distribution in porous transport layers (PTL)***. The obtained results shed new light on the transport within the PTLs, for which the transport mechanisms and patterns are still discussed [4].

- Using Gadolinium ions as a proxy for other contaminants, the accumulation over time as well as the cation movement as a function of electrolyser operation could be evidenced. These results may be used as a basis for advanced *in situ* regeneration strategies.

5 Literature

[1] P. Boillat, D. Kramer, B. C. Seyfang, G. Frei, E. Lehmann, G. G. Scherer, A. Wokaun, Y. Ichikawa, Y. Tasaki and K. Shinohara, *Electrochemistry Communications*, **10**, 546 (2008). http://dx.doi.org/10.1016/j.elecom.2008.01.018

[2] P. Boillat, G. Frei, E. H. Lehmann, G. G. Scherer and A. Wokaun, *Electrochemical and Solid-State Letters*, **13**, B25 (2010). http://dx.doi.org/10.1149/1.3279636

[3] J. Seweryn, J. Biesdorf, T. J. Schmidt and P. Boillat, *Journal of The Electrochemical Society*, **163**, F3009 (2016). http://dx.doi.org/10.1149/2.0641607jes

[4] C. Lee, J. Hinebaugh, R. Banerjee, S. Chevalier, R. Abouatallah, R. Wang and A. Bazylak, *International Journal of Hydrogen Energy*, **42**, 2724 (2017). https://doi.org/10.1016/j.ijhydene.2016.09.114