Experimental report

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Title: Operando Neutron Imaging of PEM Water Electrolyzer for Studying the Impact of the Mass Transport on the Cell Voltage at High-Load Operation

Research area: Engineering

This proposal is a new proposal

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Samples: Proton Exchange Membrane Water Electrolyzer

Instrument	Requested days	Allocated days	From	To
NEXT	4	3	19/05/2023	22/05/2023

Abstract:

Increasing concerns about climate change and energy security have stimulated hydrogen economy development. Coupling proton exchange membrane water electrolyzers (PEMWE) with renewable energy sources has emerged as one appealing option to produce green hydrogen in order to decarbonize different economic sectors. However, when operated at high current densities PEMWE faces high voltage losses. A significant part of total voltage losses at high electrical loads is attributed to mass transport losses. These losses are usually considered to be caused by the two-phase flow in the anode porous transport layer (PTL). In this work, dynamic radiography and 3D tomography measurements of electrolyzers containing different PTLs will be performed to study the two-phase flow in PEMWE PTL. Simultaneous advanced electrochemical methods and operando neutron imaging measurement, with additional model-based analysis, will allow further understanding of two-phase mass transport in the PTL and its influence on the electrochemical performance.

Operando Neutron Imaging of PEM Water Electrolyzer for Studying the Impact of the Mass Transport on the Cell Voltage at High-Load Operation

Scientific background

Driven by the aim to mitigate greenhouse gas emissions and climate change, renewable energy production has been growing significantly. However, renewable power is intermittent and requires efficient storage. Due to their characteristics, proton exchange membrane (PEM) water electrolyzers (WEs) are a favorable technology for overcoming this challenge. PEM electrolysis transforms electrical energy produced from renewables to chemical energy in the form of hydrogen. Still, the adoption of this technology is limited by its cost and performance [1]. During the operation of PEMWEs, significant voltage losses appear, especially at high current densities, increasing operating expenses. Usually, the counter-current mass transport of oxygen and water in the anodic porous transport layer (PTL) is considered to contribute to the losses significantly [2]. However, the nature of these losses remains ambiguous [3]. Especially, the influence of the periodic operation (PO) on mass transport losses, as well as the WE performance overall, is rarely studied [4, 5]. AC/DC conversion of current produced by renewable technologies is necessary before it is supplied to the PEMWEs. Since a perfect conversion is impossible, a ripple current is supplied and, consequently, PEMWEs operate periodically. It is known that the PO can result in process improvement or deterioration if compared to the steady-state operation [6].
In this study, we aimed to analyze the influence of PTL structure and PO on the overall performance and individual losses of the PEMWE, especially its effect on the two-phase transport. Thus, we have combined electrochemical measurements, allowing the performance analysis, with neutron imaging of high time and spatial resolutions for gaining information on the mass transport in the PEMWE. Both steady-state (SS) and PO of the PEMWE were analyzed for different PTLs and different operating conditions.

Experiment details

The experiments were performed at the neutron imaging instrument NeXT [7] at Institute Laue-Langevin, Grenoble, France. The high-resolution detector was employed, with a 20 µm thick Gadox scintillator, 50 mm f./1.2 Canon imaging lens in combination with 55 mm f./1.0 objective lens in infinity corrected optics configuration which were attached to Hamamatsu ORCA-Flash V3 sCMOS camera.
PEM electrolysis cells (Fig. 1.a) were designed to allow for high transmittance and sufficient contrast of images. A small active area (1 cm^2) was used to avoid spatial distributions within the cell. Commercial membrane electrode assembly (MEA) was utilized, consisting of Nafion 117 with 0.3 mg Pt cm^{-2} and 1.0 mg IrOx cm^{-2} (Ion Power), platinized titanium PTL (Bekaert), and carbon GDL (Freudenberg). Two cells were analyzed differing only in the anodic PTL porosity: WE1 with a 77% porosity PTL and WE3 with a 42% porosity PTL. The test bench (Fig. 1.b) allowed electrolysis cell operation at a constant temperature of 60°C and atmospheric pressure. Furthermore, the recirculation of water through the anodic side of the WE was realized with a flow rate of 3.25 ml min^{-1}, while nitrogen with a flow rate of 8.00 ml min^{-1} through the cathodic side assured efficient removal of the produced hydrogen. Electrochemical measurements were performed with galvanostat/potentiostat Ivium XP40. One set of measurements, termed SS measurements, was done by holding a current at constant levels of 0.1, 1, 3, 6, and 9 A cm^{-2}. The second and third sets of measurements were PO measurements at the same current densities. These measurements were performed by changing the current sinusoidally with a high perturbation amplitude and at frequencies of 50 or 32 mHz (PO1) and 1 Hz (PO2).
Both through-plane and in-plane images of the region of interest (in-plane and through-plane mark the direction of the neutron beam) were taken during each of the mentioned measurements once the quasi-steady-state operation was established. The field of view was 14.64 x 14.64 mm^2 which was a bit smaller than the active area of the cell (20 mm x 5 mm). However, the middle part of the active area could be

nicely visualized. Images were taken with a temporal resolution of 0.1 s, allowing observation of the two-phase flow dynamics. The resulting pixel size was approximately 14.30 µm.

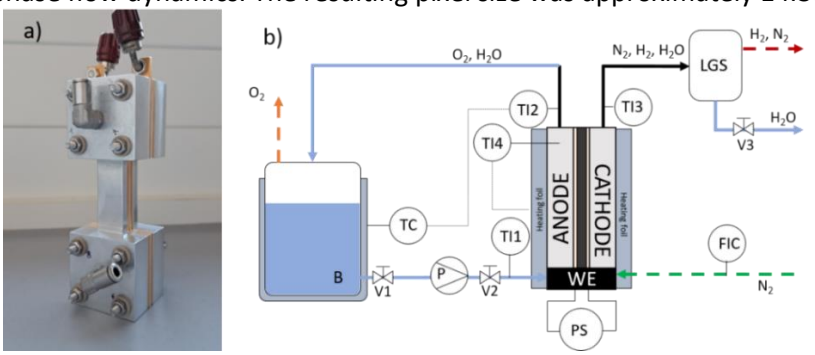

Figure 1. a) PEM electrolysis cell for neutron imaging b) Schematics of PEM electrolysis test bench

Results

Fig. 2a shows the average voltage of the WE1 and WE3 at investigated current densities. One can see that the voltage of WE3 is significantly higher than the one of WE1. Since these electrolyzers differed only in the PTL, one can deduce that PTL caused the difference in the performance. Furthermore, at higher current densities, there is a notable difference in the voltage during SS and PO. While at lower current densities, the voltage did not depend on the operating conditions, at higher current densities both PO1 and PO2 resulted in lower values of voltage. The only exception is WE1 at 9 A cm^{-2}, where a slight increase of voltage during PO2 can be seen compared to SS. Overall, the voltage of WE3 was more sensitive to the mode of operation than the voltage of WE1. The PO of the electrolyzer caused periodic fluctuations of the water thickness (WT) in the PTL, as shown in Fig 2b and 2c. One can notice, especially for PO1, a sinusoidal change in PTL WT. The fast irregular fluctuations in WT during SS are due to statistical issues (neutron flux in combination with exposure time, and count rate on the detector) and don't represent the physical phenomena. Furthermore, one can see that at higher current density (Fig. 3c), the average PTL WT during PO is lower than during SS, which is not the case for the lower current (Fig. 3b).

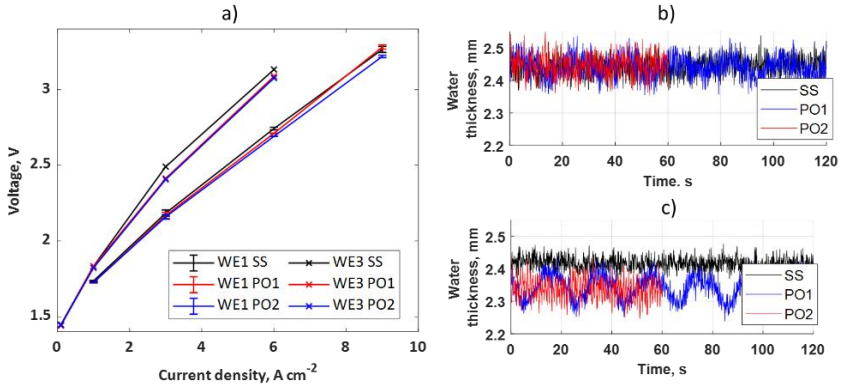

Figure 2. a) Average voltage vs. current density for WE1 and WE3; b) Average PTL saturation vs. time at 1 A cm^{-2} for WE1; c) Average PTL saturation vs. time at 9 A cm^{-2} for WE1 under different operating conditions: SS – steady state, PO1 – periodic operation at 50 mHz, PO2 – periodic operation at 1 Hz; The water thickness is obtained from the in-plane images

WT profiles for different operating conditions were determined and Fig. 3 shows average in-plane WT profiles for different current densities for WE1 and WE3. The most significant change in WT with the operating current density is observed in the anode flow channels (AFC) for both electrolyzers. At higher current densities, more oxygen is produced and, thus, more gas is present in the channels and less water. Insets in Fig. 3 show the PTL liquid saturation calculated based on the known porosity and length of the beam through the PTL. In agreement with our previous study [8], the PTL saturation is only slightly dependent on the current density. Also, a drop in the PTL saturation from the AFC towards the MEA is notable, especially for the WE1. Additionally, a couple of maxima in the PTL WT on the MEA side are present. It can be speculated that these are due to the non-uniformity of the PTL pores. Where bigger pores are present in the PTL structure, water will be better retained, and maximums in WT observed.

Next, a sharp drop in the amount of water is visible through the MEA in the direction from the AFC to the cathode flow channel (CFC). Keeping in mind that water was supplied to AFC and nitrogen was purged through CFC, this was expected. Water is observed in the cathode compartment due to the water transport through the MEA by diffusion and electro-osmotic drag. The gas diffusion layer (GDL) shows a significantly higher WT than CFC due to the hydrophilic GDL material used to prevent cathode catalyst drying out. However, the WT profiles through the MEA and cathode seem to be almost completely independent of the current density. It is also evident that WE3 has much less water in the PTL than WE1. The low porosity of the WE3 PTL is causing mass transport issues, resulting in an increased voltage of WE3. Furthermore, MEA WT is much lower for the WE3, indicating higher ohmic resistance of the membrane and lower catalyst activity. These also contribute to the difference in the voltages of WE3 and WE1. If SS and PO are compared, only a slight difference in the in-plane WT and PTL saturation is present, making it difficult to conclude if the change in the mass transport is causing the observed change in the voltage.

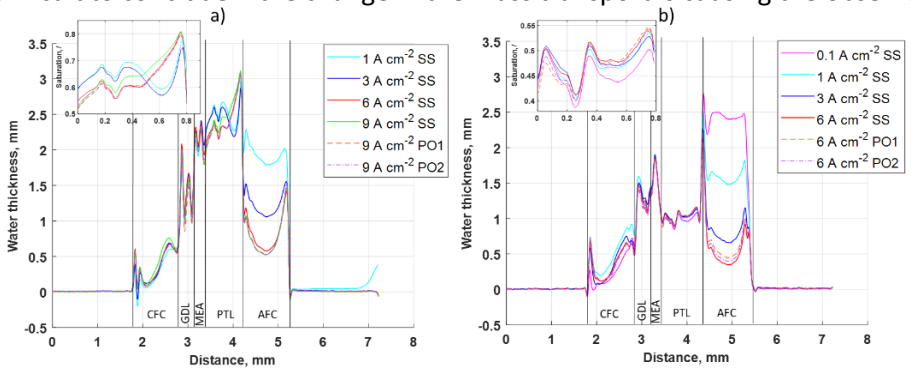

Figure 3. Water thickness profiles for different current densities for a) WE1 and b) WE3 under different operating conditions: SS – steady state, PO1 – periodic operation at 50 (32) mHz, PO2 – periodic operation at 1 Hz; Insets are showing liquid saturation through the PTL; The profiles are obtained from the in-plane images

Conclusion and outlook

In this study, mass transport in the PEMWE and its influence on the performance was investigated. While electrochemical measurements allowed the analysis of the voltage losses, operando neutron imaging was used to uncover the characteristics of the two-phase transport.

The preliminary analysis indicates that in the studied range, current density has an almost insignificant influence on the WT, except for the AFC. However, the WT and voltage of the PTL and MEA were highly dependent on the used PTL and might be correlated to the decrease in the MEA conductivity and catalyst activity. Moreover, two maxima in WT across the PTL thickness were observed. Additional analysis of the PTL structure is necessary to verify the causes of these maxima, which can be done by in-situ tomography using neutrons. Furthermore, PO resulted in a lower voltage than the SS. However, it had an insignificant influence on the in-plane WT, excluding the mass transport as a cause of the voltage decrease.

Thus, the initial conclusions are: 1) A very important factor determining mass transport and consequently the PEMWE performance is PTL; 2) PTL should allow efficient transport of water and oxygen; 3) Optimization of the PTL design is needed; 4) PO has the potential to reduce the power consumption of the electrolyzer at high current densities; 5) Further analysis is necessary to understand the origin of the PEMWE performance improvement during PO and its effect on degradation in long-term operation.

References

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