Investigation of new ion-pair-based membranes for carbon-neutral propulsion of heavy-duty vehicles

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EXTENDED ABSTRACT

Hydrogen fuel cells are a promising carbon-neutral technology for powering heavy-duty vehicles (HDVs) and could contribute significantly to the decarbonization of the transport sector. High-temperature proton exchange membrane fuel cells (HT-PEMFCs) are a class of fuel cells that can be operated with lower-purity and therefore cheaper hydrogen due to their elevated operating temperature. They require smaller heat exchangers than low-temperature (LT-) PEMFCs because the larger temperature gradient to the environment increases the cooling rate [1]. The current state-of-the-art membrane electrode assemblies (MEAs) are based on phosphoric acid-doped polybenzimidazole (PBI) membranes, which exhibit good performance at the beginning of life (BoL) but experience performance degradation over prolonged operation due to phosphoric acid leaching [1]. To mitigate this, new materials such as ion-pair-based membranes (IPMs) have been developed [1, 2].

In this study, novel IPM-based MEAs and reference PBI-based MEAs were evaluated using 100-hour accelerated stress tests (ASTs) at 160 °C, designed to simulate real-world operating conditions in heavy-duty vehicles (HDVs) [3]. The performance evaluation of the membrane material in the cell was carried out using in-situ measurement techniques, such as polarization curves and electrochemical impedance spectroscopy (EIS), which were performed in

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25-hour intervals. The ex-situ characterisation of the material was performed with scanning electron microscopy (SEM).

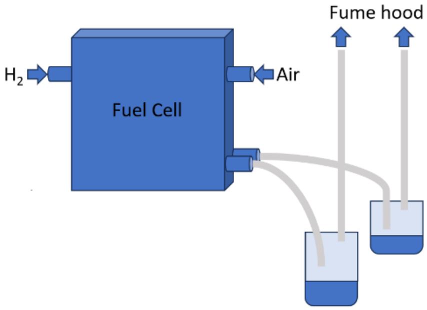

Figure 1: Schematic display of the sample collection during the AST measurement.

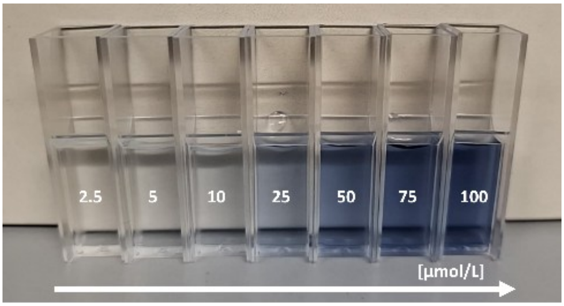

Figure 2: Molybdenum blue standards in the measuring cuvettes.

To investigate phosphoric acid (PA) loss from the two membrane types, the effluent water generated during operation was collected in a sample container connected to the cell via PTFE tubing (Figure 1) and analyzed via the molybdenum blue method [4]. In this method, a molybdenum-containing color reagent is added to the effluent, forming a blue colored complex with phosphate. The phosphate quantification was subsequently performed spectrophotometrically using a calibration curve with standards (Figure 2) and applying the Lambert-Beer law. This analytical method for the detection of phosphoric acid offers a simple and fast analysis of the effluent water sample with low limit of detection (LOD = 0.3 µmol L^{-1}) and limit of quantification (LOQ = 1.0 µmol L^{-1}), which are close to the values achieved by commercial ion chromatography measurements (LOD ≈ 0.1 µmol L^{-1}, LOQ ≈ 0.3 µmol L^{-1} [5]). The results of the molybdenum blue method were cross-validated using ion chromatography to ensure accuracy and reliability.

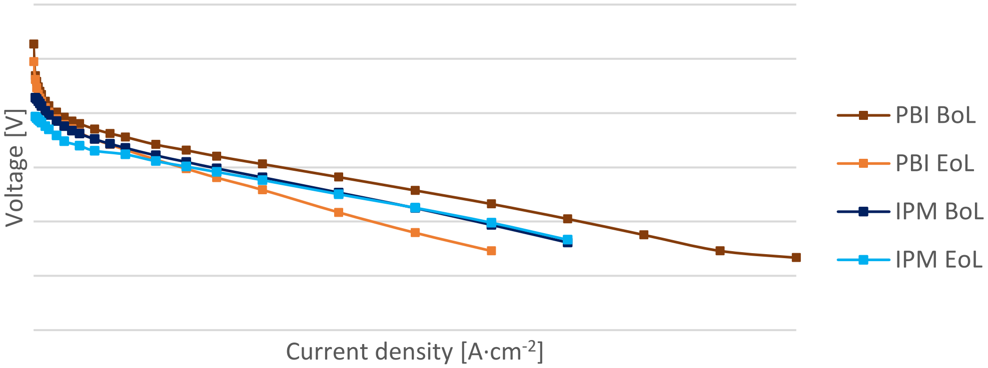

Figure 3: Comparison of BoL and EoL performances of PBI and IPM at 160 °C

At the beginning of life (BoL, 0 hours AST), the PBI-based membrane showed higher performance compared to the IPM (Figure 3). However, over the duration of the 100-hour AST, the PBI membrane experienced a more significant decline in performance, whereas the IPM demonstrated stable performance. By the end of life (EoL, 100 hours AST), the IPM-based membrane outperformed the PBI membrane.

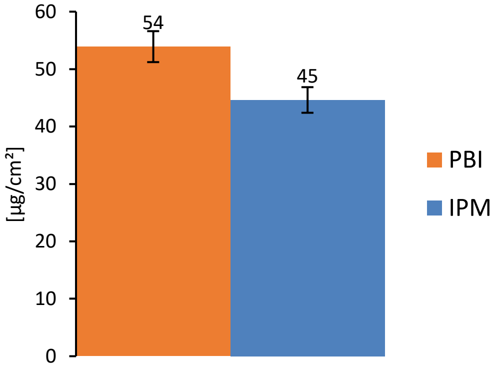

Figure 4: Determined phosphoric acid in effluent water for PBI and Ion-pair membranes after 100 h AST at 160 °C. Values given as mass of phosphoric acid, normalized for membrane area [μg_{PA} cm^2]

Furthermore, the total phosphoric acid loss observed over the 100-hour test period was higher for the PBI membrane (54 μg_{PA} cm^{-2}) than for the IPM (45 μg_{PA} cm^{-2}) shown in Figure 4. This highlights the stronger phosphoric acid retention of the IPM, due to the stronger interaction with phosphoric acid, as indicated by the higher calculated interaction energy (PBI: 17 kcal mol^{-1}; IPM: 105 kcal mol^{-1} [6]). The values obtained with the molybdenum blue method are largely in line with literature values. For the IPM, the determined phosphoric acid loss rate was in the range of 0.45 to 1.30 μg_{PA} cm^{-2} h^{-1}, and for the PBI membrane, it was in the range of 0.54 to 2.11 μg_{PA} cm^{-2} h^{-1}. Literature values report for IPM-based MEA a loss rate of 1.30 μg_{PA} cm^{-2} h^{-1} [6], whereas for PBI-based MEAs, they reported 0.24 to 61.2 μg_{PA} cm^{-2} h^{-1} [7,8].

These results suggest that the novel IPM technology is a promising alternative to conventional PBI membranes, with the potential to improve acid retention and durability of HT-PEMFCs in HDV-related operating conditions.

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