Influence of operating conditions on permeation of CO₂ through the membrane in an automotive PEMFC system

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Abstract

Fuel cell electric vehicles (FCEVs) are a possible sustainable and long-term solution to satisfy the demand for mobility. Cost targets are achieved by lowering platinum (Pt) loadings on the electrodes and using thinner membranes in the fuel cell system (FCS), maximizing the current density. Due to these measures, the FCS becomes more sensitive to contaminants, including those originating from crossover through the membrane. One of these contaminants - carbon dioxide (CO₂) - causes effects that can be reversed, however, this process negatively influences the FCS lifetime. For this reason, operating conditions should be chosen so that minimal temporary losses are caused without causing further negative effects, such as degradation, in the FCS. This paper shows the effects of CO₂ and O₂ permeation occurring during operation of an FCS and proposes the possibility of mitigating the crossover via the right choice of membrane.

Keywords

PEMFC; Membrane; Crossover; Carbon dioxide; Oxygen; Operating Conditions

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1. Introduction

In a future with a more sustainable mobility, the concept of powering a vehicle with hydrogen (H_2) based fuel cells is becoming more and more attractive. H_2 produced from renewable sources helps to avoid greenhouse gas and toxic gas emissions [1]. To achieve affordable prices for a proton exchange membrane fuel cell (PEMFC) system, cost drivers - such as noble metal catalysts - are constantly being reduced [2]. With lower Pt catalyst loadings, as demanded by the US Department of Energy [3], the FCS becomes more sensitive to impurities in the fuel. The fuel is often recirculated in an anode loop for reasons of safety, humidification, efficiency and cost, which can lead to an accumulation of impurities within the loop [4]. Furthermore, the CO_2 in the air supplied to the cathode can diffuse through the membrane to the anode side, additionally contaminating the recirculated fuel and being partly electrochemically reduced to adsorbed carbon monoxide (CO_{ad}) on the Pt catalyst layer thereby blocking its surface [5], [6].

Although recent publications promote the reverse water-gas shift (RWGS) reaction as a pathway leading to CO_{ad} [7]–[9], the amount of CO_{ad} produced via RWGS is negligible since Pt is a poor catalyst for the RWGS below 250 °C [10]. This is also in line with measurements of Giner [11] and Smolinka et al. [5] who have shown a potential dependent CO_{ad} formation, as well as a publication by Hori [12] demonstrating the electrochemical pathway between 0 – 300 mV vs reversible hydrogen electrode (RHE). In case the RWGS would be dominating the CO_{ad} formation, the RWGS would also take place at 400 mV vs RHE, because this gas phase reaction would be independent of electrode potential. However, this is not the case as adsorbed hydrogen (H_{ad}) is needed [5]. We conclude from these studies [5], [11], that the formation is electrochemically driven due to the low potential in the PEMFC anode providing H_{ad} rather than the gas phase reaction. Therefore the CO_2 in the anode feed is not negligible in terms of contamination.

CO_{ad} is strongly adsorbed on Pt up to 500 – 600 mV vs. RHE [13] before being oxidized without adding a co-catalyst such as PtRu, PtSn, PtTi, [14]–[18] and $Pt/Ti_{0.7}Mo_{0.3}O_2-C$ ($M= W, Mo$) [19] to operate at relevant PEMFC temperature.

Generally, the effect of CO_2 reduction to CO_{ad} is suppressed when there is also CO in the feed stream being adsorbed directly to CO_{ad} [5] with increasing impact along with higher CO concentration [20]. The maximum allowance for FCEV refueling is currently defined by ISO 14678-2 [21] and SAE J2719 [22] for CO and CO_2 by 0.2 ppm and 2 ppm respectively.

Temporary voltage losses caused by CO_{ad} can be recovered with the introduction of oxygen (O_2) to the anode, which oxidizes the CO_{ad} to CO_2 , freeing up the blocked catalyst surface sites. Carbon monoxide (CO) oxidation with O_2 can occur during normal operation of the FCS as well as in shut down situations, where border sites of Pt are mainly responsible for CO_{ad} oxidation [23]. During normal operation, O_2 can be brought to the anode side either by directly introducing a small amount of air (up to 2 vol % of anode feed flow) into the feed (“air bleed”) [15], [24], [25] or via permeation of O_2 from the cathode to the anode through the membrane (“internal” air bleed). During lifetime testing, an FCS faces different operating conditions with load cycling, steady state operation and shut downs according to the driver’s demands. However, only alternating steady-state operation and shut down periods are considered in this paper. During every shut down, ambient air crosses over to the anode after depletion of the remaining H_2 , which recovers the voltage for the next operation in a distinct saw tooth pattern. While this crossover of air frees up blocked Pt sites, the process also causes an elevated degradation on the cathode side, as fuel/ air boundaries can lead to in-plane currents, causing carbon corrosion [26], [27]. Consequently, the lifetime of the fuel cell system is significantly reduced [26], [28]. Avoiding these effects in the first place by mitigating the crossover of CO_2 is thus more advantageous than any later recuperating treatment of the FCS. The influence of operating conditions, membrane type and its thickness on the crossover of CO_2 and O_2 was investigated in the current work and mitigation measures for these influences were suggested.

The role of the permeation of CO_2 in an FCS with a recirculated anode loop and its consequences on the system performance are also investigated here. CO_2 accumulation at the anode side of a PEMFC is studied in the first part of this work, by, revealing for the first time, the actual gas composition in a full-size automotive fuel cell system with integrated anode loop for different load points via in situ mass spectrometry (MS) at the anode stack outlet. Subsequently, a 40 cm² flow through single cell was subjected to the CO_2 concentrations on the anode side measured in real fuel cell operating conditions. In addition to these CO_2 concentrations the amount of CO_2 present in ambient air, 400 ppm CO_2 was fed into the anode of the single cell as a worst case scenario in terms of CO_2 concentration. During each single cell test, the

cell voltage was monitored, followed by an electrochemical active surface area (ECSA) analysis to identify the amount of ECSA blocked by CO_{ad} . The voltage monitoring shows the voltage losses occurring due to CO_2 fed into the anode during the test. Cyclic voltammetry (CV) reveals the ECSA of the Pt catalyst blocked with CO_{ad} . A negative influence of the permeated CO_2 on the performance of the system was observed.

To evaluate possibilities of mitigating these permeation issues and the subsequent negative effects on the performance, the second part of this work examines the gas crossover rates for different perfluorosulfonic acid (PFSA) type proton exchange membranes (PEM), as well as one hydrocarbon membrane under different operating conditions. PFSA type membranes are widely used for long term stability reasons, but in terms of CO_2 permeation, this study shows promising results regarding the use of hydrocarbon membranes. Nevertheless, recent research shows improvement in long term durability tests [29]. Hydrocarbon based membranes are still being further developed to improve stability while maintaining high proton conductivity and mechanical stability during humidity cycling [30].

The testing conditions were chosen based on the operating conditions of an FCEV to unveil the influences in this specific operating range for ultra-thin membranes. Temperature, relative humidity (rH), pressure (p), flow rates and the type as well as thickness of the membrane were varied during the experiments. Literature on CO_2 permeation focuses primarily on thicker membranes, also along with DMFC applications, where CO_2 is primarily an indicator for cross-over methanol [31]–[35]. Recently published papers on permeation in PEMFC focus mainly on permeation of the reactants and degradation related permeation topics [36]–[43], even describing nonlinearity for H_2 permeation for low membrane thicknesses [44].

This investigation shows application relevant experiments in an automotive FCS as well as detailed single cell gas permeation measurements to study the influence of operating parameters on CO_2 and O_2 permeation employing ultra-thin ($\leq 15 \mu\text{m}$) membranes.

2. Experimental

2.1. Electrochemical Measurements

2.1.1. Full-size system

The experiments on an automotive full size fuel cell system were carried out on a research platform system for the development of Daimler AG's Mercedes Benz GLC F-Cell. It was built in a climate chamber that was kept at 20 °C during operation and particle filtered air was supplied to the system. A schematic of the operating strategy is shown in Figure 1.

The power demand by the driver ① of the FCEV defines the load required by the system. This load demand sets the operating conditions and the flow of reactants needed in the fuel cell ②. The cathode is supplied with sufficient air by the electronic turbo compressor (ETC, ③) and the anode is fed with H₂ from the H₂ storage ④. The supplied air ⑤ contained 400 ppm of CO₂, which is equivalent to the concentration in ambient air.

A fraction of the CO₂ crosses over to the anode gas stream, which gets partly recirculated ⑥ and partly purged ⑦. A part of the permeated CO₂ blocks the catalyst surface on the anode through reduction to CO_{ad}. The CO₂ concentration in the anode is governed by crossover from the cathode and the H₂ replacement strategy, which consists of regulating the purge rate as well as the fresh H₂ intake. As the anode catalyst surface is blocked, the power output of the system diminishes. Generally, the purge rate is regulated by varying the fresh H₂ supply ⑩ rate in order to have a minimum average concentration of 80 mol % H₂ at the anode outlet. To meet the power demand after the catalyst surface area has been blocked, the purge rate ⑧ rises along with an increase of fresh H₂ intake, which ultimately results in an increase of the overall average consumption of H₂ ⑨.

The FCS was operated at 7, 32, 61, 87 and 100 % of the maximum possible current density and the corresponding gas composition at the anode stack outlet was monitored via in situ MS measurements. The amount of permeated CO₂ was calculated after steady state had been reached, by averaging the measured concentration during the last 5 minutes of each operating step.

2.1.2. Single electrochemical cell

The single cell experiments were conducted to analyze cell performance losses associated with different CO₂ concentrations with respect to voltage decay and blocked ECSA. A Core Automotive Test Cell (CAT) V2 by AFCC with an active area of 40 cm² was employed for this purpose. Commercially available membrane electrode assemblies (MEAs) were used with a Pt loading of 0.05 mg cm⁻² on the anode, and 0.25 mg cm⁻² Pt on the cathode, respectively. The MEA contained a 15 µm reinforced membrane and SGL 25 BIH gas diffusion layers (GDL) were used on both sides. All tests were run with highly over-stoichiometric gas flow rates without recirculation to ensure a close to gradient free single cell operation.

CO₂ in the anode gas stream can block the catalyst surface after reduction to CO which adsorbs on Pt surface to form CO_{ad}. Other CO molecules presented in anode feed (e.g. CO coming from gas impurities) can also be adsorbed onto the catalyst sites directly. The blocked ECSA was analyzed through CV and CO stripping measurements carried out by using a Zahner IM-6 potentiostat, to determine the current necessary to remove the CO_{ad}. The scan rate in all of these CV measurements was set to 100 mV s⁻¹ in the range of 67 mV to 863 mV vs standard hydrogen electrode (SHE), with four cycles recorded for each test. The amount of CO_{ad} is analyzed via integration of the CO oxidation peak between 530 mV and 800 mV vs. RHE. To find the integration limits for these calculations, the second cycle after the CO stripping in the CV was used as the baseline, containing no CO oxidation peak [13]. Integration of the recorded current during the first CV cycle within the limits of the CO oxidation peak yielded the amount of charge necessary for oxidation of the CO_{ad} layer. This calculated charge can be related to the total amount of CO_{ad} oxidized assuming a CO monolayer oxidation corresponding to 420 µC cm⁻² ($Q_{c_{spec}}$) [45]. During CV measurements, the electrode of interest, that was contaminated before, was fed with pure Nitrogen (N₂) - being the working electrode - while the other electrode was fed with H₂ in order to operate as a combined counter and reference electrode.

Before the investigation started, the anode side ECSA was characterized by CO stripping voltammetry of a full CO_{ad} monolayer. In order to reach this maximum CO coverage, both working electrode and

counter/ reference electrode of the single cell were fed with H₂. The electrode of interest, in this case the anode, was fed with H₂ containing 10 ppm CO for four hours which blocks the catalyst sites to the maximum possible extent [46].

The test sequence for analyzing the impact of CO₂ on the performance and ECSA of the single cell with different CO₂ concentrations in the H₂ feed consisted of two parts: First, the anode was fed with H₂ containing the respective CO₂ contamination necessary for the experiments, while the cathode was fed with conditioned air for a duration of 24 hours. The voltage decay during the test was recorded for each CO₂ concentration. In the second part, the blocked ECSA was determined using CV measurements after each test.

Table 1 shows relative humidity (rH), pressure (p) and gas flow rates of the set points examined for both CV measurements (N₂/ H₂), CO saturation for CO Stripping (H₂/H₂/CO) and operation with H₂/ air. All tests were conducted at 68 °C.

Table 1: Conditions for operation used for CAT-Cell

Inlet gases an./ cath.	Current density [A cm⁻²]	rH an./ cath. [%]	p an./ cath. / [bar_a]	Gas flow an./ cath. [L_n min⁻¹]
N ₂ / H ₂	N/A	100 / 100	1 / 1	2 / 2
H ₂ / H ₂	N/A	100 / 100	1 / 1	2 / 2
H ₂ / Air	1.0	50 / 70	1.9 / 1.6	2 / 6.8

2.2. Permeation Measurements

A single cell with an active area of 25 cm² and SGL® 24 BC GDLs on both sides was employed to determine the CO₂ and O₂ permeation through the membrane, without applying any potential to the system. A gas mixture containing either CO₂ or O₂ diluted in argon (Ar) was supplied to the feed side, while a carrier gas of pure Ar was supplied to the permeate side. MS analysis of the permeate side was used to determine the gas permeation through the membrane. Ar was chosen as a background gas because it is not interfering with the m/z signals of CO₂ and O₂.

The permeation properties of four different membranes were investigated. Three of them were PFSA-based membranes with different thicknesses and properties, while the fourth was made from a hydrocarbon material. Table 2 gives an overview over all membranes used in the crossover tests.

Table 2: Overview tested membranes

Sample	Thickness (µm)	Basis
A	15	PFSA
B	15	PFSA modified
C	8	PFSA (same as A)
D	10	Hydrocarbon

The main goal of the conducted experiments was to evaluate the influence of temperature, pressure and relative humidity on the performance of the aforementioned gases in the respective range of conditions for an FCEV. The following Figure 2 shows the test bed layout which was employed.

Two test gases M1 and M2 were connected to the feed side via Bronkhorst® mass flow controllers ①, while pure Ar could be either connected to the permeate side during the measurements, or to the feed side to purge the system between measurements ②. The compositions of the test gases M1 and M2 are shown in

Table 3. Humidification of the gases was achieved by employing Bronkhorst® W-102A controlled evaporator mixers (CEMs) ③. As the used OmniStar™ GSD 320 MS system could only be operated at ambient pressure, the pressure of the gas mixture on the permeate side had to be reduced for analysis in case of higher pressure operation of the system, while the pressure within the electrochemical cell was regulated and kept constant. This was achieved by including electronic back-pressure valves ④ and pressure sensors ⑤ controlled via a computer terminal. Furthermore, water separators ⑥ were used to separate the gases from liquid water to ensure an accurate MS measurement. The OmniStar™ system was connected on the permeate side directly after the back-pressure regulator and before the secondary water separator.

Table 3: Permeation test gas compositions

Gases	CO₂	O₂	Ar
M1	0	21.01 %	78.99 %
M2	1.003 %	0 %	98.997 %
M3	18.01 %	0 %	71.99 %
M4	50.01 %	0 %	49.99 %
Ar	0 %	0 %	100 %

The permeation of CO₂ and O₂ through different membranes at various operating conditions was investigated. Depending on the membrane type, different set-points with varying temperatures, pressures and relative humidity were studied, which are listed in Table 4. In addition, tests for linear dependency of the permeability of CO₂ were conducted by varying the CO₂ content in the feed side gas for one of the membranes at selected set-points. The purpose of these additional experiments was to evaluate, whether the permeation could be extrapolated to smaller feed gas CO₂ concentrations, which could not be tested using the MS due to detection constraints at atmospheric concentrations of 400 ppm. The gas mixtures M2, M3 and M4 used for these tests are listed in

Table 3 as well.

Table 4: Overview Set-points membrane permeation investigations

	Membrane A	Membrane B	Membrane C	Membrane D
Temperature [°C]	60, 70, 80, 90	60, 70, 80, 90	60, 70, 80, 90	70, 90
Relative Humidity [rH%]	50, 65, 80	50, 65, 80	50, 80	50, 80
Pressure [bar_a]	1.3, 2.1, 2.9	1.3, 2.1, 2.9	1.3, 2.1, 2.9	1.3, 2.1, 2.9

All gases used in the permeation experiments were purchased from Messer® Schweiz AG. The composition determined by the supplier is certified according to the ISO 6143 norm for gas analysis, with a 2 % relative error on each of the gas mixture components, as listed in

Table 3. The pure Ar which was used, had a 6.0 gas purity level.

2.3. Analytical Methods – mass spectrometry systems

2.3.1. Full-size system

The high speed in situ MS integrated into the test bench for these tests was custom built with modular elements from Pfeiffer by Fraunhofer ICT, Pfingztal/ Germany. It consists of a Pfeiffer Vacuum QMG 700 with a gas tight crossbeam ion source and tungsten filament. It employs a quadrupole mass separation

with a range of 0 - 500 m/z and a 90° SEM conversion dynode (1400 V) detector. The MS also features a 0.254 mm diameter heated fused silica capillary, which is well suited for measurement of gases with high relative humidity, as they are typically found in fuel cell systems.

2.3.2. Permeation tests

An OmniStar™ GSD 300 02 was used for the conducted permeation measurements. This system comprises a Prisma quadrupole mass spectrometer with a mass range of 1 - 100 amu as well as a pump station consisting of a membrane pump and a turbo pump. A stainless steel capillary was used as gas inlet. The system was heated to 60 °C and the capillary to 130 °C during all experiments. The lower limits of detection (LLOD) for CO₂ and O₂ in Ar of the system were 10 ppm and <1 ppm, respectively.

3. Results & Discussion

3.1. Full size system analysis

As mentioned in Section 2.1, the operating conditions and the H₂ replacement strategy in the system have an influence on the CO₂ concentration in the anode loop. Figure 3 shows the CO₂ concentration on the anode side at different operating conditions of the full-size FCS. The system was started and the load was increased in 5 steps before being decreased in the same steps. The system was operated for 15 minutes at each of the load steps to reach steady state operation. With increasing load, the pressure increased as well to deliver sufficient reactants. The relative humidity and temperature also increased with increasing load due to the exothermic formation of water in the fuel cell.

The oscillation of the CO₂ signal, which can be seen in Figure 3, originates from the continuous partial replacement of the anode cycle, which is necessary to keep the minimum average concentration of H₂ on the anode at 80 mol %. Generally, the pressures re-adjusted to the new operating conditions after each load step so that the pressure gradient between two load points resulted in lower and higher concentration of CO₂ on the anode before reaching equilibrium. It is expected that permeation of CO₂ through the membrane should increase proportionally with the increasing load steps, due to increased temperature and relative humidity. The equilibrium between enrichment from crossover and replacement strategy was established for each load step after 3 minutes of operation, and a steady state condition with little oscillation was consequently reached. Peaks that occurred after these initial 3 minutes were rare and were attributed to test bench controllers.

The average permeated CO₂ on the anode side during operation was observed within a range of 130 - 155 mol ppm depending on the system load. However, considering the peaks of CO₂ amount present in the anode loop, as shown in Figure 3, values between 95 and 220 ppm were obtained. The level of CO₂ present in the system after startup was oscillating between 95 ppm and up to 162 ppm in load step ① with 7 % of the maximum load. The corresponding low flow rates and consumption rates of reactants at low loads at load points ① and ⑨ result in a higher oscillation of the CO₂ signal along with low purge and replacement of H₂. The average during load step ① is 131 ppm CO₂ for the last 5 minutes of this step when the equilibrium was settled. However, the average measured CO₂ in the anode loop only shows a significant increase after changing from 7 % to 25 % of the maximum load, as well as after changing back from 25 % to 7 %. In between 25 % and 100 % of the maximum load, the averages ranged from 145 ppm CO₂ to 155 ppm CO₂. The CO₂ amount therefore appears to be independent or at least not proportional to the applied system load in these steps. This behavior can be attributed to the replacement strategy which generally maintains a minimum of 80 mol % H₂ on the anode. This leads to the conclusion that on one hand, increased temperature, pressure and relative humidity increase the permeation of CO₂, while on the other hand, the increased purge rate decreases the CO₂ in the anode loop, finally reaching an equilibrium concentration between 130 - 155 ppm.

3.2. Single electrochemical test cell

To determine the influence of CO₂ on the catalyst sites available, the ECSA was first analyzed by CO stripping and H_{upd} analysis. The maximum possible CO coverage according to [47], [48] is about 70 % of the available Pt sites and 77% for H_{upd}, respectively. Based on this maximum coverage, the initial ECSA was determined. This initial ECSA on the anode side of the single cell MEA was calculated as 60 m²/g_{Pt}.

The blocked ECSA determined from the following measurements are understood with the maximum blocked ECSA obtained with CO stripping as reference.

In the previous chapter, CO₂ concentrations were evaluated in an FCS and were found to range from 95 ppm to 220 ppm. To determine the influence on the performance, two CO₂ concentrations, 100 ppm and 200 ppm, were added to pure H₂ and fed into an anode with a flow-through design in steady state operation in different tests. In addition to these measurements, a worst case scenario was carried out assuming 400 ppm of CO₂ on the anode side (equal to the amount in ambient air).

As discussed before, the surface coverage increased with the concentration of contaminating CO₂ at the anode. This led to the catalyst surface becoming blocked by CO_{ad}, limiting the HOR [5], which was also seen in a voltage decay. Table 5 shows the blocked ECSA after operating the cell for 24 h with different CO₂ concentrations in the anode side feed gas. Although the single electrochemical cell was operated at highly over-stoichiometric conditions, fed with pure H₂ and without recirculating the anode loop, CO₂ crossover over the 40 cm² active area was observed and led to the formation of CO_{ad} resulting in 1 % ECSA coverage.

Table 5: Blocked ECSA evaluated with CV after 24 h testing with different concentrations of CO₂ in the anode H₂ feed of a single CAT Cell test

	CO ₂ 400 ppm	CO ₂ 200 ppm	CO ₂ 100 ppm	Pure H ₂
Blocked ECSA	47 %	26 %	16 %	1 %

The impact on voltage loss by CO₂ is shown in Figure 4. The voltage decrease was more severe for higher contamination amounts in the anode feed of the cell. Decreasing the amount of CO₂ in the anode loop is therefore crucial in lowering the blocked anode ECSA, which in turn leads to a lower voltage loss. Such voltage losses caused an elevated level of H₂ intake into the anode loop to satisfy the power demand.

It can be concluded from these single cell results that the contamination of the anode loop with CO₂ has highly negative effects on the performance, presumably also during long term operation of a FCS due to CO_{ad} forming on the catalyst surface layer. CO₂ entering the anode loop via permeation through the membrane is thus to be avoided. This is especially true for an FCEV when it is often moving through tunnels where higher concentrations of air contaminants, e.g. up to 800 ppm CO₂, are expected [49], which lead to a higher crossover rate and consequently worsen the harmful effects of the anode ECSA blockage.

3.3. Single test cell permeation

3.3.1. CO₂ permeation

One possible solution to the permeation issue described in the last chapters is to choose a different membrane material for the system, which allows limiting and mitigating the permeation of CO₂ to the anode side.

For this reason, four different membranes were examined as described in Section 2.2. Membrane A was used as a base-line, to which the others were compared. The CO₂ concentration on the feed side of the cell was 1 % for all experiments (balance: argon). The permeation values measured for membrane A are shown in Figure 5. The maximum CO₂ concentration on the permeate side was 93 ppm at 2.9 bar_a, 90 °C and 80 % rH, while the lowest permeation was 26 ppm at 1.3 bar_a, 60 °C and 50 % rH. The modified PFSA-type membrane B exhibited a very similar permeation behavior, with a maximum permeation of 98 ppm and minimum of 29 ppm at the same operating conditions as membrane A.

The results for membrane C show the influence of membrane thickness on the permeation. The detected permeated gas concentration was higher, since the membrane thickness was lower at 8 µm compared to the 15 µm of membrane A and B. The measured permeation was within the range of 44 – 135 ppm with the maximum and minimum values at the same operating conditions as before. The detailed results for membrane types B and C can be found in the Supplementary Information.

Finally looking at the hydrocarbon based membrane D, a significant reduction in permeation was observed. The maximum permeation measured at 2.9 bar_a, 90 °C and 80 % rH was 14 ppm. Furthermore, the influence of pressure, temperature and relative humidity is limited as the lowest measured permeation

was found at 3 ppm. All of the obtained permeations are close to, or below the lower limit of detection (LLOD) of the OmniStar® system and thus it can be concluded that permeation through a hydrocarbon based membrane can be neglected. The results for membrane type D are shown in Figure 6.

Looking at the general influences of the operating conditions on the permeation, it can be seen in Figure 5 and Figure 6 that pressure has the largest influence on the permeation of CO₂ through all tested membranes. Temperature and relative humidity exhibited a similar but smaller influence on the permeation. Comparing the results obtained for membranes A and D, it can furthermore be concluded that by using a hydrocarbon based membrane, the permeation of CO₂ is significantly reduced.

3.3.2. CO₂ linearity results

Due to the previously mentioned LLOD of the employed OmniStar® system, the CO₂ permeation tests were conducted by employing a gas mixture content containing 1 % CO₂ rather than a lower concentration of 400 – 1000 ppm, which would represent real operating conditions of an FCEV more accurately. In order to extrapolate the obtained results for lower concentrations on the feed side, the linearity of the permeation was investigated for membrane A. For this purpose, different gas mixtures were supplied to the feed side and the permeation measured. Figure 7 shows the obtained results. The linearity of the permeation could be verified, thus allowing the extrapolation of the obtained results to other CO₂ concentrations. It is worthwhile to note that the permeation results obtained for the two different temperatures at 50% rH and 2.9 bar_a deviate from the expectation of previously obtained conclusion of increased permeation at higher operating temperatures. In fact, the permeation at 60 °C was found to be slightly higher than at 90 °C, which most likely was caused by measurement errors. Nevertheless, the linearity of the permeation was also validated for these two cases. Via this extrapolation, the maximum and minimum CO₂ permeation through membrane A in the case of a 400 ppm concentration on the cathode side are calculated as 1 and 3.4 ppm respectively.

3.4. O₂ permeation results

In addition to the experiments of CO₂ crossover, permeation experiments of O₂ were conducted for the same 4 membranes. The O₂ concentration on the feed side was 21 % for all experiments. The results for membrane type A are shown in Figure 8. The maximum detected permeation of O₂ was 379 ppm at 90 °C, 2.9 bar_a and 80 % rH, while the minimum detected permeation was 43 ppm at 60 °C, 1.3 bar_a and 50 % rH. The modified membrane B overall exhibited lower permeations, ranging from 267 ppm to 38 ppm at the same operating conditions.

Similar to the CO₂ permeation behavior observed for membrane type C, the O₂ permeation was higher than for membranes A and B and varied between 58 – 411 ppm. The detailed results for membranes B and C can be found in the Supplementary Information.

The hydrocarbon membrane D showed again significantly reduced permeation of O₂ for all operating conditions. In the case of O₂ in Ar, the LLOD of the OmniStar® system is below 1 ppm. For this reason, the measured O₂ permeations need to be considered, but due to their magnitude, the permeation can nevertheless be considered negligible for membrane type D. The detailed results for membrane type D are shown in Figure 9.

In contrast to CO₂, the observed influences of pressure, temperature and relative humidity on the permeation through PFSA-type membranes were different. While pressure still had a large influence on the permeation, the operating temperature had a larger influence than for CO₂, and the influence of relative humidity remained to be smaller compared to the others.

Furthermore, considering the feed gas concentrations, the relative permeation of CO₂ is roughly one order of magnitude larger than the relative permeation of O₂ for the PFSA-type membranes, which is in agreement with values reported in the literature [50].

The hydrocarbon membrane limits the permeation of not only CO₂, but also O₂. Preventing O₂ from crossing over mitigates the internal air bleeding effect. However, at the same time, internal air bleeding is beneficial with respect to the CO_{ad} on the anode catalyst surface, as it oxidizes the CO_{ad} to CO₂. Hence, selecting a hydrocarbon membrane is a trade-off between reducing CO₂ crossover and allowing O₂ crossover.

4. Conclusions & Outlook

The effect of CO₂ present in the cathode feed was studied in an automotive FCS. The anode loop gas composition was monitored during system operation for CO₂ permeated fractions from the air on the cathode crossing over to the anode. Permeation of CO₂ can impair the performance or make air/ air starts of the system necessary, which negatively influence the overall lifetime. However, permeation is a commonly occurring effect in fuel cells, especially when thin membranes are employed. When an anode loop is implemented, inert gases and contaminants permeating from the cathode side are increasingly accumulated on the anode. During operation of a full size system, CO₂ concentrations in the range of 100 – 200 mol ppm were observed on the anode side. The effects were studied in a single cell test with 100 mol ppm and 200 mol ppm of CO₂ in the anode feed, resulting in blocked ECSA of 16 % and 26 % respectively after flow through operation of 24h. The contamination of the anode feed with CO₂ resulted in a noticeable decay in cell performance of about 8 and 24 mV respectively. It is thus of great importance that the membrane selection accommodates the aforementioned effects during normal operation of an FCS and limits crossover to lower the CO₂ amounts on the anode.

It has been further shown in this work that this permeability, with focus on CO₂ crossover, can be influenced via the right choice of membrane type and thickness. A hydrocarbon based membrane (14 ppm CO₂ at best permeation conditions) was found to be a better permeation barrier for the investigated species than PFSA based membranes (94 ppm CO₂ at best permeation conditions) with comparable thicknesses. Furthermore, the operating conditions have shown to have a significant influence on the permeation. The pressure of the gas supply to the system has a major influence on the permeation rate, with an increased permeation rate at higher pressures. It was determined that ideally, with respect to CO₂ crossover, the system should be operated at low pressures, low relative humidity and low temperatures to minimize the CO₂ crossover to the anode side. The change of the operating conditions to the maxim of lowering CO₂ concentrations in the anode loop could cause lower overall system performance, which has to be analyzed in a tradeoff approach.

These findings may be used in future research, by employing a hydrocarbon based membrane in an FCS and examining the effects on long term performance stability and gas crossover rates as well as the general influence of permeability on the system. Further research is necessary to increase understanding of the trade-off effects between higher H₂ consumption necessary for lower anode recirculation rates and the effects of CO₂ concentration on the anode side for a consumption optimized operating strategy.

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Figure Captions:

Figure 1: Influences of the operation strategy on the CO₂ concentration in the anode of an automotive full size system.

Figure 4: Cell voltage loss for different levels of CO₂ contamination at 1 A/ cm² in single cell.

Figure 5: Measured CO₂ permeation for membrane A with 1% CO₂ concentration on the feed side.

Figure 6: Measured CO₂ permeation for membrane D with 1 % CO₂ concentration on the feed side.

Figure 7: Linearity of CO₂ permeation for membrane A for different feed side CO₂ concentrations.

Figure 8: Measured O_2 permeation for membrane A with 21% O_2 concentration on the feed side.

Figure 9: Measured O_2 permeation for membrane D with 21% O_2 concentration on the feed side.