



SELECTIVE ELECTROCHEMICAL REDUCTION OF CO₂ TO HIGH VALUE CHEMICALS

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DELIVERABLE REPORT

| 6.5 – REPORT ON BENCHMARKING OF INITIAL AEM'S | | |
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| NATURE OF THE DELIVERABLE | | |
| R | Report | X |
| P | Prototype | |
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| SUMMARY | |
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| Keywords | <i>Anion exchange membrane, electrochemical CO₂ reduction, CO evolution</i> |
| Abstract | <p>This deliverable demonstrates the effectiveness of US current-generation anion exchange membranes (AEM) with the following head groups (supplied in D6.1): trimethylamine (TMA), <i>N</i>-methylpyrrolidine (MPY), and (3) <i>N</i>-methylpiperidine (MPIP) in relation to a benchmark commercial Sustainion membrane. We tested for CO₂ electrolysis to CO using a standard Ag catalyst to allow the focus to be on the membranes. We tested for CO selectivity versus hydrogen, operating potential, ohmic resistance and CO₂ crossover in the membrane across a range of current densities 50-300 mA/cm². We tested AEMS made from 25 μm and 50 μm thickness ETFE with only the 25 μm variants being effective. We also did long term studies of 24 hours and 200 hours. The end conclusion is that the US synthesized membranes are very competitive with the commercial Sustainion membranes with the MPIP membrane showing the most promise.</p> |
| Public abstract for confidential deliverables | |

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REPORT ON BENCHMARKING OF INITIAL AEM'S

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1 INTRODUCTION

The constantly increasing emissions of CO₂ from fossil fuels have alarming consequences on the global climate. It is essential to decrease these emissions in order to avoid further environmental changes, and one potential solution is turning CO₂ into fuels and feedstock by electrochemical CO₂ reduction reaction (ECO2R). The understanding of such ECO2R devices, under realistic conditions, is constantly improving due to efforts by research. A promising configuration for ECO2R is the membrane-electrode assembly (MEA), combined with an active and selective ECO2R catalyst, allowing for high current densities. The membrane separating the cathodic and anodic compartments is an anion exchange membrane (AEM), and will be the particular focus throughout this report. Combined with the AEM, porous silver has shown high selectivity of CO₂ reduction towards CO. There are alternative membranes such as cation-exchange membranes and bipolar membranes, but these have shown difficulties suppressing HER.

An ideal membrane for the purpose of this report possesses low ohmic losses, low gas permeability, prevents flooding of the cathode and leaking, and conducts exclusively hydroxides (OH⁻). Ohmic losses can be reduced by minimizing the membrane thickness, but a corresponding fragility comes with a thin membrane as well as product crossover. Water migration across the membrane causes the cathode to flood and eventually results in a mass transfer limitation of CO₂, therefore promoting hydrogen evolution reaction (HER).

Floodings have shown to be likely to occur at GDE cathodes of MEA devices due to migration of water across the membrane from the anode according to Weber et al.¹ The floodings are considered a threat as they cause CO₂ mass transport limitations and decreased utilization of the catalyst.

Earlier research has revealed CO₂ crossover across the membrane in the form of CO₂ neutralization to bicarbonate/carbonate (HCO₃⁻/CO₃²⁻) and formate (HCOO⁻), leading to a decrease of the cathodic outlet flow. The cathodic outlet flow should in essence be constant when converting from CO₂ to CO; nevertheless, there is an apparent correspondence between the reduction of CO₂ to CO and the reduced flow rate. Conversely, when HER dominates the flow rate increases due to the addition of gaseous hydrogen in the flow. If a concentration based detection technique such as gas chromatography is used, this issue causes an overestimation of the produced CO, as the molar flow rate is lower than expected. However this can be corrected for by simply measuring the outlet flow. The basis for this is as follows. OH⁻ is produced during ECO2R and HER:



The produced OH⁻ can react with CO₂ and result to form HCO₃⁻ and CO₃²⁻:



OH⁻ is indeed produced by HER as well, but HER usually becomes significant when CO₂ is mass transfer limited. The anodic gas outlet can be measured in order to confirm the CO₂ crossover, as the ions oxidize back to CO₂ over the anode:





The main charge carrier across the AEM can be found from the anode gas outlet. Due to stoichiometry the ratio between CO₂ and O₂ is 0, 2, or 4 for OH⁻, CO₃²⁻, or HCO₃⁻, respectively. The CO₂ crossover is considered a substantial disadvantage as it can reduce the maximum conversion (CO₂ derived product out/ CO₂ in) to no more than 50% for CO and even less for more highly reduced products such as ethylene and ethanol.^{2,3} Taking into account the CO₂ crossover and the amounts of CO₂ used for production of HCOO⁻ in contrast to the CO produced, there are some considerable drawbacks of the AEM based MEA configurations.

The purpose of this report is to compare various AEMs in order to find a membrane with the ability to conduct selected ions to reduce the CO₂ lost by crossover, along with the other criteria stated above. This could increase the efficiency of the MEA significantly.

2 SCOPE

The main goal of this deliverable is to demonstrate the effectiveness of the membranes produced by US. The data produced herein will be used by the SELECTCO2 consortium for a wide variety of purposes. For partners in WP2, WP3, and WP4 the traits and characteristics of these membranes will be useful to help meet the objectives of obtaining high selectivity to CO, ethanol, and ethylene respectively, and do so at a high energy efficiency. Furthermore WP6 will use this information to develop improved membranes. WP7 can use the characteristics to get insights into modelling water and ion concentrations and the effectiveness of the membranes will also be integrated into WP8 when applying a techno-economic analysis on this technology.

In this report AEMs are tested for MEA devices. Each assembly will be introduced to some standard measurements including: a pre-test starting with low current densities, a cyclic voltammetry (CV) and capacity measurement before and after the main experiment, and the main test of various current densities from 100 mA/cm² to either 250 mA/cm² or 300 mA/cm².

The idea behind the 15 minutes pre-test is to confirm typical behaviour, i.e. the potential and the resistance are within an expected range, and to increase the conductivity of the membrane.

The CV is performed in order to find a flat area for the capacitance measurement. The capacitance measurement is performed before and after the main experiment in an effort to measure your surface area and through this find out whether the cathode is flooded or not. The interface between a solid electrode and a liquid solution causes charge to store and consequently forms a double-layer capacitor. The difference between the capacitance of the interface before and after the experiment can give an evaluation of how substantial the flooding is, and this capacitance can give an interpretation of the effective surface area.

The main experiment is a 4-5 hour experiment depending on how high current densities are applied. If there are obvious floodings of the cathode high current densities are needless as HER starts to dominate. It is clear that the

cathode is flooded if the potential suddenly starts to fluctuate. The resistance is measured in between every potential step via impedance measurements.

Each current density is applied for an hour and within this hour, there is a 30 minute flow measurement and a single Gas Chromatography (GC) injection of the cathode and anode outlet. It is important to have outlet measurements of the cathode and anode in order to determine the CO₂ crossover and the main charge carrier. The Faradic Efficiency (FE) and Partial Current Densities (PCD) are also determined for each current density, and the exact flow rate is measured to ensure accurate results.

The membranes with highest performance were introduced to a 24 hour measurement in order to see how it degrades over time. These measurements were performed at a current density of 150 mA/cm². The best performing membrane was finally put under a 200 hour durability test.

3 DISCUSSION

3.1 The Radiation-Grafted AEMs (RG-AEM) used (synthesised at US) in this deliverable

For Deliverable 6.1, Surrey supplied six different radiation-grafted AEMs (RG-AEMs) to DTU for initial testing. The AEMs were prepared by the radiation-grafting of vinylbenzyl chloride monomer onto electron-beam activated ethylene-co-tetrafluoroethylene (ETFE) polymer films followed by amination with either: (1) trimethylamine (TMA), (2) *N*-methylpyrrolidine (MPY), and (3) *N*-methylpiperidine (MPIP). Two thicknesses of RG-AEM were produced with each of the three resulting head-groups: these were fabricated from either 25 μm or 50 μm ETFE precursor films (purchased from Nowofol in Germany). Hence six RG-AEMs were supplied (ion-exchange capacities, IECs, and water contents are given in Table US1): TMA25, TMA50, MPY25, MPY50, MPIP25, MPIP50. Note that it is not currently possible to provide the thicker RG-AEMs with the same IECs as the thinner RG-AEMs, as this would require higher electron-beam radiation doses for activation of the 50 μm ETFE films, and this would result in very brittle RG-AEMs that cannot be tested in electrochemical cells in a safe manner.

Table 1: A summary of the ion-exchange capacities and water contents (λ values) of the RG-AEMs supplied to DTU in D6.1. Errors for IECs and thicknesses are from measurements on $n = 3$ samples of each RG-AEM, while errors for λ are calculated from the errors in IEC and gravimetric water uptakes (using standard error propagation rules). More properties were reported in the D6.1 report.

| RG-AEM | TMA25 | TMA50 | MPY25 | MPY50 | MPIP25 | MPIP50 |
|--|-------------|-------------|-------------|-------------|-------------|-------------|
| Thickness(hydrated) / μm | 56 ± 2 | 95 ± 2 | 72 ± 2 | 106 ± 3 | 69 ± 3 | 95 ± 2 |
| IEC / mmol g ⁻¹ | 2.20 ± 0.02 | 1.63 ± 0.09 | 2.07 ± 0.05 | 1.56 ± 0.04 | 2.09 ± 0.07 | 1.45 ± 0.04 |
| λ (average H ₂ O molecules per +ve charge in AEM) | 8 ± 1 | 6 ± 2 | 22 ± 4 | 10 ± 1 | 23 ± 5 | 9 ± 2 |

3.2 Experimental Testing Procedure

The ECO2R device consists of a MEA with an AEM as illustrated in Figure 1A, with the exact details described in Ref ³. The system includes two support blocks, two copper current collectors, a titanium flow field at the anode side, a graphite flow field at the cathode side, two gaskets of 100 μm and 50 μm at the anode and cathode, respectively, the electrodes and a membrane. A three-electrode system was used for this purpose with a working electrode (cathode), a counter electrode (anode), and a Ag/AgCl reference electrode attached to the anodic compartment. Since the focus was just on membranes, a DTU designed reactor was used instead of the standardize reactor to allow the standardized reactor to be used for other catalyst testing. However for the 200 hour durability test, we did use the standardized reactor (produced by Milestone 1) because it gave better sealing, which was important in a 200 hour test. The cathode consists of commercially available porous Ag gas diffusion electrode (GDE) from Sterlitech Corporation with a purity of 99.97% and pores with a nominal diameter of 1.2 μm with a surface area of 4 cm^2 . The anode is IrO_2/C with a surface area of 7.29 cm^2 .

Figure 1B shows the overall experimental setup. A mass flow controller (MFC) provides a 40 sccm CO_2 flow for all measurements. The gas was humidified before entering the cathode, and any production of H_2 leads to higher flow

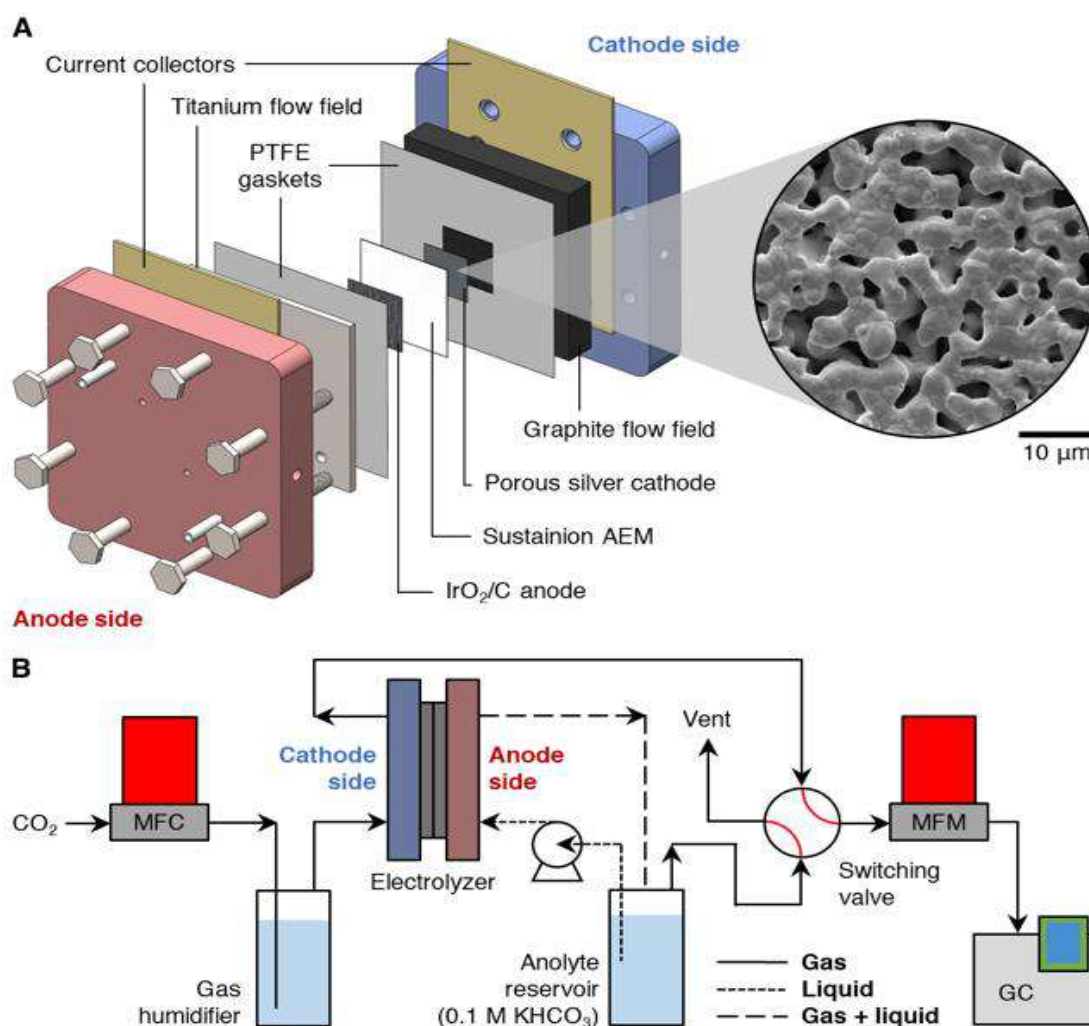


Figure 1: Cartoon describing the working set-up used for testing in this deliverable. Part A shows the reactor whereas part B shows the whole system. Figure taken from Ref ¹.

rates. A volumetric flow meter from BPC Instruments AB measured the cathodic and anodic outlet flow. The 0.1 M KHCO_3 electrolyte was pumped through the flow field at the anodic compartment.

For comparison, some experiments were performed with the commonly used Sustainion AEM. The behaviour of the MEA device is well-known using the Sustainion membrane, making it a suitable benchmark membrane. By making sure that the measurements are consistent to the expectations, it is, to some extent, possible to exclude external parameters. Hence the membrane will be the only variable for a more precise comparison.

The membranes produced by US were cut into 16 cm^2 pieces and prepared in 30 mL 1M KHCO_3 for 1 hour changing the electrolyte every 20 minutes. The preparation method was the same regardless of the membrane thickness and head group.

3.3 Testing with Different Head Groups

To help analyze the effectiveness of the membrane it is desirable to have following 1) selectivity versus current density, 2) CO_2 , O_2 , and CO_2/O_2 ratio as a function of current density on the anode and 3) current density versus voltage. We also try to determine 4) ohmic resistance in the membrane as a function of current if possible, however this information is also embedded in the total voltage, so we can see the effects of highly resistive membranes in that manner if need be.

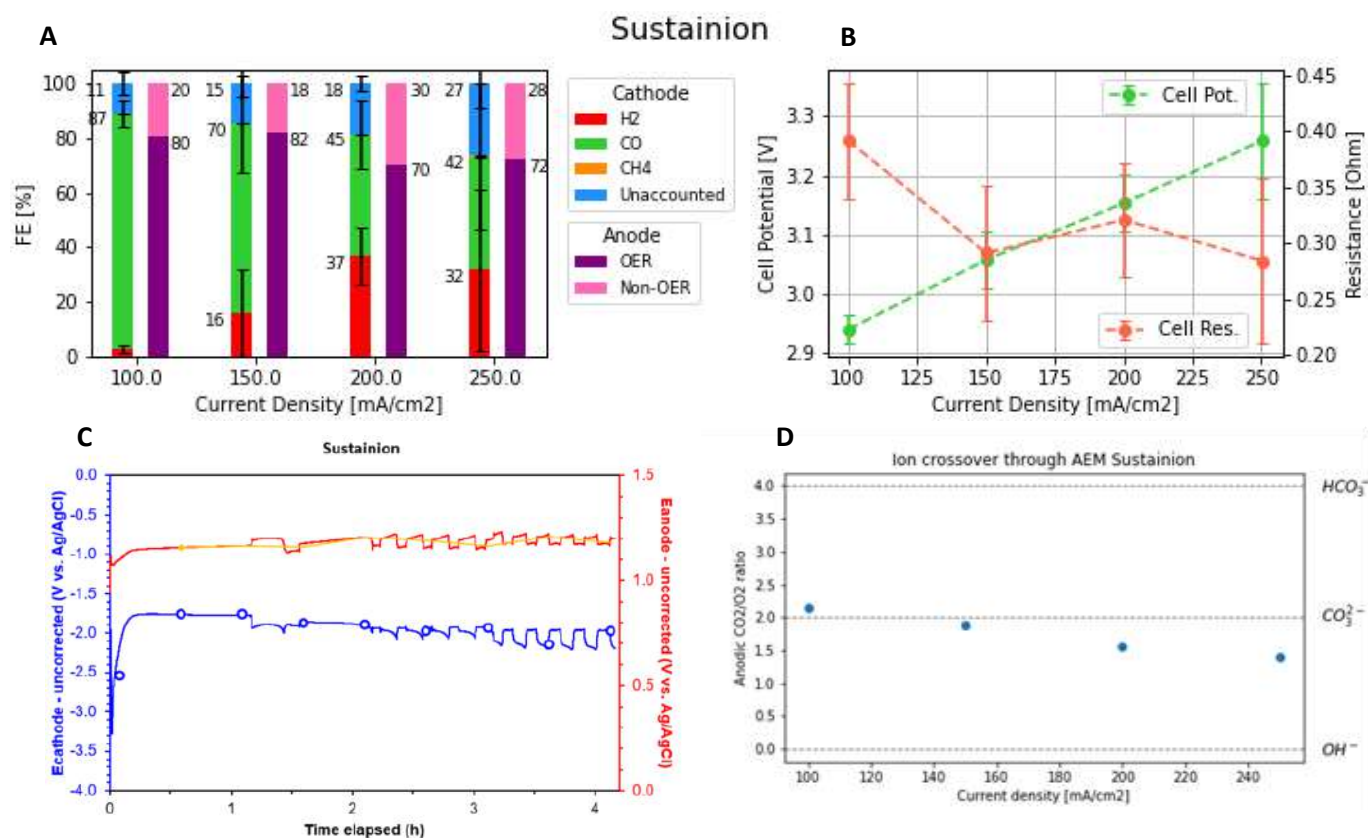


Figure 2: A) Faradaic efficiencies of Sustainion membrane at varying current densities. Both the products at the anode and cathode was measured. In these works the cathode catalysts was Ag and the anode catalyst was IrO_2 . B) The cell potential and ohmic resistance of the cell as a function of current density. C) Chronoamperometry tests operated at 200 mA/cm^2 where the potential is broken down into the anodic and cathodic components. D) The CO_2 to O_2 ratio as a function of current density. The right hand side shows the majority anion transferring through the AEM.

Three measurements were performed using a 50 μm thick Sustainion membrane to create a benchmark. Figure 2 shows the average cathodic and anodic Faradaic efficiencies and the resistance and cell potential, respectively. There were some obstacles with the anode measurements, and therefore, Figure 2A only shows anode measurements for a single experiment. The ion crossover is based on the fraction of CO_2 and O_2 from the anodic compartment, so Figure 2D is thus also only based on a single experiment.

The standard measurement with the Sustainion demonstrates a FE for CO of 87% at 100 mA/cm^2 but drops to 42% at 250 mA/cm^2 while HER begins to dominate. This correlation might be a consequence of water migration across the membrane. This would cause the cathode to flood leading to mass transfer limitations of CO_2 . As mass transport limitations seem to emerge the cell potential starts to oscillate, as Figure 2C illustrates. The dots in Figure 2C illustrate the moment where the GC injections take place. The selectivity will strongly depend on whether the GC injection takes place simultaneously with the potential value at the top or bottom of a fluctuation. At 250 mA/cm^2 assemblies with Sustainion have demonstrated FE of 62% (bottom) and 11% (top), thus indicating the extreme nature of these fluctuations in terms of selectivity.

A small fraction of the current goes to reduction of CO_2 to HCOO^- that is oxidized back to CO_2 at the anode. The “Unaccounted” in Figure 2A on the cathode side is thus most likely related to HCOO^- production. Oxidization of anions such as HCOO^- and any degradation of the carbon fiber based anode gas diffusion layer are accounted as Non-OER in Figure 2A.

The ion crossover is shown in Figure 2D by the CO_2 to O_2 ratio as a function of current density. CO_3^{2-} is the main charge carrier, since the ratio is above 2 for the first measurements and drops below 2 for current densities of 150 mA/cm^2 and higher. As CO_2 becomes mass transfer limited the OH^- becomes the main charge carrier, as a lower fraction of CO_2 is dissolved.

Figure 3 shows results for the three different head groups with a thickness of 25 μm ; MPY, MPIP, and TMA, respectively. Each experiment was performed twice using the same membrane. At least one experiment for each head group achieved successful cathodic and anodic measurements for current densities from 100 to 250 mA/cm^2 . All three show similar selectivities at low current densities. As the current density increases MPIP25 shows the best performance with a FE of 70% at 250 mA/cm^2 . TMA25 demonstrates the lowest FE of 45% at 250 mA/cm^2 . For current densities of 300 mA/cm^2 and higher, there is a tendency of HER becoming dominating concurrently with an increasing unaccounted products. Again, this is hypothesized to be correlated to the production and oxidization of HCOO^- as the amount of non-OER also increases.

The cell potential of the MPY25 shows a very counterintuitive trend in that as the current increases the potential actually decreases. However it should be noted when the current starts to increase this is when hydrogen evolution occurs. One effect that we hypothesized was happening is that at this point the MEA is becoming CO_2 limited for some reason (maybe flooding) and this is the reason for H_2 evolution. If there is a lack of CO_2 , then it would reason that the membrane would stop transferring carbonates, and switch over to OH^- . With OH^- conductivity through AEM known to be significantly more conductive than CO_3^{2-} ,⁴ this would decrease ohmic losses across the membrane, and thus decrease overall cell voltages. If one peaks ahead to Figure 5 and looks at the charge transferring across the membrane, this does show a switch from CO_3^{2-} to OH^- when the voltage starts to decrease, which gives some validation to this theory. However the extreme drop in voltages entails there is probably another effect as well. One other potential reason is that if the gas diffusion layer gets flooded, this will entail all the catalysts become active. Given that our Ag acted both as a gas diffusion layer and catalysts, once this becomes flooded the

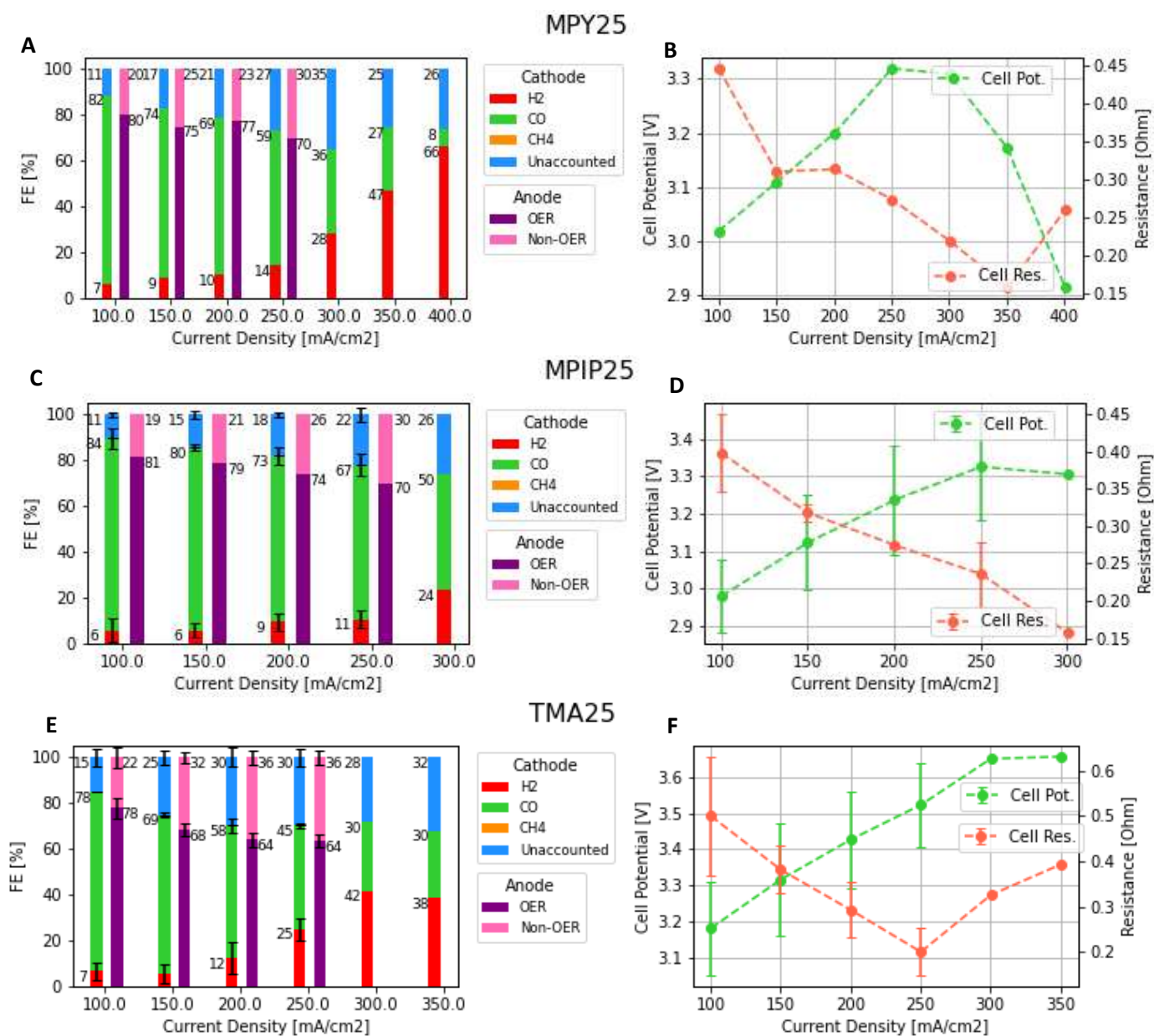


Figure 3: A, C, E) Faradaic efficiencies of various membranes as a function of current density. Both the products at the anode and cathode was measured. In these works the cathode catalysts was Ag and the anode catalyst was IrO₂. **B, D, F)** The cell potential and ohmic resistance of the cell as a function of current density. Figures A and B correspond to the MPY membrane, whereas Figures C and D correspond to the MPIP membrane, and Figures E and F correspond to the TMA25 membranes. All membranes were 25 μ m thick.

active catalyst area for electrolysis will greatly increase. Thus a drop in voltage may also be an effect of simply having much larger quantity of active catalyst sites when the gas diffusion layer is flooded.

The average cell potential and resistance are quite similar for all three membranes. The potentials are within the range of 3.1 to 3.5 V and the resistance is within 0.2 to 0.5 Ω throughout the experiment for all head groups. Nevertheless, there is a difference when observing the cell potential as function of time. Figure 4 shows the anode and cathode potentials as function of time for a variety of membranes as well as multiple experiments with the same membrane type. The difference between these two is the cell potential, but since the anode potential is rather constant the cathode potential can be representative for the cell potential behaviour.

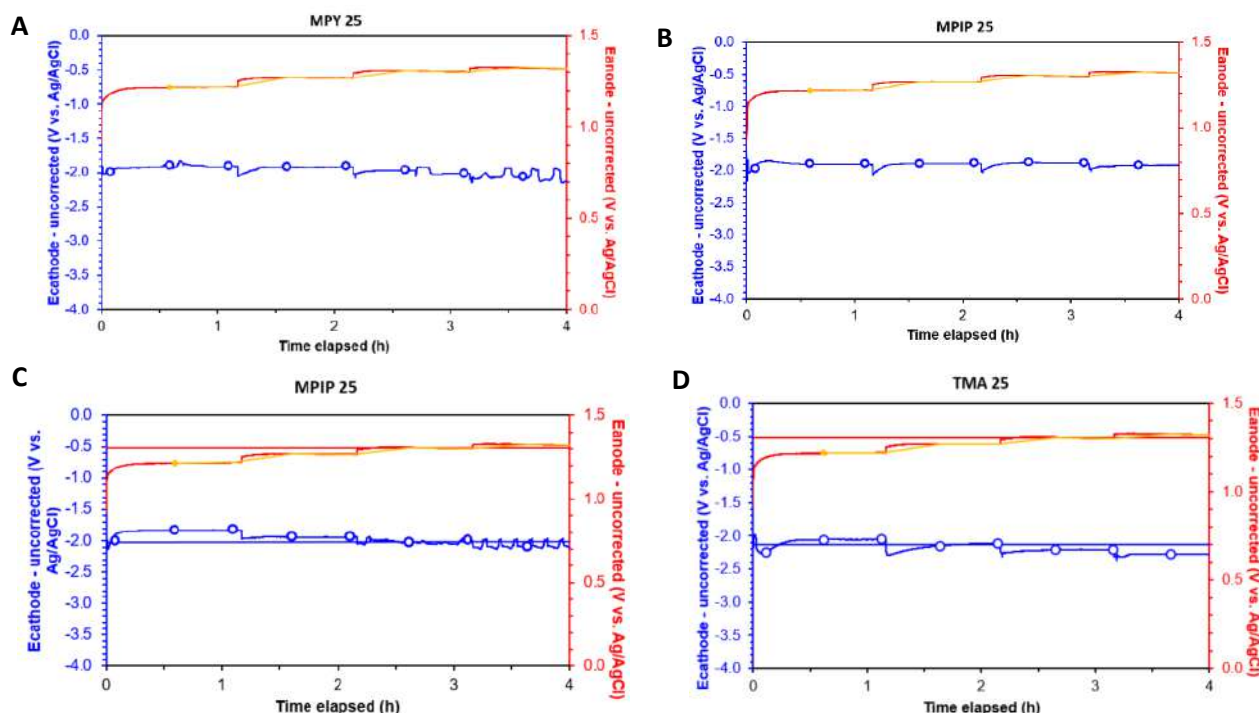


Figure 4: Anode and cathode potentials for a test with the MPY membrane (A), 2 different tests with the MPIP membranes (B, C), and a test with the TMA membrane (D). There are no obvious trends related to the membranes and the fluctuations.

The fluctuations appear for some experiments at high current densities. There are seemingly no consistencies between the presence of oscillations and a given head group. By comparing Figure 4B and Figure 4C with MPIP25 at 3 to 4 hours there are fluctuation for one of the experiments despite the fact that both demonstrate a FE of 70%. It is noteworthy that the GC injection took place at a bottom of the fluctuation. The cell potential of TMA25 in Figure 4D does not show any oscillations, and this was the case for both experiments. The cell potential of MPY25 shows oscillation towards the end, even though the FE is still around 60%, but the GC injection takes place at a low potential.

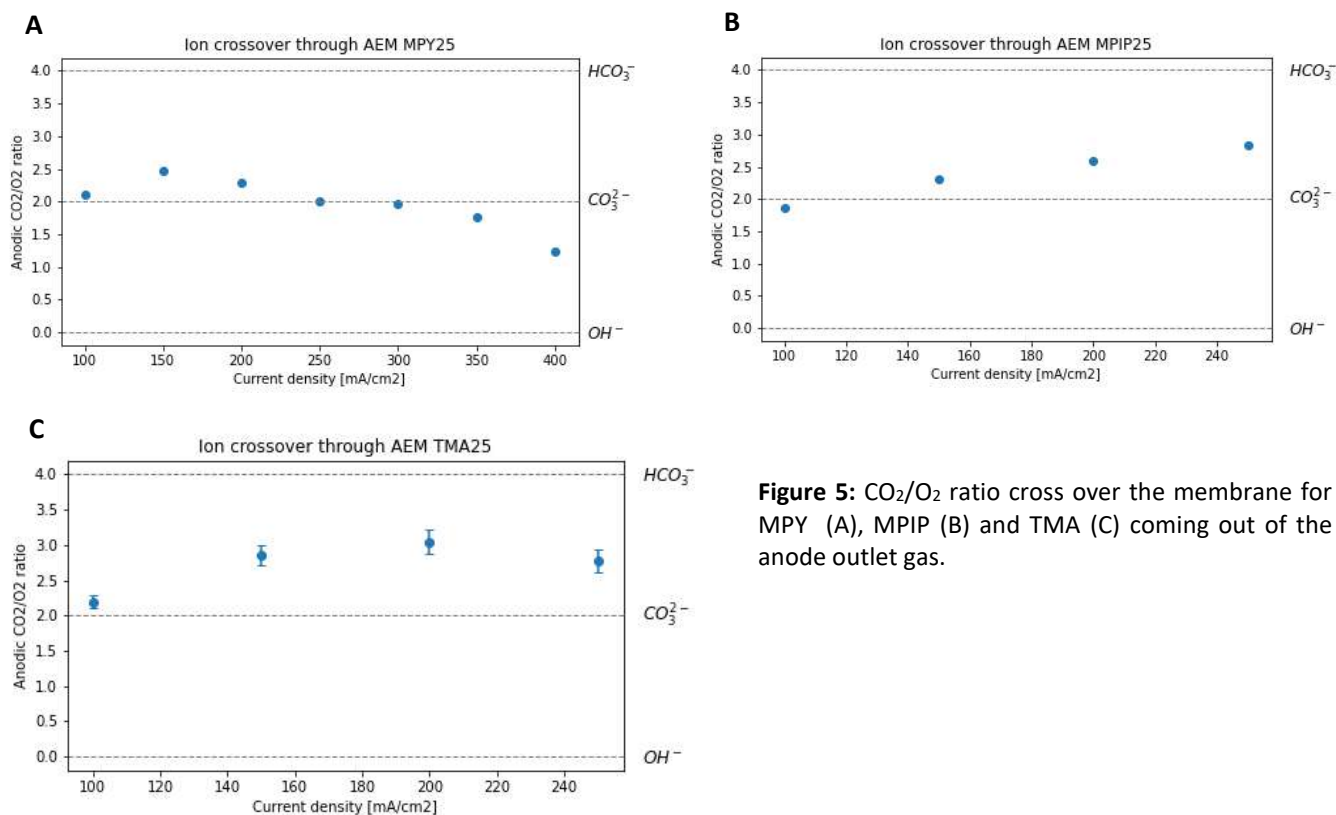


Figure 5: CO₂/O₂ ratio cross over the membrane for MPY (A), MPIP (B) and TMA (C) coming out of the anode outlet gas.

Figure 5 shows the ion crossover for the three head groups. TMA25 is the only membrane with two successful anodic measurements. However with the small standard deviations, we do not expect the general trends in the other two membranes to be distorted due to a single test. Here we see that the membrane to a larger extent conducts HCO₃⁻. For MPIP the CO₂ to O₂ ratio keeps increasing with the current density. Due to the stronger binding of carbonates compared to OH⁻ it is no surprise that we primarily have carbonate transfer across the membrane (i.e. CO₂/O₂ ratio of 2). We do see an increase of the CO₂/O₂ ratio as a function of current, which is a bit surprising since increased current density will provide a more alkaline environment which would favour carbonate even more than bicarbonate. Potentially CO₂ or carbonate could be seeping through the membrane not related to the ion exchange mechanisms or potentially there is undiscovered error in our data measurement procedures. In addition any formate production and concomitant anodic CO₂ evolution will appear here, thus increasing formate production will increase the CO₂/O₂ ratio as well. This is an area that will need further probing. However the main point is that we still have significant CO₂ crossover through the membrane in all tested membranes (both US and the benchmark Sustainion)

3.4 Testing with Different Thicknesses

Increasing from the 25 μm membranes initially used to a thicker 50 μm membranes gave significantly worse performance. We tested approximately 5 different membranes with most of them having exceedingly high voltages ($>10\text{ V}$) and were thus deemed inoperable. We did manage to have one TMA membrane that was functional and this is shown below in Figure 6. The selectivity was not good and we operated at 1 V higher than the 25 μm membranes until 250 mA/cm^2 where things went wrong. We are still struggling to figure out why these membranes are being so very ineffective. Nevertheless if a thinner membrane is already quite effective, there is no real need to investigate thicker membranes because this would be more expensive.

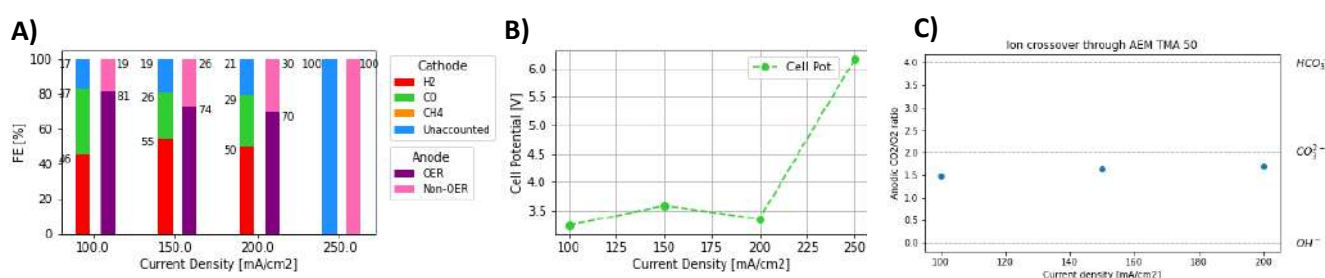


Figure 6: A) Faradaic efficiencies of the 50 μm TMA membrane as a function of current density. Both the products at the anode and cathode was measured. B) The cell potential as a function of current density C) CO_2/O_2 ratio on the anode outlet gas.

3.5 Durability Studies

The MPY, MPIP, and TMA membranes were tested for 24 hours to monitor their durability. Since we were using a porous commercial pure Ag catalyst/gas diffusion layer on the cathode and a commercial Dioxide Materials anode, we do not expect either of these to have notable degradations within a couple of hundred hours allowing us to have the durability focus just on the membrane. The electrochemical CO_2 reduction was done using the same procedures as previous, with the exception that rather than varying the current density, these samples were directly set to operate at 200 mA/cm^2 and then we monitored cathodic performance over 24 hours as well as the voltage profile. The selectivities of the MPY, MPIP, and TMA membranes as a function of time are shown in Figure 7, Figure 9, and Figure 12 whereas voltage profiles are shown in Figure 10, Figure 8, and Figure 12 **Error! Reference source not found.**, respectively. (Note in the voltage profiles for the anode and cathode we did not subtract off for any ohmic resistance.)

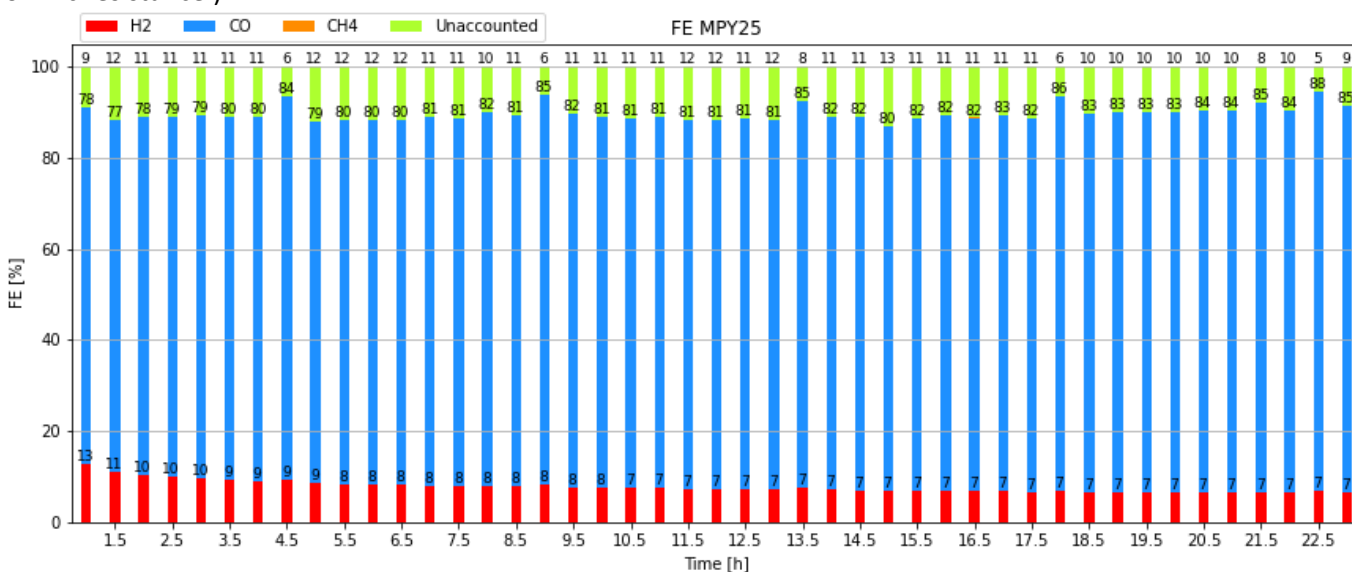


Figure 7: Product selectivity for a 24 hour test of 25 μm MPY membranes operating at 200 mA/cm^2 .

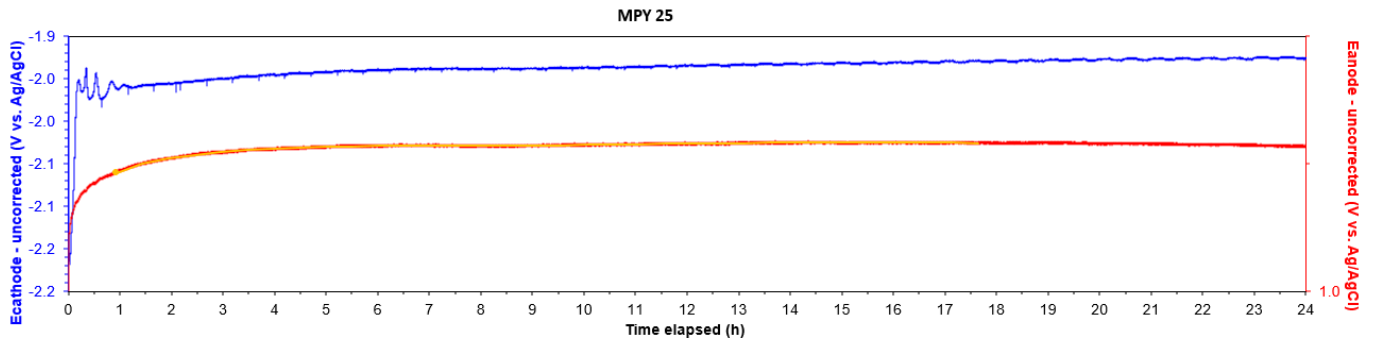


Figure 8: Voltage profile of the MPY membrane used in Figure 7.

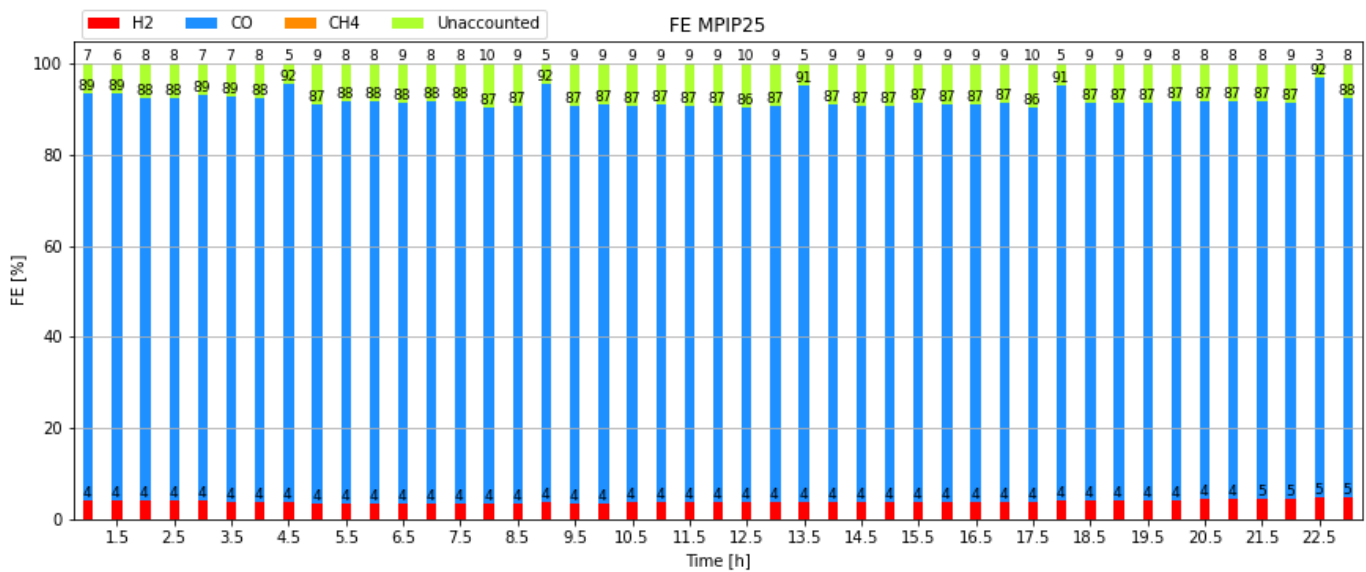


Figure 9: Product selectivity for a 24 hour test of 25 μm MPIP membranes operating at 200 mA/cm²

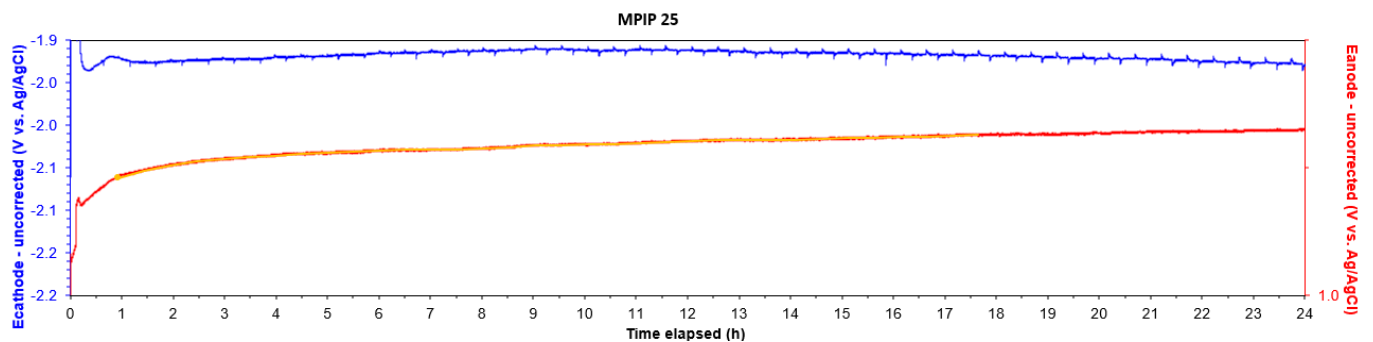


Figure 10: Voltage profile of the MPIP membrane used in Figure 9.

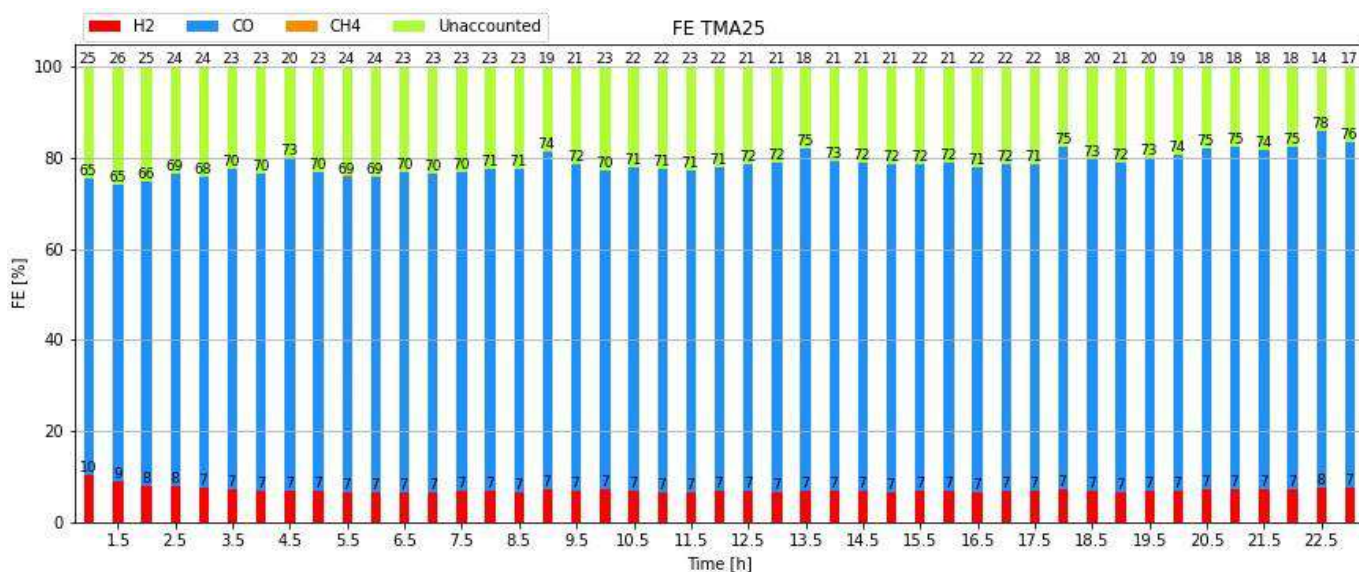


Figure 12: 24 hour test of 25 μm MPY membranes operating at 200 mA/cm²

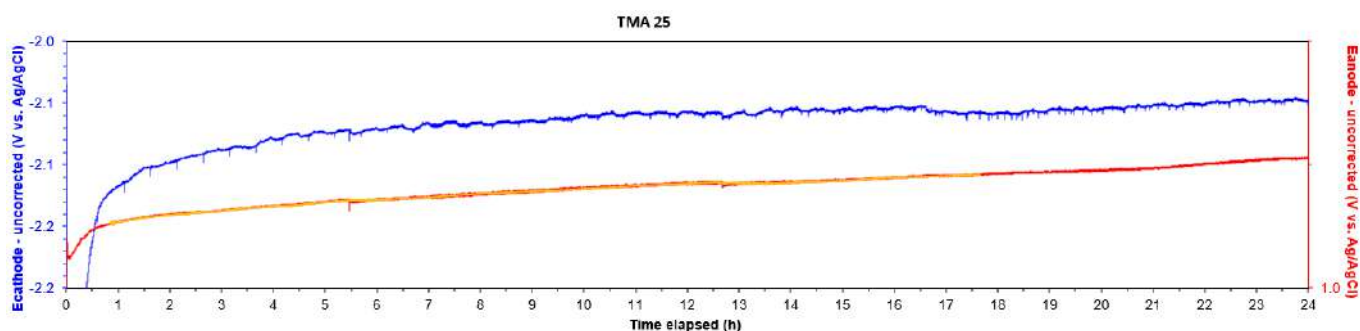


Figure 11: Voltage profile of the TMA membrane used in Figure 11

From these results we see very consistent performance. Both the MPIP and MPY membranes appear significantly better than the TMA membranes. The MPIP does operate at slightly lower overpotentials and have a higher selectivity to CO entailing these membranes are probably more conductive and induce a better local water management to help facilitate optimal CO₂ electrolysis versus water electrolysis as noted by 50% less hydrogen with the MPIP membrane. However the H₂ in both cases was quite small.

The 200 hour test was done in the standardized reactor rather than the DTU reactor since the DTU reactor had sealing issues, which led to the cell short circuiting after approximately 70 hours. The selectivity is shown in Figure 13. The slight difference in cell design may explain why there is a slight deviation in CO selectivity. Figure 14 shows the voltage profile throughout this test. This figure is a zoomed-in version of the potential showing that the operating potential varies by less than 5% during the entirety of the 200 hour test. The slight voltage jump at 180 hours occurred in the middle of the night, thus we cannot assess why this occurred. When we look at both Figure 13 and Figure 14 it is clear that these membranes are durable for at least 200 hours.

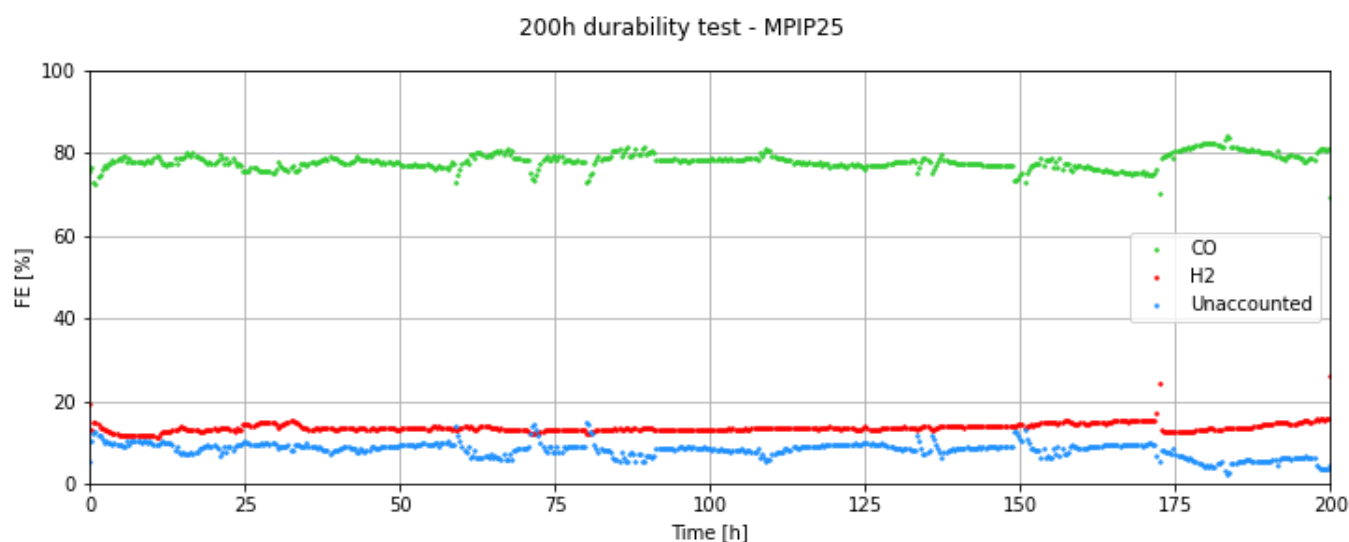


Figure 13: Product selectivity of a 200 hour test of a 25 μm thick MPIP membrane operating at 150 mA/cm^2 .

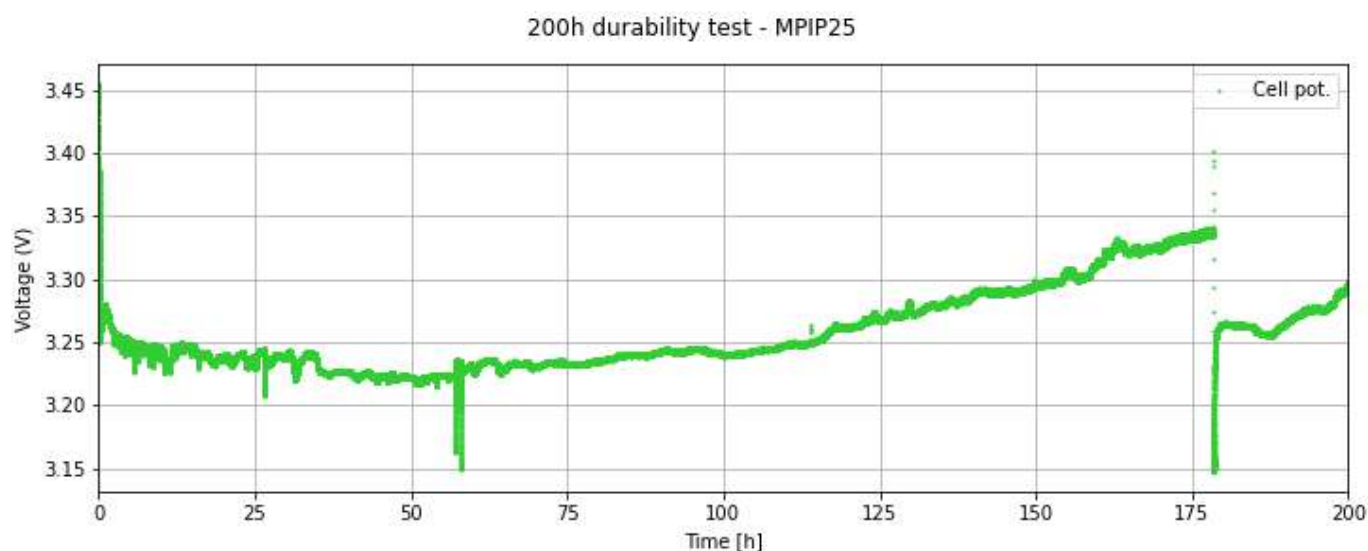


Figure 14: Voltage profile of the MPIP membrane used in Figure 13

4 CONCLUSIONS AND FUTURE WORK

With regards to membranes, there were three primary issues we focused on.

The 1st issue was whether water penetration through the membrane was too intense that it would flood the catalyst and then only hydrogen would be produced. From the selectivity results we did not see this was a major issue for the MPIP and MPA, however the TMA did show a slightly higher H₂ selectivity meaning this membrane may have a little more water penetration than the other ones. It should be noted that we always operated with a

humidified CO₂ stream and running a dry CO₂ stream or elevated temperatures could potentially have resolved this. This could potentially be followed up in future work if we find another reason to use this head group.

The 2nd issue related to the ionic conductivity in operational devices. Measuring resistance through impedance and total cell voltage gave us insight into this parameter. While the TMA had resistance and total cell voltage notably higher than the benchmark Sustainion membrane, the MPIP membranes were only slightly higher making this head group a very promising group to build on to improve performance.

The 3rd issue was analysing CO₂ crossover. While this is a very significant issues in the field, the CO₂ crossover was quite troublesome in these membranes, just like they were in the Sustainion. It was not surprising that there was a high CO₂ crossover, but it was a little interesting in that the crossover was higher than the typical 2:1 for carbonate crossover. This could potentially mean that the CO₂ electrolysis environment shifted to more neutral conditions, but since this ratio tended to increase with current density (and thus OH⁻ formation), that is highly unlikely. This may be due to a non-ion exchange mechanism to move CO₂/carbonate to the anode, however further tests would be needed to verify this.

The most important conclusion from this deliverable though was that the MPIP membranes appeared to show the most promise giving US a head group on which to base further membrane developments. The 200 hour durability is reassuring and validates that any issues relating to device performance in a standard 24 hour test will not be related to membrane stability issues.

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6 APPENDIX