





## SELECTIVE ELECTROCHEMICAL REDUCTION OF CO2 TO HIGH VALUE CHEMICALS

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## **DELIVERABLE REPORT**

6.6 – R	EPORT ON OPTIMIZED AE	Ms AND AEIs			
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SUMMARY	SUMMARY				
Keywords	Anion exchange membrane, electrochemical CO <sub>2</sub> reduction, anion exchange ionomers, reaction microenvironment, water transport, ionic conductivity, ion exchange capacity				
Abstract	This Deliverable demonstrates the effectiveness of the optimized US-synthesized anion exchange membranes (AEMs) and anion exchange ionomers (AEIs) with the following head groups: trimethylamine (TMA), <i>N</i> -methylpyrrolidine (MPY), and (3) <i>N</i> -methylpiperidine (MPIP). We conducted experiments using optimized anion exchanges membranes (based on the results of D6.3 and 6.5) with varying fundamental properties (IEC) and operational conditions (experiments at elevated temperatures). Additionally, we tested different CEIs and AEIs (including ionomer units used in AEM synthesis), coating them in single atom- or Cu-GDEs to quantify their effects on gas transport, product distribution, and stability during the performance at high current densities.				
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# DELIVERABLE 6.6 REPORT ON OPTIMIZED AEMS AND AEIS

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## **1** INTRODUCTION

Membrane electrode assemblies (MEAs) are commonly used in CO<sub>2</sub> electrolyzer devices at high current densities, as they operate efficiently due to their zero-gap design with gas-diffusion electrodes (GDEs). The catholyte compartment is filled with humidified CO<sub>2</sub>, while the anodic compartment is filled with a flowing electrolyte (usually a carbonate-based salt) to provide the necessary conductivity and cations. A membrane is placed between the electrodes to regulate water/ionic transport in the system. This approach can reduce the ohmic drop and overcome CO<sub>2</sub> mass transport limitations. However, some operational challenges, such as product crossover and water management, limit its stability and durability.<sup>1</sup>

The choice of IEM dictates the reaction environment and defines the ion-driven force across the system. Based on the charge and distribution of fixed ionic groups, membranes can be classified as cation exchange membranes (CEMs), anion exchange membranes (AEMs), or bipolar membranes (BPMs). The primary charge carriers for CEMs are  $H^+$  or alkali cations, while AEMs predominantly conduct  $OH^-$  or carbonate ions. In addition, CEMs are known for promoting primarily hydrogen evolution reactions (HER), whereas AEMs can achieve high selectivity for  $CO_2$  reduction products. Therefore, in the SELECTCO2 project, we have focused on developing a new generation of AEM for  $CO_2$  electrolysis along with some anion-exchange ionomers (AEI) for use in imparting ionic conduction in electrodes.

When the AEM/AEI is directly in contact with CO<sub>2</sub>E (MEA configuration), it is likely to affect the catalytic selectivity as it plays a significant role in ion/water transport, altering the local environment as well as pH and mass transfer properties. Therefore, some of the AEM/AEI features and properties must be optimized, which is why SELECTCO2 is interested in the development of such materials. AEM/AEI for CO<sub>2</sub> electrolysis should include high ionic conductivity, low electrical conductivity, optimized water contents and transport, inhibiting crossovers of undesired species across the AEM, mechanical and chemical robustness. The goal of WP6 (led by US), together with the collaboration of WP3 (led by DTU) and WP2 (led by TUB), was to develop AEM and AEI powders for CO<sub>2</sub> reduction applications.

Previous studies of this WP included synthesizing and testing different ETFE-based radiation-grafted AEMs (RG-AEM) with different functionalized headgroups, which resulted in some interesting trends between the cationic group, membrane properties, and CO<sub>2</sub>E performance. QA groups (TMA, MPIP, and MPY) in ETFE substate have exhibited desired transport, chemical, and mechanical properties, including high IEC (above 2 mmo/g), ionic conductivities, moderate water uptake, and low ohmic resistances (<  $0.6 \ \Omega \cdot cm^2$ ), with comparable performance to commercial ones. In D6.5, we showed that the addition of the MPIP heterocyclic headgroup in RG-AEMs exhibited improved thermal and chemical stability under different reaction conditions (e.g., temperature, pressure, or electrolyte concentration) and long-term operation for 200 h at >150 mA/cm<sup>2</sup> with high CO selectivity (80-85%) and cell voltage (-3.1 V) at ambient conditions. Detailed results of this research can be found in Deliverable D6.5 and our recent publication.<sup>2</sup>

Further studies in this WP focused on improving the MPIP-AEM by tuning its mechanical and chemical properties. Such modifications included the variation of the ion exchange capacity (IEC, to determine the optimal level), the introduction of covalent crosslinking agents, variations in the different amination procedures, or changes in different chemistries (using the same chemistries as Sustainion membranes). However, this is proving more difficult than anticipated, as none of these modifications positively affected CO<sub>2</sub> electrolysis apart from learning the need to raise IECs to higher levels. For example, adding crosslinking agents (TMHDA), or reducing the amine molar





concentration (stoichiometric) in the amination mixture used for fabrication, increased the cell potential and enhanced HER during operation. The results of the study are presented in Deliverable 6.3 of this project. While including these features was not considered for the final batches of AEMs for CO<sub>2</sub> reduction applications, further research has been conducted to optimize the synthesis method of new chemistry ETFE-MPIP-based RG-AEMs, as such strategies have proven to be beneficial in fuel cells, PEM, and alkaline electrolyzers.<sup>3</sup>

MPIP-AEMs have become the standard membrane for the SELECTCO2 project, extensively used in WP2-4, due to improved chemical stability at alkaline conditions, the ability to provide high IEC versions with facile transport of water, and ease of handling. As WP3 has extensively studied the effect of temperature in CO<sub>2</sub> electrolysis and demonstrated its potential advantages, new batches of AEMs have focused on improving thermal stability and optimizing transport properties. Those include the substitution of ETFE for LDPE as a substrate, as LDPE is thermally more stable and would allow operations at a temperature higher than 80°C, the testing of batches with higher IEC (2.1 mmol/g) and updated versions with tunable mechanical and chemical properties.<sup>2</sup>

The batches of new chemistry ETFE-MPIP-based RG-AEMs/AEI sent to DTU-EX were:

- 1. A batch of MPIP-based RG-AEM with the same chemistry as those sent in D6.1 but with different ionexchange capacities (IEC), controlled by modifying the content of inhibitor in the vinylbenztl chloride used in the grafting stage of RG-AEM fabrication.
- 2. A batch of TMA-based RG-AEM with LDPE as substrate (LPDE 25 um polyvinyl benzene (PVB) with TMA groups and IEC=2.1 mmol/g and DoG=66%) for conducting electrolysis at elevated temperatures.

The aim of these new batches of RG-AEMs for evaluation is to take advantage of operation at high temperatures with higher thermochemical and conductive membranes, suppressing electrode flooding while improving the ionic conductivity, product crossover, and overall catalytic activity. In addition, new batches have been prepared, optimizing the mechanical and transport properties (ion exchange capacity, water uptake, etc.). Studies of the AEM were done with Ag membrane catalysts using MEA configurations to ensure reproducibility and comparability with our previous results.

WP6 has also focused on synthesizing AEI powders for coating in the CL of the GDEs, as they are expected to influence the reaction microenvironment and mass transfer. Ionomers are ion-conducting polymers with functional groups that facilitate ion transport and whose functional groups are oppositely charged to the ions being exchanged. They comprise of polymer backbones and pendant functionalized groups, providing hydrophobic and hydrophilic domains. Their chemistry enables more cohesive ion and water transport pathways, increasing the activity at lower cell potentials, high ion conductivity, durability, and practicability. So far, numerous ionic groups (e.g., quaternary ammonium, imidazolium, phosphonium) and polymer backbones have been incorporated into AEIs. Still, few demonstrate satisfactory performance at high pH and temperatures, as many have limited chemical and mechanical instability or water accumulation.

The ionomers can influence selectivity due to their hydrophobicity, which regulates the electrowetting and water penetration on the catalyst surface. Furthermore, ionomers can modify the local concentrations of ions since their backbone chains provide hydrophobicity, and the charged moieties at the ends of the side chains regulate ion mobility.<sup>4</sup> By changing the microenvironment through ion transport, pH gradients are created at the electrode-electrolyte interface, suppressing mechanisms that utilize proton transfer as the rate-limiting step, thereby improving reaction selectivity. The pH gradients near electrode surfaces are explained by the mass transport system's inability to buffer the cathodic production of OH<sup>-</sup> ions. Therefore, it is possible to correlate the electrode *SELECTCO2 Deliverable Report D.6.6 – Report on optimized AEM and AEI - 28/02/2023 – Version 1* 





structure with restrictions in mass transport, manifested in local concentration gradients and further neutralization reactions, which influence selectivity during high current density operation.



Figure 1. Chemical structure of distinct ion exchange ionomer materials used in this Deliverable.

For this deliverable, we tested different CEIs (e.g., Nafion) and AEIs such as Sustainion methylimidazoliumfunctionalized styrene polymer (XA-9) or QA. QA stands for quaternary ammonium groups and includes the AEIs synthesized by the US (TMA, MPIP, MPY, TMIMID). The study of the ionomers has been divided into two primary studies. The first one was conducted by TUB, where they coated different ionomers in their NiNC catalyst layer, correlating the performance of cathode catalyst layers with their reactivity and stability in MEA electrolyzer cells. This study compared the performance using Nafion, Sustainion XA-9, MPY, MPIP, TMA, and PiperION with the MPIP-AEI obtaining a stable performance, yielding ~90% CO Faradaic efficiency up to 200 mA cm<sup>-2</sup>. Detailed information on these results can see in the manuscript submitted for this project titled "*Design of NiNC Single Atom Catalyst Layers and AEM Electrolyzers for stable and efficient CO*<sub>2</sub>-to-COelectrolysis: Correlating Ionomer and Cell *Performance*" (awaiting referee comments).<sup>5</sup>

The second study conducted by DTU included the same type of ionomers (CEIs and AEIs) but focused on Cu-GDEs. By coating ionomers in the CL, we also showed that electrodes with MPIP ionomers (10% wt.) exhibited a stable performance (as demonstrated in MS9 with a long-term performance for 200 h with higher selectivity towards carbon-derived products) at 200 mA/cm<sup>2</sup>. We attributed the such stable performance to enhanced gas transport, activity, and GDE durability by creating an optimal microenvironment, thereby reducing electrode flooding and improving mass transport rates and kinetic performance. In this deliverable, we present the results of the different ionomers, including characterization, loading studies, DLC measurements, and product distribution. In addition, DTU-EX received and tested new AEI powder containing tetramethyl imidazolium (TMIMID)-based chemistry (IEC =  $1.1 \text{ mmol g}^{-1}$ ). This is the same chemical found in Sustainion anion-exchange polymers from Dioxane materials, and it is expected to have a positive effect during the performance, as shown in the results of TUB using XA-9.

## **2 S**COPE

The main goal of this Deliverable is to demonstrate the effectiveness of the optimized AEMs, and AEIs produced by US. The SELECTCO2 consortium will use the data produced herein for various purposes. For partners in WP2, WP3, and WP4, the traits and characteristics of these AEMs will be helpful to meet the objectives of obtaining high selectivity to CO, ethanol, and ethylene, respectively, fulfilling the WPs goal. In addition, the same WPs will benefit from adding AEIs in the GDEs to enhance durability during the electrolysis. Finally, WP7 can use the characteristics to get further insights into modelling water and gas transport through the system.





In this report, new batches of AEMs are tested for MEA devices based on the results reported in D6.1, D6.3, and D6.5, while the AEI were tested from AEI powders synthesized by US and based on the chemistries used for the RG-AEMs. We tested these materials following an electrochemical protocol, including a pre-test starting at low current densities (to guarantee electrowetting), a cyclic voltammetry (CV) and capacity measurement before and after the main experiment. Also various current densities (100-500 mA/cm<sup>2</sup>) were tested. The main experimental time is around 1-2 hour experiment per each current density value if unspecified.

Deliverable 6.6 consists initially of a membrane screening at elevated temperatures (coming from the first batch of membranes with different chemistries). Then, AEM with different IECs from different batches was measured to evaluate consistency between batches and reproducibility in the experiments. Furthermore, RG-AEMs with TMA groups and different substrates (LDPE vs. ETFE) were tested to evaluate the effect of the substrate and whether the membrane could guarantee chemical stability at high temperatures. Finally, the membranes with the highest performance were introduced to a 24-hour test to see how they degraded over time. These measurements were performed at a current density of 200 mA/cm<sup>2</sup>.

AEI was tested over two types of catalysts, Ni-N-C and Cu-based electrodes. Characterization (through contact angle, hydrodynamic radius, and transmittance) was conducted. The preliminary test of these ionomers included linear sweep voltammetry (LSV) and chronopotentiometry, correlating the performance of the ionomers with their reactivity and stability in full single MEA electrolyzers.

## **3 RESULTS AND DISCUSSION OF ANION EXCHANGE MEMBRANES (AEM)**

#### **3.1 Experimental Methods**

#### 3.1.1 Materials

An Ag porous membrane with a nominal pore size of 1.2  $\mu$ m (Sterlich Inc., purity 99.97%, area 2.25 cm<sup>2</sup>) was used as the cathode for AEM testing, while Cu-based electrodes on DN908 or SG39BB were used in the ionomer testing. The anode was a commercial IrO<sub>2</sub>-coated carbon paper electrode (Dioxide Materials). The AEM were the developed MPIP RG-AEMs from US, or commercial membranes such as Sustainion.

#### 3.1.2 EC-reactor setup (Cell configuration)

The experiments were conducted on a commercial electrolyzer (Dioxide Materials) using a zero-gap MEA configuration. The assembly included loading a fresh AEM between the electrodes with PTFE gaskets for electrode protection and electrical insulation. The cell bolts are fastened with an estimated torque of 4 Nm to guarantee sufficient compression and avoid leakages into the system.

#### 3.1.3 Electrochemical Tests

The CO<sub>2</sub> gas-feeding rate (AGA, purity 4.5) in the cathode was set using a volumetric flow controller (Red-y from Voegtlin) and further humidified by sparging into a container filled with Millipore water. The anode side was fed with 0.1 M KHCO<sub>3</sub> or CsHCO<sub>3</sub> (Sigma-Aldrich, 99.995% trace metal basis) and recirculated continuously using a diaphragm pump (KNF). Another diaphragm pump for gas and liquids (KNF) was also used for the recycle line and the control of the reflux ratio. The power source was a potentiostat (Bio-Logic VSP 300 with booster unit) operated in galvanostatic mode. The standard conditions for gas flow in this work are 293 K and 1 bar, with Ag/AgCl as the





reference electrode. For high-temperature operations, a heating oven with a PSU/box interfaced with a Raspberry Pi and Audrinos was used with a PID controller. A 230 heater (GPIO pin) was connected to thermocouples for temperature measurement. A homemade Python program developed at DTU controlled the recycle loop and the reaction temperature in the reaction system.

## 3.2 Testing of new MPIP-batches (with different IEC) for CO<sub>2</sub>/CO reduction

#### 3.2.1 Electrochemical CO<sub>2</sub> reduction

As previously demonstrated in our D6.5 and MS11, the US-synthesized membranes present a new generation of AEM with  $CO_2R$ -specific properties. Experiments in both these reports have been performed at RT. For this reason and given the interest in running experiments at elevated temperatures (part of WP3), experiments with these new batches were performed primarily at  $60^{\circ}C$ .



Figure 2. 24 h experiment using Ag-based electrocatalysts and the new MPIP-AEM batch.

As shown in Figure 2 measurements of the MPIP-1.8 exhibited higher selectivities towards CO ( $FE_{CO}$ = 83% at 200 mA/cm<sup>2</sup>), with a stable cell potential of -2.8 V during the experiment and only minor oscillations during the experiment (ca. 100 mV). These results agree regarding stability and performance with those previously reported in this project. Differences in terms of ion exchange capacity (IEC) do not tend to be so significant since the previously reported data were performed using other membrane batches with higher IEC (2.1 mmol/g). However, as seen in D6.2 (in experiments comparing MPIP-1.7 and MPIP-2.3), there were no significant variations in cell voltage and selectivity (D6.2).

## 3.2.2 Electrochemical CO reduction

Given the multiple benefits of performing CO reduction over CO<sub>2</sub> electroreduction (in terms of stability and selectivity) and trying to achieve the objectives of WP3, we performed a series of experiments using CO. These experiments included the use of the MPIP-1.8 and were explicitly performed to test the versatility of these membranes for these applications as well. In addition, our experiments were performed using different substrates, including SG39BB at RT (Figure 3) and using one of DENO's formulations (WP5 in Figure 4).







Figure 3. Product distribution and cell potential profile of sputtered Cu-GDE in SG39BB in 0.1 CsOH overtime at 200 mA cm<sup>-2</sup>.



**Figure 4.** Product distribution and partial current density at different current densities using sprayed Cu-GDE DG88/77 in 0.1 KOH.

Both results show the versatility of this new generation of membranes for CO reduction. Figure 4 shows that the selectivity towards ethylene is around 25%, maintaining a constant value throughout the experiment. Likewise, the HER values are less than 10% Faradaic efficiency, which serves as a preliminary indication to show how these membranes' mechanical and transport properties help to modulate water management in the system. Since the experimental time in Figure 4 is much shorter than that typically implemented (and that within this range, any mechanism related to flooding may not be significantly observed), additional experiments were performed for different current densities (100-600 mA/cm<sup>2</sup>). Results obtained from these experiments showed stable operation, with no signs of potential electrode flooding even at high current densities. Surprisingly, our experiments have shown a selectivity greater than 80% for  $C_{2+}$  at 600 mA/cm<sup>2</sup> (with HER being less than 8%), demonstrating that some materials explicitly designed for this project (AEM from WP6 and GDL from WP5) enhanced the overall catalytic performance. It should be noted though that we attribute this breakthrough in high current density more to improvements in GDE than via the membrane.





#### 3.3 Testing of AEM at elevated temperatures

#### Initial screening of membranes at elevated temperatures

Given the results shown in D3.3 about the benefits of kinetics and mass transport in CO<sub>2</sub> electrolysis at elevated temperatures (even at 80°C), we were interested in continuing our operation in such conditions to reach SELECTCO2 goals. However, the operation at high temperatures is limited due to the chemical degradation of these materials, compromising water transport and influencing the membrane's microstructure. For this reason, we carried out measurements under elevated temperatures using different membranes and showing how temperature influences the AEM and the catalytic performance. We implemented PiperION, TMA-AEM (denoted as TMA25 from D6.5, which key properties are found in Table S1 Sustainion X37-50 RT, and MPIP-1.7 for conducting these experiments.



**Figure 5.** Screening of different AEM at 80°C regarding product distribution and cell potential profile using commercial porous Ag electrocatalyst at 200 mA/cm<sup>2</sup>.

The results in Figure 5 corroborate the limitations of current membranes for operation at high temperatures, where the PiperION membrane shows an increase in cell potential (of around -1 V overpotential) and a decay in stability. Interestingly, Sustainion X37-50 RT degraded more rapidly because the imidazolium headgroups failed to withstand these conditions, resulting in an increase in HER and the short-circuiting of the system (thus explaining the very low voltages). Furthermore, the membranes (TMA and MPIP) synthesized by US show a better operational performance, whereas the MPIP membrane provided the best performance in terms of lower cell potential (-2.85 V) and stable product distribution (around 80% towards CO) over a longer experimental time. For this reason, our experiments at higher temperatures (>80°C) were performed only with the MPIP membranes.

#### Testing new MPIP-AEM batches at higher temperatures

As previously discussed, new membranes (in this case, MPIP-1.7) were implemented for experiments at temperatures greater than 80°C to analyze their effectiveness. Initially, we conducted an experiment where we operated at 90°C for around three hours at 100% relative humidity, avoiding any potential dehydration of our membranes. Then, the other experiments were conducted at near 100°C over two different conditions (one experiment at 100% RH and the other dry).







**Figure 6.** Testing of MPIP-1.7 AEM at 90°C and 100°C regarding product distribution and cell potential profile using commercial porous Ag electrocatalyst at 200 mA/cm<sup>2</sup>.

Results from Figure 6 showed a stable operation (in terms of cell potential with a range of around -2.76 V) even at 90°C for the MPIP-AEM. However, the selectivity towards CO started to drop after 1 hour (from 82% to 15% at the end of the experiment), which we attributed to a water imbalance effect and the water activity in the gas phase compared to the liquid phase (detailed explanation and analysis of the temperature effect in the water management for  $CO_2$  electrolysis is discussed in D3.3, and our recent membrane review paper<sup>6</sup>). At 100°C, a fast degradation of the membrane was observed with the limited operation of less than 30 min for both scenarios.

Under these operating conditions, it is difficult to predict if the degradation is an effect of the functional group or if it is directly related to the substrate (ETFE). For this reason, US proposed the substitution of the substrate by LDPE, which is the one implemented in membranes for alkaline electrolyzer applications. Likewise, the variation of the functional group was made since TMA is a thermostable group that has also been previously reported in the literature.<sup>7–9</sup> Therefore, two different batches of this LDPE-TMA RG-AEM were sent to DTU to evaluate if these different components allowed operation at high temperatures (both have similar IEC, with the first being 1.80 mmol/g and the other 1.85 mmol/g).

Initially, LPDE TMA-AEMs were tested at 60°C to see if they were suited for elevated temperature operation. Then, both batches were tested for 24 hours at 200 mA /cm<sup>2</sup>, not showing significant differences in product selectivity (both started to have stability issues after 15 hours, with HER being dominant). However, in terms of cell potentials, the first batch showed some potential oscillations during the first hours of experiments (providing an overpotential of 200 mV compared to the MPIP-AEM and 250 mV compared to the second batches). Such differences aren't fully understood, but we might attribute them to differences in IEC between the samples and batches.







**Figure 7.** Testing of different LPDE-TMA AEMs batches at 60°C regarding product distribution and cell potential profile using commercial porous Ag electrocatalyst at 200 mA/cm<sup>2</sup>.

Even though these membranes do not perform better than those described in MS11 or with the MPIP-AEM (MPIP-2.1) in terms of water management and stability, they were subsequently tested at different operating temperatures. Preliminary experiments with this membrane at ambient conditions showed a stable operation (-3.1 V and selectivity towards CO higher than 70% at 200 mA/cm<sup>2</sup>) for 14 hours. Further experiments at higher temperatures and 100% RH showed, to some extent, benefits on this membrane batch compared to the MPIP-AEM. At 90°C, the MPIP-AEM lasted just three hours before seeing a selectivity change from CO<sub>2</sub>-derived products to HER. Finally, at 100°C, we could run the experiment for 4 hours. Despite having stability issues, the potential profile was stable during electrolysis, pointing to the benefits of LDPE as substrates and addressing the challenges of AEM for elevated temperature CO<sub>2</sub> electrolysis.

Finally, to demonstrate the applicability of these new AEMs batches, we switched from Ag-based GDE to Cu-GDE following the WP3 objectives. The standard measurement with the MPIP-1.8 showed, at 200 mA/cm<sup>2</sup>, an increased selectivity of CO (as expected due to the effect of temperature related to CO-desorption) initially. However, HER begins to dominate over time. This correlation might be a consequence of water migration across the membrane, causing the cathode to flood and leading to CO<sub>2</sub> mass transfer limitations. As mass transport limitations emerge, the cell potential starts to oscillate, as previously observed in multiple experiments conducted at DTU.<sup>10</sup> However, comparing the performance of these new batches with the first batches sent by US, the performance of the first batch was superior compared to the MPIP-1.7 (the one used for the experiment presented in Figure 9), which might be related to the differences between the radiation sources (Covid forced a switch in the use of electron-beam facility) and variation in some fundamental AEM properties.







**Figure 8.** Testing of LPDE-TMA AEM at ambient conditions., 90°C and 100°C regarding product distribution and cell potential profile using commercial porous Ag electrocatalyst at 200 mA/cm<sup>2</sup>.



**Figure 9.** Testing of MPIP-1.7 AEM using Cu-GDE in SG39BB at 60°C and results of main liquid and gas product distribution, including the cell potential at 200 mA/cm<sup>2</sup>.

#### 4 **RESULTS AND DISCUSSION OF ANION EXCHANGE IONOMERS (AEI)**

#### 4.1 Characterization

For Deliverables 6.1 and 6.2, US supplied RG-AEMs made via grafting of vinylbenzyl chloride monomer onto electron-beam activated ethylene-co-tetrafluoroethylene (ETFE) polymer films followed by amination with either:





trimethylamine (TMA), *N*-methylpyrrolidine (MPY), and *N*-methylpiperidine (MPIP). Results of key properties of these membranes are reported in D6.1. Subsequently five RG-AEMs were supplied (Table US1) with similar thicknesses: MPIP-1.7, MPIP-1.8, TMA, MPIP-2.1, and LPDE-TMA. For the AEIs, six different ionomers were tested, including Sustainion XI-9, MPIP RG-AEI, TMA RG-AEI, MPY RG-AEI, PiperION, and TMIMID RG-AEI, while Nafion and PTFE were also used for the experiments. For the AEIs, TUB conducted measurements of AEI-coated electrodes through contact angles, hydrodynamic radius, and transmittance (detailed data can be found in the newest TUB manuscript)<sup>5</sup>.

**Table 1** A summary of the ion-exchange capacities for RG-AEMs used this this report. Errors for IECs and thicknesses are from measurements on n = 3 samples of each RG-AEM. More properties were reported in the D6.1 report.

RG-AEM	TMA25	<b>MPIP-2.1</b>	LPDE-TMA	<b>MPIP-1.7</b>	MPIP-1.8
Thickness/ μm	56 ± 2	69 ± 3	51	52	54
IEC / mmol g <sup>-1</sup>	$2.20 \pm 0.02$	2.09 ± 0.07	2.1 ± 0.03	1.7 ± 0.04	1.81 ± 0.03

Table 2 A summary of the key properties of the different AEIs. More properties of these RG-AEIs are found in D6.2

RG-AEI	MPIP	ТМА	MPY	Sus XA-9	Pip	Nafion
Particle size / µm	$1.18 \pm 0.11$	1.96 ± 0.21	1,11 ± 0.12	N/A	N/A	N/A
IEC / mmol g <sup>-1</sup>	1.85 ± 0.05	2.09 ± 0.01	2.00 ± 0.02	0.95	2.4	0.93



**Figure 10.** Hydrodynamic radius and Transmittance of the dilute catalyst ink with different ionomers. Pictures of the contact angle of the gas diffusion electrode with different ionomers: a) without ionomer, b) Naf, c) Sus, d) PPI, e) MPY, f) TMA, and g) MPIP. Data adapted from the TUB manuscript.<sup>5</sup>

Dynamic Light Scattering (DLS) was used to characterize the catalyst ink. The average hydrodynamic radius of the catalyst powder, accompanied by different ionomers, is shown on the left axis of Figure 10. It was found that all ionomers could maintain a constant radius of around 300 nm for 10 min before the hydrophobicity was lost (comparable to the spray-coating time). However, MPY, TMA, and MPIP led to agglomeration when extended to 40 min. On the right axis of Figure 10, ink transparency represents the average powder concentration and stability of the suspension. All inks showed no phase separation within 40 mins. This can be attributed to their differing intrinsic chemical structures, added crosslinking in Sustainion (Sus), main-chain cations for PiperION (Pip), and polycationic





grafts for MPY, TMA, and MPIP groups. When bound to catalyst powders, these differences lead to structural, porosity, and morphologies variations.

#### 4.2 Testing

For the ionomer testing, we divided this Deliverable into two main sections, testing using single-atom catalysts (tests conducted by TUB) and Cu-based catalysts (performed by DTU).

#### 4.2.1 Ionomers over single atom-based catalysts

We compared six different ionomers for these experiments, one of which was a cation-exchange Nafion (Naf) and the other five being anion exchange ionomers (AEIs). These included polystyrene-vinylbenzyl-methylimidazolium (Sus), poly(arylpiperidinium) (PIP), and three ETFE-based radiation-grafted AEIs with benzyl-N-methylpyrrolidinium (MPY), benzyltrimethylammonium (TMA), and benzyl-N-methylpiperidinium (MPIP) cationic headgroups. Ionomers fulfil several roles in the CL, such as immobilizing the catalyst particles on the GDL surface (binder), altering the wettability, creating porous structures to improve mass transfers, and increasing ionic conductivity.

Characterization of the electrodes revealed only minor differences in catalyst ink states (average powder size and suspension state) over a short period. In addition, measurements of the electrochemical active surface area (ECSA) showed that Naf and Sus offered only half of the double-layer capacity compared to other ionomers, which might be related to the hydrophobic nature. Performance tests of H-Cell and MEA cells were conducted from -50 mA/cm<sup>2</sup> to -500 mA/cm<sup>2</sup> at 45 °C with 15 wt% ionomer loading. H<sub>2</sub> and CO were the major products, with a Faradaic efficiency sum of above 90% with the H-cell. In experiments using an H-cell at low current densities, the CO activity were similar, indicating similarities in intrinsic reaction kinetics and exposure of the active sites independent of the ionomers.







**Figure 11.** The catalytic performance of NiNC-IMI-based GDEs with different ionomers in MEA- electrolyzer. a) Faradaic efficiency of CO, b) Faradaic efficiency HER, c) cell potential (without iR-correction) as a function of applied current density, and d) CO partial current density as a function of cell potential. **Reaction condition**: electrolyte flow: 20 mL/min, 0.1 M KHCO<sub>3</sub>; cathode gas flow: 60 mL min humidified CO<sub>2</sub>; both chambers are separated by our RG-E-MPIP-AEM; reaction temperature: 45°C.

However, different selectivity trends were observed with the MEA configuration, such as Naf only having 50%  $FE_{co}$  and needing higher cell potentials (~ -3.5 V for 50 mA/cm<sup>2</sup>). This difference is due to the incompatibility between the cation exchange headgroups in the ionomer and the anion exchange groups in the RG-E-MPIP-AEM at 45 °C, which restricts the through-plane mass transfer during the reaction. Therefore, this screening of different ionomers showed that its chemistry (ionomer headgroups) plays a significant role in the MEA-electrolyzer.

Those could be expected as Nafion, with cation exchange headgroups, could be attached to the AEM headgroups and form a bipolar junction at the CL interface, blocking the through-plane transfer during the reaction. Fortunately, AEIs deliver better synergy with the RG-E-MPIP-AEM, exhibiting the best performance of all the RG-AEIs provided by US. Using electrodes coated with this ionomer, around 80% selectivity towards CO at 200 mA/cm<sup>2</sup> was obtained at a lower cell potential, showing some conductivity and mass transfer benefits in principle. The correlation between selectivity, stability, and IEC values becomes less significant at higher current densities. For example, Sus, with an IEC of 0.9 mmol/g, achieved promising  $FE_{co}$  at 300 mA/cm<sup>2</sup>. In contrast, TMA, MPY, MPIP, and the commercial PPI with IEC values of 2.0, 2.0, 1.85, and 2.4 mmol/g, respectively, resulted in improved mass transfer (according to cell potential) but caused "rapid flooding" during the reaction, impeding the transfer of CO<sub>2</sub> in the CL.





Therefore, it is possible to conclude that hydrophobicity is more critical than the IEC of the ionomers for the NiNC-IMI powder catalyst.



**Figure 12.** Stability test of NiNC-IMI-based GDEs with different ionomers in MEA-electrolyzer. Faradaic efficiency of CO ( $FE_{CO}$ , red, left axis), Faradaic efficiency of H<sub>2</sub> ( $FE_{H2}$ , blue, left axis), and cell voltage (grey, right axis) at 200 mA/cm<sup>2</sup> current density as a function of time. NiNC-IMI-GDE a) without ionomer, with b) Naf, c) Sus, d) PPI, e) MPY, f) TMA, and g) MPIP.

Finally, a stability test of electrodes with different ionomers was conducted at 200 mA/cm<sup>2</sup>. The bare electrode (without ionomer on the CL) constantly kept above 95% for CO for around 10 hours and displayed a gradual degradation after that (along with a rise in cell potential). Remarkably, in this comparison, the Sus ionomer was found to improve the stability to 15 hours, although its performance drastically collapsed afterward. On the contrary, the other AEIs only shortened the stability to about 5 hours. In conclusion, only the Sus AEI and TMA RG-AEI positively contributed to the catalytic reactivity, while only the Sus could extend the stability.

#### 4.2.2 Ionomers over Cu-based catalysts

Preliminary experiments of the ionomers have been conducted at DTU using AEIs in sputtered-based electrodes. Still, those showed limited performance over a short period due to inadequate ionomer loading and deficiencies in the coating method. Therefore, managing the proper coating loading and using the nanoparticulate approach instead (to keep consistency with the electrodes prepared by TUB) enable us to study the effect of different ionomers on CO<sub>2</sub> electrolysis over Cu-GDE.







**Figure 13.** : Catalyst screening through polarization curve a). Effect of different CEI and AEIs in Cu-GDE b). Effect of the ionomer loading in the catalyst activity, and c). Product Distribution of  $CO_2$  with Cu-based electrodes coated with different ionomers at 200 mA/cm<sup>2.</sup>

We first investigated how ionomer-coated Cu affects  $CO_2R$  by performing linear sweep voltammetry (LSV) at different potentials to compare the activity of bare Cu with various Cu/ionomer catalysts (Figure 13a). According to polarization curves, all catalyst containing ionomers significantly enhanced the  $CO_2$  reduction current (a 2-fold increase in total current). It was found that adding ionomers increased the activity by two-fold for Cu/PTFE, 2.8-fold for Cu/Nafion, and three-fold for Cu/MPIP compared with Cu-GDE. While LSV scan time is too short for conducting product analysis, further experiments corroborated that even at 200 mA/cm<sup>2</sup>, samples with HER remained below 10%, compared to bare Cu, which increased up to 60%. Adding ionomers in the CL might increase activity toward  $CO_2$  electrolysis caused by hydrophobicity, transport enhancement, and electric field effects. Although the reason behind this increase in current density has been thoroughly studied for this project, some literature reports have shown that PFSA or QA ions promote  $CO_2R$  through specific non-covalent interactions with  $CO_2$  intermediates (\*CO stabilization).<sup>11</sup> The effect of gas availability on gas transport has been confirmed by Garcia de Arquer et al.<sup>12</sup> and Møller et al.<sup>13</sup> through different reaction mechanisms (COR or ORR), showing such effect and reduced ionic resistance.

Furthermore, the ionomer loading was found to impact the synthesized electrodes' performance significantly. Cu/Nafion, a well-studied ionomer for  $CO_2$  reduction, was used for this study to assess the effect of the ionomer layer thickness. It was discovered that the dramatic impact of ionomer loading on the synthesized electrodes was independent of the ionomer's chemistry (Figure 13b). An increase of the loading by 10 µg/cm<sup>2</sup> caused the current density to reach 250 mA/cm<sup>2</sup> at -3 V. Loadings above 20 µg/cm<sup>2</sup> resulted in lower performance, which is likely due





to increased diffusion resistance, as increasing quantities of ionomer in the catalytic layer become a barrier to the mass transport of reactive species.

Regarding product quantification, we performed chronopotentiometry experiments at 200 mA/cm<sup>2</sup> with different CEIs and AEIs. We conducted experiments at this current density, as we have found it as a threshold for GDE-flooding, which could be interesting to evaluate the ionomer role over such conditions. Results in Figure 13c showed slight differences in the selectivity of  $C_1$  and  $C_{2+}$  for electrodes with the ionomer compared to bare Cu- GDE. The use of TMA and MPY ionomers seemed to enhance the HER (FE<sub>HER</sub>=>35%), related to their high WU and IEC. MPIP, PTFE, and Nafion showed higher selectivity towards carbon products than bare-Cu (with MPIP-AEI achieving 65% selectivity towards  $C_{2+}$  products).

In terms of ionomer chemistry, we observed minor differences between the use of CEIs or AEIs, as the distribution of products towards Cu-MPIP and Cu-Nafion has not shown any significant difference (in selectivity and cell potential). To decouple the effects on the ionomer the following logic was used. AEIs are expected to increase the local  $CO_2/H_2O$  ratio, whereas CEIs impede carbonate species from entering the catalyst microenvironment. Accordingly, the enhanced selectivity of  $C_{2+}$  products using MPIP and Nafion ionomers can be attributed to Donnan exclusion at the interface between Cu and the ionomer. This is due to the difference in background charge, which is positive for MPIP and negative for Nafion.<sup>14,15</sup>



**Figure 14.** Tracking the electrode flooding by DLC measurements as a function of the Ionomer content and current density using MPIP-AEI.

We were also interested in evaluating ionomers' effects in the DLC (Figure 14). At current densities above 200 mA/cm<sup>2</sup>, a rise in capacitance when using bare Cu was attributed to high electrowetting and GDE flooding; spikes in capacitance corresponded to an increase in HER product quantification. However, when an ionomer was added, the electrode's capacitance decreased. This is because the ionomer reduces the water/electrolyte viscosity and surface tension at the surface, allowing less water penetration through the catalyst layer.<sup>13</sup> Comparatively, samples with 10% wt. of MPIP showed more than a 2.5-fold decrease in capacitance from bare Cu (vs. 1.17 mF/cm<sup>2</sup> vs. 2.87 mF/cm<sup>2</sup>).





#### A new generation of AEI (TMIMID ionomer)

Finally, US synthesized a new ionomer powder (imidazolium-based) with similar chemistry to that provided by Sustainion XA-9, named TMIMID. For experiments with this ionomer, we just conducted chronopotentiometry measurements (200 mA/cm<sup>2</sup>) as a metric to compare the performance between the different ionomers with this new chemistry (Figure 15).



**Figure 15.** Testing of TMIDID using Cu-NPs in SG39BB and results of product distribution of main gas products, including the cell potential at 200 mA/cm<sup>2</sup>.

An exciting trend was observed during the performance of electrodes coated with TMIMID ionomer. A stable cell potential (around -3.05 V) is seen during the first 8 hours, with only minor changes in selectivity for the main products, with the HER kept below 10% and ethylene selectivity maintained (15%). Nevertheless, we noticed a voltage drop followed by potential spikes after 8 hours. After stabilizing the potential, HER increased slightly, reaching around 80% after 20 hours. Similar trends were observed by TUB using Sustainion XA-9 (which has a similar AEI chemistry).

#### **5 CONCLUSION AND FUTURE WORK**

The below summarises the work done on this deliverable and the WP6 of SELECTCO2:

- The use of cycloaliphatic groups (MPIP) in RG-AEMs still proved to be thermal and chemically stable under different reaction conditions and achieved stable operation over a long experimental time.
- The ionomer headgroups play a significant role in the MEA-electrolyzer. The CEI exhibits above 50% faradaic efficiency to unwanted HER and demands more potential for certain currents in single atoms catalysts. However, coating Nafion in Cu-based electrodes showed similar results to the MPIP-AEI.
- New AEM batches intended for high temperatures can achieve operation at 90°C but still exhibit losses in stability and selectivity over time.
- The substitution of substrate for AEM had minor effects on selectivity and cell potential, but it was less susceptible to chemical degradation while operating at elevated temperatures.
- There wasn't a correlation between the stability, selectivity, and The IEC of the ionomers during the operation at high current densities. For single atoms, Sustainion XA-9 delivered the most promising results (with a stability of around 15 h).





#### **Future work**

- An LDPE-MPIP RG-AEM will be fabricated so that there can be a more direct comparison of change in substrate (LDPE vs. ETFE). Since the Covid-derievd change in e-beam facility, LDPE could not be grafted.
   However, the most recent e-beam session (Dec 2022) has now been optimised so that LDPE can be grafted.
- Additional synthetic optimisations will be undertaken to ensure that ETFE-based MPIP RG-AEMs are consistently synthesid with IEC > 2.0 mmol g<sup>-1</sup>. This will allow for more large batches of final formulation MPIP-AEMs to be sent to partners, including to allow them to use a SELECTCO2 developed AEM beyond the project for additional impact.
- Final invetigations into RG-AEM+RG-AEI combinations, keeping in mind that the chemistry and IEC of the RG-AEIs may well be different to those of the RG-AEMs in optimised CO<sub>2</sub>E or COE cells.

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