SLUTRAPPORT

Recyclable Low Noble Metal Content MEA for Hydrogen Production

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RE:
SOURCE

Slutrapport för projekt:

Recyclable Low Noble Metal Content MEA for Hydrogen Production

Engelsk titel: Recyclable Low Noble Metal Content MEA for Hydrogen Production

Projektperiod: 2022-08-15 - 2024-08-30

Datum: 2024-10-28

Projektnummer: P2022-00344

Diarienummer: 2022-200512

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Nyckelord: 5–7 st: Elektrolys, katalys, membran, iridium, PFAS, vätgas

RE:Source är ett strategiskt innovationsprogram och finansieras av

VINNOVA Energimyndigheten FORMAS

Förord

Projektet finansierades av Energimyndigheten inom ramen för innovationsprogrammet Re:source. RISE Bio- and Organic Electronics anlitades för att utföra en LCA-analys.

Umeå universitet har anlitats för testning utav Cellfions membran i elektrolysörer.

RISE Elektrifiering och Pålitlighet – Energiomvandling anlitades utanför ramarna för detta projekt för att mäta gasbarriär hos Cellfion's membran, resultaten inkluderades i denna rapport baserat på dess höga relevans för projektet. Umeå universitet har anlitats för testning utav membran i elektrolysörer utöver det som ingick i detta projekt, där resultaten visade sig ha betydelse för detta projekt varför de nämns i denna rapport.

List of abbreviations

CCM – Catalyst coated membrane

CNF – Cellulose nanofibrils

EDX – Energy dispersive X-ray spectroscopy

EI – Environmental impact

HER – Hydrogen evolution reaction

HFR – High frequency resistance

GDE – Gas diffusion electrode

GDL – Gas diffusion layer

GWP – Global warming potential

HiPIMS – High power impulse magnetron sputtering

LCA – Life cycle analysis

MEA – Membrane electrode assembly

MPL – Micro Porous Layer

OER – Oxygen evolution reaction

PEM – Proton exchange membrane

PEMWE – Proton exchange membrane water electrolysis

PFAS – Per- and polyfluoroalkyl substances

PGM – Platinum group metals

PTE – Porous transport electrode

PTL – Porous transport layer

SEM – Scanning electron microscopy

TEM – Transmission electron microscopy

TGA – Thermogravimetric analysis

XRD – X-ray diffraction

Innehåll

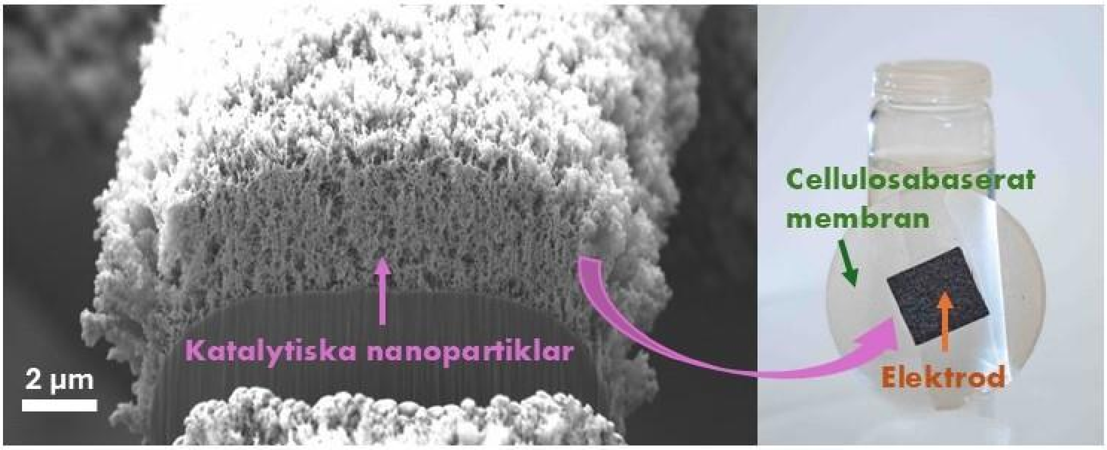
1. Sammanfattning

Protonledande membranelektrolys (PEMWE) är ett hållbart sätt att producera vätgas som potentiellt har en viktig roll att spela då användningen av vätgas som bland annat en energibärare ökar. Förutom energibärare behövs vätgas inom flera sektorer och användsningsområden och idag framställs vätgas med väldigt stora CO_2 utsläpp. Dock så använder dagens PEMWE teknik membran innehållande per- och poly-fluorerade alkylsubstanser (PFAS) samt relativt sett stora mängder av ädelmetallerna iridium och platina.

I detta projekt undersöktes möjligheten att producera mer hållbara membran-elektrod-kombinationer (membrane-electrode assembly, MEA) för elektrolys genom att kombinera biobaserade PFAS-fria membran från Cellfion med Ionautics depositionsteknik för katalyspartiklar vilken har potentialen att kraftigt reducera användningen av den mycket dyra ädelmetallen iridium.

I början av projektet utvecklades nanopartiklarnas katalytiska förmåga parallellt med membranens mekaniska och protonledande egenskaper. Som nästa steg benchmarkades de respektive komponenterna gentemot state-of-the-art material i ett PEMWE system. Slutligen kombinerades de två olika teknikerna och sammanfogades till MEAs vars prestanda också testades i PEMWE. Den generella slutsatsen är att Ionautics katalytiska skikt och Cellfions protonledande membran fungerar bra tillsammans, och kan användas för vätgastillverkning via PEMWE-teknik. Dock behöver den totala resistansen hos MEAt reduceras ytterligare för att på allvar kunna utmana nuvarande state-of-the-art. Potentiella sätt att få ner den totala resistansen har identifierats och kommer vara en del av den fortsatta utvecklingen. I projektet har även de olika komponenternas potential att bidra till en mer cirkulär affärsmodell undersökts genom marknadsundersökningar samt framtagande av en LCA-rapport. Denna rapport indikerar att båda teknikerna har stor potential att bidra till en minskad global warming impact för PEMWE-system.

Parallellt med projektet har ett flertal potentiella kunder för tekniken testat Ionautics extremt porösa iridiumoxid material i användning med traditionella PFAS-baserade membran med goda resultat. Cellfion är i kontakt med ett flertal kunder som har visat intresse att testa membranen och vill vara med i den fortsatta utvecklingen.



Vänster: SEM-bild (tvärsnitt) av IrO2 nanopartiklar på en Ti fiber. Höger: Cellulosabaserat membran med integrerad elektrod.

2. Summary

Proton exchange membrane water electrolysis (PEMWE) is a technology to produce sustainable hydrogen gas, which potentially has an important role to play with the growing use of hydrogen gas for example as an energy carrier in society. Beside the use as an energy carrier, hydrogen is crucial for several processes and applications and today, hydrogen is produced with vast emissions of CO_2. However, the current commercial PEMWE includes membranes containing per- and polyfluoroalkyl substances (PFAS) as well as relatively large amounts of noble metal such as iridium.

In this project we investigated the possibility of producing more sustainable membrane-electrode assemblies (MEA) for PEMWE by combining PFAS-free membranes from Cellfion with Ionautics technology for deposition of catalyst nanoparticles, which aim to reduce the amount of metals such as iridium and platinum needed in the system.

In the beginning of the project the catalytic performance of the nanoparticles was developed in parallel with the mechanical structure and proton conductivity of the membranes. As a next step, the components were individually benchmarked against state-of-the-art materials in a PEMWE system. Finally, the two techniques were combined and assembled into an MEA, which was also evaluated in PEMWE. In conclusion, Ionautics catalytic layer and Cellfions proton conducting membrane performes well together, and can be used for hydrogen production using PEMWE. However, the total resistance of the MEA needs to be further reduced in order to really challenge the current state-of-the-art. Potenital ways to do this have been identified and will be part of further development. In the project the circular business model for the components has also been evaluated through business case studies and an LCA report. This report indicates that

both technices has the potential to contribute to reducing the global warming impact of PEMWE systems.

In parallel with this project, several potential customers have tested and evaluated the extremely porous iridium oxide layer from Ionautics, with traditional PFAS-based membranes, with good results. Cellfion are in contact with several potential customers who have shown an interest in testing the membranes and to take part in the continued development.

3. Introduction and background

With the effects of climate change becoming more evident, the world's eyes are drawn to alternative and renewable energy storage and conversion technologies. Amongst these, hydrogen is considered the swiss army knife of energy with applications ranging from decarbonising energy-intensive industries such as steel production to storage of renewable energy. However, the best available option for producing carbon-free hydrogen, PEMWE (proton exchange membrane water electrolysis) from intermittent electricity sources such as wind and solar, is yet to be efficient or cost-effective enough to provide a viable business case. Simultaneously, the PEMWE technology's core, the MEA (membrane electrode assembly), is dependent upon expensive platinum group metals (PGM) such as Ir and Pt and a PFAS containing Nafion membrane. In fact, only 8 tons of Ir are extracted each year and if PEMWE hydrogen installations were to reach the goals set by governments, with the current noble metal content, 10-50 tons more of Ir would need to be extracted than what is possible (Minke et al 2021). The MEA does not only stand for the unsustainable usage of noble metals, but it is also the key component of PEMWE. The MEA is, therefore, the main contributor to the critical performance parameters of the electrolyzer; efficiency and lifetime.
The issue of over usage of Ir is well understood in the industry with multiple research groups and companies intending to solve the problem (HOW workshop 2021). However, solutions that intend to eliminate the usage of Ir have been proved to not work in PEMWE's harsh environments and earlier methods intended to lower the amount of coated Ir nanoparticles are not scalable and are sensitive to many parameters such as dispersion concentration, flow rates, Nafion content, making high quality and reproducibility difficult (ibid). Ionautics have tackled these issues by leveraging proprietary technology that combines HiPIMS (a physical vapour deposition technique industrially used for producing thin films) with the HiPNano (a cluster source producing nanoparticles). Together these technologies make it possible to both tailor-make nanoparticles and to collect them in extremely porous layers. In this project porous layers of IrO_2 have been successfully applied on a range of substrates such as Cellfion membranes, PFAS membranes and on to pourous transport layers (PTL). To succesfully enable sustainable large-scale usage of PEMWE it is necessary to recycle and reuse the noble metals and membrane materials. Currently the membranes limit the recycling possibilities as they are based on PFAS materials. To date, there isn't an effective commercial way to recycle the membrane. Current

methods lead to the incineration and the release of toxic gases such as hydrogen fluoride. These gases cause serious health issues if breathed in. Challenges also arise with the performance of membranes during the production of green hydrogen, due to a phenomenon called crossover (the transport of the wrong molecules) through the membrane, which leads to the production of un-pure hydrogen and degradation of devices over time. The membrane therefore also affects the efficiency of the PEMWE. Together, the membrane and the two electrodes constitute the MEA that is the core of PEMWE. Apart from individually affecting critical performance parameters, the proper integration between the two is crucial for efficiency. In 3-5 years, the MEA is expected to stand for up to 50% of the total electrolyzer cost (information from customer contacts). By contributing to lower noble metal content and increasing efficiency, the project also contributes to lowering the barrier for adopting PEMWE and hydrogen in the short run. From a long-term perspective, the project aims to work as a key enabling technology for PEMWE and scalable, carbon-free, production of hydrogen by lowering the noble metal content and applying a circular business model.

The result of this project has benefits for several audiences throughout the value chain, foremost our customers that design and develop PEMWE. From customer interactions, it is clear that the need for high performing, cost-effective and sustainable MEA's are the bottlenecks of their devices. If these issues are solved it would lead to a competitive edge and support the growth of these clean energy devices. The close collaboration with market players such as H-tec (LOI), PlugPower (mutual agreement) etc. further facilitates the possibility of rapid commercialisation. These companies have provided clear specifications on the critical performance parameters needed for purchase and also offered help with support in testing etc. so that these can be reached.

The project also presents Sweden with the opportunity to increase partnerships between SMEs that have emerging technologies and develop a sustainable value chain in Sweden for one of the world's fastest-growing markets. Critical performance parameters of the electrodes (efficiency and lifetime) are highly dependent on their integration with the membrane. Further, the economic attractiveness and scalability of the electrodes depend on them being used circularly, as they still contain noble metals. The construction of an MEA represents a higher combined value than the two technologies can produce independently and will facilitate faster adoption.

4. Implementation

This project was conducted within four separate work packages:

1. Development of nanoparticle catalysts and integration with the membrane for PEM
2. Production and characterization of CNF membranes
3. Validation of the MEA in a PEMWE cell
4. Development and preparation for enabling a Circular Business Model

Work package 1 was conducted at Ionautics laboratory at Linköping University. Membrane samples were sent from Cellfion for the parts of the work package which involved the study of the deposition of nanoparticles onto the surface of the PFAS-free membranes.

Work package 2 was conducted by Cellfion at the company's laboratory in Stockholm.

Work package 3 was conducted at Ionautics laboratory at Umeå University. Samples were sent from both Ionautics in Linköping and Cellfion in Stockholm to be tested in this work package.

Work package 4 was conducted by Ionautics and Cellfion in collaboration. RISE was contracted to perform a life cycle analysis. The work with the life cycle analysis was organized as a project where Ionautics, Cellfion and RISE worked collaboratively with regular meetings.

4.1. Development of nanoparticle catalysts and integration with the membrane for PEM

The original focus of this work package was to develop a catalytic material based on Ni and Pt for the HER reaction of the PEMWE. However, through discussions with experts in the field and potential customers, it was realized that the main bottleneck in the PEMWE is the OER reaction, and the use of the noble metal Ir. Therefore, the focus of this work package was shifted to develop the catalysts for the OER reaction, with the goal to drastically decrease the use of Ir within these. Ionautics has been in charge of this work package, and the work was carried out by combining two of their products, the HiPSTER 1 and the HiPNano. A sputtering technique called HiPIMS was combined with a hollow cathode target material, resulting in the growth of nanoparticles within the volume of a vacuum chamber.

In order to optimize the conditions for the PEMWE cell tests in WP3, a lot of collaboration and feedback between WP1 and WP3 has been carried out. Some of these are:

- Introducing O_2 into the nanoparticle growth as a reactive gas to grow nanoparticles of IrO_2, as this is the most stable form of Ir to use in the OER reaction.

- Increasing the sample sizes possible to produce from about 1 cm^2 to >5 cm^2. The reason for this was to be able to evaluate the produced nanoparticles in the PEMWE cell, as this had a size of 5 cm^2.
- Evaluating the optimal substrate to coat for assembling into an MEA. The alternatives are to either put the nanoparticles onto the membrane, or to put the nanoparticles onto a PTL. The PTL and the membrane are then sandwished together with the cathode to shape a 5-layered MEA as shown in Figure 1.

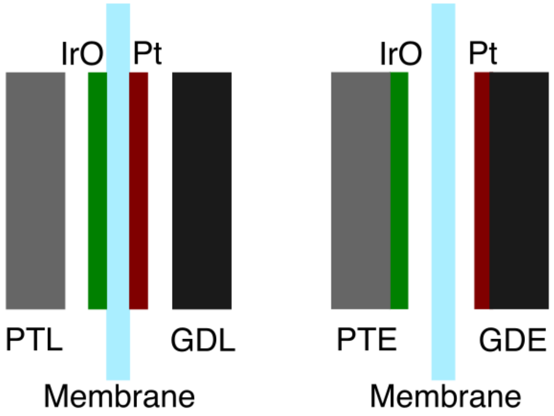


Figure 1 Two different types of 5-layered MEAs where the electrocatalysts (IrO, Pt) are coated either on the membrane (left), or on the PTL and GDL (right).

- Evaluating different GDLs, and additional protective coatings on these, to improve the performance of the full MEA.

4.2. Production and characterization of CNF membranes

In work package 2 proton conducting membranes based on chemically functionalized cellulose nanofibrils were developed and characterized. The development and production of the membranes, as well as the characterization of fundamental membrane properties were all performed by Cellfion.

The starting material in Cellfion's membrane production process is bleached softwood pulp, from which functionalized cellulose nanofibrils are obtained via chemical and mechanical processing steps. In the chemical modification step the cellulose fibres undergo chemical reactions in which functional groups are introduced into the material. These functional groups will contribute to the properties of the final membrane, and will also induce swelling of the fibers which will facilitate the mechanical processing step and reduce the related energy consumption.

In the mechanical processing step the functionalized fibers undergo high-pressure homogenization during which the cellulose nanofibrils are released from the fiber walls. The cellulose nanofibrils are obtained as a water-based gel, from which membranes can be produced via several different methods such as filtration, casting or coating, followed by drying. Membrane properties can additionally be modified via additives to form composites, or by post-modifications.

Membranes with different types of chemical functionalizations were developed with the purpose of identifying the functionalization route which would give the most beneficial membrane properties for PEMWE. In total, four different chemical modification routes were investigated during the course of the project. Additionally, the effect of some additives and post-treatments was studied. Membrane properties such as ionic conductivity and ionic selectivity were obtained and could later be correlated to the membrane performance in PEMWE, which was studied in work package 3, to give a deeper understanding of the relation between fundamental membrane properties and electrolyzer performance.

4.3. Validation of the MEA in a PEMWE cell

To evaluate the electrochemical performance of the Ir coatings, three-electrode cell measurements were conducted where the half reaction OER could be analyzed individually. These measurements only require active areas of 0.2 cm^2, and therefore was practical to begin with while developing high quality larger area coatings. The electrodes used in these experiments were standard rotating glassy carbon electrodes as well as home-made PTL electrodes, resembling those that are used in a PEMWE. In the three-electrode setups, a reference electrode (Ag/AgCl) and a counter electrode (Pt) were used to control the half-cell potential. The electrolyte was 0.5M H_2SO_4 (pH~0) to simulate the acidic environment present in a PEMWE. For these measurements we used a Iviumstat.h (Ivium) potentiostat with integrated frequency response analyzer. Benchmark tests were done using commercial RuO_2 as well as Ir and IrO_2 nanopowders, mixed to low concentrated dispersions that were applied and dried onto the electrodes.

The full performance of integrated MEAs were evaluated with a Scribner cell fixture (5 cm^2). Here, the combined performance of Cellfions membranes and Ionautics Ir coating can be studied for PEMWE. This cell has rod-heated aluminum end plates, platinized Ti anode flow plate, graphite cathode flow plate and a gold coated current collector. The cell is assembled with 8 bolt screws and has inlet and outlets of gas and water. A thermocouple was placed inside the anode flow plate to maintain the cell temperature. Swagelok type fittings were used for water and gas transportation in and out of the cell. The cell fixture was mounted in a Scribner PEM 600 electrolyzer test system, which controls and monitor gas and water flows, temperature and voltage/current measurments. This system also includes a frequency response analyzer for electrochemical impedance spectroscopy measuremenents, which are used to evaluate the resistance of each component in the MEA, and especially the membrane. Using impedance spectroscopy, the membrane's ability to conduct protons from the anode to the cathode is determined, which is the core purpose of the membrane. The water needs to be very pure and was ultra pure water (Milli-Q) while all the parts in the re-circulation loop are made of 316L stainless steel or PFA plastic, for minimal contamination. Additionally, the recirculation loop includes a mixed bed resin for filtering the water. The quality of the water is monitored live by measuring its conductivity. Benchmarks tests were done with Nafion 115 membranes (127 µm), and the cathode were carbon paper GDLs commercially coated with Pt/C (0.3 mg/cm^2) in all measurements for high reproducibility.

4.4. Development and preparation for enabling a Circular Business Model

In work package 4 the possibility of achieving a circular business model for actors within the electrolyzer value chain was investigated. This work included conducting a thorough overview and summary of the market for electrolyzer components as well as a life cycle analysis (LCA) for the components developed during the project.

5. Results and discussion

During the project results have been produced which are valuable for the continued development within both Ionautics and Cellfion. The most important results from each work package are presented below. Additional details and confidential results are submitted as an appendix to this report.

5.1. Development of nanoparticle catalysts and integration with the membrane for PEMWE

5.1.1. Development of catalyst coatings

The nanoparticle generator HiPNano was originally designed to deposit nanoparticles onto a surface of approximately 1 cm^2, as this is usually a suitable sample size for academic studies of the generated particles. Analysing equipment such as SEM, TEM, EDX and XRD can all be used for samples of this size. However, within this project, the nanoparticles are also evaluated through their catalytical activity within a PEM cell. The smallest typical size of such a cell is 5 cm^2

(approximately 2.25x2.25 mm) of active area. Therefore, the HiPNano was redesigned in order to be able to collect generated nanoparticles over a larger surface area. The original, cone shaped stainless steel mesh that encloses the plasma growth zone of the HiPNano was replaced with a solid stainless steel cylinder. The stationary substrate holder was replaced with a rotating one, in order to smoothen out any inhomogenety within the deposition pattern on the substrate surface. Also, the static electric potential that was originally used to attract the generated particles onto the substrate, usually referred to as the "substrate bias" was replaced with a pulsing potential that was synchronized with the pulse of the HiPSTER 1. Whis was made possible by the so called "HiPSTER Sync Unit", developed by Ionautics. All of this combined, resulted in a larger deposition area with more homogenous nanoparticle loadings.

Ionautics has further developed the nanoparticle catalysts by introducing oxygen into the deposition process. Figure 2 shows the images of the nanoparticles produced at different O_2 flows. The reaction of oxygen with Ir resulted to a change in both the structure and size of the particles. The oxygen acts as an impurity and enhances the nucleation of nanoparticles. Without oxygen, the particles appeared as individual spherical particles. By increasing the oxygen, smaller particles are produced but also agglomeration happened. The formation of the more stable IrO_2 using medium O_2 flow is confirmed via x-ray diffraction (XRD) as shown in Figure 3. There are no peaks associated with pure Ir which means that the Ir particles were fully oxidized during the deposition process.

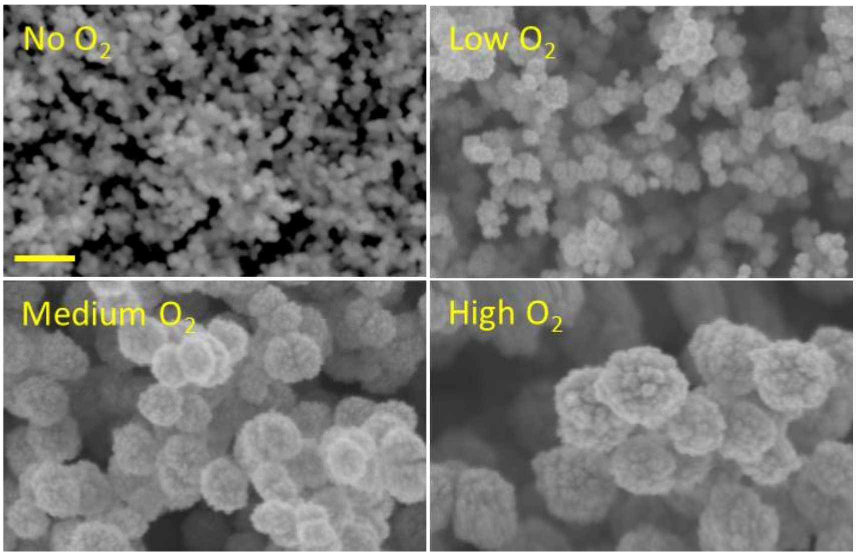


Figure 2. Ir and iridium oxide particles produced (a) without O_2, (b) low O_2, (c) medium O_2, and high O_2.

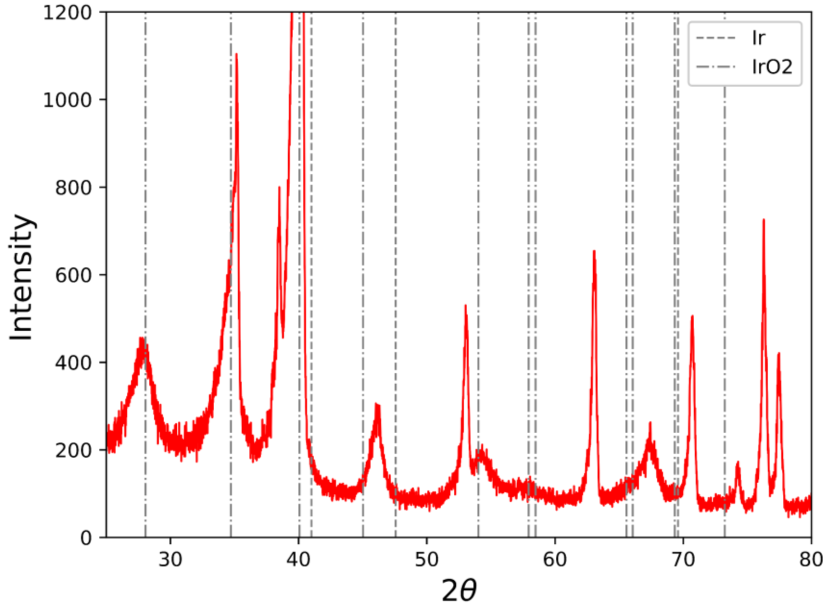


Figure 3. XRD of iridium oxide nanoparticles produced with medium O_2 flow. The peaks for Ir and IrO_2 are marked while the rest of the peaks belong to either Ti or Pt. No peaks can be associated with Ir.

The collection of nanoparticles on conducting and non-conducting substrates was investigated. The nanoparticles obtain a negative charge due to collision with electrons in the plasma discharge. This allows the nanoparticles to be influenced by electric fields, in this case with the use of an applied substrate bias voltage and cylinder voltage. The results of nanoparticle collection on conducting and non-conducting substrates are shown in Fig. 4. Nanoparticles often appear as dark coating due to the diffusion of light on rough surfaces. A circular pattern of nanoparticles is formed when collecting on a conducting substrate, but this pattern changed when the particles are collected on a non-conducting surface. It is clear from Fig. 4 that there is an area in the middle of the non-conducting substrate that has less coating while a more homogenous coating can be achieved when a conducting substrate was used. These results were obtained using the same deposition parameters and experimental set-up, which highlights the extent of the difference in nanoparticle collection between these two types of surfaces. It is possible to further optimize the collection of particles by adjusting i.e. the substrate bias and geometry between the source and the substrate. Fig. 5 shows the image of proton-conducting membranes such as Cellfion and Nafion membranes after a test deposition of Ir nanoparticles. This result shows that it is possible to use our deposition method to apply electrocatalyst nanoparticles directly on membranes. The results in Fig. 4 and 5, however, helped us conclude that we should use conducting substrates to maximize the collection and have a better control of the arrival of nanoparticles on the substrates. Thus, it became preferable for us to coat directly on PTLs, rather than directly on membranes.

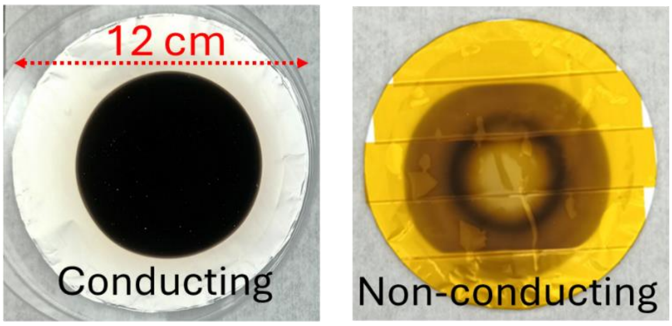


Figure 4. Ir nanoparticles collected on conducting and non-conducting surfaces using the same deposition parameters and experimental set-up.

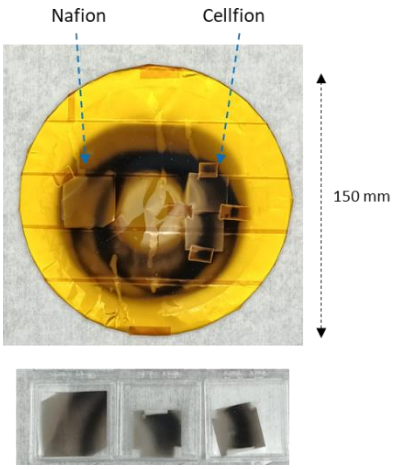


Figure 5. Image of Cellfion and Nafion membranes after a trial coating with iridium oxide nanoparticles.

The homogeneity of the nanoparticle distribution on the substrate has been improved during the duration of the project. Currently, it is possible for Ionautics to collect particles in a circular area which can be adjusted and refined by changing, i.e substrate bias voltage, source-to-substrate distance and offset between the HiPNano and substrate. Fig. 6 shows the effect of substrate rotation and offset on the homogeneity of particle distribution. Normalized EDX peak intensities from the nanoparticles across a line through the coated area confirmed the improvement in particle distribution. The improvements made in the nanoparticle collection and coating homogeneity made it possible to deposit on large substrates accurate loadings fit for PEMWE tests.

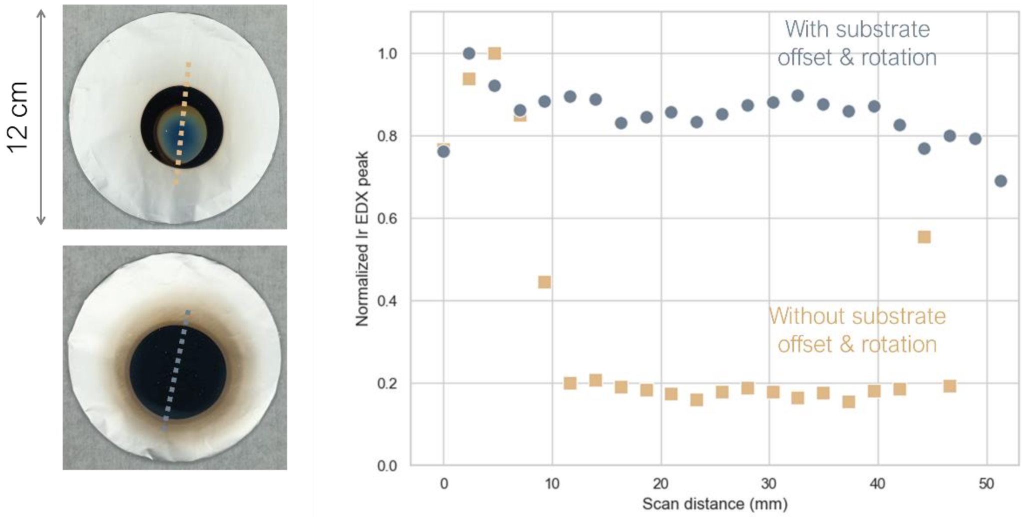


Figure 6. Images of the substrate after deposition with and without substrate offset and rotation and normalized peak intensities from the EDX of Ir nanoparticles.

5.1.2. Electrochemical testing for oxygen evolution reaction

In the early stages of the project when the coated area was small, we analyzed the nanoparticles in three-electrode cells. During this time metallic iridium nanoparticles were made, which were relatively large in average crystallite size (14 nm), determined from XRD. To measure the electrochemical performance, we collected and dried nanoparticles from coated substrates, dispersed them in commonly used alcohol/Nafion solutions that were finally drop-casted on glassy carbon electrodes. Initial tests of using Cellfion ionomer solutions was conducted but caused large agglomerations and therefore only Nafion solution was used. The overpotential for reaching a current density of 10 mA/cm^2 is a common measure for such electrodes and is shown in figure 7 (a-b) for several samples. In Figure 7, we used commercial RuO_2, Ir black and IrO_x nanopowders as reference catalysts for comparison. Since the weight increase on such small electrodes from our coating technique is exteremely difficult to measure, we also measured the electrochemical surface area (roughness factor) to improve the analysis. In this way, we could correlate the activity against the amount of material we used. In Figure 7 we see that our nanoparticles perform almost as good as the commercial high surface area Ir-black reference, which have nanoparticle sizes as small as 3 nm. We also notice that RuO_2 is the best catalyst for this short-term tests as expected, but since this metal is known to be unstable for long opretions it is therefore not used commercially in PEMWE. This is also the case for metallic Ir and therefore we tried to anneal the metallic Ir nanoparticles to form Ir oxides. We used a highest temperature of 450 °C to avoid oxidizing the substrate and sintering the nanoparticles into larger particles. We concuted termogravimetric analysis (TGA) to investigate the annealing behaviour, as viewed in Figure 7c. We noticed that our nanoparticles start to oxidize at higher temperature than the 3 nm small reference Ir black, which is expected from the particle size. Therefore, we unfortunately noticed an efficiency decrease and no evident Ir oxide formation, as seen in Figure 7d, after annealing our metallic nanoparticles. The performance of the annealed particles is displayed by the crossed and dashed circles in Figure 7(a-b).

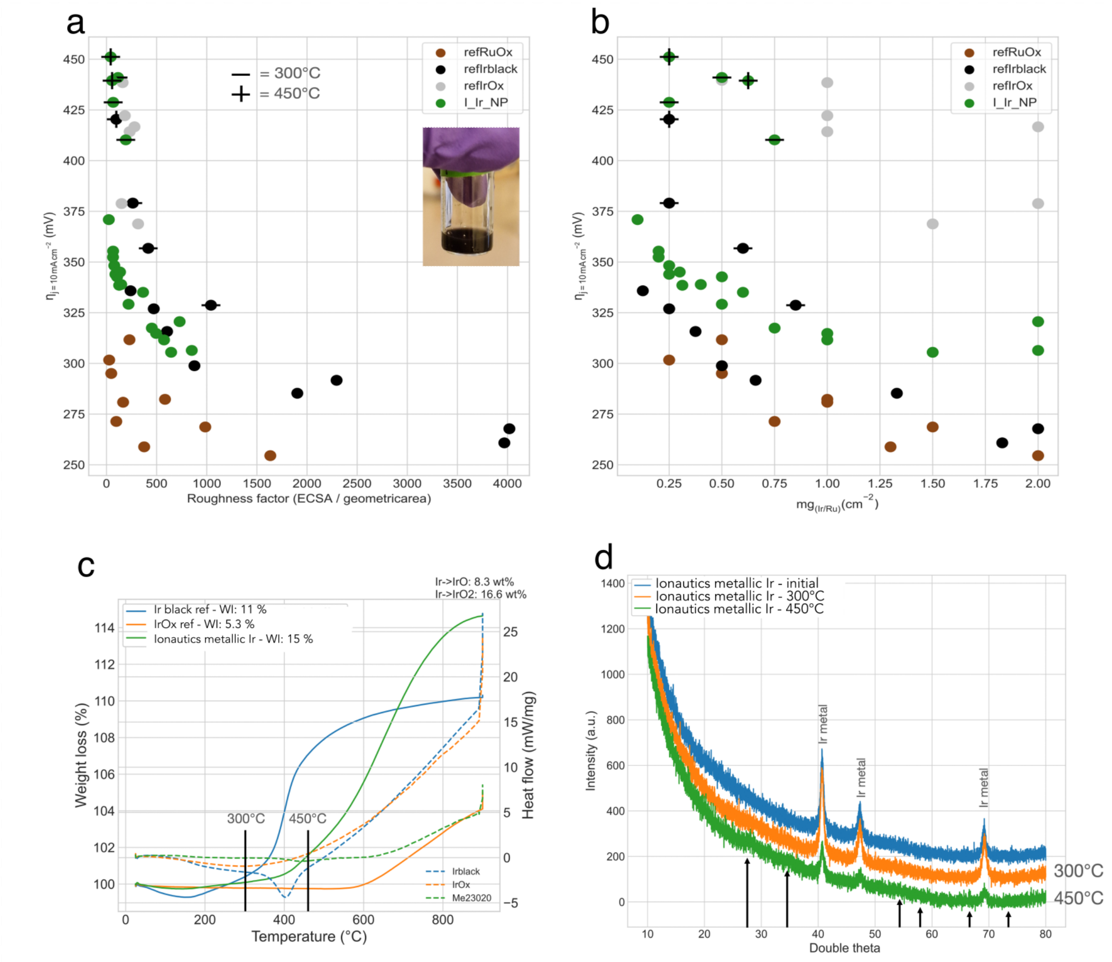


Figure 7. (a-b) Three-electrode test data of collected nanopowder, dispersed and drop-casted on glassy carbon electrodes. (c) TGA of Ionautics metallic Ir nanopowder. (d) XRD data for Ionautics initial and annealed metallic Ir powder.

To analyze the advantages of our technique we also coated glassy carbon electrodes directly, rather than dispersing the nanoparticles. In Figure 8a the overpotential at 10 mA/cm^2 is shown for such nanocoatings compared to drop-casted didsperions (nanopowder) and two reference materials. We see that for a similar roughness factor, our direct deposited coatings perform better than the drop casted electrodes. This is an indication of very porous, active and homogenous films but since we were not able to calculate the loading on each electrode, we could not show the trend for these electrode as in Figure 8b. However, compared to previous measurements on similar parameters, we believe that none of these electrodes had a loading above 0.2 mg/cm^2. Overall, we were very excited by these results.

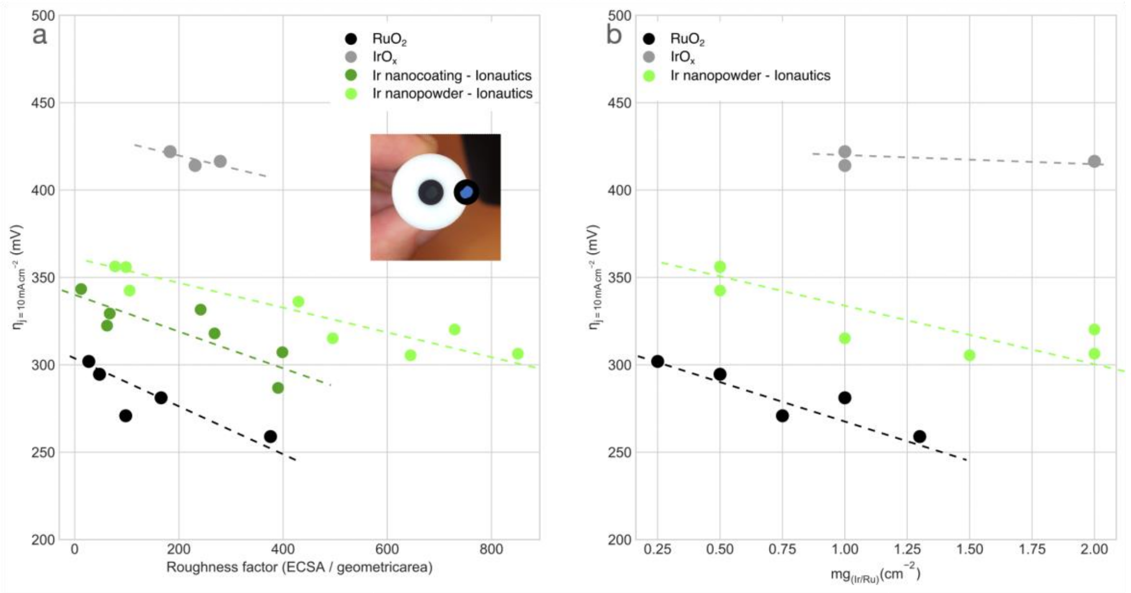


Figure 8. (a-b) Three-electrode test data comparing drop casted dispersions to Ionautics direct deposited nanocoatings on glassy carbon electrodes. Note that the nanocoating does not cover the whole glassy carbon surface area (blue marking in inset) and that the loading of nanocoatings could not be measured.

5.1.3. Integration of the coating with a MEA

After increasing the coating area to 5 cm^2 it was possible to construut MEAs for PEMWE measurements. After this milestone was achieved, we characterized the coatings exlusively in PEMWE, which is the intended application. In a PEMWE, much alrger current densities can be obtained because of the solid electrolyte and high temperatueres. In Figure 9a, the HFR-corrected potentials at a current density of 2 A/cm^2 are shown for different MEAs between 2023-2024. Here the HFR-free potentials display the kinetic potential of the MEA, disregarding the membrane performance, and is a good measure for the catalyst efficiency. During the project time, Ionautics have developed and improved the catalyst coatings consistently, as evident by the decreasing potentials. This was achieved by reaching several important milestones, which are marked in Figure 9a and are further summarized here. In milestone (i) PEMWE meaurements were initialized and the MEAs were made by collecting and drying nanoparticles for spray-coating the PTLs. In this period, we also investigated different ionomer contents on the electrodes. At milestone (ii) we succeeded to deposit Ir directly on to the PTL with an area of 5 cm^2, which lead to a drastically increase in performance. At the start of milestone (iii) we developed coatings containing iridum oxide, with much smaller sized nanoparticles. Here we also improved the overall MEA and changed to a better and more reliable cathode electrode. In milestone (iv) the PEMWE measurement protocol was improved to match industrial standards and simultaneously we developed more homogenous and higher performing coatings leading to continusly decreasing potentials and higher efficiencies. Finally, milestone (v) was reached by using magnetrons for up-scaling purposes. The catalyst coatings at this stage include ultra small semi-crystalline Ir oxide nanoparticles (<2 nm) to higher degrees of crystalline IrO_2 with slightly larger nanoparticles. The coating area is now also increased to ~100 cm^2 with improved homogeneity. A cell potential of ~1.65 V is needed for 1 A/cm^2 using a N115 membrane, which is state-of-the-art performance compared to literature data. By using more optimal membranes with lower resistance, we should reach 3 A/cm^2 below 1.8 V, which is the DOE efficiency target for 2026. As an example, we need a total HFR of 80 $mOhcm^2$, reachable with a commercial Nafion N112 membrane. This HFR is what we need to aim for with the new cellulose based MEA to be able to finally reach the target values for commercialising global scale PEMWE.

To evaluate the performance of Ionautics PTEs compared to industrial standard, commercially coated state-of-the-art CCMs with high Ir oxide loadings of 2.0 mg/cm^2 (Fuelcellstore) have been measured and is shown in Figure 9b. We found that the MEAs using Ionautics electrodes outperform the commercial benchmark CCM, both in terms of cell potential (efficiency) and resistance, while using less than 10 times lower Ir loading. These results show that Ionautics' PTEs are now competitive to state-of-the art CCM-MEAs, but also that PTE type MEAs has the possibility to replace the commonly used CCM-MEAs in PEMWE. While CCM is the most commonly used MEA today, Ionautics' PTE MEAs have several advantages over these such as high reproducibility, low waste, high purity and control, extremely porous and optimal electrical connection of the nanoparticles to the PTL.

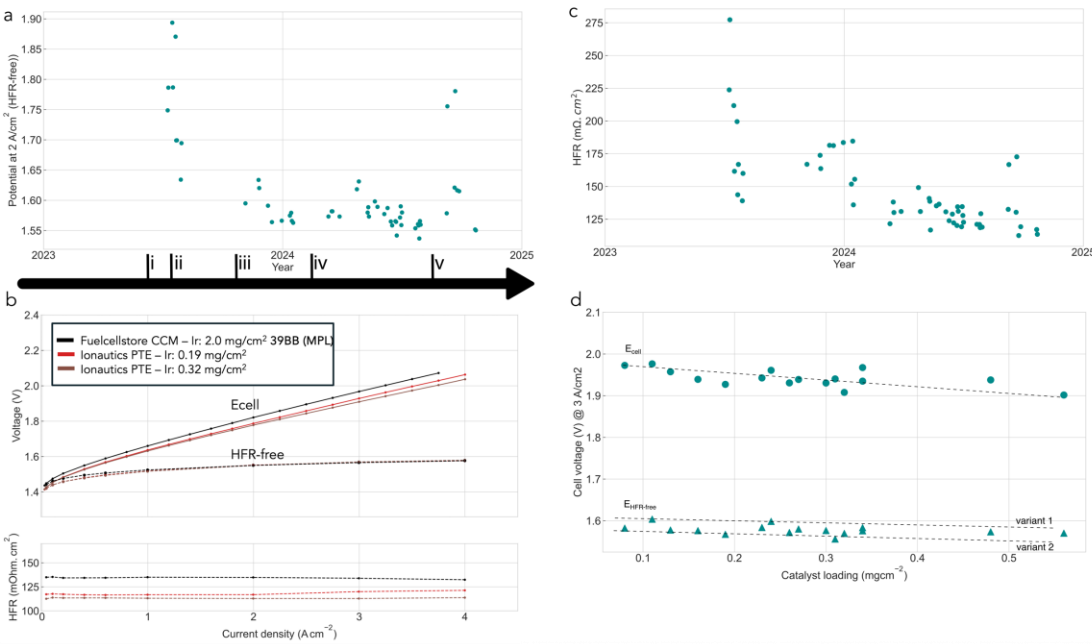


Figure 9. PEMWE results over time. In (a) the HFR-free potential at 2 A/cm2 is shown and in (b) two of Ionautics PTE MEAs using Nafion is shown against a commercial benchmark. (c) the HFR measured for the MEAs in (a) are shown over time. In (d) the cell potential and HFR-free pontential for several samples are shown with different Iridium loadings. Important milestones in coating development as well as in MEA production and testing protocol are marked in (a) with i-v explained in the main text.

While the overall trend in Figure 9a is clear, the performance of the MEAs is also dependent on the HFR and the catalyst loading. In figure 9c, we see that the HFR also has decreased simultaneously as the HFR-free data, which means that the cell voltage of the whole MEA has improved even more than the HFR-free voltage over time. In all MEAs, we use GDLs with a MPL containing teflon for high reproducibility and cost-effectivness. However, this GDL increases the overall HFR by up to 25 $mOhcm^2$, and even lower potentials can be reached by optimizing the cathode GDL. We have carefully studied the effect of Ir loading by comparing similar type of IrO coatings and varying the amount. In figure 9d the cell potential and HFR-free potential at 3 A/cm^2 for Ionautics coatings are displayed. It is evident that the performance improves with higher loading, which is a clear indication that the whole catalyst layer is used, and not only the top surface layer. Additionally, this shows that our measurements and coatings are highly reproducible with very small potential differences between samples. While the decreasing trend with respect to loading is even more clear for the cell potential, the HFR-free potentials levels out for samples at higher loadings since they display a simultaneous decrease in HFR as viewed in Figure 9c. This is in fact a good thing, because if the HFR decreases with loading, we are sure that the coatings are indeed highly electrically and ionically conducting, which is of high benefit in PEMWE. This is further confirmed by the low HFR compared the benchmark MEAs tested in our lab.

5.2. Production and characterization of CNF membranes

In this work package, cellulose-based proton conducting membranes were developed and characterized by Cellfion with the aim of achieving properties suitable for use in PEMWE such as high proton conductivity, chemical stability, and mechanical stability. Several different types of chemical modifications of the cellulose were evaluated in this project, as well as some routes to enhance membrane properties such as crosslinking and functional additives. The different chemical modification routes included functionalization with weak-, strong- and multi-proton acid groups. The membranes were characterized in-house at Cellfion with respect to some important properties, which were later evaluated in relation to the performance of the membranes in the PEMWE as studied in work package 3.

Flat membranes were successfully assembled from the modified cellulose nanofibrils using dead-end filtration followed by hot pressing to dry the membranes. Figure 10 shows representative photos of chemically modified cellulose nanofibril gel (left) and dry freestanding nanocellulose-based membrane (right). An optimal procedure for the production of all types of membranes used in this project was developed which was then used throughout the project.

Figure 20: Representative photographs of cellulose nanofibril gel and cellulose nanofibril membrane respectively.

It was found that the chemical functionalization route used to modify the starting material had a large effect on several membrane properties such as ionic conductivity, swelling and mechanical stability. The detailed results are described in a confidential appendix to this report. Crosslinking was found to be a successful strategy to reduce swelling, but to the price of a highly reduced ionic conductivity. The membranes with sufficiently high ionic conductivitites were chosen for further characterization in WP3.

In addition to the properties mentioned above, for one of the membrane types the hydrogen gas barrier was evaluated and benchmarked with a commercial Nafion212 membrane as a reference. This work was conducted by RISE with external funding, but the results are mentioned here as they are highly relevant to the project. A good hydrogen gas barrier is a requirement for a membrane in a PEM electrolyzer to prevent the produced gas from crossing over through the membrane. The hydrogen gas barrier was measured via crossover current in a fuel cell setup. It was found that the cellulose-based membrane has good hydrogen gas barrier properties, similar to or better than the commercial Nafion212 membrane, under the conditions tested. Plots of crossover current density vs potential obtained at 40°C are shown in figure 11 for Nafion212 and two different Cellfion membrane respectively.

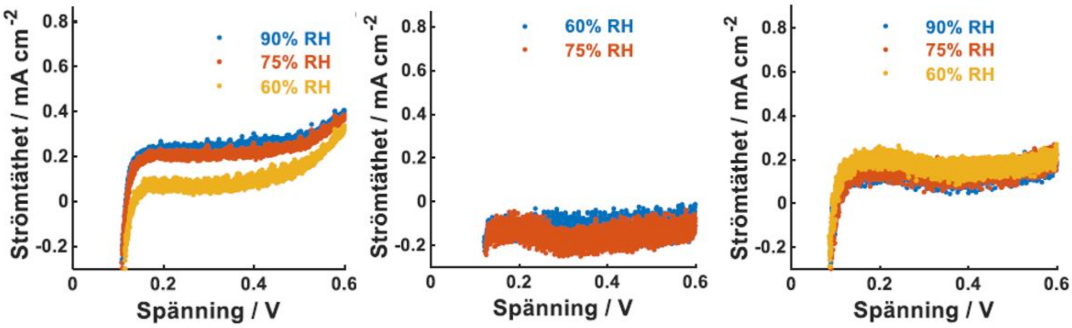


Figure 11: Crossover current density vs potential for membranes at 40C. Left to right: Nafion212, C4-M0-1, C4-M0-2.

5.3. Validation of the MEA in a PEMWE cell

Initial MEA studies for PEMWE were conducted by Ionautics using spray-coated reference catalyst materials to benchmark the performance of the membrane against Nafion membrane references. However, the nanoparticle dispersions were not stable with Cellfion ionomer and therefore Nafion ionomer was used in the catalyst dispersions. Using Nafion Ionomer is not an optimal solution but is needed to be able to spray-coat homogenous layers of the catalysts onto the membrane or PTL. While the catalyst coating was succesfull, all the membrane variants tested in this period were too fragile and caused short-circuits by perforated membranes. As comparison, we have therefore only used a Nafion based MEA together with Ionautics electrode.

After the initial difficulties with using the cellulose based membranes in the electrolyzer, Ionautics improved the cell assembly methods to be able to measure more fragile membranes by removing high pressure points. In the meantime, Cellfion initiated a study to understand the requirements for successfully running the electrolyzer with such membranes. This study was conducted at Umeå University via consulting. The results indicated that the activation process in the electrolyzer is crucial for the function of some variants of the cellulose membrane as a PEM in the electrolyzer. This knowledge was used to implement changes in the test procedure in the following parts of this project.

While ionomer solutions are mixed with catalyst nanoparticles to create adequate dispersions for spray-coating, Ionautics coating technique does not require this. Therefore, this technique is optimal for evaluating Cellfions membranes as we were able to analyze these without adding any Nafion in the catalyst layer. In Figure 12, PEMWE polarization curves at 60°C of Ionautics electrodes combined with three different Cellfion membranes variants are shown together with a Nafion 115 (127µm) membrane MEA benchmark. Details regarding the membrane types are given in the confidential appendix. All MEAs use an Ir loading around 0.3 mg/cm^2, and any small differences in loading should not affect the performance noteworthy. We see that among these three membrane variants, C1-R and C1-M1 perform best reaching the highest current densities. After removing the HFR resistance, which is mainly from the membrane, these two MEAs perform comparable to the Nafion reference, which means that the catalyst efficiency is maintained with the membrane. However, while the Nafion MEA was conditioned for 12 hours prior to the measurement, the Cellfion-based MEAs were recorder directly. The electrochemical results from the full measurement protocol of the Cellfion based MEAs can be seen in Figure 13a where the cell voltage, current density and measured HFR are shown over time.

A similar activation procedure was conducted as was developed in the collaboration between Cellfion and UmU for all measurements. However, we did not notice any activation for the membranes, except for the C3-M0 variant, which also was tested at UmU. This means that the three different membranes behave differently, and the break-in/activation protocol should be developed separately. Furthermore, as mentioned no Nafion solution was added to the MEA, which could affect the performance. As evident, the activity of the C1-R and C1-M1 membranes was initially greatest and decreased over time, mainly from an increasing HFR, which normally is accounted to membrane degradation or membrane/catalyst interface deterioration. At this moment, we are nor sure what caused the degradation, but for sure the interface must be studied and optimized for a more honest evaluation of the membrane performance.

While the C3-M0 could be partly activated by the protocol, we were not able to perform the full protocol because the cell voltage limit of 2.1 V was exceeded. Furthermore, we see that the activity of C3-M0 variant is initially very poor compared to the other variants, even if the membrane resistance (HFR) is lower. After compensating for the HFR, the HFR-free potential of the cell was therefore still much larger. We suspect that the proton transportation is limited by water diffusion in this membrane as evident by the shape of the Nyquist plot at 0.04 A/cm^2 in Figure 13b. It may be that the HER mechanism changes from $2H^+ + 2e^- \rightarrow H_2$ to a less favorable $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ reaction pathway in this membrane at the higher current densities, leading to the "s-shaped" polarization curve. A lack of protons at the cathode could lead to this behaviour. Interestingly, we see that this membrane activates after a short period, which was also noticed in the study performed at UmU. The reason for this activation and if it is consistent over time must be studied more. However, we further noticed that this membrane type (C3-M0) swelled from ~70µm to over 1 mm thickness and was not mechanically stable. This may cause puncturing, dissolution or other problems in long-term PEMWE operations. Therefore, according to our tests, this membrane is not suitable for PEMWE.

The impedance measurements in Figure 13(b-c) of C1-R and C1-M1 look promising and show similar characteristics as for Nafion 115 membrane. While the HFR is higher than the Nafion reference, the charge transfer resistance is comparable to Nafion, which indicates that the reaction mechanism of the water splitting reaction is fast and similar as in Nafion based MEAs. Since these membrane variants displayed a HFR above 2000 mOhmcm^2, far above the needed 80 mOhmcm^2, future work should be made into either improving the membrane proton conductivity or the interface between the catalyst and the membrane. At this moment, it is unclear what causes the high HFR. Understanding the casue fot he high HFR of the MEAs to be able to improve it is crucial for making the MEA competitive in global-scale PEMWE where Ir shortage is the main limiting factor. Since the electrodes did not attach very well to the membranes. compared to Nafion, we suspect that the interface between them could be improved. This could either be done by alternating the chemistry of the membrane, the production parmaters of the MEA or inclusion of Cellfion ionomer solution into the catalyst layer.

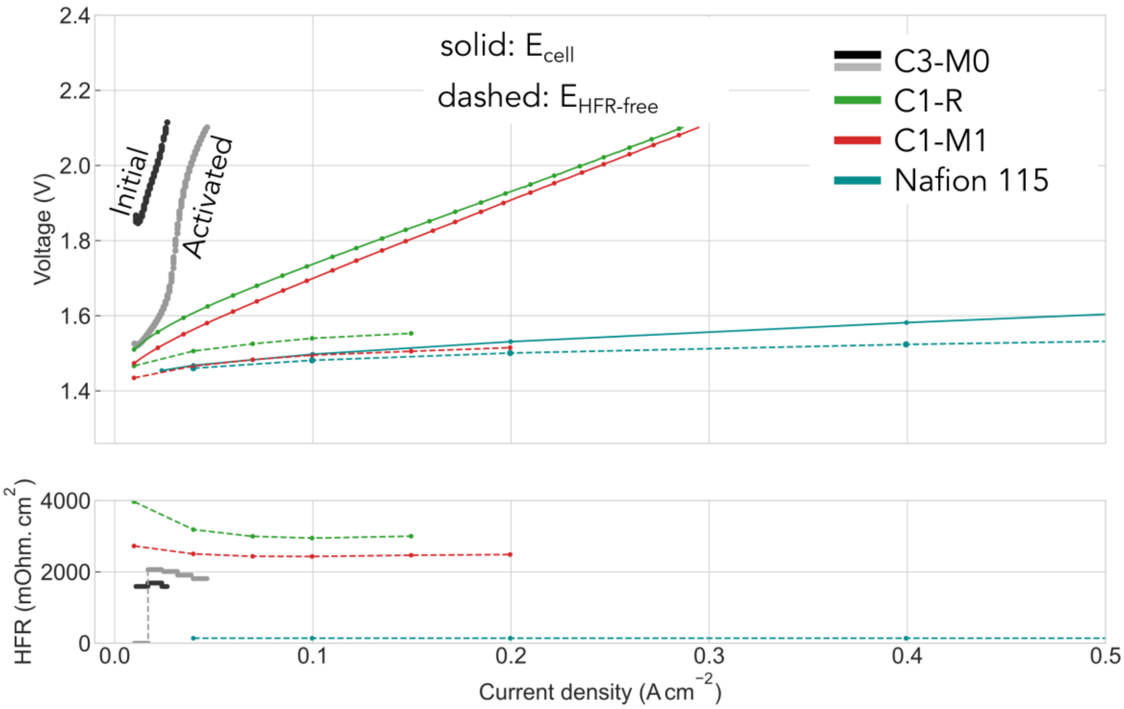


Figure 12. Polarization curves and HFR data for MEAs using Ionautics electrodes and Cellfion membranes at 60°C. A Nafion membrane benchmark with Ionauitcs electrode is included. Note that for C3-M0, the HFR is calculated at a single frequency of 10k Hz while for the others, the crossing of the Nyqust plots.

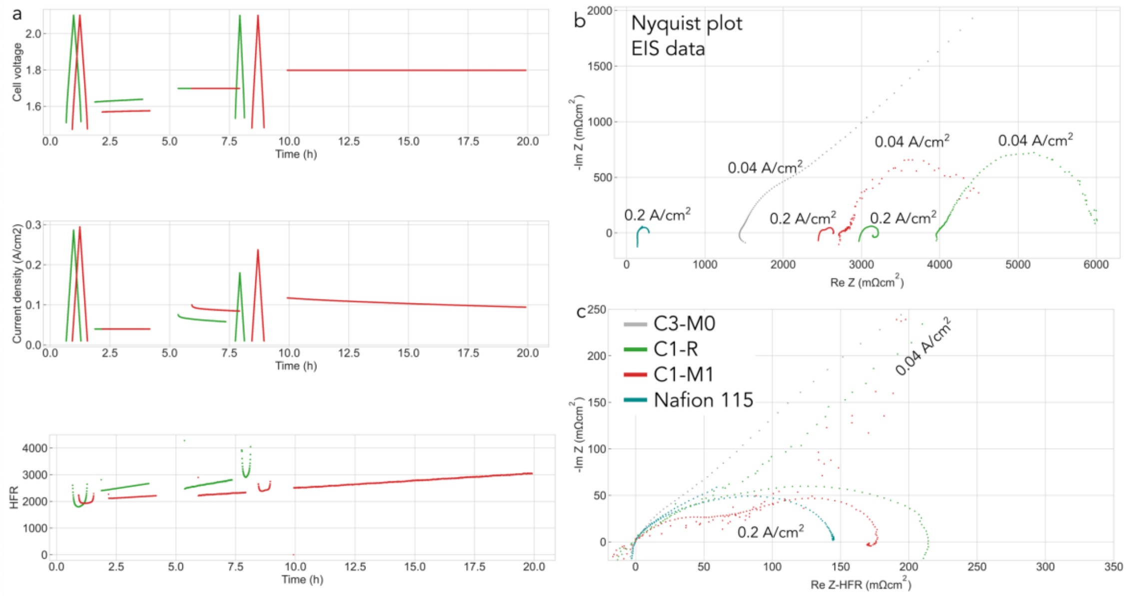


Figure 13. In (a) the cell voltage, current density and measured HFR (at 10k Hz) is shown over time for the whole measurement protocol. In (b) nyquist plots are shown for two different current densities and in (c) the Re(Z) is shofted to zero for the same data as in (b). Note that for C3-M0, the protocol was terminated because of E overload and is not shown.

5.4. Development and preparation for enabling a Circular Business Model

In the first part of work package 4 the business case was evaluated through a thorough analysis of the PEMWE market, resulting in a business case report that has been submitted as an appendix to this report.

The second part of work package 4 consisted of doing a full life cycle assessment for the components developed within the project. RISE was appointed to conduct the LCA, and the work was organized as a project with close collaboration between RISE, Ionautics and Cellfion. The LCA was separated into one part for the case of the catalyst nanoparticles and one part for the cellulose-based membranes. Besides the LCA analysis, the report included potential recycling scenarios, as well as comparisons to current state-of-the-art commercial components.

Main conclusions from the LCA study:

- The Ir particles have the largest environmental impact in the membrane-particle product.
- The main contribution to the environmental impact in the Ir particle production is the metal itself.

- The HiPIMS process used by Ionautics has a negligible environmental impact compared to iridium production, with electricity being the primary source of environmental burden and oxygen contributing the least.
- The main hotspots for the cellulose membrane were the use of isopropanol in the chemical functionalization process, as well as chemical waste handling.
- Besides the production of CNF, the main contribution to the EI was the drying of the membrane. The drying had a moderate contribution to the GWP, but a major contribution in several other impact categories.
- Scenario analysis:
  - Case 1A: Paper recycling of the membranes had a small effect on the EI, while a hypothetical CNF recycling process showed a major reduction in EI.
  - Case 1B: Recycling reduces iridium's environmental impact by nearly 75%. However, iridium remains the largest contributor to the overall impact, and its impact would need to decrease by 50 to 100 times to match other components.
  - Case 2: When comparing the EI to produce a cellulose membrane to that of a PFSA membrane, the cellulose membrane had a 40% lower GWP compared to the PFSA membrane. This difference became more noticeable, reaching less than 20%, when accounting for the lack of waste handling processes in the PFSA model. It should be noted that in many of the other impact categories, the trend was the opposite.
  - Case 3: The scenario explored the change of solvent in the chemical functionalization process, and showed that replacing the currently used solvent with a viable alternative resulted in a 10% lower GWP.

The full LCA report can be found as a confidential appendix.

6. Conclusions and future work

Several conclusions can be drawn from the results obtained in this project.

- The process developed by Ionautics has been scaled up so that larger areas can be covered, and has also been improved so that both conducting and non-conducting substrates can now be used.

- The performance of Ionautics’ coatings has been improved such that it is now comparable, or outperform, state of the art catalyst coated membranes in the litterature. The nanoparticles are best suited to be coated on the PTLs instead of the membrane, putting Ionautics in a rather unique position on the market.

- Cellfion’s membranes can be used as proton conducting membranes to produce hydrogen gas via PEMWE. The proton conductivity of the membranes needs to be increased for the performance of the membranes to reach commercially interesting levels.

- The type of chemical modification used to functionalize the cellulosic starting material has a large influence on the performance of the cellulose-based membranes in a PEMWE, and should be chosen with care to optimize performance.
- Functionalizing cellulose-based membranes using e.g. crosslinking or functional additives is a way to control and tune properties which can be used to enhance membrane performance in PEMWE.
- The life cycle analysis conducted within the project shows that both the components developed by Ionautics and Cellfion can have large benefits over their commercial counterparts in terms of reducing global warming potential.
- Combining Ionautics coatings with Cellfion membranes work well together forming a functioning MEA for PEMWE, compared to reference catalyst coatings. However, the overall resistance of the MEA needs to be reduced. Futher work must be done on the interfaces and the membrane conductivity.

7. Project communication

The project has been communicated through our own homepages, LinkedIn and by attending relevant conferences in order to establish contacts with potential customers.

Homepage:

https://www.cellfion.se/news/cellfion-and-ionautics-team-up

Conferences:

Hydrogen Americas Summit 2022, Washington DC

European Hydrogen Week 2022, Brussels

244th ECS 2023, Gothenburg

Hydrogen Tech Expo 2023, Bremen

245th ECS 2024, San Fransisco

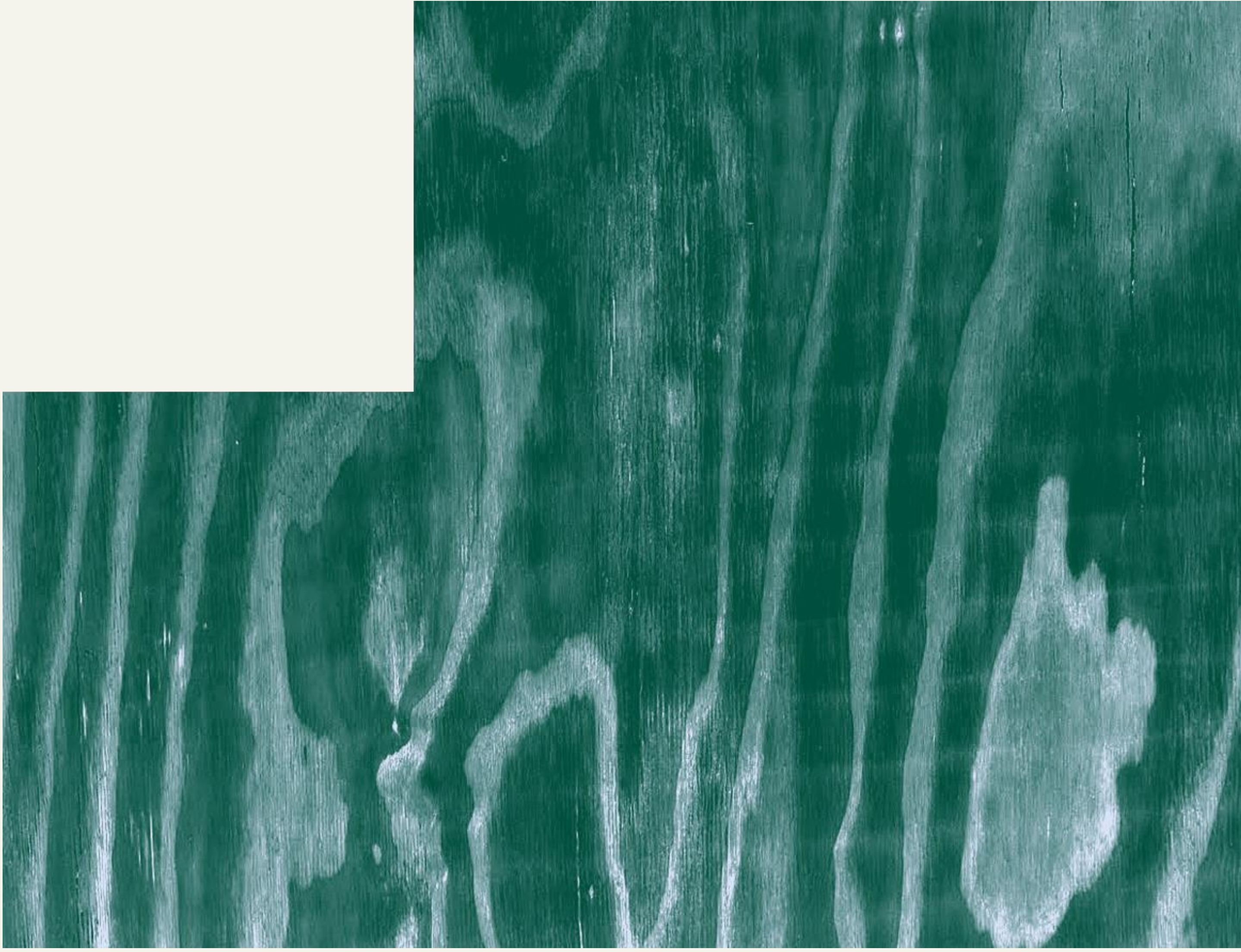
8. Appendix

The following appendices are attached to this report:

Business case

EJ SPRIDNING Results

EJ SPRIDNING LCA



RE:Source är ett strategiskt innovationsprogram som fokuserar på att utveckla cirkulära, resurseffektiva materialflöden. Vårt mål är att uppnå en hållbar materialanvändning där vi håller oss inom planetens gränser.

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