Deliverable D3.9: EC Production protocols

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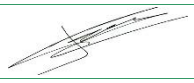
		Approval by coordinator	

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Table of contents

GLOSSARY

Symbol or acronym	Unit	
AL	-	Active Layer
CCM		Catalyst-Coated Membrane
EC		Electrochemical Core
EFC		Electric and Fluidic Core
GDL	-	Gas Diffusion Layer
MEA		Membrane Electrode Assembly
PEMFC		Proton Exchange Membrane Fuel Cell
SEM		Scanning Electron Microscopy
XRF		X-Ray Fluorescence

PUBLISHABLE SUMMARY

This public deliverable aims at presenting good practice for Electrochemical Core preparation and fabrication. The manufacturing steps, protocols and characterization tools are described to ensure the quality of the final objects.
The Electrochemical Core concept in the DOLPHIN project corresponds to the classical Catalyst-Coated Membrane which can be then coupled with the Micro-Porous Layer.

This overall process is presented for a reference case and it can be then adapted for the integration of new components (catalysts, membrane and/or ionomer).

LIST OF FIGURES

1. INTRODUCTION

This public deliverable aims at presenting good practice for Electrochemical Core preparation and fabrication. The manufacturing steps, protocols and characterization tools are described to ensure the quality of the final objects.
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2. EC FABRICATION FOR LABORATORY DEVELOPMENTS

2.1. Fabrication of Catalyst-Coated Membrane

In the DOLPHIN, CEA has in charge to study and optimize the CCM manufacturing process to be integrated and tested in large single cell and in stacks. Hereafter, CEA has focused on the blade-coating deposition to manufacture the DOLPHIN components and the CCM by decal transfer method has been chosen. The overall manufacturing steps are illustrated in ***FIGURE 1***.

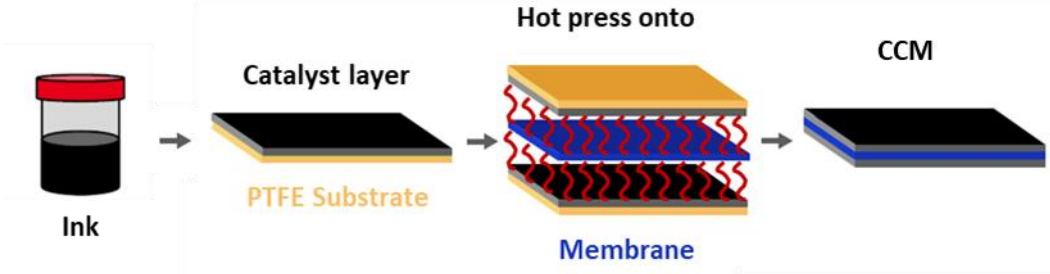

FIGURE 1: MAIN STEPS FOR CCM MANUFACTURING BY DECAL TRANSFER

The reference CCM/MEA components were chosen among state-of-art materials at the beginning of the project (see ***TABLE 1***).
At the anode and at the cathode, state-of-art Pt/C catalysts with Vulcan carbon support can be chosen as reference since it is widely used in literature. Hereafter, TEC10V50E from Tanaka will be considered for the guidelines for CCM manufacturing process.

TABLE 1: *REFERENCE COMPONENTS*

	Commercial reference	Comments
GDL (both sides)	Sigracet 22BB SGL	215 µm thickness
Membrane	CHEMOURS reference	15 µm thickness
Anode Cathode CEA reference catalyst	Pt/C TEC10V50E from Tanaka	Reference carbon support (Vulcan XC72) Pure Pt (not alloyed) Pt loading 47% wt. Anode loading : 0.1 mg_{Pt}/cm^2

The anode manufacturing protocol by blade coating has already been described in a previous publication[1] and will be summarized hereafter.

As a first step, an ink is prepared by mixing the Pt/C catalyst powder with ultra-pure water and ethanol (12.5 : 1 as volume ratio). Then, the Zr beads are added to the slurry and the flask is mixed using a roller mill (IKA Roller 10 basic, see ***FIGURE 2***) at 30 rpm overnight (> 10 h) at ambient temperature. Nafion® D2020 ionomer solution is then added to reach a Ionomer to Carbon (I/C) ratio of 0.7. The ink is then further mixed by roll milling with the same parameters for at least 10 hours.

The ink can be also prepared in a one-pot method by adding all components followed by roll milling overnight (> 10 hours) for homogeization before deposition[2].

FIGURE 2: ROLL MILLER (IKA ROLLER 10 BASIC) USED FOR INK HOMOGENIZATION

After homogenization, this ink is coated on a PTFE sheet which is fixed on a vacuum and heating plate at 60°C. The coating speed is set typically between 5 and 20 mm s^{-1} for the blade (ELCOMETER, see ***FIGURE 3***). The layer is then dried for 5 min on the plate. In our case, the anode loading is classically set at 0.1 mg_{Pt} cm^{-2} for all MEA whatever the cathode composition and/or loading for both reference and/or DOLPHIN specific CCM integrating new catalyst or other components.

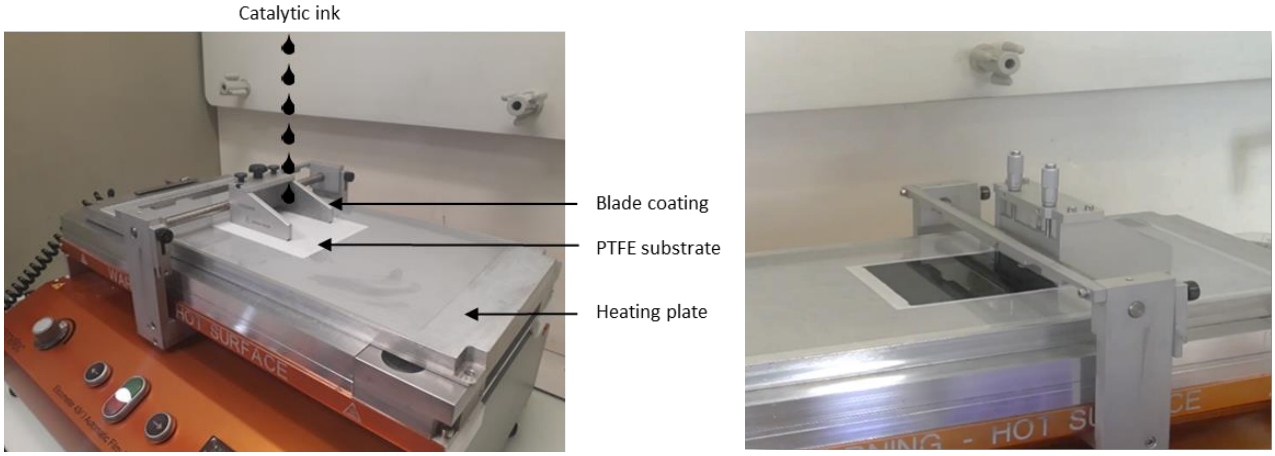

FIGURE 3: ELCOMETER BLADE COATING EQUIPMENT

[1] R. Riasse *et al*. Journal of Power Sources 556 (2023) 232491

[2] R. Sgarbi *et al*. Ind. Chem. Mater., 2023,1, 501-515

The cathode electrode can be prepared similarly to the anode. The height of the blade has to be adjusted in order to obtain the desired catalyst loading (typically 0.3-0.4 mg_{Pt} cm^{-2}) to reach satisfying performances and durability with the state-of-art and commercial catalysts.

Finally, the actual loading of each layer is measured and controlled by weighing and by X-Ray Fluorescence (XRF). This method also makes it possible to check the homogeneity of the loading before the decal-transfer step. Optical and/or Scanning Electron Microscopy (SEM) can also be used to control the surface state of the electrodes to verify the absence of defects such as cracks, holes and agglomerates as illustrated in ***FIGURE 4***. The coated area is usually larger than the specifications and this allows to avoid and rule out areas with unsuitable loadings (too low or too high) usually on the borders.

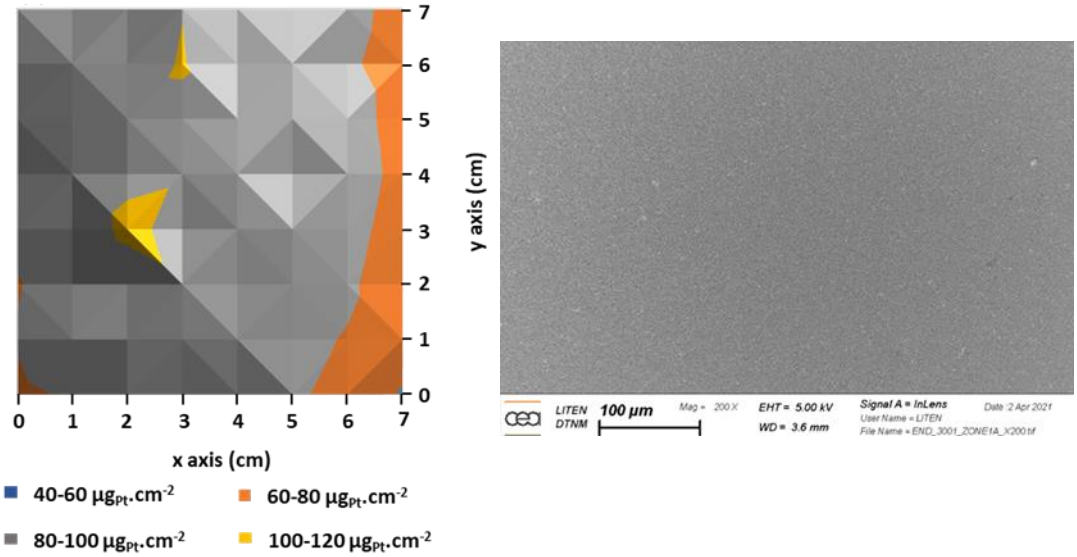

FIGURE 4: EXAMPLE OF HOMOGENEITY QUALITY CONTROL ON ANODIC LAYERS (25 CM²) MADE BY BLADE COATING BY XRF MAPPING MEASUREMENTS (LEFT) AND SEM OBSERVATION TOP VIEW (RIGHT).

The typical range of parameters for the decal step used for the DOLPHIN reference CCM are mentioned in ***TABLE 2***. A pre-heating step is usually applied to the transfer mould to heat homogeneously the whole hardware before the actual transfer step. This pre-heating step can be ajusted depending on the mould size and thermal inertia. Similarly, the transfer temperature as well as the transfer duration can be varied to optimize the decal process.

TABLE 2: TYPICAL RANGES FOR DECAL TRANSFER STEP PARAMETERS FOR REFERENCE CCM WITH PT/C MATERIALS[1-2]

	Temperature	Pressure	Duration
Pre-heating step	145-160	50 N	3 min
Transfer step	145-160	1-2 MPa	3 -10 min

The mould is finally cooled down to ambient temperature to remove the CCM.

Cross-section images for the reference CCM can be observed to check the quality of the active layer|membrane interfaces related to the hot decal transfer step (see ***FIGURE 5***). The

homogeneity within the active layers is also important to verify the absence of agglomerates, the good dispersion of the ionomer and the homogeneity of active layer thickness.

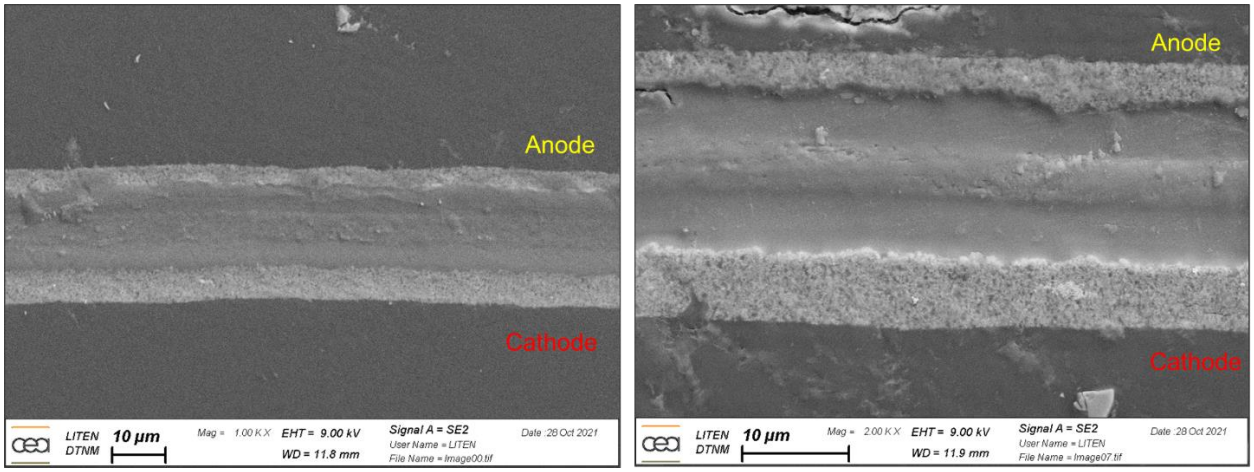

FIGURE 5: EXAMPLE CROSS-SECTION IMAGES BY SEM TO CONTROL THE CCM HOMOGENEITY AFTER THE DECAL TRANSFER STEP AT TWO DIFFERENT SCALES.

The CCM can be then coated with the MPL layer to form the EC and/or combine with the GDL components to obtain the full MEA to be inserted in the PEMFC.

2.2. Fabrication of Micro-Porous Layer

The well known Doctor Blade coating, as well as the air brush spraying methods were applied for fabricating MPLs. Thus two individual inks, consisting same composites, but different proportions were mixed. The MPL ink in both cases is primarily composed of demineralized water as the solvent, carbon black, and PTFE. Additionally, methylcellulose serves as a thickening agent, and Triton X-100 acts as a surfactant. Acetylene black which is composed of 99.99% pure long-chain carbon with particle size of 0.5 µm and a relative density of 1.95 is applied as the main component of the ink. Polytetrafluoroethylene (PTFE) from is used as a binder and hydrophobic material for balancing the wettability of MPL in the ink. For this purpose 3M™ Dyneon™ PTFE Dispersion TF 5135GZ which is a milky-white, water-based fluoropolymer dispersion, and has a solids content of approximately 58% with an average particle size of 190 nm is applied. The PTFE mass fraction reaches 20 wt.% of the final MPL layer for both methods. To achieve optimal rheological properties for the coating of the ink, the M0512 methylcellulose from Sigma-Aldrich® was used in the MPL ink. It has an approximate molecular weight of 88,000 and an approximate viscosity of 4000 mPas in a 2% aqueous solution at 20°C. The high solubility of M0512 in water makes it a good thickening agent, which can simultaneously improve the rheological properties of the ink. For the MPL ink, diluted Triton™ X-100 Laboratory grade (0.2 $ml_{Triton\ TM\ X\text{-}100}$ / g) from Sigma Aldrich was used. Besides, to improve the water balance in the cell environment, three different surface structure, the porous structure of the MPLs were modified by applying monodisperse polymethylmethacrylate (PMMA) particles. The structure of the modified MPLs is perforated either homogeneously with PMMA. The compositions for inks, as well as the MPL characteristics are summarized in the ***TABLE 3*** below.

TABLE 3: INK SPECIFICATION AND DECISICVE CHARACTERISTICS OF THE FABRICATED MPLS.

Coating method	Carbon / g	Triton / g	Methylcellulose / g	Demineralized water / g	PTFE / g	PTFE Proportion / weight%	Solid content / weight%
Doctor blade	4.80	0.59	0.58	25.60	2.07	20	17.84
Air brush spray	2.16	2.87	0.65	25.45	0.93	20	8.42

For each mixing process, the components (except the binder) are placed in a container, sealed airtight, and mixed in the DAV 600.2 VAC-P planetary centrifugal mixer from SpeedMixer™. The mixing method involves simultaneous rotation of the ink container around its own axis counterclockwise, combined with the rotation of the spinning container clockwise around the axis of the mixer to apply centrifugal forces in different planes and obtain a homogenous mixture. The ink is mixed twice for two minutes each at 2000 rpm before adding the PTFE. Between each mixing cycle, a cooling period of two minutes is provided. For cooling, the mixing container is removed from the mixer and placed in an ice bath at 0°C. This sequence of mixing and cooling ensures that the temperature of the ink, increased by mixing, remains below the cloud point of Triton™ X-100 (63°C-69°C). After adding the PTFE to the ink, the ink undergoes six additional mixing/cooling cycles, resulting in a homogeneous viscous ink ready for coating. The homogeneously mixed ink is applied either to the gas diffusion medium (substrate, Freudenberg H14) for conventional GDL fabrication, or on a flat glass for a standalone MPL fabrication independently on the doctor-blade or air brush spray technique. For doctor-blade coating, the substrate is fixed on the backing glass plate of the motorized film applicator from Ballard. A 100 µm gap is set between the substrate/glass and the blade, and the ink placed in front of the blade on the substrate is applied at a speed of 1 cm/s. The coated layer is dried in a convection oven at 80 °C. in case of the air-brush spray method, a heating tape set at a temperature of 80 °C was placed under the robot table, so that each sprayed layer could get dried directly. After drying, the coating is subjected to thermal treatment in a forced-air oven with heat supply. During this heat treatment, all additives (Triton X-100, methylcellulose, and pore formers) This thermal treatment process is based on recommendations from the manufacturer of the PTFE dispersion used. The temperature profile of the thermal treatment (***FIGURE 6***) is as follows: The MPL is heated from room temperature to 200 °C at a rate of 10 °C/min, followed by a slower heating rate of 2.5 °C/min to 250 °C. The temperature is then held constant for 10 minutes and then increased to 330 °C at a rate of 10 °C/min, followed by a slower heating rate of 2.5 °C/min to the final temperature of 380 °C. The temperature is maintained constant for 30 minutes during the sintering process and then cooled to room temperature. Triton X-100 begins to decompose at 200 °C, and the surfactants are completely removed from the coating at 330 °C. While methylcellulose starts decomposing below 200 °C, nearly 10% of methylcellulose remains in the coating until the end of the sintering process are decomposed, and the PTFE particles in the coating are sintered.

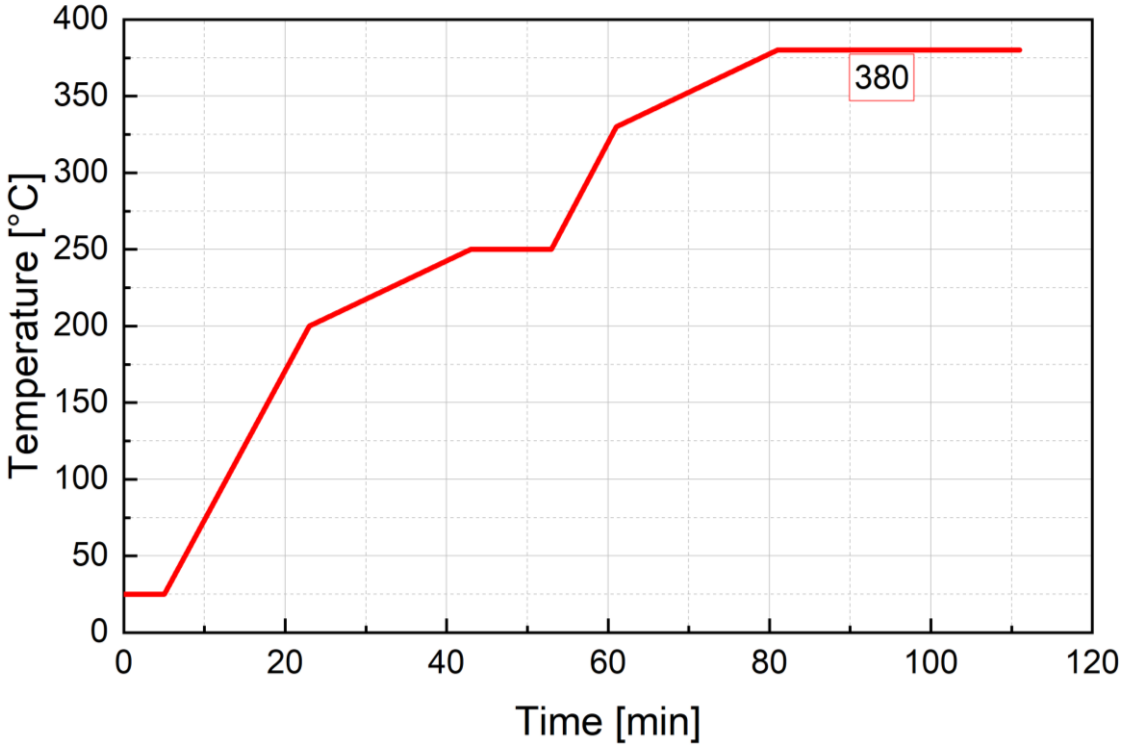

FIGURE 6: TEMPERATURE PROFILE FOR STEPWISE MPL SINTERN PROCESS

3. INDUSTRIAL PROCESS – EC PRODUCTION

3.1. Membrane coating

Membrane is firstly coated with the two electrodes (anode and cathode). The coating technique chosen is a direct slot-die coating for it has the advantage of being a direct, no-contact, fast and precise technique with the following characteristics:

- No intermediate foil (Cost advantage: no waste, no production by-product, low maintenance level)
- Minimum damage on membrane (Cost advantage: no contact between the printing head and the support, less defect → minimum production scrap)
- Challenging cycle time of 1 seconds per cell with coating speed up to 5m/min (Cost advantage: minimum quantity of machines required)
- Discontinuous coating and good precision level on the coating thickness between 100nm and 100µm (Cost advantage: minimum ink process scrap)

The coating technique chosen is compatible with a roll-to-roll process that enables the capacity of the process to meet the requirements of 20M cells per year with only one machine. The oven, used to dry the coating, being the limiting factor of the speed used in the process, its length is chosen to enable the maximum coating speed on the process.
A scheme of the coating station is represented in the ***FIGURE*** below.

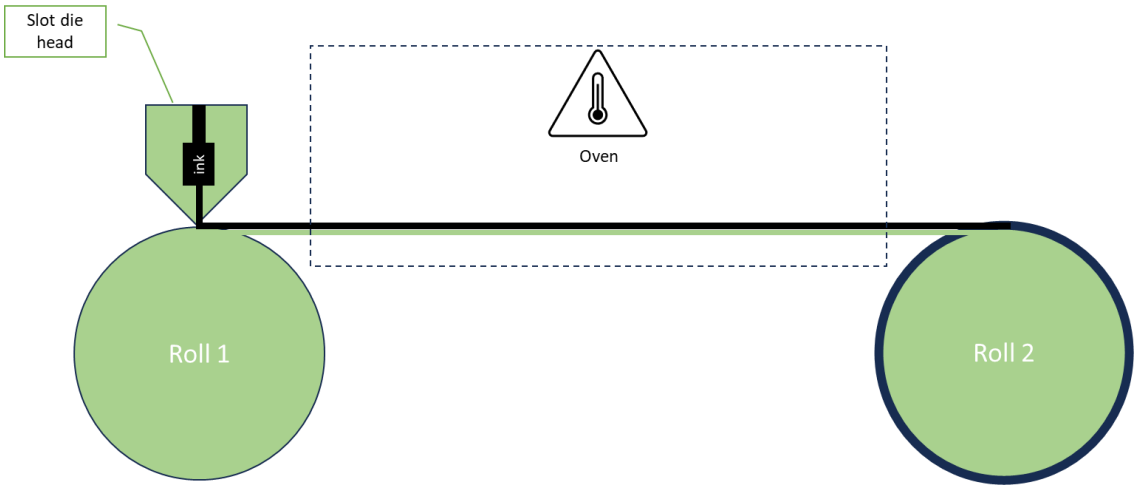

FIGURE 7: DIRECT SLOT DIE COATING ON ROLL-TO-ROLL CONFIGURATION

3.2. Assembly

The coated membrane is cut from its roll along the borders of the coated area and assembled in a double layer film, the subgasket, constituted of 25µm of polymer coated with 15µm heat activable glue on one side. A hot compression is used to seal the coated membrane within the double layer film. Then, anode gas diffusion medium is die-cut from the roll and glued with pressure activated glue on the surface of the double layer film and a final cut is performed around the MEA. The operations are done step by step in a high-rate automatic assembly machine. Visual controls of the catalyst coated membrane in the subgasket involving back diffusion lights and camera and geometrical assessment of the final parts constitute the in-line quality controls of the line. Several lines in parallel (at least three) will be needed to meet the rate of one cell per second. The scheme of the final assembled MEA is represented in the ***FIGURE*** below.

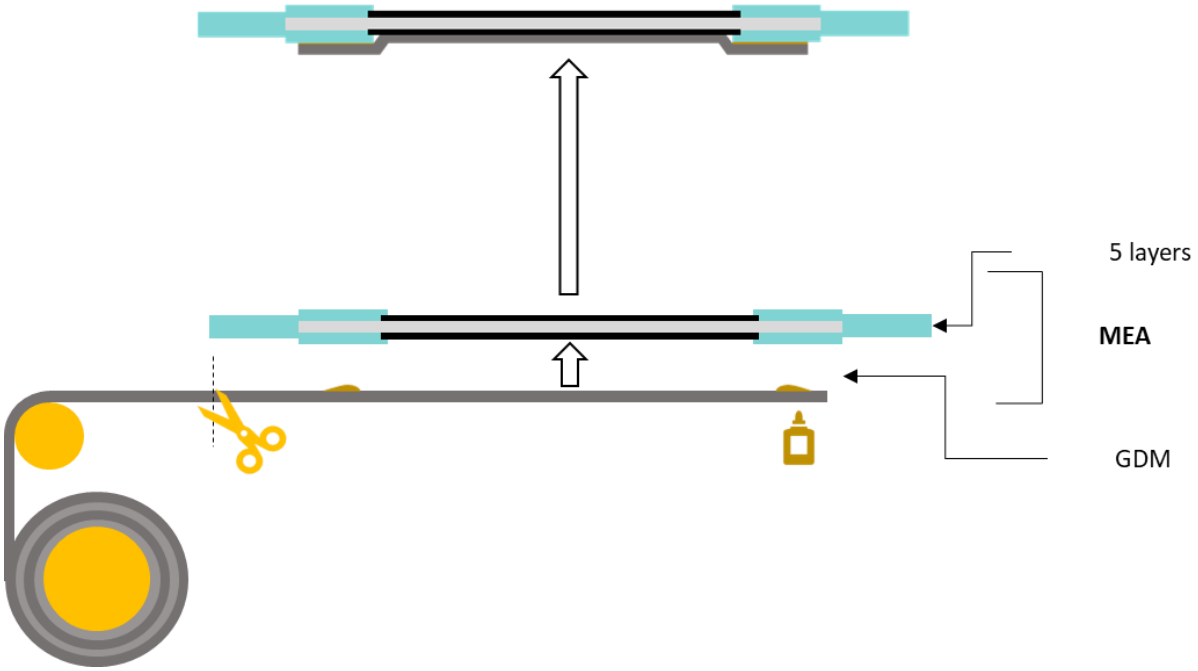

FIGURE 8 - ASSEMBLY SCHEME OF THE MEA

4. CONCLUSIONS

This public deliverable presents good practice and guide for Electrochemical Core preparation and fabrication. A reference case is presented to prepare Catalyst-Coated Membrane (CCM) components with state-of-art catalysts, membrane and ionomer materials.

The quality control and the corresponding techniques are presented to guarantee the properties of the final object related to the initial specifications in terms of Pt loading and surface state-homogeneity. These general protocols can then be adapted to produce CCM with new and innovative components.

5. ACKNOWLEDGEMENTS

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