MASS MANUFACTURE OF MEAS USING HIGH SPEED DEPOSITION PROCESSES

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DELIVERABLE REPORT 1.5

D1.5 – NON-SELECTED TECHNIQUES: REPORT ON POSSIBLE IMPROVEMENTS	
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O	*Other*	

D1.5 – Summary	
Keywords	Casting, dip coating, spin coating, spray coating, bar coating, doctor blading, screen printing, gravure printing, printed CCM, catalyst, ionomer
Full Abstract (Confidential)	In WP1, deposition techniques are reviewed and assessed. In D1.5 the technologies that are evaluated as not completely suitable for CCM manufacturing are described with the explanation of their limiting factors. In particular the less promising techniques individuated are casting, dip coating and spin coating. Spray coating, bar coating and doctor blading are more promising than the previous ones but still not acceptable. Lastly, screen printing and gravure printing are described. These two techniques are down-selected but not implemented for high-throughput production. Some possible improvements like ink adaptation and defoamer utilization for screen printing and having a high particle loading in the ink with a fast evaporation of the solvent for gravure printing are discussed.
Publishable Abstract (If different from above) ***For publication on website***	In WP1, deposition techniques are reviewed and assessed. In D1.5 the technologies that are evaluated as not completely suitable for CCM manufacturing are described with the explanation of their limiting factors. In particular the less promising techniques individuated are casting, dip coating and spin coating. Spray coating, bar coating and doctor blading are more promising than the previous ones but still not acceptable. Lastly, screen printing and gravure printing are described. These two techniques are down-selected but not implemented for high-throughput production. Some possible improvements like ink adaptation and defoamer utilization for screen printing and having a high particle loading in the ink with a fast evaporation of the solvent for gravure printing are discussed.

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0.1	24.06.2019	UNIMORE	First draft with outlines
0.2	26.03.2020	ENAS	Dip coating, screen printing and gravure printing described
0.3	09.06.2020	UNIMORE	Casting and spin coating described, comments added
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1.2	31.01.2021	TUC	Minor changes – duration of the project

D1.5 – NON-SELECTED TECHNIQUES: REPORT ON POSSIBLE IMPROVEMENTS

CONTENTS

1. INTRODUCTION

In WP1, deposition techniques are reviewed and assessed in order to identify at least two of them that can be suitable for CCM manufacturing. In previous deliverables the best ones were described while this D1.5 is focused on the not selected techniques. They are evaluated with the explanation of their limiting factors. The less promising are casting, dip coating and spin coating. Spray coating, bar coating and doctor blading are more promising than the previous ones but still not acceptable for CCM manufacturing. Lastly, screen printing and gravure printing are described. These two techniques are down-selected but not implemented for high-throughput production. Some possible improvements like ink adaptation and defoamer utilization for screen printing and having a high particle loading in the ink with a fast evaporation of the solvent for gravure printing are discussed. These two techniques are down-selected but not implemented for high-throughput production. Slot-die coating and inkjet printing are not described here, because these two techniques are used for CCM manufacturing within the project MAMA-MEA.

2. DISCUSSION ON THE LESS PROMISING TECHNIQUES

2.1. CASTING

It is the simplest film-forming technique and it consists to casting a solution onto a substrate followed by drying [1] (Figure 1). A very horizontal work surface is the only equipment needed [1].

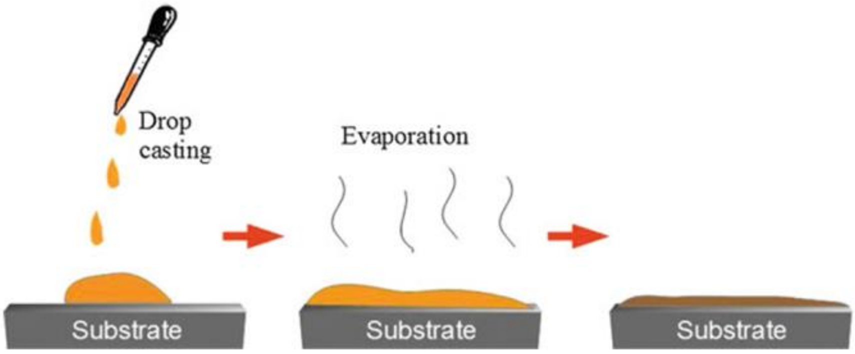

Figure 1 Casting [2]

With this technique it is possible to obtain good quality films and thick films, however, it suffers from a lack of thickness control [1]. In addition, picture framing effects can be observed near the edges of the film or precipitation during drying [1]. When the liquid surface tension dominates, the drying is inhomogeneous [1]. If crystallisation or precipitation are to be avoided the material to be coated must have high solubility in the used solvent [1].

Table 1 Comparison between features of casting vs. requirements for CCM manufacturing

Features of casting	Requirements for CCM manufacturing
No patterned inking of objects	✘ Patterned inking of object
Layer thickness difficult to control	✘ Defined layer thickness
✓: is matching / ● : o.k. / ✘ : mismatch	

Despite its simplicity, this technology doesn't match the requirements of additive manufacturing requirements of CCM manufacturing. Other deposition technologies performing better than casting should be preferred.

2.2. DIP COATING

The basic principle of dip coating is shown in Figure 2. An object (e.g. a white sheet of material) is dipped into a container (blue) containing an ink (black). For some dipping time and while insertion and removal, the ink is coating and penetrating the object. When removing the object, the remaining layer thickness can be varied by the removal speed. After removal from the ink reservoir the inked object need a drying cycle. Further information can be found in [3-4]

The features of a dip coating process are:

- Omnidirectional inking of object (even of 3D-shaped ones)
- Variation of layer thickness by process parameters (ink viscosity, inking time, removal speed, …)
- No patterned inking (except by use of masks)

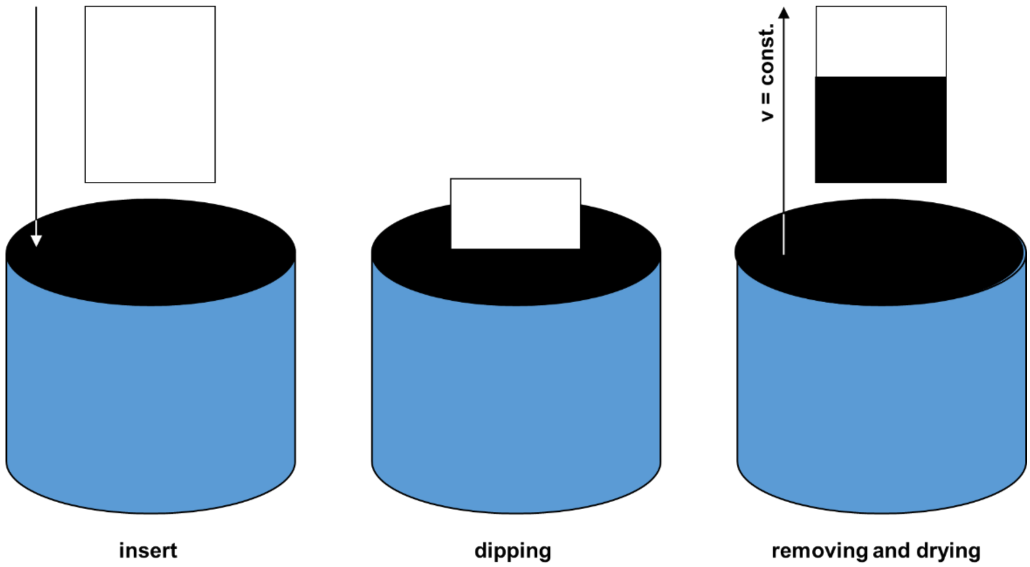

Figure 2 Schematic representation of dip coating process (blue: ink container; black: ink; white: substrate)

Dip coating is state-of-the-art in industry e.g. for inking car bodies or coating windows glasses. Also textile industry uses dip coating for soaking fabrics with chemicals or inks. All these industrial implementations have the target to ink material homogenously without any pattern. The volume of the ink reservoir is matching the application. Using chemicals or inks in these processes is a considerable financial effort. The features of this technology don't match the requirements of additive manufacturing requirements of CCM manufacturing. These aspects are shown in Table 2.

Table 2 Comparison between features of dip coating vs. requirements for CCM manufacturing

Features of dip coating	Requirements for CCM manufacturing
Omnidirectional inking of object	✘ One side inking of object ✓ One side only in special setup
No patterned inking	✘ Patterned inking of object
Layer thickness determined by process parameters	✓ Defined layer thickness
Sheet-based / can be web-based	● Web-based
✓: is matching / ● : o.k. / ✘ : mismatch	

Summarising the features of dip coating for an application in CCM manufacturing, the challenges arising are hard to overcome. As long as there are deposition technologies available performing much better than dip coating, they should be preferred for this application.

2.3. SPIN COATING

The typical spin coating operation consists in the application of a liquid to a substrate and its consequent acceleration to a chosen rotational speed [1] Figure 3.

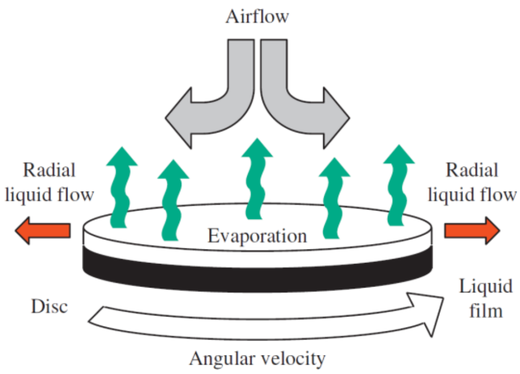

Figure 3 Spin Coating [1]

Despite film formation complexity, spin coating allows highly reproducible formation of films and it has various advantages over other coating techniques during drying, allowing the formation of very homogeneous films over area with a diameter up to 30 cm [1]. The final film thickness, morphology and surface topography from a particular material in a given solvent at a certain concentration are very reproducible [1]. The final thickness can be calculated with the formula 1 [5]:

$$h \propto \left(\frac{e\eta_i}{mf_s\rho_i\omega^2}\right)^{1/3} \quad (1),$$

where mf_s is the solvent mass fraction in the ink, ω is the angular velocity, ρ_i is the density, η_i is the viscosity and e is the evaporation rate of the ink [5]. Spin coating is extremely useful as an experimental technique on a laboratory scale but is difficult to apply for high volume production because it is a serial technique where substrates need to be handled individually, therefore it is not roll-to-roll compatible, and it does not allow the patterning of the formed film [1]. In addition, spin coating is not parsimonious with respect to ink usage [1] and the shear forces, higher at the edges of the sample compared to the centre, lead to thickness anomalies [5].

Table 3 Comparison between features of spin coating vs. requirements for CCM manufacturing

Features of spin coating	Requirements for CCM manufacturing
No patterned inking	✘ Patterned inking of object
Layer thickness determined by process parameters	✓ Defined layer thickness
Individual substrates	✘ Web-based
✓: is matching / ● : o.k. / ✘ : mismatch	

For these reasons spin coating doesn't match the requirements of additive manufacturing requirements of CCM manufacturing. Other deposition technologies performing better than spin coating should be preferred.

3. Spray coating

Spray coating is a well-known industrial technique used for producing thin films, and is often applied to making laboratory scale catalyst coated membranes (CCMs) [6]. The process can be used to produce continuous coatings or well-defined discrete patches if used in conjunction with a print mask (see Figure 4).

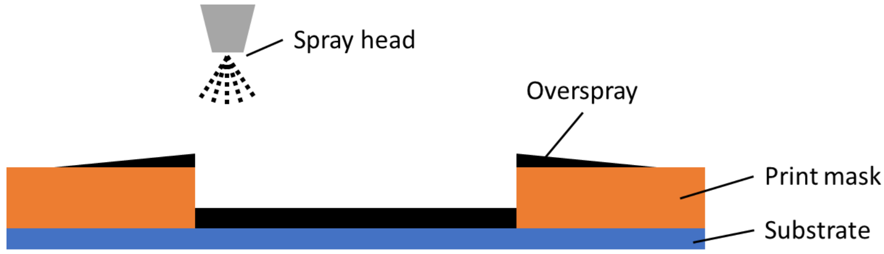

Figure 4 Spray coating of discrete patch

The spray is produced by propelling the ink out of a fine nozzle using a carrier gas. The coating width of each head is relatively small and so a single head is rasterised across the part to give complete coverage, or multiple coating heads are used. Because the ink fans out from the spray head, the resulting layer deposited will have a variation in loading, with the loading diminishing with increasing distance from the point directly below the spray head. This variation in the coating also requires the use of a print mask if a well-defined discrete shape is required. Although print masks allow well-defined shapes to be produced, it is at the cost of wasted ink that coats the mask, and the shape definition can be damaged when the mask is removed. Inks optimised for spray coating are low in solids as there is a requirement for a low viscosity for coating. This then reduces the coating speeds possible, as the coated inks need to be laid down in several layers and each layer needs to be completely dried before the next layer is coated; if the previous layer is not dried fully, the layer is disrupted by the flow of gas over the surface caused by the spraying process. Generally, a heated coating bed is used to dry the ink quickly after coating. This rapid drying is helpful for depositing porous catalyst layers but causes issues with membranes that must be gas tight. The need to dry the ink as it is coated, and the deposition of multiple layers, limits the production speeds that can be achieved using this technology. A comparison of the features of spray coating vs. the requirements for CCM manufacturing is shown in Table 4.

Table 4. Comparison between features of spray coating vs. requirements for CCM manufacturing

Features of spray coating	Requirements for CCM manufacturing
Loading control for catalyst needed	✗ Good loading distribution
Discrete shapes possible with print mask	● Patterned image
Sheet-based and web-based	● Web-based
✓: is matching / ● : o.k. / ✗ : mismatch	

4. K-BAR COATING

K-bar (Mayer bar) coating is a simple metered-off process that controls the layer thickness by using a wire-wound bar that sits on the surface of the substrate to coat a specific layer thickness. The bar is pushed into contact with the web in order to limit the ink flow under the bar. It is possible to operate with the bar pressing into a backing roller/plate or simply to tension the substrate over the bar. A reservoir of ink is placed up web of the bar and as the web moves under the bar a controlled amount of ink flows under the bar, though the exact amount of ink coated depends on the bar, ink viscosity and coating speed. This means that small variations in the raw materials can alter the coating thickness achieved. Because of the need for a reservoir of ink before the bar, only continuous coatings can be produced with this method. One of the main issues encountered with bar coating multilayers is the previous layers being damaged as the bar is dragged over the surface; this has a tendency to 'plough up' the areas where the bar is in contact with the previous layer, due to the relatively high pressure seen at the contact points. A comparison of the features of K-bar coating vs. the requirements for CCM manufacturing is shown in Table 5.

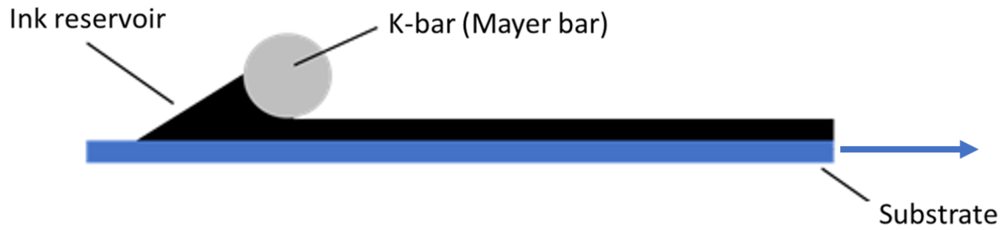

Figure 5 K-bar coating of a continuous film.

Table 5. Comparison between features of K-bar coating vs. requirements for CCM manufacturing

Features of K-bar coating	Requirements for CCM manufacturing
Loading control for catalyst	● Metered off process
Contact coating method → previous layers easily damaged by bar	✘ intact layers
Discrete shapes possible but continuous coating only	✘ patterned imaging
Sheet-based and web-based	✓ both possible
✓: is matching / ● : o.k. / ✘ : mismatch	

5. Doctor blading

Doctor blading (tape casting, knife coating) is a well-known additive layer manufacturing technique in many industries including paper, plastic, paint, and thin ceramic or metallic film manufacturing. Doctor blading technique is roll-to-roll compatible and can be scaled up for large area deposition. The technique is able to coat a substrate with a variation of wet film thickness from 10 to several hundred microns with the speed up to several meters per minute. The thickness of the layer is governed by the height of the doctor blade upon the substrate. [7-8] Additionally, for a desirable layer formation the ink viscosity has to be controlled: the ink should be viscous enough to avoid uncontrolled splashing and at the same time liquid enough to allow continuous flow.

The schematics of doctor blade techniques for coating plastic films is shown in Figure 6. It consists out of blade, tank containing the ink, and moving web of substrate with fixed blade. Alternatively, the substrate is fixed on a plain carrier and the blade is moved across it. The blade spreads the ink and determines the wet layer thickness. Then this wet film dries transforming into a solid thin film of lower thickness when solvent evaporates. In its simplest configuration, doctor blading technique does not have any fully closed ink reservoir. This may cause changes in the ink chemistry over printing time. [9]

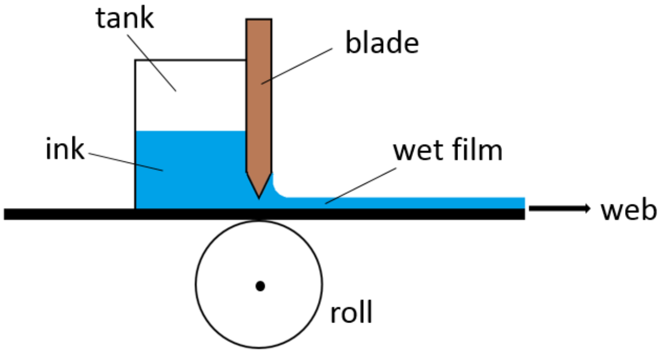

Figure 6 Schematic representation of doctor blading for plastic foil, adapted from [9]

Although doctor blading is a promising technique (Table 6) for deposition of catalyst and ionomer layers, it was not selected due to the absence of the corresponding equipment on roll-to-roll bases. Instead JMFC explored slot die coating, which has a similar approach (ink outlet defining the web film layer thickness) but offering much better control about the process parameters.

Table 6 Comparison between features of doctor blading vs. requirements for CCM manufacturing

Features of doctor blading	Requirements for CCM manufacturing
No patterned inking of object	✘ Patterned inking of object
Layer thickness determined by process parameters	✓ Defined layer thickness
Sheet-based and web-based	✓ Web-based
✓: is matching / ●: o.k. / ✘: mismatch	

6. Discussion on down-selected techniques not implemented for high-throughput production

6.1. Screen printing

The basic principle of flatbed screen printing is shown in Figure 7 as a side cut. The substrate is fixed to a flat base plate. In some distance over the top of the substrate is a screen mounted. The screen tension is caused by fixation to a metal screen frame. The screen mesh usually consists of a polymeric or metallic thread material. Thread thickness and frequency determine the ink volume that can be transferred from the top of the mesh to the beneath substrate. The ink is pushed down by a squeegee also causing a pressure onto the screen in a way that it touches the substrate only at the transfer line. By moving the squeegee from one side of the screen to the other, the ink is deposited on the substrate.
Patterning is realised by an emulsion when crafting it, closing the open screen at defined areas. The remaining open areas are for patterning the deposited ink on the substrate.
Further information can be found e.g. in [10].

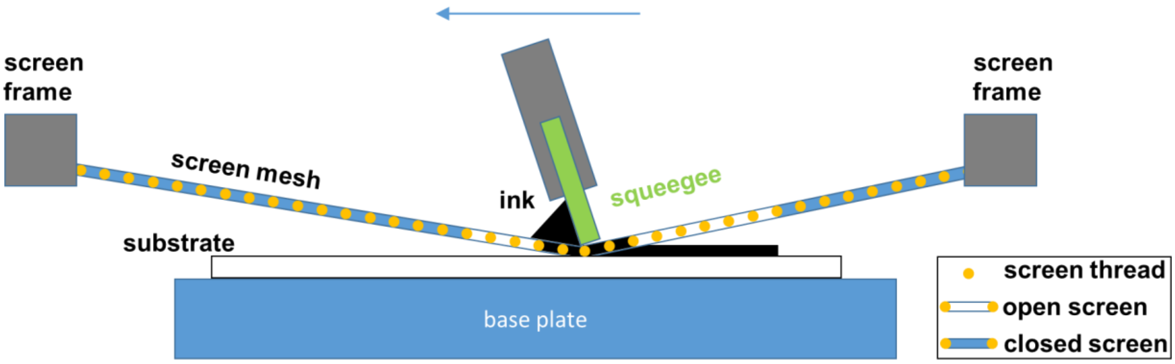

Figure 7 Schematic representation of screen printing

Another setup (without a schematic representation) is employing a screen in form of a rotating cylinder. In this plot the substrate can be web-based and large areas can be processed. This setup is used e.g. in textile industry for colouring fabrics.
In Table 7 the features of screen printing and requirements for CCM manufacturing are compared.

Table 7 Comparison between features of screen printing vs. requirements for CCM manufacturing

Features of screen printing	Requirements for CCM manufacturing
Patterned inking of object	✓ Patterned inking of object
Layer thickness determined by process parameters	✓ Defined layer thickness
Sheet-based (fled-bed) or web-based (rotary)	✓ Web-based
✓: is matching / ● : o.k. / ✗ : mismatch	

In the MAMA-MEA project, this technology has been down-selected as potential deposition technology. Based on this outcome, experiments had been performed to apply catalytic ink onto membranes.
The obstacle experienced was a non-homogenous layer formation due to inclusion of air bubbles. When squeezing the ink through the screen a high shear stress is introduced. So it may happen that the filling of the screen material doesn't eliminate the present air between the threads completely. This remaining air bubbles are transferred onto the substrate and remain in the material layer when drying.
Due to the project focus on the process evaluation rather than on ink development, there had been the decision to stop activities in the direction of screen printing. The necessary development step would be to modify and optimize the ink employed for screen printing. One approach would be to utilise defoamers to prohibit air bubble formation. These have to be compatible with the CCM functionality. Another approach would be to adjust the solvent composition within the ink to facilitate the degassing after printing. All efforts in modification of the ink should be accompanied by optimising the printing process itself by adjusting parameters like printing speed, mesh size, lift-off, etc. as well as pre-processing of the printing substrate.

6.2. Gravure Printing

The basic principle of gravure printing is shown in Figure 8. The printing form is a metal cylinder with engraved image elements (cells). These cells are cavities below the surface of the cylinder. The rotating cylinder is moved along the ink in an ink fountain bath. This bath could also be enclosed within a chamber to limit evaporation of solvent. The ink is not only filling the cavities but also wetting the whole surface of the cylinder. Therefore, a metal doctor blade is used to hold back any surplus material on the surface that is not filling the cavity. After the doctor blading there is a direct contact with the substrate under pressure impact caused by an impression roller. For generating a very good pressure line, the impression roller is covered by a rubber coating to have the contact between a hard (i.e. gravure cylinder) and a soft (i.e. impression roller) surface. In between the substrate is passed. By the pressured contact the ink is transferred from the cells onto the substrate. Additional information is given e.g. in [10].

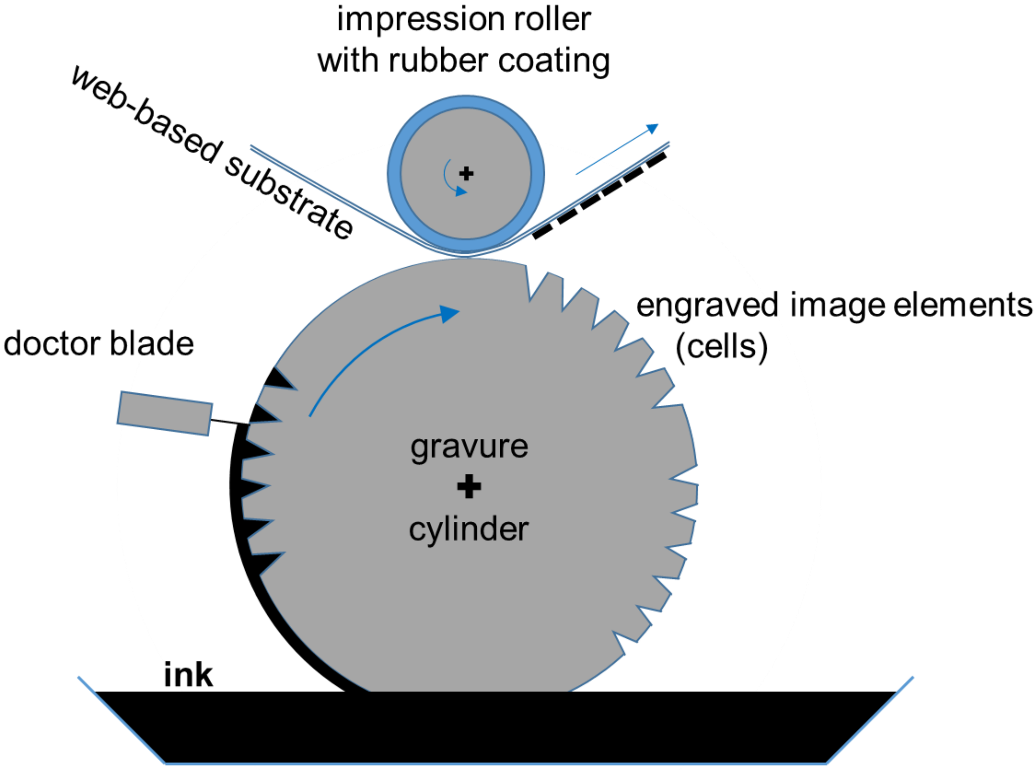

Figure 8 Schematic representation of gravure printing

In Table 8 the features of gravure printing and requirements for CCM manufacturing are compared.

Table 8 Comparison between features of gravure printing vs. requirements for CCM manufacturing

Features of gravure printing	Requirements for CCM manufacturing
Patterned inking of objects	✓ Patterned inking of object
Layer thickness determined by process parameters, typical layer thickness 1 µm	● Layer thickness > 5 µm
Web-based	✓ Web-based
High pressure for ink transfer → may damage beneath layers	● Moderate / low pressure
✓: is matching / ● : o.k. / ✘ : mismatch	

Gravure printing, used e.g. for magazine printing, is a technology delivering square meters of deposited ink within a second. In the view of high volume production this feature is very attractive for catalytic layer manufacturing. There are two restrictions of gravure printing that led to the decision within MAMA-MEA to focus on slot die coating and inkjet printing instead.

The typical layer thickness of gravure printing is in the order of 1 µm. Comparing this thickness with the requirements of CCM manufacturing, it is about only 20 % of the requirement. TU Chemnitz had demonstrated some years before the MAMA-MEA project that by an optimised machine setup, a layer thickness in one printing pass of more than 5 µm is achievable. That investigations were done by employment of an optimized ink and matching modifications of the printing unit. In MAMA-MEA there is the focus on deposition methods rather than on ink science. Therefore, the efforts needed for development could not be covered by the project. The approach would be to have a high particle loading in the ink with a fast evaporation of the solvent after printing. There is the requirement of an encapsulated printing unit to avoid fast evaporation and failure of the printing cylinder. Therefore, a strong focus in this direction would be required.

The more important reason to stop activities with gravure printing was the involvement of high pressure for ink transfer. As long as the substrate is any polymeric film of appropriate mechanical strength properties, it's rather easy to deposit one layer of material. As soon as there exists already a layer of material, new challenges arise. Besides chemical compatibility requirements also mechanical stress has to be withstand. In the topic of MAMA-MEA the approach is to generate the membrane by printing technology on top of a catalytic layer. The catalytic layer is slightly brittle and therefore tends to be destroyed in this printing step.

7. Conclusions

The not selected techniques were described in this deliverable, starting from the simplest and not suitable for the CCM manufacturing, to the very attractive ones but that were abandoned in order to focus on the most promising. In particular, screen printing and gravure printing showed very interesting performances and probably can be used in high throughput production of fully printed CCMs or at least single layers of it. A possible improvement for screen printing is to modify and adapt the ink to this deposition technology e.g. using defoamers or changing solvent composition. Regarding gravure printing, the approach would be to have a high particle loading in the ink with a fast evaporation of the solvent. There is also the requirement of an encapsulated printing unit to avoid fast evaporation and failure of the printing cylinder. Due to the described obstacles, and despite these two deposition technologies show specific benefits in CCM production, they were not further investigated within the MAMA-MEA project. The required efforts could not be spent to use these technologies, instead the manpower was focused on further improvement of slot die coating and evaluation of inkjet technology.

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