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Overview of Membrane Electrode Assembly Preparation Methods for Solid Polymer Electrolyte Electrolyzer

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http://dx.doi.org/10.5772/52947

1. Introduction

In search for improved overall efficiency, higher current density, lower membrane cost and maximized utilization of relatively expensive catalytic materials, the scientific community has produced hundreds of publications, assisting those looking for the opportunity to turn electrolyzer prototypes into commercially viable products [1]. While other chapters of this book focus on the development of catalysts and proton conductive membranes, this chapter describes the principle functions of "membrane electrode assemblies" (MEAs), followed by an overview of methods designed and developed to produce effective MEAs. The process conditions chosen during the preparation/production of MEAs have a great impact on the logistics of proton-, electron-, reagent- and product-transport. Each different method is aimed at achieving an architecture yielding optimal accessibility, stability and numbers of ''three phase boundaries'' (TPB) that contribute to the productivity and efficiency of the electrolyzer system. Proper design of the MEA is essential since the true potential of the most appropriate membrane and the most active catalysts will only be revealed in a successful MEA configuration.

List of abbreviations:

MEA - membrane electrode assembly
TPB - three phase boundary
SPE - solid polymer electrolyte
PEMFC - polymer electrolyte membrane fuel cell
Pt/C - carbon supported platinum
CL - catalyst layer
CCG - catalyst coated GDL

CCM - catalyst coated membrane
GDL - gas diffusion layer
PFSA - perfluorosulphonic acid
PTFE - polytetrafluoroethylene
PVD - physical vapour deposition
CVD - chemical vapour deposition
ES - electro spraying
EPD - electrophoretic deposition
MWNT - multi walled carbon nano tube
TEM - transmission electron microscope
SEM- scanning electron microscope
NML - noble metal loading
EASA - electrochemical active surface area
MT - mass transfer

2. The principle functions of the MEA

In both Solid Polymer Electrolyte (SPE) and Fuel Cell MEAs the principle function of the MEA is to efficiently control the flow of electrons liberated at the electron donating reaction (the anode) to the electron accepting reaction (cathode). This is typically achieved by separating the cathodic reaction from the anodic reaction by using a membrane that conducts protons (H^+) only. Electrons are channelled through an external circuit from the anode to the cathode. By controlling the flow and direction of electrons, H_2O can either be used to produce H_2 and O_2 (Electrolysis) or can be produced from H_2 and O_2 (fuel cell). The anode and the cathode reaction for an SPE electrolyzer are shown in equation 1 and 2 respectively;

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad \text{(anode, electron donating reactions)} \qquad (1)$$

$$4H^+ + 4e^- \rightarrow 2H_2 \qquad \text{(cathode, electron accepting reactions)} \qquad (2)$$

Since the enthalpy of H_2 and O_2 is higher than the enthalpy of H_2O, a sufficiently high electrical potential has to be applied between the two electrodes to force a flow of electrons from the anode to the cathode. One of the aims in SPE MEA design is to minimize power losses during the electrolysis process. Hereafter, SPE MEAs will be referred as MEAs in this chapter. Total power losses are related both to the material properties of MEA components and the MEA production methods (the way the components are put together). The various components in a typical MEA are listed in Table 1;

Different groups of researchers have been optimizing the properties of each component. Components with the most promising properties have been assembled into MEAs. The most commonly used membrane is Nafion® 115 with mainly commercial IrO_2 as anode catalyst, and commercially available carbon supported Pt as cathode. Ti-fibre as anode backing and E-TEK / Toray carbon paper/cloth as commercial backing on the cathode. Typically, MEA performance is given as the current density as function of applied potential. Table 2 gives an

overview of various published MEA performances with listed components and production methods used.

No	MEA COMPONENT	PROPERTIES
1	Membrane	Conductance (1/S), gas permeance, electroosmotic properties (all as function of temperature)
2	Cathode catalyst	Catalytic activity of the specific material, electrical resistance of the cathode layer, particle size
3	Anode catalyst	Catalytic activity of the material, electrical resistance of the anode layer, particle size
4	Cathode backing layer	Mass transfer of reactants and reaction products
5	Anode backing layer	Mass transfer of reactants and reaction products

Table 1. MEA components and their main properties

The results reveal that the true potential of the MEA is not only determined by the properties of the individual components but mainly by the MEA production method. Before describing various MEA preparation methods, the concept of TPB is explained in conjunction with the logistics around electrons, protons, reactants and products.

3. Logistics at three phase boundaries

Since MEAs have no significant capacitance, accumulation of protons or electrons at either surface of the MEA is negligible. Therefore, both half cell reactions will happen at exactly the same rate. In order for an MEA to function, the following conditions must be met;

a. The combined electrode overpotential should be low enough for the reactions to occur at a reasonable rate, typically <2V.
b. Each electron liberated at the anode catalyst in accordance with equation 1 has to find its way to a cathode catalyst particle in order to recombine in accordance with equation 2. For the electrons to flow, a path of sufficient electro conductivity running from the anode catalyst particle to the cathode catalyst particle must be available. Concurrently, a path with sufficient proton conductivity must be available to transport the H^+ from the anode catalyst, through the membrane, to the cathode catalyst.
c. For the reactions to continue, reactants (water) should be supplied continuously to the anode catalyst site (that holds both required protonic and electronic connection with the cathode catalyst). Products such as O_2 and H_2, need to be removed on a continuous bases from the anode and cathode respectively.

The three dimensional interfaces where catalyst, ionomer and reactant convene to meet all three conditions, are called the three phase boundaries (TPBs). From conditions B and C it can be concluded that not only the number of TPBs are important but also the logistics of proton-, electron-, reagent- and product-transport. Both factors determine the rate and efficiency at which the MEA can produce H_2 and O_2 from water. A schematic representation of the TPB is shown in Figure 1.

Ref	MEA Size (cm²)	Production Methode Anode	Production Methode Cathode	Pmin (Mpa)	Pmax (Mpa)	Time (Sec)	Tmin (oC)	Tmax (oC)	Electrolyte	Thickness (mm)	Catalyst type Anode	Catalyst type Cathode	Loading (A/C/IA /IC*)	Backing Anode	Backing Cathode	Test Cell clamping force
2	100	CCM (spray)	CCS (paste spreading)						Nafion 115	127	IrO2 (inhouse)	30%Pt/C ETEK	3/0.6/33/33	Ti-grid 260	GDL ELAT	15kg/cm2
2	100	CCM (spray)	CCS (paste spreading)						Nafion 115	127	IrO2 (inhouse)	30%Pt/C ETEK	3/0.6/33/33	Ti-grid 500	GDL ELAT	15kg/cm2
2	100	CCM (spray)	CCS (paste spreading)						Nafion 115	127	IrO2 (inhouse)	30%Pt/C ETEK	3/0.6/33/33	Ti-grid 500	GDL ELAT	25kg/cm2
2	100	CCM (spray)	CCS (paste spreading)						Nafion 115	127	IrO2 (inhouse)	30%Pt/C ETEK	3/0.6/33/33	Ti-grid 500	GDL ELAT	25kg/cm2
3	100	CCM (spray)	CCS (spread)						Nafion 115	125	IrO2 (inhouse)	30%Pt/C ETEK	2.5/0.5/33/33	Ti-Mesh	GDL ELAT	25kg/cm2
4	100	CCM (spray)	GDE Etek						Nafion 115	125	IrO2 (inhouse)	GDE Etek	2.5/0.6/?/33	Ti-Mesh	Carbon Cloth	7Nm
4	5	CCM (spray)	CCS (paste spreading)						Nafion 115	125	IrO2 (inhouse)	30%Pt/C ETEK	3/0.6/33/33	Ti-Mesh	GDL ELAT	9Nm
4	5	CCM (spray)	CCS (paste spreading)						Nafion 115	125	IrO2 (inhouse)	30%Pt/C ETEK	3/0.6/33/33	Ti-Mesh	GDL ELAT	9Nm
5	X	CCM (spray)	CCS (paste spreading)						Nafion 115	125	IrO2/TiOx	30%Pt/C ETEK	1/ 1 /33 /33	Ti-Grid - mod	GDL ELAT	75kg/cm2
5	X	CCM (spray)	CCS (paste spreading)						Nafion 115	125	IrO2/TiOx	30%Pt/C ETEK	1/ 1 /33 /33	Ti-Grid - mod	GDL ELAT	75kg/cm2
6	160	prototype Giner GS-10 electrolyzer, no details provided														
6	160	prototype Giner GS-10 electrolyzer, no details provided														
7	27		CCS (x)						Nafion 115	127	IrO2	Pt	x /x / x/ x	Ti-Felt (Pt mod)	Toray TGP-H-090	
7	27		CCS (x)						Nafion 115	127	IrO2	Pt	x /x / x/ x	Ti felt (Pt mod)	Toray TGP-H-090	
8	5	CCM (spray)	CCS (paste spreading)						Nafion 115	127	IrO2 (inhouse)	30%Pt/C ETEK	2.5/0.5/33/33	Ti-Mesh	GDL ELAT	
9	2500	No details							Nafion 112	50	No details					
10	4	CCS (spray on silicon rubber)		4	17	90	168	198	30PES SPEEK	127	Ir Black	20% Pt/C (JM)	5/1.5/15/x	Ti mesh 40	Toray CP	
10	4	CCS (spray on silicon rubber)			8	90	130		Nafion 115	127	Ir Black	20% Pt/C (JM)	5/1.5/15/x	Ti mesh 40	Toray CP	
11	5	CCM (spray)			10	x	140		Nafion 1035	89	Ir0.4Ru0.6O2	RuO2/C (25%)	1/0.5/25/25	Toray TGP-H-060	Toray TGP-H-060	
11	5	CCM (spray)			10	x	140		Nafion 1035	89	Ir0.4Ru0.6O2	Pt/C (28%)	1/0.5/25/25	Toray TGP-H-060	Toray TGP-H-060	
12	4	CCS (spray on silicon rubber)			8	90	130		Nafion 112	50	Ir black	Pt Black (JM)	3.8/2.3/13/11	Ti mesh 40	Toray CP	
13	50	CCS brush coating	CCS SPD		x	x	130		Nafion 115	127	Ir black	20%Pt/C	0.3/x/x/5	Ti-Mesh (Pt mod)	Porous CP	
14	100	CCS brush coating	CCS SPD		x	x	130		Nafion 115	127	Ir black	20%Pt/C	0.3/0.4/x/5	Ti-Mesh (Pt mod)	Porous CP	
14	9	CCS brush coating	CCS SPD		x	x	130		Nafion 112	50	Ir black	20%Pt/C	0.3/0.4/x/5	Ti-Mesh (Pt mod)	Porous CP	
15	X	CCS (ink "applied" to GDL)			5.5	180	140		Nafion 112	50	Pt & Ir black 85:15		4/4/20/20	LT140W Elat	LT140W Elat	
16	27	Hot pressed electrodes to membrane							Nafion 112	50	Pt & IrO2 mixed			Ti felt (Bekinit)	Toray 090	
17	4	CCM (spray)							Nafion 115	127	Ir0.6Ru0.4O2	20% Pt/C (JM)	2/0.4/5/10	Ti sinter	Ti sinter	
18	4	CCM (spray)							Nafion 115	127	IrO2	20% Pt/C (JM)	2/0.4/5/10	Ti sinter	Ti sinter	
19	4	CCM (spray)							Nafion 115	127	IrO2	20% Pt/C (JM)	2/0.4/5/10	Ti sinter	Ti sinter	
20	5	CCGDL							Nafion 115	127	IrO2	30% Pt/C (JM)	3/0.6/33/33	Carbon cloth	Carbon cloth	
21	5	CCM (spray)							Nafion 115	127	IrO2	40% Pt/C (JM)	2/0.5/33/33	Carbon cloth	Carbon cloth	
22	1	CCGDL							Nafion 212	51	IrO2/SnO2	40% Pt/C (JM)	1.5/0.3/30/30	Carbon cloth	Carbon cloth	
23	100	CCM		hot press					B2-type	51	IrO2	40% Pt/C (JM)	4/2.4/25/25	GP CP	GP CP	
24	5	CCM (spraying)		catalyst on sprayed nafion layer					Nafion 115	127	IrO2	Pt black	2.5/2/30/30	GP CP	CP	

X=missing details; GP=Gold plated; CP= Carbon paper; GDL= Gas diffusion layer; CCM= Catalyst Coated Membrane CCS= Catalyst Coated Substrate; SPD=Screen Print Diffusion

Table 2. MEA performance, components and production methods (Ref [2-24])
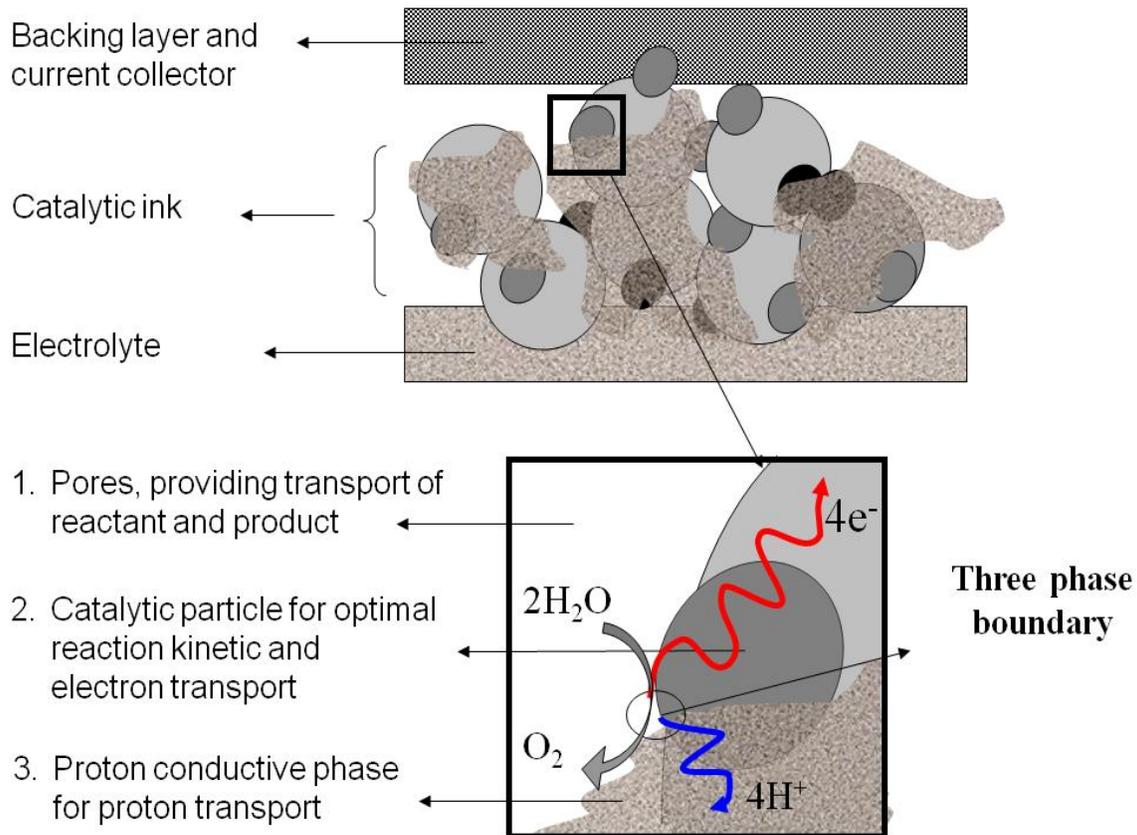
Figure 1. Schematic overview of the three phase boundary

For the cathode of a SPE electrolyzer, the catalyst layer (CL) structure is similar with that for PEMFC. Normally, carbon supported platinum (Pt/C) catalysts are used in these CLs. For the anode of a SPE electrolyzer, the CL differs somewhat from that for PEMFC due to the unavailability of carbon support in anode catalyst. For example, oxides such as IrO2, Ir–Ru, Ir–Sn, Ir–Ta, Ir–Ru–Sn and Ir–Ru–Ta etc were widely used as oxygen evolution electrocatalysts in anode CL. Particles of supported catalysts are well dispersed and extend deep into layers of carbon particles, which requires more ionomer to extend the TPB whereas in unsupported catalysts, the catalyst layer is only one to two layers thick and therefore requires less ionomer for optimum TPB.

The principle functions of the MEA are summarized in the left column of Table 3. The right column provide parameters that influences these functions

4. Membrane electrode assembly production methods

As mentioned in the previous section, each MEA preparation method is aimed at achieving a MEA architecture with an optimal accessibility, stability and number of TPB. Generally the approaches taken to produce MEA can be divided into A and B as depicted in Figure 2. Catalysts are either applied directly onto the proton conductive membrane or onto the electrically conductive supports. The different ways catalysts are applied on either surface is discussed in the following paragraphs.

No	FUNCTIONS OF THE MEA	
1	Separate cathode and anode reactions	Membrane properties (gas permeance)
2	Channelling electrodes from the anode to the current collector and from the current collector to the cathode	Catalyst type, electrical resistivity of the membrane material
3	Provide optimal electrochemical activity	Catalyst type
4	Provide optimal number of TPBs	MEA preparation method, catalyst type
5	Provide structure that facilitate electron transport from current collector to TPBs at the minimal overall electrical resistance	MEA preparation method, catalyst type, support type, ionomer type and loading
6	Provide structure that facilitates proton transport from TPBs to PEM with the optimal proton conductivity	MEA preparation method, ionomer content, ionomer type
7	Provide structure that allows for products to be transported away from TPBs, as accumulation of products will have a negative impact on the rate at which reactants can reach the TPBs	MEA preparation method, ink composition including hydrophobic / hydrophilic components
8	Provide structure that allows for reactants to reach TPBs	MEA preparation method, ink composition including hydrophobic / hydrophilic components

Table 3. MEA components and their main properties
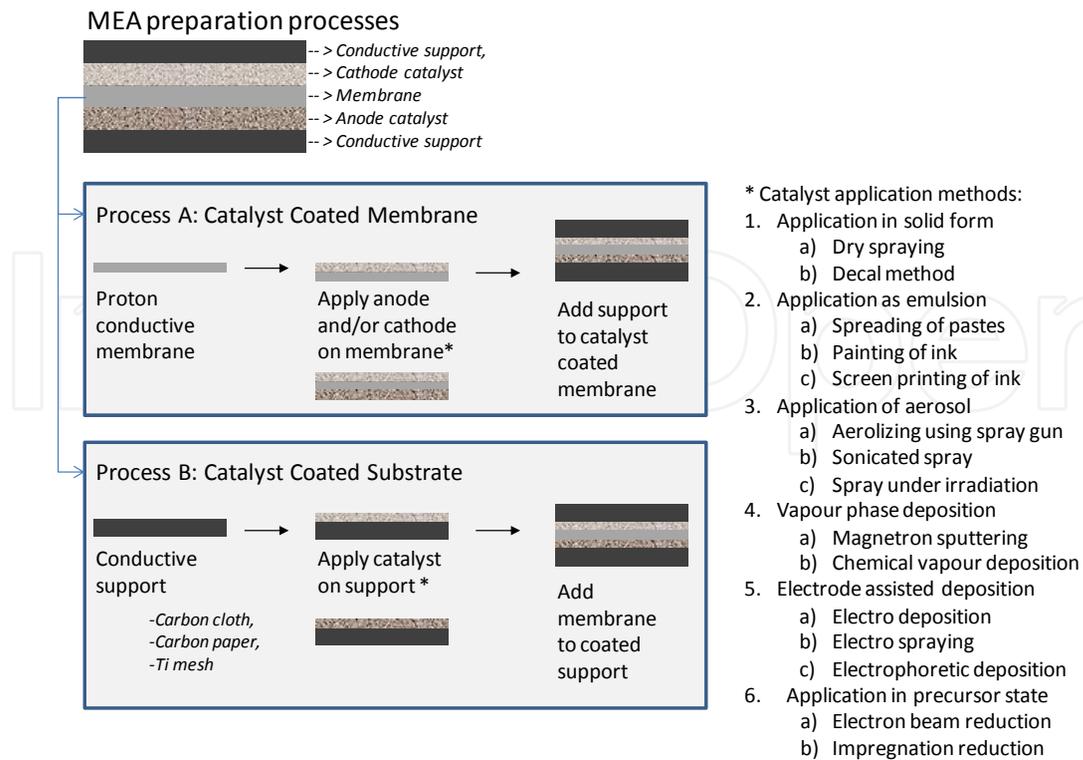
Figure 2. Schematic of catalyst-coated GDL (CCG) and catalyst-coated membrane (CCM) structures.

5. Application of the catalyst in solid form

a.   Dry spraying

Dry spraying is a method of depositing CL from dry powder electrode material, based on the adaptation of a rolling process. After mixing the reactive materials (catalysts, PTFE, PFSA powder and/or filler materials) in a knife mill, it is then atomized and sprayed in a nitrogen stream through a slit nozzle directly onto the GDL or membrane. This reactive layer is fixed and thoroughly connected to the membrane by passing them through a calender. Although adhesion of the catalytic material on the surface is strong, the layer is further fixed by hot rolling or pressing to improve the electric and ionic contact. Depending upon the degree of atomization, a completely, uniformly covered reactive layer with thickness down to 5 µm can be prepared with this technique [25]. A consistent particle size distribution is a reason for using dry spraying. The procedure is simple and, as a dry process, avoids the use of any solvents and drying steps.

b.   Decal method

Decal method is the most commonly used route for fabricating CL on either side of SPE membrane [26-27]. In this method, the catalyst ink (electrolyte ionomer, catalysts and solvent mixture) is coated on a decal that has precisely the same dimensions as that of the active area in the water electrolyzer. The widely used decal material for this purpose is fiberglass reinforced Teflon (200-300 mm thick). Prior to catalyst coating, the decal surface must be cleaned with a solvent, then treated with a Teflon release agent and dried at room temperature. Desired catalyst loading can be achieved by repeated painting and drying of the decal. Drying the slurry-coated decals at high temperature (100-150 $^{\circ}$C) in a vacuum oven for 30-60 minutes between each coating ensures complete solvent evaporation and ionomer redistribution. The pretreated membrane is sandwiched between two catalyst-coated decals, with the catalyst-coated sides facing each other. The decal/membrane assembly is then enveloped between two PTFE blanks, followed by sandwiching two stainless-steel sheets and compressed using a preheated hot press at a compression pressure for few minutes. The next step is transfer of CL from the decal to the PEM to produce a CCM. This is done again at high temperature and pressure using a hot press. After cooling the hot-pressed assembly to room temperature, the decals can be peeled away from the membrane, then two thin casting layers of catalysts are left on the membrane. The GDLs can then be added to the CCM either by hot-pressing or without the need for hot-pressing, if a uniform compression force and low contact resistance can be ensured during the cell assembly.

6. Application of the catalyst as emulsion

Various techniques have been categorized as application of the catalyst as emulsion including spreading, painting and screen printing. These techniques involve one of the following routes as discussed earlier: coating the CL on the membrane (CCM) or coating the CL on the GDL (CCG). In either route, the first step is the preparation of catalyst-electrolyte

ionomer-solvent emulsion, which will be coated as slurry or paste on the SPE membrane or GDL.

a.   Spreading of pastes

In this technique, the previously prepared catalyst emulsion is spread onto a membrane or wet-proofed GDL using a heavy stainless-steel cylinder (spreading mill) on a flat surface or by rolling-in between two rotating cylinders [28]. The thickness of the prepared CL can be controlled by adjusting the distance between the rolling cylinders. The roller-pressed CLs are uniformly thin and the catalyst loading is directly proportional to the CL thickness. The CCM or CCG thus prepared must be hot-pressed with the GDL or SPE membrane to fabricate the MEA.

b.   Painting of ink

In the painting method, the catalyst ink is brush-painted directly onto a dry ion-exchanged membrane in the Na^+ form and then baked in an oven to evaporate the solvent in the ink. A more uniform CL might be difficult to achieve through this method as there could be a significant distortion on the membrane during painting and drying. This can be overcome by drying the membrane in a special vacuum table heating fixture. Also the bulk of the solvent is removed at a lower temperature to alleviate cracking, and later the final traces of solvent are rapidly removed at higher temperature (> 80 °C). In the last step, the catalyzed membranes are rehydrated and ion-exchanged to H^+ form by immersing them in slightly boiling sulphuric acid followed by rinsing in deionized water.

c.   Screen printing of ink

The screen printing method has not been widely used for MEA preparation as much as spreading or painting for SPE water electrolyzer. Four items are essential for screen printing: the printing medium (catalyst ink), a substrate onto which the print will be made (GDL or membrane), a screen to define the required patterns, and a squeegee to force the ink through the screen [29]. In this method, a screen sieve is held above the substrate, while the pre-prepared catalyst slurry or ink is applied over it. As the squeegee travels over the screen, it presses it down into contact with the substrate pushing the paste through the screen thus depositing the catalyst ink onto the substrate surface. The pore size in the screen must be optimized to be about the same size as that of catalyst particles to get an optimum print quality. The limitation of this method is that larger particles tend to get clogged and could produce irregularly printed patterns on the substrate surface.

7. Application of the catalyst as vapour

The vapour deposition methods also yield thin CLs, but unlike the slurry (ink)-based preparation methods, vapour deposition does not yield a uniform layer of electrolyte matrix in the CL. Here the unsupported catalyst is deposited as a metal on the SPE membrane or GDL from its vapour phase. The need for an electrolyte matrix (ionomer) inside the CL is altogether eliminated in vapour deposition processes owing to their ability to fabricate ultra-

thin CLs (as low as 1 μm). The most common vapour deposition methods are physical vapour deposition (PVD; e.g., magnetron sputtering) and chemical vapour deposition (CVD).

a.   Magnetron sputtering

Sputtering is a PVD process in which the atoms from the source material (target) erode and get deposited on the substrate. It is performed in a vacuum chamber or in a controlled environment chamber that uses argon plasma. Despite the ability to produce CLs as thin as 1 mm, the performance of MEA prepared using sputter-deposited CLs varies by several orders of magnitude primarily due to the variation in CL thickness and particle size (<10 nm). Sputtering thick CLs (>10 um) is disadvantageous because of the absence of ionomer inside the CL [30]. In such cases, impregnation of PTFE and carbon power into the porous substrate is crucial to enhance ionic transport. Methods to create three dimensional reaction zones from two-dimensional thin film structure have demonstrated improved performance. Although the sputtering technique provides an easier way of direct deposition of CL, the main drawback of this technique is the poor adherence of platinum to the substrate. As a result, the catalyst is prone to dissolution and sintering under variable operating conditions and is often not durable enough to meet the long-term requirements of the MEA application. So far, published material related to magnetron sputtered MEA were related to PEMFC MEAs.

b.   Chemical vapour deposition

Chemical vapour deposition is similar to a PVD process in many aspects, but instead of using solid precursors (targets) to deposit a thin film of solid material, it uses gas-phase precursors. This process chemically transforms the gaseous precursor molecules into a solid material in the form of thin film or powder on the substrate surface. In essence, the CVD method enables the platinization of the dispersed carbon particles and does not directly produce a CL. Platinum particles selectively deposit on the surface defects produced by the acid pretreatment of the carbon particles; hence, the particles are small (<5 nm) and highly dispersed [31].

8. Electrically assisted catalyst deposition

The electrically assisted catalyst deposition is a novel technique for electrode fabrication under the influence of electric field (electrochemical processes), including electro deposition, electro spraying (ES) and electrophoretic deposition (EPD). Similar to vacuum deposition methods, the electrochemical methods provide the feasibility of fabricating ultra-thin CLs with superior properties.

a.   Electro deposition

Electro deposition process for MEA preparation involves several steps including impregnation of the porous GDL with ionomer, exchange of cations in the ionomer with a cationic complex, followed by electro deposition of catalyst from this complex onto the

support [32]. This results in the deposition of catalyst only at sites that are accessible by both support and ionomer, thus providing good utilization. This technique is capable of producing loadings as low as 0.05 mg cm^{-2}. Another method of electro deposition process involves deposition of catalyst from the electrolyte through the membrane and the catalyst is deposited where it encounters the electrically conducting carbon. This process deposits the metal catalyst only at locations where both protonic and electronic conduction are possible, thus yielding a loading as low as 10 μg cm^{-2}.

b.   Electro spraying

Electro spraying is as the name indicates, spraying a jet of catalyst ink from a capillary tube under the influence of high electric field [33]. The ES apparatus consists of a capillary tube (similar to a spray gun) in which the catalyst ink is forced to flow by using a pressurized inert gas (nitrogen or argon) toward the substrate. Very high electric field (3–4 kV) is applied between this capillary tube and the substrate. A jet of catalyst ink emerging out of the capillary tube is converted into a jet of highly charged particles under the influence of electric field. Owing to solvent evaporation and coulomb expansion (droplet division resulting from high charge density), the droplets of electro sprayed ink reduce in size before reaching the substrate. Thus a thin layer of catalyst-ionomer is deposited onto the GDL, which can then be hot-pressed with the membrane. Both morphological and structural improvements have been observed that contribute to a better catalyst utilization compared to more conventional methods.

c.   Electrophoretic deposition

Electrophoretic deposition is a process in which charged particles in a colloidal suspension move toward oppositely charged electrodes under the influence of a high electric field [34]. The particles coagulate into a dense mass during deposition, which can produce complex geometries and functionally graded materials, suitable for preparing graded CLs. The catalyst suspension must possess good electrochemical stability to avoid any parasitic faradaic reactions even at very high cell voltages. For preparing a MEA using electrophoretic process, the catalyst-ionomer CL can be directly coated onto the membrane (CCM) without the need for hot-pressing or decal transfer.

9. Application of catalyst in precursor state

a.   Electron beam reduction

The electron-beam reduction for electrode preparation is a novel method that utilizes the idea of reducing ions of the catalyst species right on the carbon cloth fibers and the multi walled carbon nano tubes (MWNTs) via direct electron-beam bombardment [35]. The basic procedure of the method involved an ionic solution, such as $PtCl_4$, then wetted onto the TEM specimen copper grid and dried in the air. The air-dried copper grid on the specimen holder inserted the whole module into the TEM column. With an accelerating voltage of 80 kV and a 2×10^{-6} Torr vacuum, the Pt^{4+} ions were struck by 80 keV electrons (e^-) and reduced to Pt^0 nanoparticles on the copper grid. Meanwhile, the $Cl_2(aq)^-$ and $H_2O(l)$ were

transformed into $Cl_2(g)$ and $H_2O(g)$ and were immediately removed by the TEM vacuum pump. In this process, high energy electron-beams emit from transmission electron microscopes (TEM), scanning electron microscopes (SEM), or electron-beam writers, so basically this method transforms the TEM or SEM into a device that fabricates catalyst particles for electrodes.

b.   Impregnation reduction

This process is also known as electroless deposition [36]. In this method, the membrane is ion exchanged with NaOH to the Na^+ form. It is then equilibrated with an aqueous mixture of hydrazine $(NH_3)_4PtCl_2$ and a co-solvent of H_2O/CH_3OH, in an impregnation step. Following impregnation, the vacuum-dried PFSA ionomer membrane in the H^+ form is exposed to air on one face and to aqueous reductants such as hydrazine N_2H_4 or $NaBH_4$ on the other face, during which the platinum ions are reduced to form metallic platinum, in the reduction step. This method has been found to produce catalyst loadings on the order of 2–6 mgPt cm^{-2}. Following the reduction step, the fabricated CCM is equilibrated with 0.5 mol L^{-1} sulphuric acid prior to hot-pressing step with the GDL. Note that a carbon-coated membrane is an essential precursor for this process in order to provide support to the catalyst particles.

10. Application of the catalyst as aerosol

a.   Aerosolizing using spraying gun

Similar to spreading and tape casting, the prerequisite for this technique is the catalyst ink. Spraying is one of the most popular methods for CL fabrication [37]. In this method, the catalyst ink is sprayed using an air-brush onto the membrane or GDL using a pressurized stream of inert gas such as argon or nitrogen. Unlike the spreading method, spraying is done in multiple steps in order to achieve the desired loading or thickness. The sprayed catalyst ink is then evaporated, and sometimes sintered at 80-120 ^{o}C, before spraying the next coating of thin layer. Manually sprayed CLs are not as uniform as the roller-pressed ones, but computer-controlled industrial sprayers are known to produce uniform layers.

b.   Sonicated spraying

Sonicated spraying is a novel technique for electrodes preparation based on ultrasonic and sonoelectrochemical devices [38-40]. In the process, the catalyst inks are first inserted in a sonicated syringe prior to atomisation in a nozzle and sprayed at a flow rate up to 2.4 ml min^{-1}. Various passes are performed in view of obtaining the appropriate loading. Here, the ultrasonic spray incorporate an ultrasonic atomizing nozzle, vibrating at high frequency ultrasound (120 kHz) created by piezoelectric transducers inside the nozzle's titanium housing. The catalyst inks are pumped through the nozzle and are atomized into a fine mist at the nozzle tip to produce highly repeatable thin films of micron-sized droplets, with coating thicknesses from 200 nm to 500 μm. The ultrasonic-spray method distribute the catalyst ink more evenly leading to better catalyst utilisation compared to the hand-painted method and this is further evident at lower catalyst loadings.

11. Factors influencing the MEA performance

In addition to the MEA preparation methods, the MEA performance also depends on key physical properties such as the membrane glass transition temperature, pressure distribution across and within the MEA, feed water quality, gas crossover (especially at high pressure), gas departure, contact resistance between the sublayers, catalyst loading, ionomer content, and the long-term stability of the sublayers.

Pressure Distribution

Uniform and optimal pressure distribution is essential during the design, engineering, and assembly of an electrolyzer or stack. Nonuniform pressure distribution, especially for MEA with big-size, could cause performance issues such as gas leakage, high contact resistance, malfunctioning of cells, or even physical damage to stack components. Uneven pressure distribution may also result in localized hot spots creating pinholes in the membrane, which could have a detrimental effect on the electrolyzer performance.

Water Quality

The conductivity of water supply for SPE electrolyzer has very important effect on the long-term performance of MEA. Due to the use of titanium materials and IrO_2 catalyst at the anode, the corrosion or aging of the MEA was not likely to happen in the primary operation. Therefore, the performance degradation in the primary running is mainly caused by a contamination from the feed water. There is considerable accumulation of ionic species in the feed water with the process of water electrolysis, the main reason leading to short period performance decline of the MEA. These ionic species mainly originate from the water tank, piping and other components of the test stand, which can be dissolved in water in trace amounts , and not only concentrated with the water being electrolyzed, but also added from time to time with refilling the water tank. To maintain good performance, it is therefore crucial to use high quality feed water.

Electrochemical Active Surface Area (EASA)

The EASA is the important parameter that determines the MEA performance than the catalyst loading itself. Higher EASA would result in better catalyst utilization although it is not always guaranteed. The performance of water electrolysis also depends on the type of materials used for the MEA components, bipolar plates, and other stack components. Although the operating conditions also play an important role in determining the performance of electrolyzer, it can be conclusively said that the MEA has a more dominant role. A water electrolyzer polarization curve consists of three regions, namely the activation (kinetic), ohmic, and mass transfer regions. The myriad of material, chemical, and electrochemical properties of each MEA sublayer have a profound influence on the performance in each of these regions. This is conceptually described in the polarization curve shown in the Figure 3.

Activation Polarization

The activation polarization loss (kinetic loss) occurs because of the sluggishness in oxygen evolution kinetics at the anode and can be minimized by using a high active catalyst. The CL

properties such as catalyst loading, type of catalyst, utilization, electrochemical active area, and the stability of the catalyst support are some properties that play a role in determining the water electrolysis performance in the activation region of the polarization curve.
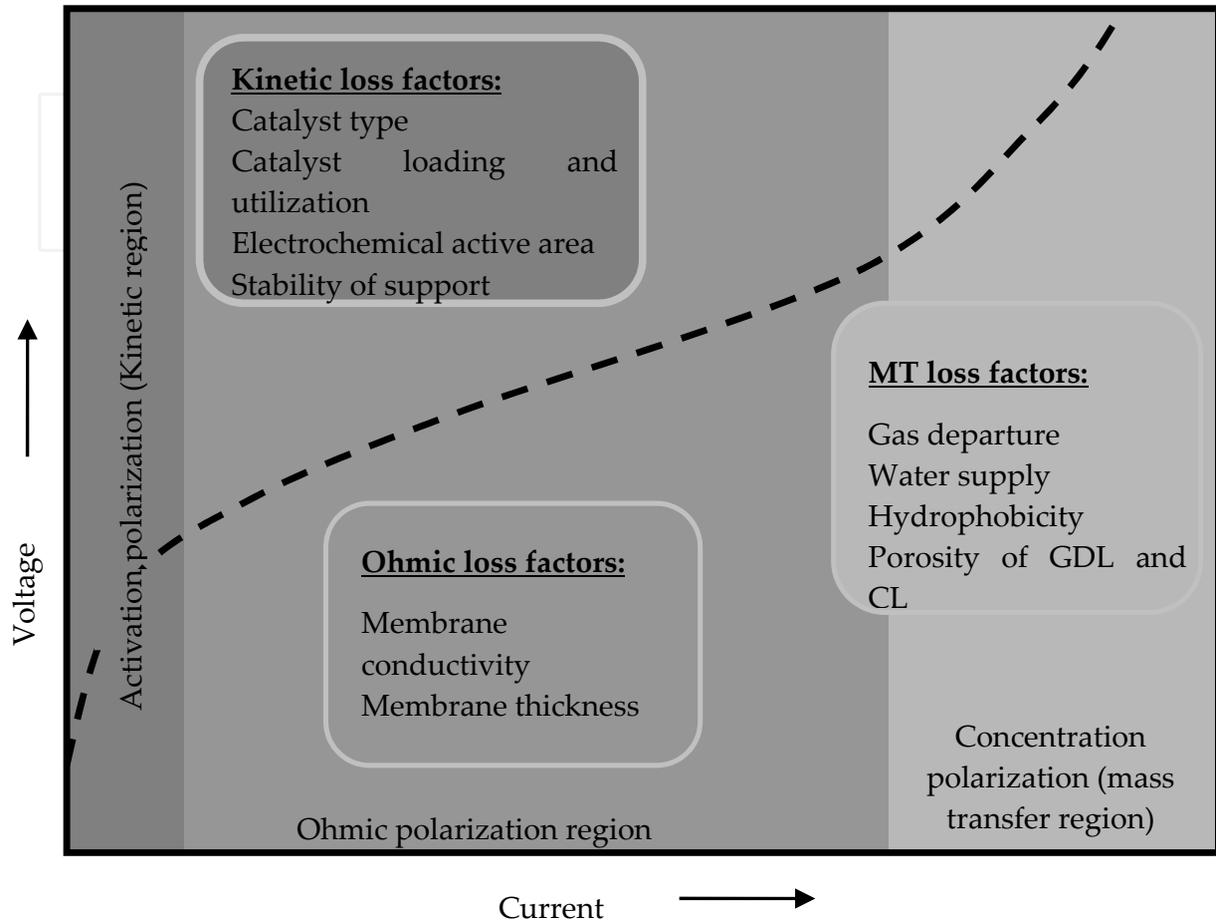
Figure 3. Conceptual representation of performance influencing MEA properties in the activation, ohmic, and mass transfer (MT) regions of an electrolyzer polarization curve.

Ohmic Polarization

The performance of MEA in the ohmic region is largely dependent on the electrical conductivity of stack components especially the bipolar plates. In the case of a single cell, the membrane ionic conductivity is the single most dominant factor to influence the ohmic polarization behavior. Properties such as membrane ionic conductivity, thickness, contact resistance between the MEA sublayers, compression pressure, and the electronic conductivity of the GDL are some key factors that play a role in determining the performance in the ohmic region of the polarization curve.

Concentration Polarization

At high current densities, the MEA performance is affected by mass transfer limitations for the diffusion of gaseous products and water transport inside the pores of MEA sublayers. One must ensure effective two-phase transport inside the pores of bilayer GDL and CL in order to keep the MEA dry under wet operating conditions. Properties such as PTFE content

(hydrophobicity), porosity, pore size, and compression pressure (which determines the interfacial gaps between the MEA sublayers during different compression load cycles during operation) determine the MEA performance in the mass transfer region of the polarization curve.

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