Preparation methods of membrane electrode assemblies for proton exchange membrane fuel cells and unitized regenerative fuel cells: A review

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Amit C. Bhosale[1*], Prakash C. Ghosh[2], Loïc Assaud[3*]

[1]Department of Hydro and Renewable Energy, Indian Institute of Technology Roorkee, Haridwar, Uttarakhand-247667, India

[2]Department of Energy Science and Engineering, Indian Institute of Technology Bombay, Mumbai-400076, India

[3]Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO) – ERIEE, Université Paris-Saclay, CNRS, Rue du Doyen Georges Poitou, 91400, Orsay, France

Abstract

Hydrogen technologies will become more and more prominent in the next coming years, in particular systems operating at close to ambient temperature, in the context of sustainability and renewable energies. Membrane electrode assembly (MEA) has been the most primary part of the conventional polymer electrolyte fuel cells as well as unitized regenerative fuel cells. This paper summarizes the important steps and latest developments in the preparation of the assembly such as membrane treatment, preparation of electrodes followed by hot pressing for low temperature (< 100°C) polymer electrolyte fuel cells and unitized regenerative fuel cells. Various possibilities in the membrane selection for the assemblies are detailed out and their performances are compared with respect to the preparation method. Catalysts play a very important role in supporting oxygen reduction as well as evolution reaction and primarily differentiate the MEAs of the cells. Hence, they are tabulated along with the possible supports. Also, importance of wet

proofing the gas diffusion backing along with preparation of microporous layer with different materials and processes is also reviewed. Hot pressing which is conventionally used for preparing the assemblies makes a great difference when used with optimized operating parameters such as pressure, temperature and time during the pressing. A comparison between the various techniques used for MEA fabrication is summarized and is believed to be useful for researchers. In addition to an extended review on the preparative techniques for MEA manufacturing, the authors underline the performance of a unitized regenerative fuel cell (area = 22.5 cm^2) by incorporating the salient steps involved during the preparation of membrane electrode assemblies.

Keywords: Gas diffusion layer, catalyst, membrane electrode assembly, proton exchange membrane, unitized regenerative fuel cell

*Corresponding author

E-mail: loic.assaud@universite-paris-saclay.fr (L. Assaud); achbhosale@hre.iitr.ac.in (A. C. Bhosale)

Abbreviations

BHC	Bifunctional hydrogen catalyst
BOC	Bifunctional oxygen catalyst
BPP	Bipolar plate
CCE	Catalyst coated electrode
CCM	Catalyst coated membrane

1	CCS	Catalyst coated substrate
2	CNF	Carbon nano-fiber
3	CNT	Carbon nanotube
4	CVD	Chemical vapor deposition
5	DI	Deionized water
6	GDB	Gas diffusion backing
7	GDL	Gas diffusion layer
8	GNF	Graphitic nano-fiber
9	Ir	Iridium
10	IrO_2	Iridium dioxide
11	IPA	Iso-propyl alcohol
12	MEA	Membrane electrode assembly
13	MPL	Microporous layer
14	OER	Oxygen evolution reaction
15	ORR	Oxygen reduction reaction
16	PEMFC	Polymer electrolyte membrane fuel cell
17	PPy	Polypyrrole
18	Pt	Platinum

1	PTFE	Polytetrafluroethylene
2	SPE	Solid polymer electrolyte
3	TCR	Thermal contact resistance
4	Ti	Titanium
5	TiC	Titanium carbide
6	TPB	Triple phase boundary
7	URFC	Unitized regenerative fuel cell
8		
9		

Highlights:

- Possible varieties of membranes used commercially are summarized.
- New as well as commercial catalysts including catalyst base are detailed out.
- Various gas diffusion layers and microporous layers along with their preparation methods are discussed.
- The governing parameters during conventional hot press method are summarized along with characterization of single cell of URFC (area: 22.5 cm^2) fabricated in the laboratory.

1. Introduction

The increasing penetration of renewables in the power grid is demanding improvements of technologies for energy storage to smooth the intermittent profile of power generation as well as reduce the carbon footprint and greenhouse gas (GHG) emissions [1,2]. Batteries [3] and fuel cells [4,5] are some of the energy storage technologies under consideration to meet the demand of today's power-hungry world. Chemical batteries expansion, especially the emerging technologies such as lithium-ion batteries, is restrained by the limited availability of rare chemical elements [6], and needs complementary technologies like hydrogen based systems for energy generation and storage. On another hand, fuel cells are driven by more vastly available resources, typically hydrogen [7]. However, it has to be mentioned that these technologies are expensive to manufacture due to the high cost of catalysts (Pt, IrO_2). New catalysts are emerging as replacement of precious metal, such as catalysts resulting from bioinspired processes or molecular electrocatalysts consisting of a non-precious metallic center (Co, Ni, Fe), however, they still need optimization to be implemented into areal water electrolysers due to the lack of durability and chemical stability because of the operating conditions (low pH, high current densities, temperature etc.) [8]. Moreover, there is still a lack of infrastructure to support the distribution of hydrogen. Also, a lot of the currently available fuel cell technology is in the prototype stage and not yet validated.

Despite such disadvantages, fuel cell technology finds its place in niche applications because their abilities like noiseless operation, quick start, high-power density and an absence of greenhouse gases make them favorites among others [9,10]. Fuel cells are basically the electrochemical devices that allow hydrogen (fuel) to react with oxygen (oxidant) indirectly and generate electrical power during the operation. The protons generated by catalyzing oxidation of

hydrogen channelized using a bipolar plate (BPP) [11,12] at anode pass through the electrolyte i.e. membrane and combine with electrons and oxygen to form water at cathode. Such a technology is close to commercialization however, hindered by high cost and hydrogen infrastructure [13]. Many efforts are being done to improve the performance of many types of fuel cells, such as alkaline fuel cells (AFCs) [14], solid oxide fuel cells (SOFCs) [14], PEMFCs [15] and URFCs [15]. This review covers the scientific efforts on the last two types in terms of recent advancements in their components, issues and detailed overview of preparation of membrane electrode assemblies.

Unitized regenerative fuel cells (URFCs) [16,17] are the extension of conventional proton exchange membrane fuel cells with the additional ability of electrolyzing the water with the help of heat and electrical energies as an input (Fig.1a). In other words, when operated in fuel cell mode (FC mode) of operation, it undergoes hydrogen oxidation and oxygen reduction reactions (HOR and ORR) at respective electrodes i.e. hydrogen and oxygen electrodes. However, the same cell is observed to undergo hydrogen evolution [18] and oxygen evolution reactions (HER and OER) at the said electrodes respectively when supplied with water and energy as mentioned earlier. The proton exchange membrane fuel cell (PEMFC) uses a water-based, acidic polymer membrane as its electrolyte. PEMFCs operate at intermediate temperature (below 100°C) and can tailor electrical output to meet dynamic power requirements. URFCs can be operated first in fuel cell mode by supplying the reacting gases to produce energy and then switched to electrolysis mode to use the surplus energy available from primary energy sources to produce the gases. URFCs are therefore, neither affected by depth of discharge nor determine the storage. The power (size of the cell) and energy stored (size of storage tanks) thus, are not linked to each other [19]. Therefore, the technology potentially sees applications where energy saved/power

used per unit weight of total system matter the most [20,21]. Fig. 1a schematically explains the working of a URFC in respective modes. PEMFCs are a mature technology and have found themselves in marine applications [17,18], portable power sources [19,20], aerospace [21], vehicles etc. [22]. URFCs, being relatively new technology, have been claimed to be suitable for standalone applications [23] and further extended to aerospace applications [24,25].

In order to use such electrochemical cells in a long run, both PEMFCs and URFCs have a common component, the so called membrane electrode assemblies (MEAs) that should be effective and durable. The MEAs are the heart of such cells as the entire reactions viz. proton and electron generation, distribution and consumption take place within the MEA The effectiveness of MEA therefore defines the performance as well as the life of cells. They should, therefore, be prepared with utmost care and correct protocol [22]. S.J. Peighambardoust et al. [23] extensively reviewed the solid polymers as an electrolyte for both low as well as high temperature polymer electrolyte fuel cells (PEMFCs).

MEA breaks into four main components: the polymer electrolyte membrane, the catalyst layer, the gas diffusion layers and the bipolar plates [24]. The polymer electrolyte membrane (solid acidic polymer) allows for the hydrogen to be dissociated as protons going through the membrane and react at each electrodes. The catalyst layer is in direct contact with the membrane and the gas diffusion layer. It has been of major interest in the past years to develop efficient cells. The gas diffusion layer consists of a porous layer that allows for an efficient removal of reactants and products from the electrode. Finally, bipolar plates uniformly distribute fuel gas and air, and conduct electrical current to the cell.

The objective of the study is therefore to present the exclusive report including recent developments in the field of preparation of MEAs including their protocol and different methods

related to PEMFCs and URFCs. This review paper is organized as follows. Section 2 describes the importance as well as different variety of membranes in the respective cells including heat transfer and proton conduction in them. Section 3 covers the materials and methods for electrode preparation. The methods adopted for MEA preparation are discussed in detail in section 4. Section 5 analyzes the assembling methods discussed in section 4 and compares them with each other. Section 6 delivers the conclusions.

Regarding the membrane, various alternatives such as modified Nafion® composite membranes, functionalized non-fluorinated membranes as well as acid-base composite membranes were detailed out. Authors also highlighted the possible candidates for PEMFCs based on specific properties of solid polymer electrolyte (SPE) such as proton conductivity, water uptake, gas permeability etc. M. Gabbasa et al. [25] summarized possible alternatives for membranes, catalysts, microporous layer (MPLs) and BPPs for URFC stacks. Similar review summarizing bifunctional hydrogen catalyst (BHC), bifunctional oxygen catalyst (BOC), gas diffusion layer (GDL) and BPPs for URFCs was reported by Y. Wang et al. [26].

However, despite simpler management of gases, the bi-functionality of electrodes is observed to degrade the URFCs (Fig. 1a). Researchers, therefore, opted a different approach based on unchanging the redox function of the electrodes in URFCs (Fig. 1b) [27]. S. Dihrabet et al. [19] highlighted the graphite and coated metallic BPPs for PEMFCs and URFCs respectively. MEAs for respective cells were also addressed by the authors.

Several reviews on membranes [28–30], catalysts [31], GDLs [31–33] and BPPs [22,34,35] cover the most in terms of materials' point of view. S. Dihrab et al. [19] while reviewing membrane and BPPs for PEMFCs and URFCs briefed about MEAs for the respective cells. Apart from that, extensive summary on the preparation of MEAs is not available to best of

authors' knowledge. The objective of the study is therefore to present the exclusive report including recent developments in the field of preparation of MEAs including their protocol and different methods related to PEMFCs and URFCs.

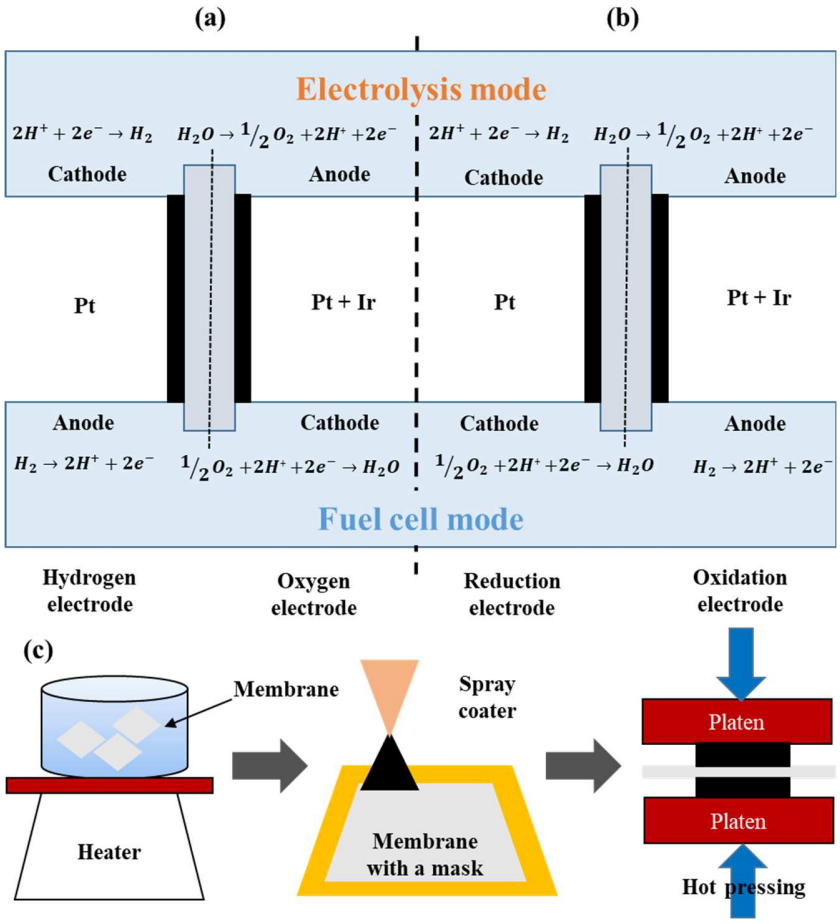

Fig. 1. Schematic working of URFC in (a) conventional way and (b) unchanging redox function of the electrodes (redrawn with permission from Elsevier [27]); (c) general protocol for the preparation of MEA.

Since the general protocol for the preparation of MEAs involves treatment of membranes, preparation of electrodes followed by the pressing (Fig. 1c); each of the processes is explained in following sections.

2. Membranes

The function of heart i.e. membrane of conventional PEMFCs or URFCs is to transfer the protons from anode to cathode [36,37]. Minimum travel distance between the two electrodes for a given electrolyte conductivity shall offer the least resistance offered by the membrane thereby enhancing the performance of cells (Table 1). Also, the membrane is also expected to isolate the electrodes from each other and avoid any crossover of the gases [38]. Protons are ideally made to flow through sea of water molecules (discussed in following section). However, issues associated with formation of water and its accumulation lead to several other problems like ionomer dissolution, membrane swelling as well as formation of ice [13].

2.1 Proton conduction in the membranes

Proton conduction is the most important criteria as the ohmic drop in the characteristic curve of any fuel cell is measure of ion conduction in the membrane [39,40]. In general, the conduction of protons through the membrane can be generalized into two categories [23] hopping mechanism (Grotthus mechanism) and diffusion mechanism (Vehicular mechanism).

Hopping mechanism (Fig. 2a) is one in which protons hop from one hydrolyzed ionic site (SO_3^- H_3O^+) to other. When the protons are generated from the oxidation of hydrogen, they combine with water molecule to form hydronium ion inside the membrane [41]. Thus, protons travel from one hydronium ion to other. Such mechanism is observed in perflourinated sulfonic acid membranes such as Nafion®. Whereas, in case of vehicular mechanism (Fig. 2b), the hydronium ions pass through the aqueous medium with the help of one or more water or methanol molecules [42]. The transfer occurs through the membrane by electro-osmotic drag in which the water or methanol molecules form a vehicle for the protons. Such protons when combined with water or

methanol form H_3O^+, $H_5O_2^+$, $CH_3OH_2^+$. However, availability of free volumes in polymeric chains of membrane is required for effective functioning of vehicular mechanism.

Apart from proton conduction mechanisms, the hydration level in the membranes also plays a vital role. Reduction in membrane thickness reduces the possibility of water drag/crossover and thus enhances the performance [43]. Moreover, the distance travelled by protons also gets reduced thereby adding to the performance. Thinner membranes therefore can be easily hydrated. However, loss of potential due to fuel crossover increases with thinner membrane.

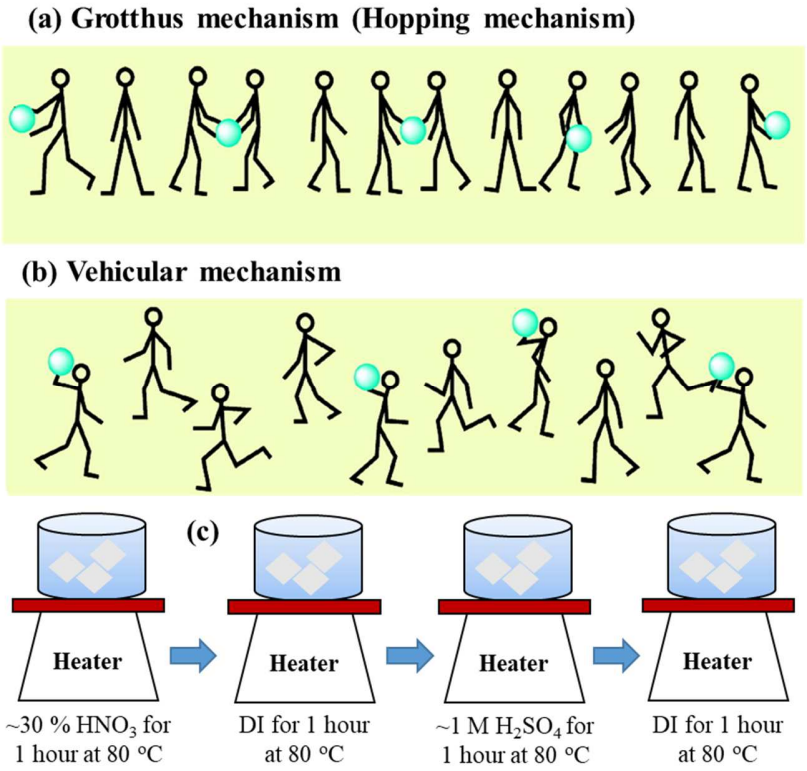

Fig. 2. Proton exchange in membranes using (a) Grotthus; (b) vehicular mechanism and (c) treatment of membranes (Reprinted with permission from [41]. Copyright (2008) American Chemical Society).

2.2 Heat and water management in membranes

As explained earlier, water has been the main component to transport the proton from anode to cathode. It also helps in hydrating the membranes which in turn maintain their proton conductivities over time. The electro-osmotic coefficient for Nafion® membranes responsible for number of water molecules transported per unit proton is about 2.5. Therefore, water that is lost at anode due to electro-osmotic drag should be restored by supplying the gases with optimized relative humidity. Also, water flooding at cathode should be avoided for excessive loss in power especially in mass transfer zone [44].

Thermal management is considered as an important issue in case of PEMFCs or URFCs. More generation of current leads to more loss in terms of heat thus bringing down the overall efficiency close to 50% [45]. Low temperature PEMFCs and URFCs typically operate at 60-70°C as further increase in temperature of operation shall dehydrate the membranes. Moreover, temperature below 50°C condenses the water inside the cell causing mass transfer losses due to water flooding effect.

2.3 Treatment of membranes

Membranes are supposed to be treated with different acids [46,47] to oxidize the impurities present on the surfaces as well as sulfonate the membranes. Commonly used oxidizing agents [48] are HNO_3 (~35 wt%) and H_2O_2 (~5 wt%) whereas, H_2SO_4(~1 M) is used to increase the proton content in the membrane. Membranes are first treated with the oxidizing solution for approx. 1 hour at 80°C ensuring impurity free membranes followed by washing them in deionized water (DI) for similar temperatures and time. Treatment with sulfuric acid [49] at mentioned temperature and time increases the proton content in the membrane after which

1 washing with DI removes weakly bonded protons from the membrane surface. The entire process
2 can be summarized in Fig. 2c.

3 **2.4 Membranes used for PEMFCs and URFCs**

4 Nafion® (Dupont, U.S.A.) is conventionally used as an electrolyte for the cells for its better
5 proton conductivity and durability. However, efforts have been put to replace the highly priced
6 Nafion® membranes by researchers in case of low temperature PEMFCs and URFCs. Since,
7 Nafion® membranes lose their physical and chemical strength at high temperatures (> 100ºC),
8 different membranes have been synthesized/used and characterized for the performance,
9 durability and sustainability of the fuel cell technology. Unlike PEMFCs, crossover is marginally
10 higher in URFCs because of which slightly thicker membranes are used in the cell/stack. Table 1
11 details out the membranes used for conventional and regenerative fuel cells. The electrolyte
12 conductivity of the membranes have been reported to underline its importance. Although
13 decrement in membrane thickness enhances its conductivity, it is also prone to fuel crossover
14 specially in case of URFCs during electrolysis mode of operation [50]. It is therefore suggested
15 to used comparatively thicker membrane in such cells. Furthermore, cell resistance is also
16 reported to take care of electrolyte as well as contact resistance of the cell apart from activation
17 and mass transfer resistances. The resistance emerging from the component interconnect
18 contributes almost 50% of the total ohmic resistance of the cell [51].

19

Table 1. List of different membranes used in the PEMFCs and URFCs.

Ref.	Membrane	Catalyst Loading on H_2/O_2 (mg cm^{-2})	GDL	Area (cm^2)	Preparation method of MEA	Best result	Electrolyte conductivity (S cm^{-1})	Cell resistance (Ω cm^2)	Salient feature of the work
[52]	Nafion 115	0.4(Pt) /0.4(Pt)	Carbon paper	50	CCM	1 A cm^{-2} @0.6 V	0.074	0.6	Water transport plate was used as BPP which could be used to supply or drain out the water at cathode.
[53]	Nafion 211	0.12(Pt) /0.2(Pt)	-	25	CCM	1.25 A cm^{-2} @0.6 V	0.13	0.48	Dual catalyst layer on cathode side improved the overall Pt utilization as well as mass transfer loss.
[54]	Nafion 211	0.5(Pt) /0.5(Pt)	Carbon paper	45	Decal transfer	1.3 A cm^{-2} @0.6 V	0.13	0.4615	Low temperature decal transfer with an additional layer of Nafion ionomer (0.2 mg/cm2) on the top of catalyst layer followed by hot pressing (1000 psi, 130 ^oC, 3 min) showed better results than the conventional method.
[55]	Sulfonated polyether (SPES50)	0.2(Pt) /0.2(Pt)	Carbon paper	25	Decal transfer	Negligible decrement in OCV for SPES50.	-	-	SPES50 was observed to perform better than Nafion® HP and Nafion® 212 because of least gas permeability.

[56]	Aquivion (20 μm)	0.3(Pt) /0.3(Pt)	Carbon paper	5	CCM	2.5 A cm^{-2} @0.6 V	-	0.24	Low thickness aquivion membrane directly coated on GDLs using a spray reported highest power density of 1.6 W/cm^2.
[57]	Nafion 212	0.4(Pt) /0.4(Pt)	Carbon paper	5	CCE	1.45 A cm^{-2} @0.6 V	0.1	0.4138	Water stream supplied conditioning done for 2.5 hr improved the performance of the MEA than the conventional conditioning methods.
[58]	Nafion 212	0.4(Pt) /0.4(Pt)	Carbon paper	16	CCM	0.5 A cm^{-2} @0.6 V	0.1	1.2	The cell is observed to be affected by mass transfer losses and water flooding due to carbon corrosion.
[54]	Nafion 115	0.35(GO) /0.35(GO)	Carbon paper	1	CCE	0.2 A cm^{-2} @0.6 V	0.074	3.0	Graphene oxide (GO) was synthesized can investigated as an alternative to conventional catalysts.
[59]	Nafion 212	0.35(GO) /0.35(GO)	Carbon paper	25	Decal transfer	0.6 A/cm^2 @ 0.6 V	0.1	1.0	Effect of ionomer addition for various catalyst loading was found to add to water flooding effect.

[60]	Nafion/sepiolite composite membrane	0.6(Pt) /0.6(Pt)	Carbon paper	50	CCE	0.8 A cm^{-2} @0.6 V	-	0.75	The composite membrane performed better in terms of operation as well as fuel crossover than conventional Nafion 112.
[61]	Nafion 211	0.03 (Pt)/ 0.03(Pt)	Carbon paper	5	CCM	1.125 A cm^{-2} @0.6 V	0.13	0.53	Experiment with pattern morphology revealed its high dependence on the performance.
[62]	Nafion 112	0.5(Pt)/ 4(PtIr)	-	5	CCE	1.6 A cm^{-2} @0.6 V	0.1	0.37	Pt deposited Ti BPP exhibited better performance and durability than carbon based BPP.
[63]	Nafion 112	Pt/PtIr	Carbon cloth		CCE	1.5 A cm^{-2} @0.632 V	0.1	0.42	Graphitized carbon was investigated for better MPL material than conventional amorphous carbon.
[17]	Nafion 212	0.5(Pt)/ 0.5($PtIrO_2$)	Carbon paper	22.5	CCE	0.634 A cm^{-2} @0.6 V; 0.55 A cm^{-2} @1.8 V	0.1	0.95	Investigation in degradation of URFC revealed adverse impact of higher temperature of water supplied during electrolysis mode

[64]	Nafion 212	0.2 (Pt)/ 0.8(PtIr)	Carbon paper	10.89	CCM	0.64 A cm^{-2} @0.6 V; 2.18 mA cm^{-2} @1.8 V	0.1	0.94	Optimized catalyst loading was found to be 0.2 and 0.8 for respective H_2 and O_2 electrodes. Also, hydrophobic nature of O_2 electrode was optimized to 26.95 %.
[65]	Nafion 115	0.3 (Pt)/ 0.5(Pt-IrO_2)	Carbon cloth	5	CCM	0.1 A cm^{-2} @0.6 V; 0.54 A cm^{-2} @1.8 V	0.074	6.0	The performance was achieved by depositing Pt on IrO_2 without changing the oxidation status of Ir.
[66]	Nafion 115	Pt/(Pt-IrO_2)	Ti-felt	27	CCE	0.55 A cm^{-2} @0.6 V; 0.63 A cm^{-2} @1.6 V	0.074	1.09	Ti powder on Ti felt as a GDL was observed to manage the water along with effective distribution of pore size.
[67]	Nafion 212	0.5 (Pt)/ 1(Pt-Ir/TiO_2)	Carbon paper	5	CCE	1.3 A cm^{-2} @0.6 V; 0.9 A cm^{-2} @1.6 V	0.1	0.46	Synthesized Ir-TiN as a MPL along with catalysts (Pt-It/TiO_2) showed better performance and durability than unsupported Pt-Ir black.
[68]	Nafion 1135	0.8 (Pt)/ 2(Pt-Ir)	Ti-felt	256	CCM	0.5 A cm^{-2} @0.55 V; 0.5 A cm^{-2} @1.74 V		1.1	The 7-cell stack highlighted the potential of URFC system in real life applications.

[69]	Nafion 115	Pt/ (Pt/IrO_2)	Ti-felt	27	CCE	0.65 A cm^{-2} @0.6 V; 0.75 A cm^{-2} @1.6 V	0.074	0.92	Larger fiber diameter of Ti-felt was observed to affect the cell performance in EL mode.
[70]	Nafion 115	0.35 (Pt)/ 1.5 (Pt-Ir)	Ti-felt	7	CCM	1.0 A cm^{-2} @0.6 V; 1.75 A cm^{-2} @1.8 V	0.074	0.6	$Ir_{0.5}Pt_{0.5}$ among various combinations was found as a better catalyst for BOE.
[71]	Nafion 212	0.5 (Pt)/ 1 (Pt-IrO_2)	Carbon paper	22.5	CCE	0.25 A cm^{-2} @1.6 V	0.1	6.4	Effect of operating pressure on ICR and cell performance was modeled.
[72]	Nafion 115	0.4 (Pt)/ 0.5 (Pt-IrO_2)	Carbon cloth	5	CCM	0.18 A cm^{-2} @0.6 V; 0.35 A cm^{-2} @1.6 V	0.074	3.33	ATO as a support to catalysts was explored and found better than Ebonex as a commercial base.
[73]	Nafion 1110	0.8 (Pt)/ 2 (Pt-IrO_2)	Ti-felt	250	CCE	0.3 A cm^{-2} @0.6 V; 0.6 A cm^{-2} @1.8 V		2.0	Prototype stack of URFC was developed and tested in the view of "GenHyPEM".
[74]	Nafion 212	0.25 (Pt)/ 0.25 (Pt/Graphite)	-	9	CCM	0.11 A cm^{-2} @0.6 V; 0.1 A cm^{-2} @1.6 V	0.1	6.0	Graphitized carbon supported Pt as BOE was synthesized and tested for URFC.
[75]	Nafion 212	0.2 (Pt)/ 1 (Pt-IrO_2)	-	5	CCE	1.625 A cm^{-2} @0.6 V; 1.0 A cm^{-2} @1.6 V	0.1	0.37	The synthesized Pt-IrO_2 performed better than conventional mixture of Pt and IrO_2.

3. Electrode preparation

Once the membrane is treated and stored in DI for further usage, next task is to prepare the electrodes for the cell. The catalyst layer could either be coated on membrane directly (catalyst coated membrane, CCM) or on the GDL (catalyst-coated electrode, CCE). The coating on membrane offers an advantage of catalyst being close to electrolyte thus forming a strong interfacial contact in an electrode-electrolyte pair [76]. CCMs are normally coated with a spray coating technique or a decal transfer method whereas catalyst coated electrodes (CCEs) could be coated either with spray or brush coating method [33]. The GDLs should be selected based on minimum bulk and through plane resistance apart from porosity and morphology. The measured resistance (R_z) of GDL could be calculated using following Eq. 1 [77]

$$R_z = \frac{2R_{ICR}+2\rho_z d}{A} \quad (1)$$

Where, $R_{ICR}$is interfacial contact resistance, ρ_z through plane resistivity, d is the thickness of the GDL and A is the sample area.

The electrode preparation predominantly involves teflonization of backing layer followed by deposition of microporous layer (MPL) as explained in following sections.

3.1 Teflonization of the gas diffusion backing layer

A gas diffusion layer (GDL) is expected not only to diffuse the fuel but also to conduct the electrons from catalyst layer to current collector or bipolar plate (BPP) or vice versa. Fuel cells require electrodes that are hydrophobic in nature so as to take out the water generated due to reaction at TPB at the oxygen side [78]. The microchannels present in the GDL provide passage for the generated water from TPB to its outer surface. Polytetrafluoroethylene (PTFE) has been found to be the best candidate to do the job. However, greater the concentration of PTFE in

electrode substrate (e.g. carbon paper/cloth), lower will be its electrical conductivity as PTFE will hinder the flow of electrons from catalyst layer to the diffusion layer. Therefore, 15 wt% of PTFE has been chosen to be optimized value for teflonization [79]. Carbon paper/cloth is generally pretreated with a mixture of PTFE, ammonia solution (NH_3(aq)) and water for a specific time to change its wettability.

Fig. 3 illustrates the variation in weight of substrate sample (carbon paper in this case, 2 x 2 cm^2) with that of PTFE, ammonia solution, water and time. It could be observed that increase in PTFE (60 wt%) and dipping time increased the weight of sample. However, addition of water and ammonia diluted the mixture and thereby decreased the increase in the weight of sample. It should be noted that the temperature of the mixture was maintained below 10°C and ensured of constant stirring to achieve uniformity in the solution.

Thus, the ratio of concentrations of PTFE, NH_3(aq), DI and time (min) was optimized to 1:2:4:2. Sintering melts PTFE and thus helps in distributing the same uniformly across the entire volume of the substrate.

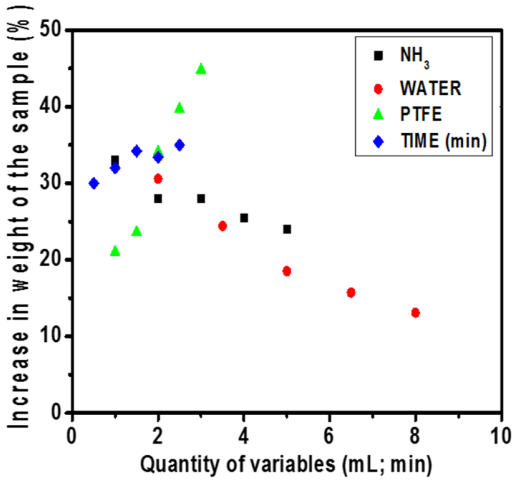

Fig. 3. Effect of variation in governing parameters of teflonization.

3.2 Preparation of Microporous layer (MPL)

Microporous layer drew much of attention after Papagin et al. [79] developed it by using a homogeneous suspension of carbon powder (Vulcan XC-72) with the desired amount of PTFE which was coated on the substrate (carbon paper/cloth) [33]. Such a layer develops a better contact between the catalyst layer and gas diffusion backing (GDB). It also helps in better water transport [77] and diffusivity of gases along the surface as the pore size of carbon paper/cloth gets reduced. The layer along with substrate also hinders the path for contaminations to reach the catalyst layer [80].

T. Sadhasivam et al. [63] synthesized graphitized carbon (Gr-carbon) as a MPL for URFCs using high temperature annealing. They observed the Gr-carbon to perform better than amorphous carbon in terms of round trip efficiencies and durability. Tatsumi Kitahara et al. [81] prepared a carbon paper based GDL with triple coatings. The first layer composed of PTFE (10 wt%) and carbon black whereas, second and third layers were made from mixture of PTFE (20 wt%) carbon black and a hydrophilic layer. The comparison of triple coated MPL with single and double coated ones showed that hydrophilic layer helped expelling excess water from triple phase boundary (TPB) thus reducing oxygen transport resistance. The said coating had layers of mixtures of PTFE and carbon black with 10 and 20 wt% of PTFE followed by a hydrophobic layer.

Table 2. List of different MPLs used in PEMFCs and URFCs.

Ref	Substrate	MPL material	PTFE conc. (%)	Best performance
[82]	Carbon paper	Vulcan XC-72R	20	800 mA cm^{-2} @0.6 V
[77]	Carbon paper	Vulcan XC-72R	20-30	350 mA cm^{-2} @0.6 V
[83]	Carbon paper	Vulcan XC-72R	30	400 mA cm^{-2} @0.6 V
[84]	Copper sheet (12.5 μm thick)	-	Self-assembled monolayer on Cu substrate	800 mA cm^{-2} @0.6 V
[85]	Carbon paper	Vulcan XC-72R	0-20	Thermal contact resistance (TCR) observed to decrease over compression for a given PTFE and MPL loading. (0.8 K W^{-1} @10 bar)
[86]	Carbon paper	Self-supported MPL	5-30	~1000 mA cm^{-2} @0.6 V
[87]	Hybrid GDL	-	-	~1000 mA cm^{-2} @0.6 V (air as oxidant)
[88]	Synthesized diffusion layer (eGDL)	-	Trichloro(1H,1H,2H-perfluorooctyl) silane as a hydrophobic agent	Cell resistance of 0.2 Ω at 1000 mA cm^{-2}
[89]	Carbon paper	Vulcan XC-72	27	1800 mA cm^{-2} @0.6 V
[90]	Titanium sheet	Titanium powder	-	1250 mA cm^{-2} @1.8 V (Electrolyser)
[91]	Thin titanium LGDL	-	-	1300 mA cm^{-2} @1.6 V (Electrolyser)
[92]	Carbon paper	TiC and $IrTiO_x$	15	500 mA cm^{-2} @0.6 V and 500 mA cm^{-2} @1.6 V (URFC)
[63]	Carbon cloth	Graphitized carbon	20	1750 mA cm^{-2} @0.6 V and 1200 mA cm^{-2} @1.6 V (URFC)
[93]	Titanium felt	-	10	550 mA cm^{-2} @0.6 V and 650 mA cm^{-2} @1.6 V (URFC)

Effect of PTFE loading in the MPL was investigated by O.M. Orogbemi et al. [94]. Carbon was used as the candidate for MPL. The authors found a decrement in the gas permeability with increase in carbon loading. They also found the PTFE loading to affect the through-plane gas permeability [95,96]. Effect of GDL on cell performance based on PTFE loading, compression pressure and MPL were investigated by Chao Si et al. [97]. Validated Leverett function was used in the investigation. The group observed PTFE with 20 wt% to perform better than the rest. However, more compression pressure decreased the porosity and thereby decreasing the cell performance. Table 2 summarizes different MPLs used in PEMFCs and URFCs.

3.3 Electrode coating methods

Despite various coating methods available; rolling, spraying and brushing methods have been adopted both for small (< 50 cm^2) as well large size (> 50 cm^2) GDLs during preparation [17,98–100]. In case of PEMFCs, carbon paper or cloth is predominantly selected as base substrate for coating MPL (usually made from Vulcan XC-72). However, in case of URFCs, carbon paper or cloth cannot be used because of high corrosive environment leading to oxidation of carbon over time. Hence, porous Titanium sheet [69,101] is preferred as a backing layer because of its high anticorrosive property, better electrical conductivity and excellent machinability. MPL is generally a Titanium powder [66,102] or sometimes noble metals IrO_2 [103] or a combination with a Ti as a base such as Ti/IrO_2 [104], IrO_2/Ta_2O_5 [105], $TiC/IrTiO_x$ [92]. Addition of little quantity of PTFE is also observed to improve the performance of URFCs despite making the GDLs hydrophobic in nature [106]. This could be attributed to balancing of the water removal from triple phase boundary (TPB) during fuel cell mode and vice-versa during electrolysis mode.

Fig. 4a schematically explains the preparation of MPL over a wet proofed GDL (carbon paper) using a brush coating method [17,71,107]. Accordingly, efforts were put to prepare the MPL

over a sintered carbon paper with the carbon loading of 1.5 mg cm^{-2} [108]. In brief, Vulcan XC-72 was suspended in IPA and sonicated for 30 min for homogeneity. 15 wt% of PTFE (60%) suspended in ammonia was then added and sonicated again in an ice bath until PTFE is uniformly dispersed in the solution. The slurry was then brush coated on sintered carbon paper whose difference in initial and final weight after drying underlined the desired loading of carbon. The coated paper was sintered at 350°C for 30 min for better results.

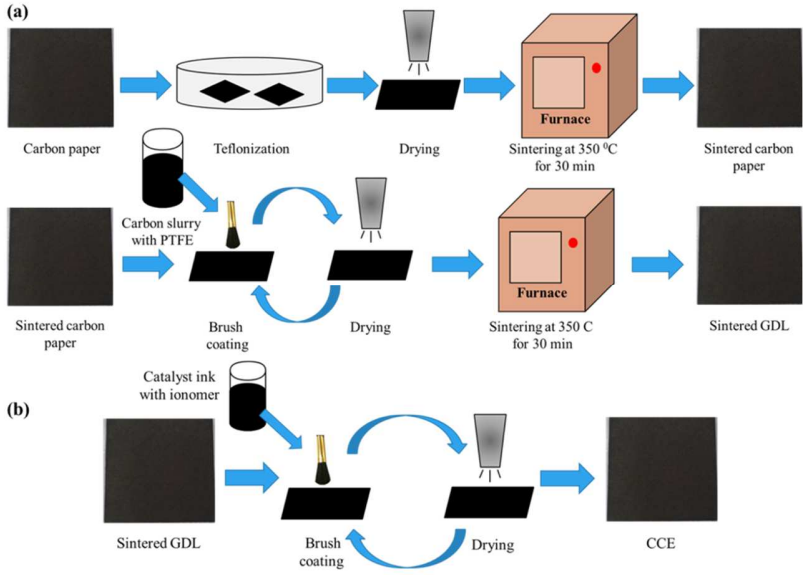

Fig. 4. Schematic representation of (a) fabrication of gas diffusion layer with MPL and (b) preparation of catalyst-coated electrode (CCE) using brush coating method.

3.4 Preparation of catalyst layer

Catalyst can also be coated either on GDL (CCE) or on membrane directly (CCM). Although similar coating methods could be used as mentioned in coating of MPL, the major difference lies in the preparation of ink/slurry for the catalyst. In brief, ionomer (Nafion® solution) is added to the catalyst ink instead of PTFE as ionomer creates path for protons to travel from TPB to electrolyte. Also, it acts as an adhesive between GDL and membrane (Fig. 4b).

In case of PEMFCs, Pt has been commercially accepted as a catalyst both for hydrogen as well as oxygen electrode (Table 1) [109,110]. Modifications such nanotubes and nanoparticles along with efficient preparation methods [111–113] have also been proved to be viable options to conventional Pt/C. On the other hand, URFCs need to have catalysts that support both ORR and OER as mentioned earlier. Table 1 summarizes various combinations of catalysts used. Deposition of Pt on porous IrO_2 was carried out by Fan-Dong Kong et al. [114]. The group observed 28% higher electrochemical activity of the synthesized catalyst towards OER than commercially available Pt/IrO_2. Another study involving preparation of TiC supported Pt-Ir for URFCs using plasma reduction process was found to be more active than the one prepared using chemical reduction process [115]. Fig. 5c-5f showcases using scanning electron microscope (SEM), the various catalysts such as graphene, carbon nanotubes, fibers synthesized by researchers [116,117].

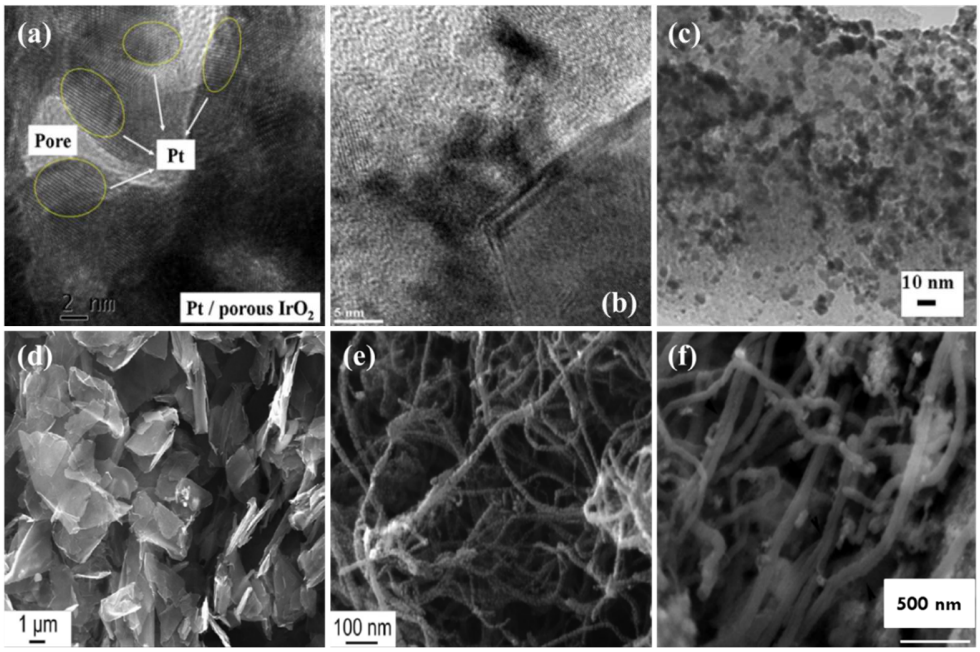

Fig. 5. Catalysts prepared by (a) F.D. Kong et al. (reproduced with permission from Elsevier [114]), (b) S. Sui et al. (reproduced with permission from Elsevier [115]) and (c) S.A. Grigoriev et al. (reproduced with permission from Elsevier [118]); Different modifications on carbon that include (d) graphene, (e) nanotubes (CNTs) and (f) nanofibers (CNTs) (reproduced with permission from Elsevier [116,117].

The former process helped the production of fine nanoparticles with their uniform distribution over the base i.e. TiC which increased the activities towards URFC reactions. Catalysts used for water electrolysis can also be used in URFCs along with some option left in the support of ORR. S.A. Grigoriev et al [118] deposited Pt and Pd nanoparticles on graphitic nanofibers (GNFs) and compared their performances with that of supported by carbon black. The GNFs synthesized using a chemical vapor deposition (CVD) method was found to be better base than the carbon black because of structured layer of catalyst in case of GNFs.

3.5 Support for catalysts

Catalysts mentioned earlier function only when they are well supported [119]. The support is mainly functionalized to provide sufficiently large area for catalyst nanoparticles to create

maximum number of reaction sites (Fig. 5a, 5b and 5c) [116,120,121]. Apart from that, the support should be i) highly electrically conducting, ii) highly porous, iii) corrosion resistant and iv) good at water handling. Carbon, in many forms [117,122–128], has been conventionally used as a support for catalysts both in conventional as well as unitized regenerative fuel cells because of its ease of preparation, high surface area (~250 $m^2\ g^{-1}$ for Vulcan XC-72) and other satisfying conditions [120][129]. Its family includes modified structures such as nanoparticles, nanofibers etc. (Fig. 7d, 7e and 7f).

However, it is prone to oxidation particularly during electrolysis mode of URFCs because of high operating potential by the virtue of following reaction (Eq. 2) [67]:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \qquad (E^o = 0.207\ Vvs.NHE\ at\ 25\ C^o) \qquad (2)$$

Hence, new supports for catalysts including modifications in existing/established materials were investigated across the globe. Table 3 lists out some of the important contributions made in the name of catalyst supports for low temperature PEMFCs and URFCs.

Table 3. List of different catalyst supports investigated.

Ref.	Catalyst support	Preparation method	Observations
[130]	Pt/graphene nanocomposites	chemical oxidation and graphite oxide exfoliation	Post characterizations indicate formation of the composite and its compatibility to form composite membranes.
[131]	Ta-TiO_2	Modified sol-gel method	More stability than that of pure Tantalum based electrocatalyst and comparable ORR activity to commercial Pt/C.
[132]	Antimony doped Tin Oxide (ATO)	Polyol process	Surface area = 50 $m^2 g^{-1}$; lower performance than that of commercial carbon; better corrosion resistance.
[133]	Teflonized carbon paper	Direct deposition method	The deposited paper revealed high activity towards ORR with low catalyst utilization.
[134]	Hierarchical porous carbons containing numerous nitrogen atoms (HPCs-N)	Inclusion complexes of cellulose hosted by urea hydrates	Better ORR activity than that of Pt/C; synthesized catalyst support showed 393 mW cm^{-2} against carbon support with 322 mW cm^{-2}.
[135]	PBI grafted on graphene (PBI/graphene) and carbon black (PBI/XC-72)	Surface-initiated polymerization	Synthesized supports reveal excellent ORR activity as well as durability.
[136]	Porous carbon nanofibers (PCNFs)	Polyol process	Better distribution of catalyst than Vulcan XC-72. Almost double power density observed at 0.6 V for synthesized support than that of Vulcan.
[137]	TiO_2@C		Carbon shell enhances the support for TiO_2 making mounting of Pt nanoparticles easier; increased stability over carbon.
[138]	Functionalized carbon nanofibers (CNF-f)	Thermocatalytic decomposition method	50% higher performance compared to Vulcan XC-72.
[139]	TNTS-Mo	Modified polyol method	Better performance and stability than commercial Pt/C
[140]	Modified carbon aerogel	Acid/base treatment	Reveal HOR and ORR activity

[141]	CNFs on activated carbon fibers (CNF/ACF)	Catalytic growth	Heat treatment of the synthesized supported catalyst enhanced the stability and corrosion resistance.
[142]	SiO_2	Ultrasonic method	Self-humifying support helped MEA resist the dehydration over time.
[143]	TiO_2		Better thermal and electrical conductivity; good corrosion resistance of the support than conventional carbon
[144]	SiC	Shape memory synthesis method	Better stability and supports bigger size of catalysts (8 nm of Pt in this case); results in low catalyst loading
[145]	Polypyrrole (PPy)	Chemical oxidative polymerization	Better corrosion resistance and double ORR activity than Pt/C
[146]	Co based nanowire networks (NWNs)	Surfactant-assisted soft template synthesis procedure	Better networking with average wire diameter of 2 nm; enhanced ORR activity Pt/Co than Pt/C
[147]	Ti_4O_7	Low temperature process	PtIr supported by the synthesized support showed better stability and enhanced activity towards ORR and OER.
[148]	Reduced graphene oxide (rGO)	Spray pyrolysis method	Enhanced stability and activity after heat treatment at 600^{o}C
[149]	PtRu	Pulse electrodeposition method	10 mol% Ir on 90 mol% PtRu exhibited highest round-trip efficiency for the URFC.
[150]	Carbon		Porous structured PtNi/C found to be highly active towards ORR and OER with very low overpotential in respective reactions.
[151]	CNTs		The oxidized CNTs offered more surface area.
[152]	SiO_2-SO_3H	Chemical method	800:650 mA cm^{-2} for synthesized catalyst: Pt/C at 0.7 V
[153]	Titanium carbonitride (TiCN)	Polyol process	Support to offer more stability and delay catalyst dissolution over time.
[154]	Vulcan XC-72		Introduction of Ir in AuIr catalyst reduces the size of Au; stable and better performance compared to Au/C and Ir/C and combined.
[155]	s-IrO_2	Template-assisted method	Current density of Pt/s-IrO_2 compared to Pt/commercial IrO_2 be 215.9 and 151.5 mA mg^{-1} at 1.65 V respectively.
[156]	TiN		TiN found to be better support than TiC and TiCN
[157]	TiCN		Better stability and corrosion resistance than TiC (as a support) due to heat treatment

[158]	Sb-doped SnO_2 (ATO)	Sol-gel method	High specific area (216.7 m^2g^{-1}) and better performance and stability compared to Vulcan XC-72.
[159]	CNTs and CNFs	DC magnetron sputtering system	Better support in terms of stability than Vulcan
[160]	$Ir_x(IrO_2)_{10-x}$	Adams fusion method	High surface area (24.74 m^2g^{-1}) and better activity towards OER; follows four-electron mechanism
[161]	Ir nanodentrites	Wet chemical method	Core-shell structure; better distribution of Pt; good interaction between Pt and Ir
[162]	CoB/ZIF-8	Reduction method	Excellent phase structure; good activity towards HER

4. Assembly preparation

The last step in MEA fabrication is sandwiching the membrane between the electrodes prepared. Once the CCEs are ready, they are coated with a fine layer of a mixture of Nafion® ionomer and iso-propyl alcohol (IPA) (v/v = 1:1). This step creates extra pathways for protons to flow from TPB to electrolyte thereby enhancing the catalyst usage [76]. It also ensures better bonding between electrodes and membrane during hot pressing. Care should be taken that additional layers of such mixture do not cover up the catalyst. In case of CCMs, the catalyst layer is present on membrane surfaces and it takes care of TPB. Unlike CCEs, GDLs are therefore not required to be coated with mixture of ionomer and IPA and are ensured of definite electrical contact with catalyst layers.

4.1 Milestones achieved in MEA protocol

The primary requirement of any polymer-based fuel cell is to have better contact between electrodes and the electrolyte. It could be achieved by bringing them close to each other with an external force or pressure. The conventional method, therefore, involved sandwiching the electrolyte between electrodes at a certain pressure, temperature and time. The temperature was normally kept little lower than the glass transition temperature of the electrolyte to ensure its softening yet maintaining its solid phase. The softened electrolyte/polymer makes an easy pair with electrodes under specified pressure and time. Although a lot of improvements have been done across the globe, Fig. 6 displays various techniques that set benchmarks in fabricating MEAs for different cells.

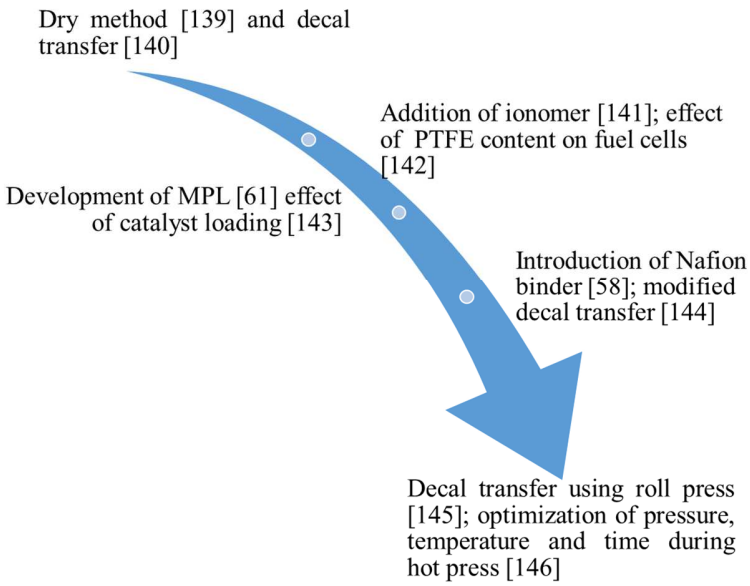

Fig. 6. Milestones achieved in preparation of MEA.

4.2 Different methods adopted in MEA preparation

Different category MEAs were examined at different temperature and pressure conditions [163], and it was found that better performance could be achieved with an additional layer of sputtered platinum on the oxygen side. Huaneng Su et al. [164] studied MEAs with different membranes and catalyst loading. The results showed that best performance for electrolysis was obtained using 60 wt% Pt/C and Nafion®212 membrane with the cell. However, stability test of membranes revealed that thinner membrane (Nafion® 211) failed due to insufficient strength for heat impact, pressure of the gases etc.

The wet method (glue method), that Z.X. Liang et al. [76] developed, introduced a binding agent, i.e., Nafion® solution, between membrane and electrodes. The conventional hot pressing method that involved pressing at high temperature and pressure didn't achieve a true interfacial contact. The treated Nafion® solution was applied over the surface of the membrane and was sandwiched

between respective electrodes at 60ºC with the pressure of 0.4 MPa for 30 min. The MEA fabricated with glue method was found to perform better than that of the dry method.

Lindermeir et al. [165] investigated the performance of the MEA prepared by applying catalytic layers directly onto the membrane and found that performance was improved than that of conventional MEA fabricated. A low-temperature decal method was developed by Jae Hyung Cho et al. [166] with which MEA fabricated was compared with other fabrication methods such as conventional decal method (Fig. 7a), a direct spray coating method etc. MEA fabricated by catalyst coated membrane (CCM) method had improved catalyst/membrane interface, better utilization of catalysts and superior formation of the ionomer network (i.e., 5% Nafion® solution) over catalyst coated substrate (CCS; substrate: carbon cloth/paper) method. Various methods of improving membrane and catalyst layer such as graded electrode method, deposition on porous membranes, patterned coating etc. and their impact on cell performance have been discussed in detail in the work reported by Matthias Breitwieser et al. [167].

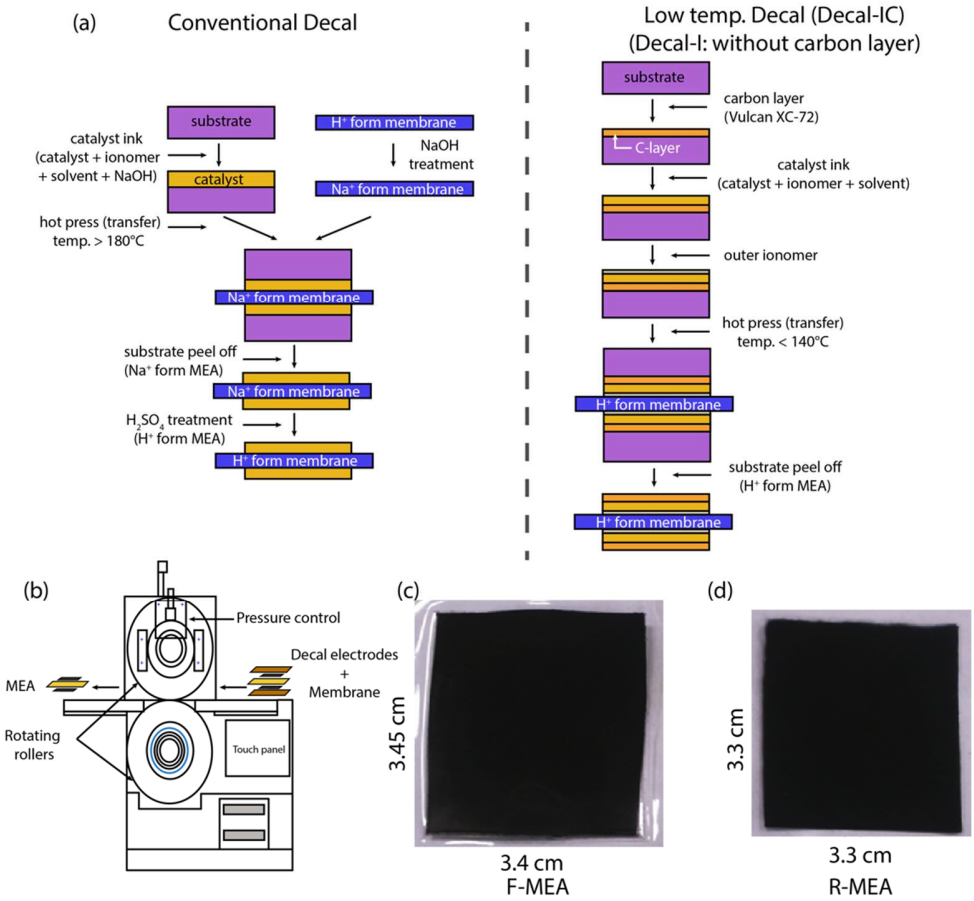

Fig. 7. (a) Schematic diagram of conventional high-temperature decal process and low-temperature decal method (reproduced with permission from Elsevier [166]; (b) schematic diagram of a roll-press machine; photographs of MEAs; presenting changes in geometrical s shape with (c) flat decal method and (d) roll press (reproduced with permission from Elsevier [172]).

The problem with CCS method is that the catalyst layer cannot be transferred on membrane while hot pressing whereas in CCM method, membrane undergoes severe swelling while spraying/applying catalyst on the membrane. This was also proved by S. Thanasilp et al. [168] who fabricated the MEAs by direct spray on the substrate (CCS-DS), membrane (CCM-DS) and by decal transfer. MEA (CCM-DS) was found to swell severely while spraying. This could be removed by using iso propyl alcohol (IPA) as the primary liquid media and ethylene glycol as the

active additive during CCM-DS. Also, low-temperature decal process was adopted to avoid the formation of oxides of the electrocatalyst. The MEA prepared by the methods were hot pressed at 137^{o}C at 65 kg cm^{-2} for 2.5 min.

Shubo Wang et al. [169] also investigated the ABPBI based MEA performance fabricated through CCM method and compared with that of CCE method. The authors found that CCM method was optimum for fuel cell applications. All MEAs were hot pressed with 29.3 MPa at 150^{o}C for 6 min.

Guobao Chen et al. [170] also studied the effect of variation in fabrication of bifunctional catalyst layers (BCLs) for URFC to understand the origins of performance variations. It was observed that fabrication method affected the fuel cell operation to agreater extent than that of electrolyser mode. Spraying catalyst on GDL was found more effective than on membrane since Pt layers formed by spraying onto GDL showed more homogeneous and porous surface than that sprayed onto the membrane which prevented the URFC from water flooding at high current density in fuel cell mode.

The group [171] also tried a different approach for improving the efficiency of URFC by using a novel MEA. Here, GDE coated with Pt was pyrolysed at 320^{o}C for an hour. This addition to conventional MEA fabrication decreased the hydrophilic behavior of Nafion® present in the electrode, thus reducing the flooding effect during fuel cell mode.

Asad Mehmood et al. [172] developed a new roll-press (Fig. 7b-7d) for MEA fabrication and compared the performance of respective MEAs with that of conventional flat press decal method. The method was found to be more productive and could transfer maximum catalyst on the membrane with Kapton as a transfer medium as there were no stability issues.

Since various parameter such as pressure, temperature and time affect the quality of MEA, Osman Okur et al. [173] studied the effect of such parameters on MEA fabrication using the response surface method (RSM). RSM is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables. Thus, the optimum pressure, temperature and time found were 66 kg cm^{-2} (6.42 MPa), 97°C and 3.56 min with a remark that pressure affected more than the other two parameters. Shidong Song et al. [174] developed a five layered CCM for water electrolyser by adding Nafion® as a binder between conventional three-layered CCM and GDLs (135°C, 10 MPa, 3 min). The performance of such five layered CCM was compared with conventional three-layered CCM and protonated one. The newly developed CCM proved to perform better than the other two because of better TPB and lower contact resistance.

An innovative way of reducing the membrane and charge transfer resistance was found by spray coating the ionomer dispersion on the catalyst layer followed by spraying catalyst layer [175–177]. The average coating sequence (Fig. 8a) involved coating of an anode/cathode on GDL, followed by spray coating the ionomer dispersion for definite number of turns to develop uniformly thick membrane over the area. The other electrode was then spray coated by masking the solid membrane. The technique has so far, been successful in creating the layer of membrane of 10-12 μm thus reducing the membrane resistance multifold (Fig. 8b and 8c). Moreover, the electrode-electrolyte interaface is found better than the conventional MEAs. The only drawback with such cells seen so far is the huge hydrogen crossover campared to conventional cells [177].

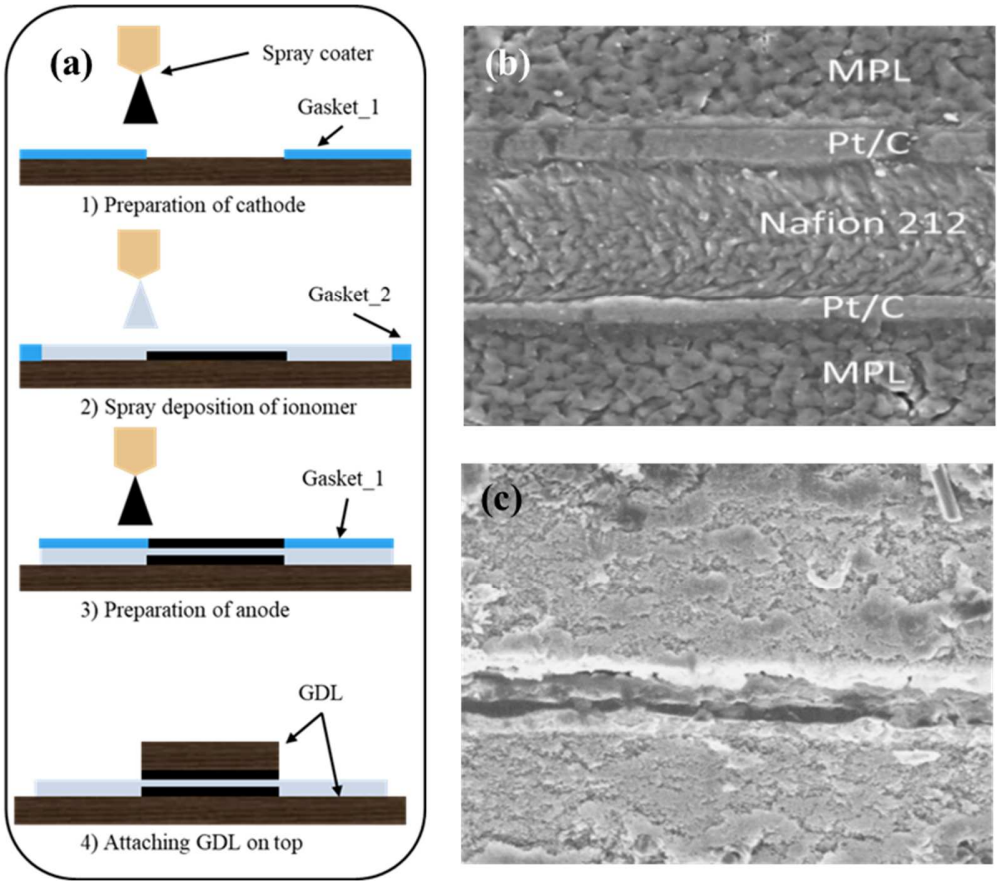

Fig. 8. Cross-sections of (a) conventional MEA and (b) spray coated MEA (reproduced with permission from Elsevier [177]); (c) schematics of the process of spray coated MEA.

Fig. 9a, by and large, summarizes the different coating techniques used in preparation of MEAs; whereas, differentiation based on usage of pressure is showcased in Fig. 9b. The former class of MEA preparation underlines the most types of methods used viz. CCE and CCM. CCE being most robust method, involves coating of catalyst on wet proofed GDL using brush coating or spray coating method. MEAs with areas < 50 cm^2 (discussed in Table 5) are normally fabricated using the said technique. The primary reason for employing CCE method is its ease of fabrication (specially brush coated CCEs) compared to other techniques. The said method is also proven to have least loss of catalyst as discussed earlier. CCM, on the other hand, is also well established technique commonly used for fabricating MEAs of larger active areas thereby reducing the

catalyst loss per unit area. TPB created using the technique is also claimed to be better as the catalyst layer is brought much closer to the membrane compared to CCE. CCM method involves a dedicated equipment for coating the catalyst over membrane surface and therefore is found exorbitant. The coating is normally done using 1) inkjet printing, 2) spraying and 3) drop casted method [177].

The classification of MEA preparation methods based on pressure as a parameter is shown in Fig. 9b. The ionomer dispersion method being most recent one involves layered fabrication of MEA as discussed earlier (Fig. 8a). The other set of pressure based MEA preparation method highlights typical platen based and roll based pressing method in which former method is employed for pressing the entire set of MEA components at same time whereas latter method is a measure of pressing the MEA components gradually (Fig. 7b). Decal transfer method uses a substrate (typically Teflon sheet) on which the catalyst ink is coated and then transferred onto the membrane surface by sandwiching the assembly at low (<140°C, low temperature decal process) or high temperatures (>180^{o}C, conventional decal transfer) (Fig. 7a) as discussed earlier.

The major difference between preparation of MEAs for conventional and URFCs is the use of catalysts (Table 1). GDLs and membranes in most of the cases are found similar. Moreover, pressure, temperature and time during hot pressing have been found most important and are summarized in Table 4. Fig. 10 compares the performance of MEAs fabricated with CCM and CCE method underlining CCM as a promising method for low Pt loading [178].

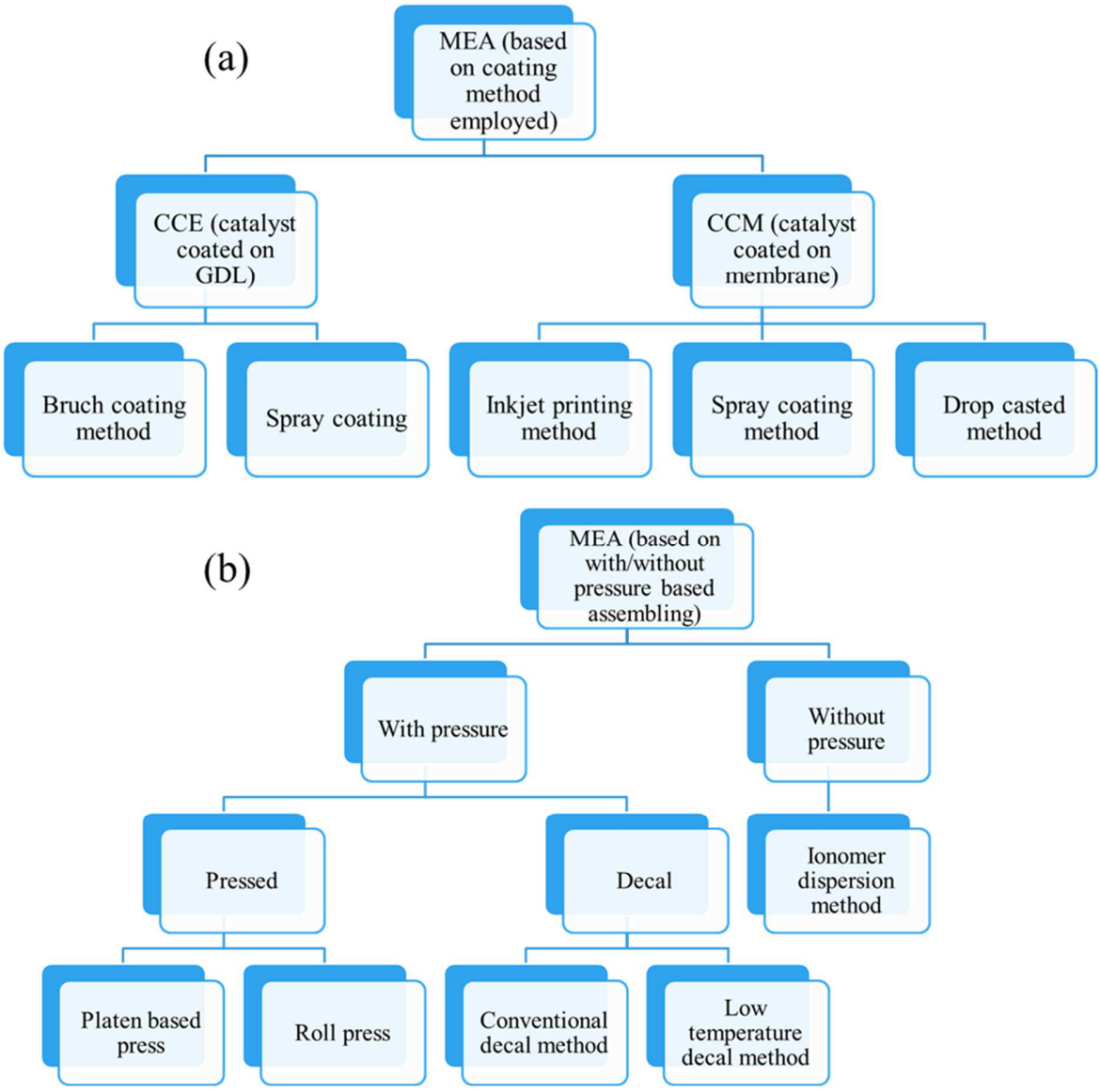

Fig. 9. Classification of MEAs based on (a) coating methods employed during the preparation and (b) the pressure used while sandwiching the membrane between electrodes.

Table 4. Various combinations of parameters used in hot pressing.

Ref.	Pressure ($kg.cm^{-2}$)	Temperature (^oC)	Time (min)	Area (cm^2)	Preparative technique
[179]	50	140	2	11	CCE
[61]				5	CCM
[180]	20	80	2	5	CCM
[181]				25	CCM
[182]		140	4	25	CCM, Decal transfer
[183]	200	140	1.5	25	CCM, spray coated
[184]				12.96	CCM, membrane and catalyst layer were prepared by spray coating on carbon paper in specific order.
[185]		130	2	5	CCE, Atomic layer deposition (ALD)
[186]				10.89	CCM
[187]				7	CCM, spray coated
[188]	10.19	120	7	5	CCE, brush coated
[189]				75	CCM, spray coated
[190]				25	CCM, spray coated
[191]		110	10	9	CCM, spray coated
[192]	45.88	140	2~3	5.309	CCM, layer by layer technique
[184]				4	CCM, membrane was prepared by spray coating the ionomer on catalyst coated electrodes.
[193]	635	125	90	1	CCM, spray coated
[194]				5	CCE, sputtering deposition

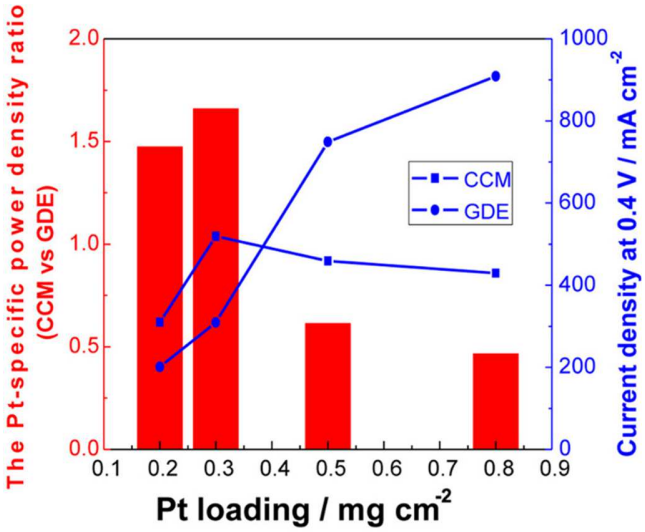

Fig. 10. Comparison of Power and current density for different Pt loading using CCM and CCE (GDE) method of MEA preparation (reproduced with permission from Elsevier [178]).

5. Results and discussion

Having highlighted the different preparation methods, a comparison chart is prepared and shown in Fig. 11. The comparison, on a scale on 1 to 10 with 10 being highest, is based on different parameters such as quality of TPB produced, time of preparation, instruments required, catalyst loss etc. Decal transfer, although seems similar to that of CCM, is compared separately as the preparation method is different from conventional spray coating method (CCM). CCE being an established method, is found cost effective as well since there are no dedicated instruments required compared to other techniques. CCM and ionomer spray method are comparable in terms of most of the parameters listed, however, differ in crossover and maturity with ionomer spray method having higher crossover and low maturity. It is probably due to the thickness of membrane claimed by the method by spraying iononer is very less (5-10 µm) compared to commercially available membranes (~50 µm) as discussed earlier.

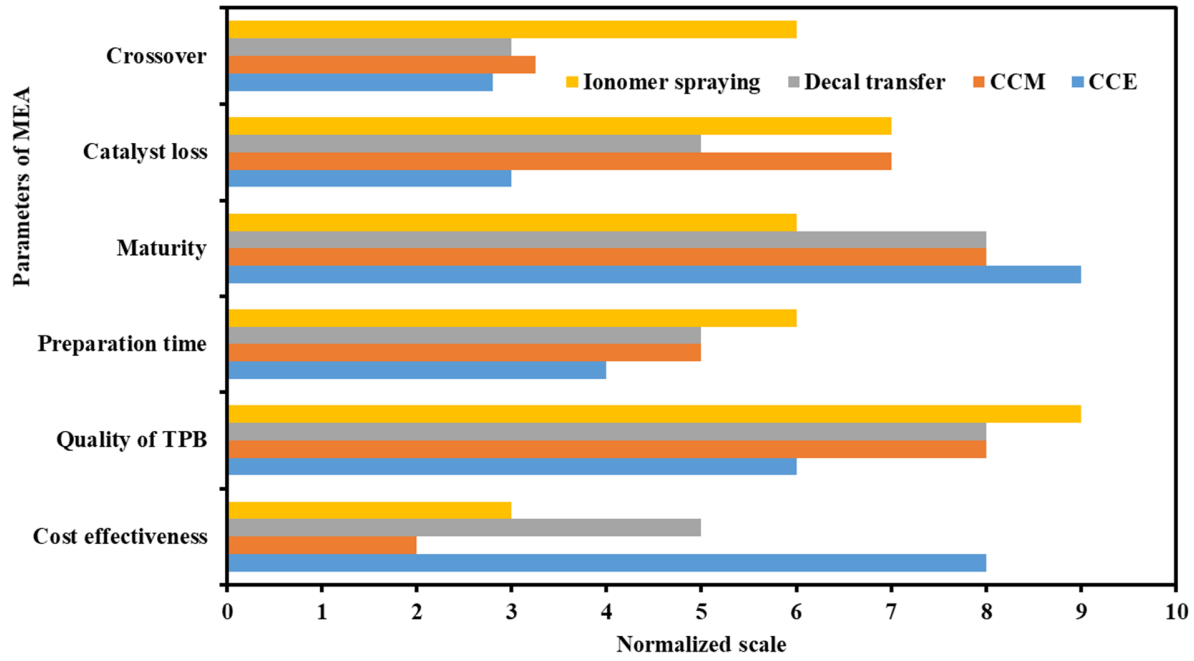

Fig. 11. Quantitative comparison of MEAs based on different parameters.

Decal transfer, though uses a substrate to transfer the catalyst layer on the membrane surfaces, produces a comparable TPB to that of CCM. Furthermore, it also saves considerable quantity of catalyst being lost. All methods by and large require same time for setting up the process except conventional CCE method as there is no necessity of a dedicated equipment to be ready. CCE, however, would consume same time if the catalyst is coated by a coating machine.

Table 5 compares these methods on the basis of equipment required and coating area. Smaller size MEAs (<50 cm^2) would be preferred by CCE if brush coating is used as large size GDLs would be difficult for the coating using brush. Ionomer coatings although use similar coating techniques to that of CCMs, haven't matured enough for scaled up cells and therefore limited by the coating dimensions (<50 cm^2). In case of CCMs, the catalyst loss per unit area coated increases with decrease in the MEA size. It is therefore, suggested to use the technique for higher coating area [195].

Table 5. Comparison of different MEA fabrication methods.

Parameters	MEA preparation methods			
	CCE	**CCM**	**Decal transfer**	**Ionomer spraying**
Instrument required	No	Yes	Yes	Yes
Preferred MEA size (cm^2)	<50 (brush coating)	>50	>20	<50

To realize the importance of various steps and parameters on cell performance, authors characterized the single cell of URFC (Effective area = 22.5 cm^2) with in-house made MEA [17,71]. In brief, the membrane was dried properly before it is put up in a hot press (FME10, FLOWMECH, India) to avoid any further shrinking and dimensional mismatches. The electrodes were properly placed beneath and on the membrane center ensuring their overlapping each other before their positions were frozen. The entire assembly was cushioned appropriately and was then placed at the center of the press the platens maintained at 130°C which is higher than the glass transition temperature ($T_g \approx 110.3$°C; [196]) during the pressing. The MEA was hot pressed for ~3 min. That made the membrane little softer resulting in partial penetration of electrodes in the membrane, making them as one piece together. Moreover, the cushions being thermal insulators, restricted the heat flow to the membrane as overheating could result in the changes of structural properties as well as the ionic conductivity of the membrane [197].

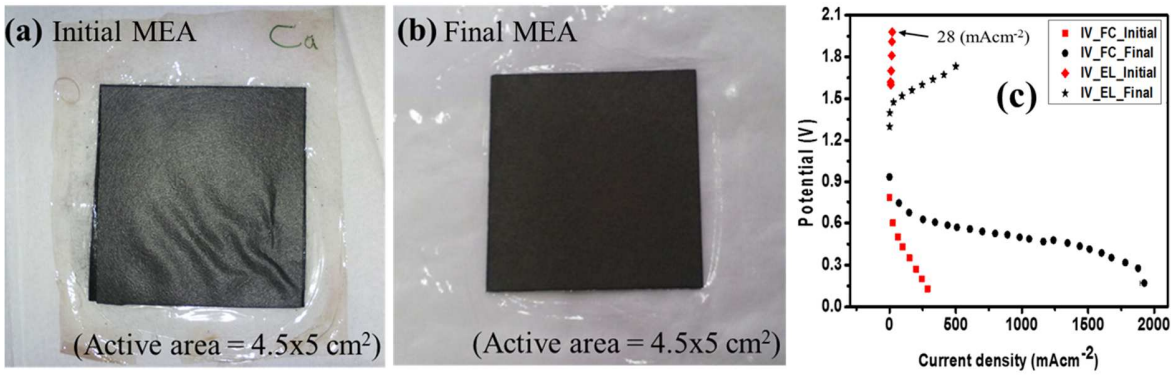

Fig. 12. (a) initial and (b) final MEA; (c) performance comparison of the MEAs.

The pressure, temperature and time for which pressing was done are 60 kg cm^{-2}, 130°C and 3 min [168]. Gradual pressure rise was ensured for better results. The entire pack of cushioned MEA was taken out and allowed to cool down after which cushioning was removed by applying deionized water (DI) with soft hands on both sides of MEA.

Although parameters like pressure, temperature and time could be found from literature, their effect on MEA could be different with different machines/hot presses used. Also, small steps in the MEA preparation that are normally not discussed in the literature are of great help and come through experience. Fig. 12 underlines the importance of such steps in the view of the performance.

6. Conclusions

MEAs being the heart of the cells, are supposed to be fabricated with appropriate techniques and care. Here, authors summarize the importance of MEAs along with the materials that could be used in various preparation methods. Membranes being the major contributor in ohmic resistance of the cell, have to be as thin as possible yet managing the crossover of the fuel in PEMFCs (<50 µm). However, in case of URFCs, since the gases are generated during the electrolysis mode at high pressure, the thickness the membranes could be higher (> 50 µm) to avoid the

crossover and gas leakage. Researchers also suggested various catalysts for PEMFCs (Pt) and URFCs (IrO_2, RuO_2) along with the supports (Vulcan XC-72, SnO_2, TiO_2 etc.),

MPLs and the backing layer control the diffusivity of the fluids as well as the electric conductivity of the cells and hence should be prepared/chosen wisely. Carbon based GDLs serve the purpose in case of PEMFCs however, they get oxidized in acidic environment during electrolysis mode of URFCs. Titanium based GDLs seem to have a satisfactory performance for such cells primarily due to their strong anticorrosive properties.

Various ways of fabrication of MEAs are discussed in detail here in this report with the focus on CCE method of preparation due to its robust nature as well as widely accepted and used method. The importance of controlling parameters such as pressure, temperature and time of pressing has been detailed out with pressure being the game changer in the process. The approximate values of such parameters have been reported to be 60 kg cm^{-2}, 130^{o}C and 3 min respectively. The authors, considering the importance of materials as well as process, have shown the comparative performance of MEAs made using the CCE method.

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