A comprehensive review on PEM water electrolysis

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Abstract

Hydrogen is often considered the best means by which to store energy coming from renewable and intermittent power sources. With the growing capacity of localized renewable energy sources surpassing the gigawatt range, a storage system of equal magnitude is required. PEM electrolysis provides a sustainable solution for the production of hydrogen, and is well suited to couple with energy sources such as wind and solar. However, due to low demand in electrolytic hydrogen in the last century, little research has been done on PEM electrolysis with many challenges still unexplored. The ever increasing desire for green energy has rekindled the interest on PEM electrolysis, thus the compilation and recovery of past research and developments is important and necessary. In this review, PEM water electrolysis is comprehensively highlighted and discussed. The challenges new and old related to electrocatalysts, solid electrolyte, current collectors, separator plates and modeling efforts will also be addressed. The main message is to clearly set the state-of-the-art for the PEM electrolysis technology, be insightful of the research that is already done and the challenges that still exist. This information will provide several future research directions and a road map in order to aid scientists in establishing PEM electrolysis as a commercially viable hydrogen production solution.

1. Introduction

The implementation of the so-called “Hydrogen Economy” [1–4] has been, since its first statement, disrupted by the fact that hydrogen does not exist in its molecular structure in nature. Hydrogen must be produced by means of an energy input, and to date, hydrogen is mainly produced by steam reforming natural gas or other fossil fuels, such as propane, gasoline, diesel, methanol, or ethanol [5,6]. This is achieved in a processing device called a reformer in which water vapor at high temperature (~700–1100 °C) is reacted with a fossil fuel, in the presence of a metal-based catalyst (usually nickel) [5,6]. However, steam reforming of fossil fuels produces low purity hydrogen with a high concentration of carbonaceous species such as carbon monoxide. More importantly, steam reforming does not relieve dependencies on scarce fossil fuels or reduce their pollutants, ultimately, not contributing to the establishment of a “carbon-balanced” energy matrix. High-quality hydrogen (=100% hydrogen) can be produced by the electrochemical conversion of water to hydrogen and oxygen through a process known as water electrolysis. The reaction with the thermodynamic energy values is described in Eq. (1):

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tricity has hindered and/or postponed the production of H2O sources like photovoltaics, and wind turbines. In this scenario, electrolytic hydrogen can not only be produced from a renewable energy source, work as an energy vector/carrier, and work as an energy storage medium, but also overcome the intermittency of typical renewable energy resources. Over the past decades, the ever increasing price of electricity has started a green transition. In Denmark, this is particularly more important and necessary, since the Federal Government has decided to stop the production of nuclear energy by 2022 and moreover, decisive targets for the share of electricity produced from renewables has been established (Fig. 1). In order to achieve those targets, the full reorganization of the energy matrix with renewable sources will require a high degree of energy availability and storage capacity \([14,15]\) (load leveling \([16]\)) of secondary fuels for the electricity industry and the transport sector.

### 1.1. Alkaline water electrolysis

Since the electrolysis phenomenon was discovered by Troostwijk and Diemann in 1789 \([17]\), alkaline electrolysis has become a well matured technology for hydrogen production up to the megawatt range, and constitutes the most extended electrolytic technology at a commercial level worldwide \([18]\). It brings Denmark a step closer to the target of 100% renewable energy in the energy and transport sectors by 2050 \([13]\).

In many ways, Denmark has started a green transition. In 2012 an energy agreement was signed, resulting in a target by 2020 where at least 50% of the electricity consumption is to be supplied by wind power, and more than 35% of the final energy consumption is to be supplied from renewable energy sources. The agreement contains a wide range of ambitious initiatives, bringing Denmark a step closer to the target of 100% renewable energy in the energy and transport sectors by 2050 \([13]\).

\[
\text{H}_2\text{O}(\text{aq}) + 237.2\text{kJ mol}^{-1} + 48.6\text{kJ mol}^{-1} \rightarrow \text{H}_2 + 1/2\text{O}_2 \quad (1)
\]

Over the past decades, the ever increasing price of electricity has hindered and/or postponed the production of electrolytic hydrogen \([7]\). This figure is about to change with the recent growth in energy capacity based on renewable sources like photovoltaics, and wind turbines \([8]\). In this scenario, electrolytic hydrogen can not only be produced from a renewable energy source, work as an energy vector/carrier, and work as an energy storage medium, but also overcome the intermittency of typical renewable energy resources \([9,10]\).

In many ways, Denmark has started a green transition. In 2012 an energy agreement was signed, resulting in a target by 2020 where at least 50% of the electricity consumption is to be supplied by wind power, and more than 35% of the final energy consumption is to be supplied from renewable energy sources. The agreement contains a wide range of ambitious initiatives, bringing Denmark a step closer to the target of 100% renewable energy in the energy and transport sectors by 2050 \([13]\).

In Germany, this is particularly more important and necessary, since the Federal Government has decided to stop the production of nuclear energy by 2022 and moreover, decisive targets for the share of electricity produced from renewables has been established (Fig. 1). In order to achieve those targets, the full reorganization of the energy matrix with renewable sources will require a high degree of energy availability and storage capacity \([14,15]\) (load leveling \([16]\)) of secondary fuels for the electricity industry and the transport sector.

### Nomenclature

- \(\Delta G\): Gibb’s free energy, J mol\(^{-1}\)
- \(A\): membrane surface area, m\(^2\)
- \(C_i\): molar concentration of species \(i\)
- \(C_{\text{H}_2}\): bulk proton concentration, mol cm\(^{-3}\)
- \(C_{\text{H}_2}\): proton conc. in surface diffusion, mol cm\(^{-3}\)
- \(D_{\text{eft}}\): effective diffusivity of transport media
- \(D_{\text{G}}\): proton Grothuss diffusion coefficient, m\(^2\) s\(^{-1}\)
- \(D_{\text{en masse}}\): proton en masse diffusion coefficient, m\(^2\) s\(^{-1}\)
- \(D_{\text{pt}}\): proton surface diffusion coefficient, m\(^2\) s\(^{-1}\)
- \(E\): open circuit voltage, V
- \(E_{\text{activation}}\): activation energy of electrode, J
- \(F\): Faraday’s constant, C mol\(^{-1}\)
- \(H_i(T)\): enthalpy of species \(i\) at temperature \(T\)
- \(I\): cell current, A
- \(i\): current density, A cm\(^{-2}\)
- \(i_0\): exchange current density, A cm\(^{-2}\)
- \(J\): diffusion flux, mol m\(^{-2}\) s\(^{-1}\)
- \(L\): length of a single pore, m
- \(n\): number of electrons transferred in reaction
- \(P\): pressure, kPa
- \(Q\): volumetric flow rate, m\(^3\) s\(^{-1}\)
- \(R\): universal gas constant, J K\(^{-1}\) mol\(^{-1}\)
- \(R_{\text{eff}}\): total electrical resistance of cell, \(\Omega\)
- \(S_i(T, P_0)\): entropy of species \(i\) at temp \(T\) and 1 atm
- \(T\): temperature, K
- \(T_{\text{el}}\): electrode temperature, K
- \(V\): cell voltage, V
- \(x\): spatial coordinate in direction of diffusion

### Greek symbols

- \(\alpha\): charge transfer coefficient
- \(\delta_c\): Stefan–Maxwell diffusion ratio
- \(\delta_{\text{mem}}\): thickness of membrane, m
- \(\lambda\): water uptake coefficient
- \(\mu\): dynamic viscosity of water, Pa s
- \(\sigma_{\text{mem}}\): proton conductivity of membrane, S m\(^{-1}\)
- \(\tau\): tortuosity factor
- \(\epsilon_i\): membrane porosity

### Abbreviations

- BMG: bulk metallic glass
- CCM: catalyst coated membrane
- CNT: carbon nanotube
- CV: cyclic voltammetry
- DSA: dimensionally stable anode
- ECSA: electrochemical surface area
- GDL: gas diffusion layer
- HER: hydrogen evolution reaction
- HHV: higher heating value, kJ mol\(^{-1}\)
- MEA: membrane electrode assembly
- MPL: microporous layer
- NSTF: nanostructured thin film
- OCV: open circuit voltage
- OER: oxygen evolution reaction
- ORR: oxygen reduction reaction
- PEM: polymer electrolyte membrane
- PFS: perfluorosulfonate polymer membrane
- PGM: platinum group metals
- RDE: rotating disk electrode
- SHE: standard hydrogen electrode
- SOEC: solid oxide electrolysis
- SPE: solid polymer electrolyte
- TPF: thermoplastical forming
- UPD: under potential deposition

\[
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\]
is characterized by having two electrodes immersed in a liquid alkaline electrolyte consisting of a caustic potash solution at a level of 20–30% KOH. The two electrodes are separated by a diaphragm (Fig. 2), which has the function of keeping the product gases apart from one another for the sake of efficiency and safety. The diaphragm must also be permeable to the hydroxide ions and water molecules. Table 1 lists the state-of-the-art for the specifications of an alkaline electrolyzer.

Three major issues are normally associated with alkaline electrolyzers, low partial load range, limited current density and low operating pressure. First, the diaphragm does not completely prevent the product gases from cross-diffusing through it. The diffusion of oxygen into the cathode chamber reduces the efficiency of the electrolyzer, since oxygen will be catalyzed back to water with the hydrogen present on the cathode side. Additionally, extensive mixing (particularly hydrogen diffusion to the oxygen evolution chamber) also occurs and must be avoided to preserve the efficiency, as well as safety. This is particularly severe at a low load (<40%) where the oxygen production rate decreases, thus drastically increasing the hydrogen concentration to unwanted and dangerous levels (lower explosion limit >4 mol% H₂) [19]. The second drawback for alkaline electrolyzers is the low maximum achievable current density, due to the high ohmic losses across the liquid electrolyte and diaphragm. The third problem, also attributed to the liquid electrolyte, is the inability to operate at high pressure, which makes for a bulky stack design configuration.

1.2. Solid oxide electrolysis (SOEC)

In the 1980s, Dönitz and Erdle were the first to report results from a solid oxide electrolyzer (SOECs) from within the HotElly project at Dornier System GmbH using a supported tubular electrolyte [21]. Since then, SOECs have attracted a great deal of interest because they can convert electrical energy into...
chemical energy, producing hydrogen with high efficiency. In this program, single cells have been operated with current densities of 0.3 A cm$^{-2}$ achieving 100% of Faraday efficiency at a voltage as low as 1.07 V [21,22]. Later on, Westinghouse Electric Corporation Research and Development Centre contributed to the development of SOECs with great interest. SOEC is nowadays still under development but research has grown exponentially in the last decade, companies, research centers and universities around the world have shown interest in this field. Another remarkable project funded by the European Commission is the Relhy project, including 7 European partners [21,22]. These preliminary lab-scale studies are mainly focused on the development of novel, improved, low cost, and highly durable materials for SOECs. They are also focused on the development of the inherent manufacturing processes, and the integration in an efficient and durable SOEC. Also interesting, is that SOECs, due to the chemical flexibility of those devices and high temperature of operation, could be used for the electrolysis of CO$_2$ to CO, and also for the co-electrolysis of H$_2$O/CO$_2$ to H$_2$/CO (syngas). The SOEC technology has a huge potential for the future mass production of hydrogen, if the issues related to the durability of the ceramic materials at high temperature and long-term operation are solved. For future developments, the understanding of the structure and electrochemistry of the materials is essential in order to solve these drawbacks.

### 1.3. PEM water electrolysis

The prognostics to overcome the drawbacks of alkaline electrolyzers changed when General Electric, in the 1960s, developed [23] the first water electrolyzer based on a solid polymer electrolyte concept. This concept was idealized by Grubb [24,25], where a solid sulfonated polystyrene membrane was used as an electrolyte. This concept is also referred to as proton exchange membrane or polymer electrolyte membrane (both with the acronym PEM) water electrolysis, and less frequently as solid polymer electrolyte (SPE) water electrolysis.

The polymer electrolyte membrane (Nafton®, fumapem®) is responsible for providing high proton conductivity, low gas crossover, compact system design and high pressure operation. The low membrane thickness (~20–300 μm thick) is in part the reason for many of the advantages of the solid polymer electrolyzer.

#### 1.3.1. Positive aspects

PEM electrolyzers can operate at much higher current densities, capable of achieving values above 2 A cm$^{-2}$, this reduces the operational costs and potentially the overall cost of electrolysis (Tables 1 and 2). Ohmic losses limit maximum achievable current densities, with a thin membrane capable of providing good proton conductivity (0.1 ± 0.02 S cm$^{-1}$) [26] higher current densities can be achieved. The solid polymer membrane allows for a thinner electrolyte than the alkaline electrolyzers.

The low gas crossover rate of the polymer electrolyte membrane (yielding hydrogen with high purity), as described in Table 2, allows for the PEM electrolyzer to work under a wide range of power input ( economical aspect). This is due to the fact that the proton transport across the membrane responds quickly to the power input, not delayed by inertia as in liquid electrolytes. As discussed above, in alkaline electrolyzers operating at low load the rate of hydrogen and oxygen production reduces while the hydrogen permeability through the diaphragm remains constant, yielding a larger

<table>
<thead>
<tr>
<th>Table 1</th>
<th>State-of-the-art for the specifications of alkaline and PEM electrolyzers as reported in the NOW-study [20].</th>
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</thead>
<tbody>
<tr>
<td>Specifications</td>
<td>Alkaline electrolysis</td>
</tr>
<tr>
<td>Cell temperature (°C)</td>
<td>60–80</td>
</tr>
<tr>
<td>Cell pressure (bar)</td>
<td>&lt;30</td>
</tr>
<tr>
<td>Current density (mA cm$^{-2}$)</td>
<td>0.2–0.4</td>
</tr>
<tr>
<td>Cell voltage (V)</td>
<td>1.8–2.4</td>
</tr>
<tr>
<td>Power density (mW cm$^{-2}$)</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Voltage efficiency HHV (%)</td>
<td>62–82</td>
</tr>
<tr>
<td>Specif. energy consumption:</td>
<td>4.2–5.9</td>
</tr>
<tr>
<td>Stack (kW h Nm$^{-3}$)</td>
<td>4.5–7.0</td>
</tr>
<tr>
<td>Specif. energy consumption:</td>
<td>20–40</td>
</tr>
<tr>
<td>System (kW h Nm$^{-3}$)</td>
<td>&gt;4</td>
</tr>
<tr>
<td>Lower partial load range (%)</td>
<td>H$_2$ production rate:</td>
</tr>
<tr>
<td>Cell area (m$^2$)</td>
<td>Lifetime stack (h)</td>
</tr>
<tr>
<td>Stack-system (Nm$^3$ h$^{-1}$)</td>
<td>Lifetime system (y)</td>
</tr>
<tr>
<td>Degradation rate (μV h$^{-1}$)</td>
<td>3–14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Advantages and disadvantages of alkaline and PEM electrolysis.</th>
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<tbody>
<tr>
<td>Advantages</td>
<td>Alkaline electrolysis</td>
</tr>
<tr>
<td>Well established technology</td>
<td>High current densities</td>
</tr>
<tr>
<td>Non noble catalysts</td>
<td>High voltage efficiency</td>
</tr>
<tr>
<td>Long-term stability</td>
<td>Good partial load range</td>
</tr>
<tr>
<td>Relative low cost</td>
<td>Rapid system response</td>
</tr>
<tr>
<td>Stacks in the MW range</td>
<td>Compact system design</td>
</tr>
<tr>
<td>Cost effective</td>
<td>High gas purity</td>
</tr>
<tr>
<td>Dynamic operation</td>
<td></td>
</tr>
</tbody>
</table>

| Disadvantages | Alkaline electrolysis | PEM electrolysis | SOEC electrolysis |
|-----------------|--------------------------------------------------|
| Low current densities | High cost of components | Laboratory stage |
| Crossover of gases (degree of purity) | Acidic corrosive environment | Bulky system design |
| Low partial load range | Possibly low durability | Durability (brittle ceramics) |
| Low dynamics | Commercialization | No dependable cost information |
| Low operational pressures | Stacks below | |
| Corrosive liquid electrolyte | MW range | |
concentration of hydrogen on the anode (oxygen) side thus creating a hazardous and less efficient conditions [27]. In contrast with alkaline electrolysis, PEM electrolysis covers practically the full nominal power density range (10–100%). One could speculate that PEM electrolysis could reach values over 100% of nominal rated power density, where the nominal rated power density is derived from a fixed current density and its corresponding cell voltage. This is due to the low permeability of hydrogen through Nafion® (less than $1.25 \times 10^{-4}$ cm$^3$/s cm$^{-2}$ for Nafion® 117, standard pressure, $80^\circ$C, 2 mA cm$^{-2}$) [27].

A solid electrolyte allows for a compact system design with strong/resistant structural properties, in which high operational pressures (equal or differential across the electrolyte) are achievable [28]. Some commercial models have claimed to reach pressures up to 350 bar [29]. The high pressure operation [28,30] of an electrolyzer brings the advantage of delivering hydrogen at a high pressure (sometimes called electrochemical compression) for the end user, thus requiring less energy to further compress and store the hydrogen. It also diminishes the volume of the gaseous phase at the electrodes thus significantly improving product gas removal which follows Fick’s law of diffusion [31]. In a differential pressure configuration, only the cathode (hydrogen) side is under pressure, this can eliminate the hazards related to handling pressurized oxygen and the possibility of self-ignition of Ti in oxygen [32]. The pressure increase minimizes the expansion and dehydration of the membrane, preserving the integrity of the catalytic layer [31]. The increase in the operating pressure also results in higher thermodynamic voltages (100 mV every two order of magnitude or 44 mV dec$^{-1}$), however, with only slight improvement in overall efficiency, especially at high current densities [33].

1.3.2. Negative aspects

Problems related to higher operational pressures in PEM electrolysis are also present, such as cross-permeation phenomenon which increases with pressure [33,34]. Pressures above 100 bar will require the use of thicker membranes (although more resistant), and internal gas recombiners to maintain the critical concentrations (mostly H$_2$ in O$_2$) under safety threshold (4 vol.% H$_2$ in O$_2$) [33]. Lower gas permeability through the membrane (crossover) can be obtained by incorporating miscellaneous fillers inside the membrane material [35], but this normally leads to less conducting materials.

The corrosive acidic regime provided by the proton exchange membrane requires the use of distinct materials. These materials must not only resist the harsh corrosive low pH condition (pH $\approx 2$), but also sustain the high applied over voltage ($\approx 2$ V), especially at high current densities. Corrosion resistance applies not only for the catalysts used, but also current collectors and separator plates. Only a few materials can be selected that would perform in this harsh environment. This will demand the use of scarce, expensive materials and components such as noble catalysts (platinum group metals-PGM e.g. Pt, Ir and Ru), titanium based current collectors, and separator plates (Figs. 2 and 3).

Iridium has one particular limitation, since it is one of the rarest elements in the Earth’s crust, having an average mass fraction of 0.001 ppm in crustal rock. Conversely, gold and platinum are 40 times and 10 times more abundant, respectively [36–38]. The major commercial sources of iridium are

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**Fig. 3** – Component overview for a typical PEM water electrolyzer. Catalyst layer inlay reproduced from ref [39] with permission from Elsevier.
found in pyroxenite and the sulfide ore laurite in South Africa, as well as pentlandite from nickel mining regions in Russia and Canada. Iridium demand has recently increased due to its use on crucibles employed to fabricate LEDs for smartphones, tablets, televisions and automobiles. It is consequently expected that a high penetration of the PEM electrolysis technology in the market would considerably affect the demand for iridium and consequently the price.

Since the first studies by GE [23], research groups have tried to overcome the high cost issue with innumerable alternatives. However, the number of published papers related to PEM electrolysis is low (Fig. 4), especially when compared, for example, to PEM fuel cells R&D. Nevertheless, important achievements were accomplished, and in summary, we will attempt to outline a road map for electrocatalysts and component development over the years as well as helpful insights for the years still to come. Based on the current state-of-the-art of R&D in PEM electrolysis, we will attempt to draw opportunities and guiding directions on how the technology can be further developed, the durability enhanced and the costs further reduced, in order to ultimately contribute to a future hydrogen based economy.

2. Electrocatalysts for PEM water electrolysis

The first PEM electrolysis journal publication was done by Russell et al., in 1973 at GE using a PEM electrolysis cell [23]. However, in this study, voltage–current profiles (VI Curves) from 1967 until 1972 are also presented, showing the R&D development over the early years (Fig. 5) [23].

It is also interesting to note that in this publication of 1973, key words such as, “future hydrogen economy,” “hydrogen as energy storage,” “solar energy systems,” and hydrogen being “tomorrow’s energy power system” were already being used. Regarding the empirical aspect, these early PEM electrolysis systems were already considerably efficient, presenting performances of 1.88 V @ 1 A cm$^{-2}$ or 2.24 V @ 2 A cm$^{-2}$. They also had already presented a cell life of over 15,000 h without substantial performance degradation [23]. The authors also addressed concerns related to the high costs of catalysts used, and for these early systems, catalyst layers were based on Ir and Pt black with high metal loading. They suggested that capital costs could be reduced by reducing the loading and/or substituting the expensive noble materials used for the fabrication of catalyst layers and hardware [23]. Catalyst developments for water electrolysis using liquid acid electrolytes were already present, for both hydrogen (HER) and oxygen evolution reactions (OER). Earlier in 1966 for example, Damjanov et al. studied the kinetics of the OER on Rh, Ir, and Pt–Rh alloys using a liquid electrolyte, showing activities in the following order: Pt < Pt–Rh < Rh < Ir [40].

Important and valuable understandings related to electrocatalysis for the OER and the HER were obtained in two series of studies. The first was a series on the OER that was done by Burke and Moynihan (Part 1 to Part 8, from 1971 until 1976) [41–48]. The second was a series on the HER that was presented by Furuya and Motoo (Part 1 to Part 6, from 1976 until 1979) [49–54]. In Tables 3 and 4 the main findings from these studies are summarized. However, it is important to note that the research can be found in greater detail directly in these publications [41–54].
Table 3 – Summary of studies performed by Burke et al. for the OER.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Oxygen evolution reaction</th>
</tr>
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<tbody>
<tr>
<td>[41]</td>
<td>The formation of oxide film on the Pt metal surface follows Elovich kinetics.</td>
</tr>
</tbody>
</table>
| [42] | OER over ruthenium:  
  * Vigorous corrosion was observed under highly anodic conditions with a variety of oxidation states.  
  * d-band vacancies are essential for oxygen chemisorption, the concentration of such vacancies in ruthenium is too great. |
| [43] | Coverage of the elec. surface by OH radicals is not at any time regarded as being very large as the conversion to an oxide film occurs, possibly via peroxide intermediate. OER is assumed to occur via similar mechanisms. |
| [44] | Ru has the ability to form oxide bridges with two three-centre molecular orbital bond. This accounts for the metallic conductivity of RuO₂, and is involved in the support of Ru in the oxide film on Pt. Reduction of these oxide bridges would lead to loss of Ru and a diminution of catalytic activity. |
| [45] | The loss of storage capacity when the activated Ir surface is anodized for a short time above 1.60 V is attributed to loss by corrosion of the outer active layer from the Ir surface. |
| [46] | The rate of OER was considerably faster on Ir vs. Pt in both acidic and basic media. Under constant E conditions a continuous decrease in I vs. t was observed in the case of Pt. This effect is due to continuous slow oxidation of the metal substrate with consequent inhibition of e- transfer or of radical reaction at the elec. surface. |
| [47] | The charge storage properties of an Ir elec. activated by potential cycling are attributed to stoichiometry changes in an oxide film. The rate of growth of this film in acid solution decreased with increasing frequency. These results are explained in terms of nucleation of corrosion centers at low potentials and subsequent irreversible oxide formation in pitted regions at more anodic potentials. |
| [48] | For RuO₂/Ti, the charge involved in the Cyclic Voltammetry (CV) and the OER rates are dependent on the true (rather than apparent) area of these electrode surfaces, and also on the pH of the solution. The charge associated with CV sweeps is accounted for in terms of surface redox processes rather than bulk penetration of protons into the oxide. |

In the following years, studies on PEM water electrolysis had been focused on the survey of electrocatalysts in order to mitigate the drawback of the OER irreversibility and slowness. Attempts have been extensively made to find a more reversible oxygen catalyst, but not forgetting that the electrocatalyst would have to be resistant to the harsh oxidative environment of a PEM electrolyzer. Miles and Thomason demonstrated a summary of activities for a variety of elements for the HER and the OER using cyclic voltammetric techniques (Fig. 6) [55]. It is clear in this study that when using single elements alone, the HER and the OER will be essentially dependent on noble elements for the sake of efficiency. For the HER it was found that in 0.1 mol L⁻¹ H₂SO₄ at 80 °C the catalytic activity order was Pd > Pt > Rh > Ir > Ge > Os > Ru > Ni. For the OER, the order was Ir ≈ Ru > Pd > Rh > Pt > Au > Nb. However, the authors discussed that oxides of each catalyst for the OER seem to have a dominant factor in affecting their electrocatalytic activities [55]. In fact, RuO₂ was discovered to exhibit oxygen overvoltages much lower than any other material tested [56], which is consistent with many observations found in the early studies [57–61]. As an example, the overvoltage for the OER is much lower with RuO₂ or Ru than with Pt [59]. The presence of platinum adversely affects the electrocatalytic activity for the OER due to the high resistance oxide film that forms on the platinum surface (the same effect applies for palladium) [56].

Among the transition metal oxides, RuO₂ and IrO₂ exhibit high metallic conductivity, with a value in the order of 10⁴ cm⁻¹Ω⁻¹ (single crystals) [59]. The value for the metal−metal distance and the radius of the cation in these oxides are such that overlap of the inner d-orbital is possible, the d-electrons in these d-bands are responsible for the electron conduction [57].

A major drawback with RuO₂ is that it corrodes at an appreciable rate with oxygen evolution. Kötzt et al. presented a model (Fig. 7) for the anodic oxidation of Ru and RuO₂ electrodes in acid electrolyte where it is said that RuO₂ corrodes by

Table 4 – Summary of studies performed by Furuya and Motoo for the HER.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Hydrogen evolution reaction</th>
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<tbody>
<tr>
<td>[49]</td>
<td>The rearrangement from disordered to ordered surface structure of Cu ad-atoms on Pt takes place in the E range from 0.2 to 0.6 V (RHE) resulting in the decrease of the recombination of adsorbed H, reducing HER rate.</td>
</tr>
<tr>
<td>[50]</td>
<td>The activity of As deposition on Pt has been found to depend not on the amount of deposited As but on the number of vacant sites. The difference in the effects of As and of Cu on HER is attributed to the difference in the affinity of the ad-atoms for hydrogen.</td>
</tr>
<tr>
<td>[51]</td>
<td>Using a Pt−Au system, the HER activity is predominantly controlled by the surface and not by the bulk. In general the decay for HER depends on the number of Pt sites occupied by an atom (Sn, Pb, Ge) or of the ad-atom species.</td>
</tr>
<tr>
<td>[52]</td>
<td>HER on a Pt elec. proceeds through the atom + atom step which needs pairs of 2 nearest neighbor sites available for HER. HER activity decreases with the decrease of the # of pairs of Pt sites with the deposition of foreign ad-atoms. The rate of hydrogen evolution is reduced in a manner same as that of the reduction of the pairs of nearest neighbor sites available for hydrogen adsorption.</td>
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</table>
forming RuO₄ in acid electrolytes. In this model Ru is leached out of the catalyst layer [63] and into the membrane, in ionic form, or by electrophoretic action, where Ru is finally precipitated and deposited. Ru ions which may be complexed, even to the negative ionic state, back-diffuse from the cathode either, dissolved in the swollen membrane, in cracks, or in the gas passages [64]. Using x-ray photoelectron spectroscopy Kötz et al. found that during the OER on Ru, a highly defective hydrated oxide is formed as a result of corrosion. Since RuO₂ is more abundant than the IrO₂, researchers over the years have attempted finding alternatives to stabilize RuO₂ against corrosion/dissolution [64–71]. These alternatives were mainly approached by introducing other elements or oxides into the Ru catalyst structure, so that this solid solution could reduce the erosion rate of Ru. When mixing IrO₂ with RuO₂, Kötz and Stucki hypothesized the existence of a common band between the IrO₂ and RuO₂ orbitals. In this scenario the electrons available on IrO₂ sites could be shared with RuO₂ sites, thus the oxidation potentials of Ru would be raised [65].

Researchers have demonstrated that an admixture of IrO₂ significantly improves the stability of RuO₂ during the OER. Relatively small amounts of IrO₂ (20%) had a dramatic effect and reduced the corrosion rate of the oxide to about 4% of the original value [65]. Besides Ru, Ir exhibits the best catalytic properties for the OER in acid electrolytes when compared to other noble metals, but not presenting severe corrosion like Ru. In this sense, the great majority of studies on PEM water electrolysis for the OER have concentrated on Ir based catalysts (appendix A). For the HER, platinum based catalysts are the most commonly used.

Fig. 8 shows a representation of the performances (cell voltage @ 1 A cm⁻²) of the PEM electrolysis studies published since 1970. At a current density of 1 A cm⁻² the majority of the activation losses will originate from the anode reaction, as the cathode normally exhibits good kinetics at these current densities [68].

It is important to mention that the different publications might have different experimental conditions (temperature, pressure, electrode size, and stack compression/torque), and also different materials or components (membrane, ionomer, catalysts, current collectors and separator plates). This means that a direct performance comparison is not trivial, since the different conditions and materials will directly influence the performance. However, the main objective of these studies, regardless of the used materials and conditions, was to improve performance, which in general means decrease the cell voltage and improve current densities. In this sense, a subjective comparison is worthwhile, and could bring important insights.

Cell voltage has not decreased considerably over the years and a few points have to be considered that could explain this observation. First, when compared to alkaline electrolysis, the initial PEM electrolyzers already had good performance using platinum group metal (PGM) based catalysts and Nafion® membranes. This means that further reductions on cell voltage would be rather challenging. Second, early studies were not only aimed to improve the performance or reduce the cell voltage, but also to reduce the costs, which frequently means reducing the loading of the catalysts and/or using alternative, less noble catalyst systems. Therefore, research in loading reductions and noble metal substitution usually results in decreased performance levels. In Fig. 9, the values of catalyst loading are presented for the same publications found in Fig. 8.

Early on the catalyst loadings for the cathode were considerably high. The loadings dropped quickly, after the realization that high amounts of catalysts for the HER were not necessary (since the OER is the dominant reaction). To date catalyst loadings for the cathode side have been reduced to a range of 0.5–1 mg cm⁻². For the anode side, where the OER takes place, the catalyst loadings have not reduced as much over the years, due to the continuous dependence on low utilization and low surface area iridium catalysts. Currently, the loadings for the anode catalyst layer range around 2 mg cm⁻².

2.1. Electro catalysts for the oxygen evolution reaction

As previously discussed, Ir (IrO₂) is generally recognized as the state-of-the-art for the OER in PEM electrolysis. Ru (RuO₂) is...
more active than Ir (IrO₂), but the problems related to instability (corrosion) limit its use. Until the early 1990s PEM electrolysis publications concentrated mainly on the use and understanding of Ru and Ir catalysts, and their alloys, for the OER. With the aim of improving efficiency, stability, and reducing the costs, researchers in the following years began trying different catalyst alternatives for the OER.

The first approaches were concentrated on mixing IrO₂ with a cheaper “diluent” forming a solid solution with less expensive and more durable materials that could be easily manufactured. This would considerably reduce the capital costs. In 1995, De Pauli and Trasatti [73] prepared mixed oxide layers of SnO₂ and IrO₂ which were electrochemically characterized in a liquid acidic regime. They found that with only 10% Ir, the surface of the SnO₂ was almost fully saturated with Ir [73,74]. Unfortunately, no OER results were demonstrated.

Other studies were performed with an addition of less expensive oxides to the IrO₂ catalyst. Materials such as Ta₂O₅ [75,76], Nb₂O₅ [77], Sb₂O₅ [78], and their mixtures (e.g. SnO₂–IrO₂–Ta₂O₅ [79]) were also published. Chen et al. made an important comment on the electrode stability in relation to the electron conductivity [78]. They suggested that there are many factors that can affect electrode stability, one of which is the coating conductivity. In an article by de Oliveira-Sousa et al., a Ti/IrO₂ coated electrode was prepared using three different methods, and tested for the OER in acidic media [80]. The tests indicated good stabilities and durability of the coatings. Low electron conductivity will result in a high electric field inside...
the coating and thus cause a quick migration of $O^2-$ ions toward the substrate. The quick $O^2-$ migration may then accelerate formation of an insulating TiO$_2$ layer at the interface between the titanium substrate and the coating, leading to electrode passivation. A lower electrode stability at low mol % Ir$_x$O$_y$ for most Ir$_x$O$_y$-based coatings, is normally associated with insufficient coating conductivity [78].

In the research by Hu et al., it was concluded that on Ti/IrO$_2$-Ta$_2$O$_5$ electrodes, three modes of destruction are present during electrolysis: (i) dissolution of the active component, (ii) penetration of the electrolyte through the porous structure of the thermally prepared oxide layer, and (iii) dissolution and anodic oxidation of the Ti base. It was also concluded that the electrocatalytic activity of the oxide catalyst decreases slowly with electrolyzer operation, and no sudden or sharp deterioration occurs [76].

Ardizzone et al., using a mixture of SnO$_2$-IrO$_2$-Ta$_2$O$_5$ oxides, evidenced the superior properties of the ternary mixtures and the key role of tantalum (even at low molar fraction) in, expanding the surface area, improving the electronic conductivity, increasing the charge storage capacitance and promoting the surface enrichment of iridium [79]. The excellent electrocatalytic properties for the OER in acid electrolyte, even at low Ir content (15 mol%), were highlighted [79]. However, since most of these catalysts were coated/supported on solid Ti plates, those electrodes could not be used in a membrane electrode assembly (MEA) or catalyst coated membrane (CCM) configuration, due to the impermeability of the solid catalyst plate.

Terezo et al. suggested that the active surface sites play a dominant role both in the capacity charging process and in the transport component of the impedance [77]. In other words, a catalyst with high surface area (or electrochemical surface area – ECSA) would enhance performance and ionic conductivity. Unfortunately, this was not the case for those Ti coated catalysts, since the coating process usually produces very low surface area electrodes.

In order to evaluate the activity of these catalyst systems in a PEM electrolysis cell, a method to produce catalysts in a “free standing” form with high surface area had to be developed together with methods to incorporate the porous catalyst structure on the electrolyte membrane. In the beginning, noble metal catalysts were directly reduced or electroplated on the membrane surface or inside its structure (appendix A). This method resulted in poor catalyst utilization, low surface area, and consequently low performance. In the early studies, different methods to prepare and apply powdered catalysts were used to produce CCMs and MEAs (section 7), most of which came from fuel cell R&D. Dimensionally stable anode (DSA) type electrodes were not suitable for CCM preparation due to the difficulty in obtaining a good membrane and electrode contact, as opposed to ultrafine catalyst nanoparticles where membrane-electrode contact is enhanced [81]. The ideal catalyst layer should then provide high catalyst utilization, high electron conductivity, and high mass transport. More importantly, it should present high durability.

Marshall et al., using a modified polyl method, produced and characterized nanocrystalline oxide powders of Ir$_x$Sn$_{1-x}$O$_2$. The study suggested that the crystal properties of Ir$_x$Sn$_{1-x}$O$_2$ powders, depend on the method used to prepare these materials [82]. Adams fusion method results in an oxide consisting of at least two separate oxide phases, with one of these containing mostly SnO$_2$. Alternatively, the modified polyl method was believed, in this publication, to form a solid solution between iridium and tin oxide, with the lattice parameters increasing linearly with tin content. Comparing the electrical resistivity of these oxides, it was shown that for the Adams fusion method the addition of SnO$_2$ increases the resistivity, while for the polyl method the formation of a solid solution reduces the effect of SnO$_2$ on the resistivity. By making simple estimations of possible ohmic losses in a PEM water electrolyzer, the authors suggested that the limit for SnO$_2$ addition is around 50–60 mol% [82]. Regarding the synthesis procedure, the authors also pointed out that iridium rich colloids have a low zeta potential and therefore will agglomerate at lower pH values than tin rich colloids. Therefore, to ensure that homogenous agglomerate is obtained, high pH values should be used to ensure all colloidal material is present in the agglomerate [82].

In another study also using Ir$_x$Sn$_{1-x}$O$_2$, Marshall et al. added that the inclusion of tin oxide to iridium oxide particles for the OER resulted in a dilution of the more expensive iridium oxide at all examined current densities [83]. Using Ir$_x$Ru$_y$Ta$_z$O$_5$, Marshall et al. showed no better activities for the Ta added catalysts compared to Ir$_x$Ru$_y$O$_2$ due to the very poor activity of TaO$_2$ toward the OER [68]. However, when Mo was added, forming Ir$_{x}$Ru$_{y}$Mo$_{z}$O$_5$, smaller particle size and larger active surface area compared to Ir$_x$Ru$_y$O$_2$ was observed. The authors explained that the reason for the reduced particle size is that Ir and Ru ions at the interface can connect with Mo by Ir(Ru)—O—Mo bonds around the rutile crystalite, which inhibits the growth of crystallite grains during the Adams fusion method process [70].

Using the sulfite complex route, IrO$_2$ with a small particle size (2–3 nm) were produced by Siracusano et al. [84,85]. This was a considerable reduction, since most of the published research using IrO$_2$ nanoparticles range from 7 to 12 nm [86]. The authors claimed a reduced sintering phenomena, since no particle sintering was observed after the single cell tests. However, information on the homogeneity and representative long-term operation tests, or accelerated durability tests were not presented in this study. Most of these studies suggest that the “non-noble” oxides (such as TiO$_2$, SnO$_2$, Ta$_2$O$_5$, Nb$_2$O$_5$, Sb$_2$O$_3$) do not contribute actively to the OER. Xu et al. concluded that the Tafel curves of IrO$_2$ with SnO$_2$ showed that the addition of Sn effectively suppressed adsorption of hydroxyl species which is directly involved in the OER [72]. The addition of SnO$_2$ not only promoted the dispersion of the nanoparticles but also efficiently removed adsorbed hydroxyl species and released more active reaction sites of IrO$_2$.

In a study using IrO$_2$ supported on tantalum carbide (TaC), Polonsky et al. commented that a negative aspect of a NaTaO$_3$ surface film, characterized by low conductivity, may be overcome by applying a sufficient amount of IrO$_2$ (in this particular case the metal loading was 50 wt.% or more) [87]. In more recent research, interesting materials and material structures have appeared that might change this picture. In one publication, RuO$_2$ supported on ATO (Sb doped SnO$_2$ nanoparticles) were prepared via a colloid method with only 20% ruthenium content, while maintaining high performance (1.55 V @
1 A cm\(^{-2}\)) [88]. The authors concluded that the enhancement was attributed to the reduction of catalyst particle agglomeration and increasing electron conductivity of the RuO\(_2\) by ATO, but also pointing out that ATO is believed to be an inert material for the OER.

In a recent European project that was completed in July 2012, PrimoLyzer [89–91], the OER was studied by molecular modeling or density functional methods. The investigated catalysts consisted of pure metal oxides (IrO\(_2\), RuO\(_2\), and SnO\(_2\)) with rutile structures, binary structures (Ir-RuO\(_4\) and RuIrO\(_4\)) and tertiary metal oxides (Ir-RuSnO\(_3\)) with rutile-like structures. According to the report, Mixed Ir–Ru oxides were the most active binary and Ir–Ru–Sn the most active tertiary oxides catalysts. The stability of the mixed Ir–Ru oxide was verified in a dissolution cell in 0.5 M H\(_2\)SO\(_4\) at 1.85 V vs. SHE and 80 °C in a CCM configuration (single cell tests). Pt and PtPd supported on carbon black and multi walled carbon nanotube were also studied for the HER. 10 wt% was found to be the optimal noble metal loading in liquid H\(_2\)SO\(_4\) electrolyte reaching the activity of 1.5 A cm\(^{-2}\) at 40 mV (vs. SHE) at room temperature. In the single cell tests, IR-corrected polarization curves of the optimized CCMs showed performances higher than the project target [1.64 V @ 1.2 A cm\(^{-2}\)] for CCMs with less than the targeted catalyst loadings [Present loadings: Anode: 0.3 mg cm\(^{-2}\), Cathode: 0.5 mg cm\(^{-2}\) – Target loadings: Anode: 1.0 mg cm\(^{-2}\), Cathode: 0.5 mg cm\(^{-2}\)]. For single cell tests, at 70 °C, Ambient pressure, Nafion\textsuperscript{®} 115, C: 0.6 mgPt cm\(^{-2}\), A: 0.6 mgIr cm\(^{-2}\), and performance of 1.72 V @ 1 A cm\(^{-2}\), after 2000 h of operation, the degradation rate was <30 μV h\(^{-1}\) [89–91].

In summary, by diluting the noble metal content, the metal oxides contribute to the stability of the noble metal particles against corrosion. They essentially work as a support material for the active catalyst; however, to date, the real phenomena are not completely clear. Since these corrosive resistant oxide materials generally present low electron conductivities [92], high loadings (over 50%) of the active materials [72,93], high particle size, low homogeneity, and consequently low noble metal utilization, there is a necessity to apply high metal loadings on the preparation of the CCM.

### 2.2. Electrocatalysts for the hydrogen evolution reaction

The challenges related to the OER in PEM electrolysis have concentrated the R&D efforts on the development of electrocatalysts systems for the anode side. In most of the early studies, researchers used platinum black as a standard catalyst on the cathode side (HER). Later on, due to the experience on the development of catalysts for PEM fuel cells, researchers started to use platinum nanoparticles supported on carbon black (Pt/C) from different manufacturers (ETEK/BASF, Tanaka, and Johnson & Matthey) as their standard catalysts for the HER. However, despite the lower platinum loadings compared to the anode side loading (appendix A), the cathode catalyst still represents a considerable portion of the total system cost, especially if degradation or corrosion of the carbon support occurs.

Today, loadings for the cathode side range between 0.5 and 1 mg cm\(^{-2}\) and further reductions will always be desired, with the potential of reaching values below 0.2 mg cm\(^{-2}\). Since 2005, few studies exist attempting to reduce the platinum loadings, improve catalysts utilization (homogeneity, particle size), and potentially substitute (creating the so-called platinum free catalysts). When studying the cathode catalyst, due to the dominance of the OER, experimentation is usually done in a liquid electrolyte half-cell or three electrode apparatus to isolate the contribution of only the cathode.

Hinnemann et al. experimentally studied MoS\(_2\) as an alternative catalyst for the HER [94]. These experiments were done by preparing a MEA with standard Pt on one side and MoS\(_2\)/graphite on the other. It was shown that MoS\(_2\) is a reasonable material for the HER but with significantly lower current densities compared to conventional Pt cathodes. MoS\(_2\) nanoparticles on reduced graphene oxide (RGO) have also been evaluated [95]. The MoS\(_2\)/RGO hybrid exhibited superior electrocatalytic activity in the HER but only relative to the other MoS\(_2\) catalysts and still not comparable to Pt. MoS\(_2\) nanowires have also been evaluated for HER [96], however, a comparison between these materials and conventional Pt electrodes is unfortunately missing. The same observation applies for the study with Cu\(_2\)xN\(_x\)WO\(_4\) [97].

Heteropolyanions of tungstophosphoric acid (PWA) hybridized with carbon nanotubes (CNTs) were tested for the HER by Xu et al. [98]. It was concluded that the new catalyst alternative presented activities up to 20% of the activity of Pt/CNTs. Xu et al. also notes that PWA is more abundant than noble catalysts. WO\(_3\) nanorods were also demonstrated for the HER, and are produced with a high yield while using a simple step method [99,100]. The catalyst is presented as an active alternative for the HER, however, no comparison against standard Pt was presented.

A family of macrocycles has also recently received attention for the HER because of their potential use as molecular electrocatalysts for many electrochemical reactions. Due to their activities, Co and Ni glyoximes were evaluated by Pantani et al. [101] where the possibility of these immobilized metals (Co and Ni) in the HER was investigated [101]. The authors commented that their activities remained stable but results are still not comparable to Pt [101]. The redox potentials must be shifted to higher voltages, closer to 0 V vs. the standard hydrogen electrode (SHE), by chemically modifying the ligands bonded to the metal active sites. It was also suggested that these compounds must be dispersed onto an appropriate electronic conductor to increase the contact area between the catalyst and the electrolyte. Before these glyoximes can be seen as a viable Pt replacement the reaction rate and stability must be improved, and in order to achieve this a better understanding of the HER mechanism is needed [101,102].

Pd/CNTs have also been tested for the HER, but no consistent difference was obtained compared to Pt/CNTs [102–104]. CNTs are commonly used as a support because they are generally recognized as having higher electron conductivities and corrosion resistance when compared to conventional carbon black. In the work by Raoo et al. a poly(8-hydroxyquinoline) film was formed on the surface of a glassy carbon disk [105]. Cu nanoparticles were then complexed into the polymer matrix and Cu was then replaced by Pt, forming Cu/Pt-p(8-HQ) on GC [105]. The material is active for the HER, however lower performances are obtained when compared to a bare Pt electrode.
2.3. Promising alternatives

Based on the positive results of electrocatalysts recently developed for PEM fuel cells, analogous catalyst materials and methods could be studied and employed for PEM electrolysis. Well-grounded knowledge is available in many publications related to PEM fuel cells and electrochemical systems, such as batteries and solar cells. This knowledge can be potentially assigned to PEM water electrolysis as well, in order to further develop/establish PEM electrolysis.

2.3.1. Core-shell catalysts

Core-shell catalysts essentially consist of atomic metallic mono layers (such as Pt) supported on a metallic core substrate (such as Cu) [106]. Core-shell structures provide beneficial effects of bimetallic catalysis, tuning the surface and catalytic reactivity of these catalysts for different electrochemical reactions. Core-shell systems are prepared by preferential dissolution (removal) of the electrochemically more reactive component from a bimetallic alloy. In other words, in a Pt @ Cu configuration, Cu will be removed from the surface and concentrated on the core of the catalysts structure, with Pt being concentrated on the outer shell of the catalyst. According to Strasser et al. the dealloyed Pt @ Cu nanoparticles have presented uniquely high catalytic reactivity for the oxygen—reduction reaction (ORR) in fuel cell electrodes, with pure Pt as the preferred catalyst [107]. In FEM fuel cells, the ORR is slow, which is why high Pt loadings are required, thus increasing costs. The authors also pointed out that the core—shell catalysts meet and exceed the technological activity targets in realistic fuel cells, and can reduce the required amount of Pt by more than 80% [107]. In order to decrease the metal loadings used in PEM electrolysis, core—shell structures could be a good and promising alternative. Pt—Cu core shell catalysts could be used in the cathode side, drastically reducing the loading to values under 0.2 mg cm$^{-2}$, and still improving the efficiency. Ir and/or Ru core—shell structures could be developed for the anode side as well. In fact, a few studies already exist for fuel cells using Ir and Ru [108,109], but to the best of our knowledge, this has not been evaluated for PEM electrolysis yet. However, one has to bear in mind, that the non-noble core of those catalyst systems has to be kept completely covered by the noble metal in order to avoid the dissolution of the non-noble catalyst and posterior poisoning/deactivation of the catalysts and membrane and ionomer, as it is discussed in section 6.

2.3.2. Bulk metallic glasses (BMGs)

It is generally recognized in catalysis that high surface area multicomponent nanowires alloys are particularly promising for increasing the activity and utilization of precious metal catalysts. These improvements are due to ensemble effects that arise when dissimilar surface atoms induce electronic charge transfer between themselves, thus improving their electronic band structure [107]. However, the common strategies or processes to produce advanced catalyst systems with these characteristics involve complex synthesis methods due to the difficulty in fabricating these advanced nanostructures with high dispersion and noble metal utilization. Carmo et al. [110] and Mukherjee et al. [111] recently demonstrated a catalyst alternative for fuel cells, which are bulk metallic glasses (BMGs). BMGs exist in a wide range of compositions and can be thermoplastically formed (TPF) into complex geometries over a length scale ranging from 10 nm to a few centimeters [112,113]. The absence of grain boundaries and dislocations in the BMG amorphous structure result in a homogenous and isotropic material down to the atomic scale, which displays very high strength and elasticity combined with good corrosion resistance. Carmo et al. also used a top-down approach to fabricate Pt-BMG nanowires in an economical and scalable way [110]. This study also showed that Pt-BMG properties, composition, and geometry are possibly suitable for high-performance electrocatalysts. Furthermore, the high level of controllability of Pt-BMG during thermoplastic formation in the highly viscous supercooled liquid region results in high catalyst dispersion without the need for a high surface area conductive support (e.g., carbon black). Therefore, developing specifically tailored alloys of BMGs and using specific engineered BMG compositions could result in transformative improvements for PEM electrolysis.

2.3.3. Nanostructured thin films (NSTFs)

One example using advanced structures developed for PEM fuel cells on PEM electrolysis are the nanostructured thin films (NSTF) from 3M$^®$. According to Viestlicht et al. and Debe et al., NSTF catalysts have been shown to eliminate or significantly reduce many of the performance, cost, and durability barriers standing in the way of cathodes and anodes for H$_2$/air PEM fuel cells [114,115]. NSTF catalysts specific activities and durability seems to be significantly higher than conventional carbon supported Pt catalysts, and mass activities are closely approaching the 2015 DOE targets of 0.44 A mg$^{-1}$ at 900 mV [116]. The NSTF catalysts are formed by vacuum sputter deposition of catalyst alloys onto a supported monolayer of oriented crystalline organic-pigment whiskers. Whiskers are corrosion resistant, therefore eliminating the high voltage corrosion affecting carbon blacks. According to the study by Debe et al., the NSTF whisker is immune to chemical or electrochemical dissolution/corrosion, because the perylene dicarboximide pigment is insoluble in typical acids, bases and solvents while its single crystalline nature confers it with a “band-gap” that does not support electrochemical corrosion currents above 2 V [114,116]. NSTF catalysts with low catalyst loadings (cathode: Pt$_{50}$Ir$_{50}$ and Pt$_{50}$Ir$_{25}$Ru$_{25}$) were assembled in a single cell and short stack PEM electrolyzer. The catalysts were tested for performance and durability at Pt loadings of 0.10—0.15 mg cm$^{-2}$ (not including Ir and/or Ru loading) [116]. According to the authors, NSTF catalyst alloys showed good OER and HER activities. The cathode performance of NSTF Pt$_{50}$Co$_{29}$Mn$_{3}$ and sputtered NSTF Pt$_{50}$Co$_{29}$Mn$_{3}$ catalysts were claimed to be equivalent to that of standard Pt-blacks having loadings an order of magnitude higher and with durability exceeding 4000 h [116]. Anode performances of sputtered NSTF Pt$_{50}$Ir$_{50}$ and Pt$_{50}$Ir$_{25}$Ru$_{25}$ catalysts were found in single cell tests to be nearly equivalent to that of standard PtIr-blacks having loadings an order of magnitude higher, and with durability tests reaching up to 2000 h [116]. The authors make a valuable suggestion that NSTF alloy catalysts having only ~10% of the loadings of standard PGM blacks is a promising result, and with further
catalyst refinement, membrane and GDL optimization, both overpotential and stability can be improved [116].

3. Ionomer and polymer exchange membrane

3.1. Ionomer

The addition of polymer solutions with ionic transport properties (e.g. Nafion® ionomer) in the catalytic layer has two contrary impacts on the electrode in PEM electrolysis. One effect is to promote the proton transport from the bulk of the catalyst layer (nanoscopic level) to the membrane, enhancing the overall efficiency by decreasing the ohmic losses. The ionomer also acts as a binder providing a three dimensional stable catalyst structure, giving mechanical stability and consequently durability to the electrode [39,117]. On the other hand, it decreases the electronic conductivity of the catalyst, since the polymer is electron resistant. The ionomer in the catalyst layer also makes the catalyst layer more hydrophilic, potentially reducing mass transport out of the catalyst layer. Therefore, an optimization of the triple-phase-boundary and ionomer layer characteristics is necessary.

To the best of our knowledge, there is no reference to an ionomer layer in PEM electrolysis prior to the work presented by Shao et al. [118]. With the addition of the ionomer to the catalyst layer, clear improvement in the performance was seen, but no information regarding the ionomer loading is usually presented (appendix A). To date, only a very few studies [39,117–119] have concentrated on this topic, and it can be generally recognized that the ionomer loading ranges from 20 to 30% over the dry catalyst weight.

In research by Zhang et al., it was concluded that the interfacial resistance between the membrane and electrode, or the catalyst and ionomer, was considered to be a major factor leading to the differences in the performances of MEAs. The method of ink and MEA preparation has a significant influence on the interfacial resistance [120]. The optimal Nafion® ionomer loading was found to be 25 wt% for the anode and 20 wt% for the cathode [39]. Other studies could be made in order to further optimize the triple-phase-boundary [121].

3.2. Membrane

In PEM electrolysis, a thin (≈100 μm) perfluorosulfonate polymer membrane (PFS) is used as a solid electrolyte [18,23,117,122]. The commercial Nafion® membrane from Dupont® is ordinarily used due to its excellent chemical and thermal stability, mechanical strength, and high proton conductivity [18,117]. However, with this there are disadvantages, namely its cost and disposal. Their disposal when disused, can also be expensive due to the contained fluorine in the backbone structure [122].

Research groups have been concentrating their efforts to make less expensive proton exchange membranes, but also focusing to improve their ion exchange characteristics and durability for PEM electrolysis. Nafion™ membranes have been extensively studied in PEM fuel cells [114,123]. However, the hydration state of the membrane differs between fuel cell operation and electrolysis operation. During PEM fuel cell operation, the membrane is humidified by the humidified gases and equilibrated with water vapor, whereas during PEM electrolysis operation, the electrolyte membrane is exposed to liquid phase of water and fully hydrated during water electrolysis [124]. Despite these different boundary conditions the water uptake and performance of the membrane may or may not be effected as there is contradictory evidence in the literature [125–127].

Many studies already exist seeking a hydro-carbon membrane as an alternative for PEM water electrolysis. Masson et al. developed non-fluoro membranes by radiation grafting of styrene groups on a polyethylene matrix, followed by chemical sulfonation of the resulting polymer [128]. Linkous et al. and Wei et al. evaluated different types of engineering polymers and identified a few options that could withstand the conditions found in PEM water electrolyzers [122,129]. Of these, polybenzimidazoles (PBI), poly(ether ether ketones) (PEEK), poly(ether sulfones) (PES) and sulfonated polyphenylquinoxaline (SPFQ), were selected for sulfonation into ionomers/membranes to be used for PEM electrolysis. Jang et al. chose SPEEK and sulfonated block copolymer of polysulfone (PSF) and poly(phenylene sulfide sulfone) (SPSfco-PPSS) to make SPEs for water electrolysis [130]. SPEEK polymer is considered to have high strength and it is an easy membrane-forming material. SPEEK also has a fairly high degree of sulfonation, which enables high proton conductivity. Unfortunately, SPEEK membranes tend to swell excessively or even dissolve at elevated temperature. An alternative would be to reinforce the SPEEK membrane with other polymer structures and/or fillers [122].

Nevertheless, these alternative membranes have shown rather low current densities and low durability compared to standard Nafion® [117] membranes. Another drawback of PFS membranes is that they are known to loose water, and thus ionic conductivity, at temperature above 100 °C [131], which prohibits them from being used for higher temperature water electrolysis. The increase in the temperature of operation offers several advantages from thermodynamic, kinetic and engineering points of view. When the temperature is increased, the electrode kinetics will be enhanced and therefore the overpotentials will be reduced [18,132]. If water is reacted above 100 °C in the gaseous form, the electrolysis process will be thermodynamically less energy demanding [133]. The reversible voltage of the electrolysis cell is 1.23 V at 25 °C, considerably higher than at 200 °C for steam water (1.14 V). Better membrane hydration and proton conductivity characteristics can also be obtained when the electrolysis system is pressurized. A higher operation pressure would also be favorable for PEM electrolysis since it would reduce the gas pressurization constraints for storage purposes [18]. Hence, it would be important to develop membranes that can sustain a higher temperature of operation and higher pressures (>350 bar) [29].

Composite or reinforced membranes (with SiO₂, TiO₂, or WO₃) would allow an increase in the operating temperature and pressure of the electrolyzer [35,134]. These alternative composite membranes would also decrease the cross-over of the gases through the membrane [35,134]. The high temperature operating condition is allowed by the water retention
properties of the composite membrane due to the presence of inorganic hygroscopic fillers inside the polymeric matrix [135]. It is well known that the high ionic conductivity of Nafion® membranes can be maintained under dehydrating conditions if water is replaced by a less volatile proton solvent, such as ionic liquids [136,137] or phosphoric acid (PA) [137]. Studies have already demonstrated the operation of PA doped Nafion® membrane at temperatures up to 200 °C with those membranes exhibiting proton conductivity of around $10^{-2}$ S cm$^{-1}$ [138]. In the last decades, PA doped poly[m-phenylene-bis(5,5'-benzimidazolazole)] (PBI) membranes have emerged as a promising PEM material for applications in fuel cells operating at temperatures of up to 200 °C [139–141]. The rigid aromatic backbone of these PBI membranes provides the necessary chemical and thermal stability. However, In PBI/PA systems, the proton conductivity is strongly dependent on the acid doping level [139,142], being the PA concentration together with the high temperature, responsible for a critical corrosion limiting condition for the overall system [143,144]. Nevertheless, many studies have appeared in order to improve the characteristics and properties of PBI systems. The main idea is to improve the mechanical strength, and to keep the same level of PA doping over time. Essentially, PBI systems still do not keep the same level of performance due to membrane degradation and drops in the PA concentration [145]. A few alternatives include the synthesis of PBI analogs, composites, or different cross-linked polymer structures [132,145–149]. A few research groups have also attempted to fabricate cross-linked membranes by mixing PBI and different acidic polymers like sulfonated polysulfone [150], sulfonated poly(etheretherketone) [151], or sulfonated partially fluorinated arylene polyethers [152]. However, to date, R&D on membrane materials for PEM electrolysis is still scarce. For future studies, the focus has to be orchestrated for the extension of lifetime, performance, and the decrease of the cost of these materials. The new concepts presented above have a high potential to overcome the drawbacks presented by the benchmark membranes. These alternative concepts could in the future bring significant innovations in PEM electrolysis.

4. Current collectors

In a PEM water electrolyzer, water is usually fed (at the same working temperature of the cell = 80 °C) in the anode side of the cell, where the oxygen evolution reaction takes place. The water travels via channels in the separator plates and diffuses through the current collector. The water reaches the catalyst layer and the molecules are split into electrons, diatomic oxygen, and protons. The oxygen gas has to flow back through the catalyst layer and current collector to the separator plates (against the water flow) then out of the cell. The electrons travel from the catalytic layer, through the current collector, separator plates, and then go to the cathode side. The protons leave the anode catalytic layer through the ionomer, reaching the membrane and crossing to the cathode side, after reaching the catalytic layer they will combine with electrons to form H$_2$. The hydrogen gas then has to flow across the cathode current collector, cathode separator plate and leave the cell. This overall phenomena leaves a few important aspects to be considered for the development of current collectors [153]. (i) Due to the high overpotential, the presence of oxygen, and the acidic environment provided by the solid acid electrolyte, the current collectors used must be corrosion resistant. (ii) They also have to have good electrical conductivities, and not passivate over time. (iii) The current collectors must also provide mechanical support to the membrane, especially under operational differential pressures. (iv) The gases have to be effectively expelled and water must effectively reach the catalytic sites in counter flow. This is more important at high current densities where mass transport is the limiting factor. In this regard, current collectors with large porosity will promote facile gas removal, but will decrease the electron transport and consequently decrease efficiency. Large porosity will also decrease the amount of water trapped into the catalytic layer. Conversely, small porosity will obstruct gas removal and increase mass transport resistances. Due to the need of an optimized pore size distribution, research methods have been developed for PEM fuel cells that could easily be applied to electrolysis to analyze the contact area as well as the mass transport aspects of the current collectors [154,155].

Therefore, an optimized current collector is required, and variables such as pore structure and design; pore size and distribution, electron conductivity, and corrosion resistance are key factors. Due to the corrosive condition, carbon materials (e.g. carbon paper, cloth, and fleece) used as gas diffusion layers/current collectors (GDLs) in fuel cells, cannot be applied in PEM electrolysis. The high overvoltage imposed at the anode side (~2 V) and high concentration of oxygen, water and low pH (~<2) will overtime easily promote the oxidation of carbon or graphite materials to CO$_2$. In this condition carbon will rapidly corrode, being especially severe at the oxygen side. Therefore, current collectors materials for PEM electrolysis are typically prepared by thermal sintering of spherically shaped titanium powder; the parameters are listed on Table 5. In many studies, stainless steel grids or Ti grids are also used, but the performances are lower compared to sintered Ti particles, and might not be sufficient for long-term operation. Carbon materials (carbon cloth, paper) are anyhow used, but can be only considered for short tests or electrocatalysts characterization purposes, not representing the performance of a real PEM electrolyzer at long-term operation. Although some studies suggest that carbon current collectors could be used in the cathode side, further research is however still necessary in

| Table 5 – Parameters of current collectors for PEM water electrolyzers [160]. |
|-----------------|-----------------|
| Thickness of current collectors | 0.8–2 mm |
| Porosity | 20–50% |
| Pore size | 5–30 μm |
| Particle size | 25–250 μm |
| Gas permeability | $1 \times 10^{-9}$–$1 \times 10^{-11}$ m$^2$ |
| Specific electric resistance | 5–10 mΩ·cm |
order to understand how these materials would perform in a real condition, and with differential pressure over time.

Another issue is that hydrogen embrittlement takes place on the cathodic current collector and separator plates. Hydrogen embrittlement of materials follow the sequence (Ti = Ta > Nb > Zr > graphite) [158]. This issue is usually solved by using gold plated materials in the cathode side, but resulting in an obvious increase in capital costs [159].

Grigoriev et al. performed an optimization of current collectors from both experimental and modeling approaches [160]. According to this study, and as expected, the microstructure of porous titanium plates used as current collectors in PEM water electrolysis cells plays a significant role on the overall cell efficiency. Results presented in this paper show that an optimum spherical powder size value of 50–75 microns is required. The authors also have shown that an inadequate pore structure of the current collectors can increase the cell voltage by up to 100 mV at 2 A cm⁻². They also concluded that CCMs prepared with electrocatalytic layers deposited directly onto the membrane surface are slightly more efficient than those prepared with electrocatalytic layers deposited onto the current collectors surfaces (MEAs) [160].

Marshall et al. pointed in another study, that both perpendicular and lateral conductivity is required as the electrical contact to the layer is achieved through a porous support rather than a solid and flat electrode [83]. Differences in the lateral and perpendicular conductivity will arise from the different particle vs. particle contact pressure in each direction. In this study, the porous titanium current collectors used had porosities around 50%, and therefore a loss of 50% in active surface area may be reasonable, if the lateral conductivity is very low [83]. In other words, that is a reason for the addition of a micro porous layer (MPL) to PEM fuel cell gas diffusion layers, to smooth the contact between the catalytic layer (nano-level) and current collectors (micro-level).

Millet et al. also noted that the main challenge in stack configuration is to reduce parasitic ohmic losses which appear at contact points between cell components such as separator plates, current collectors, and electroactive layers, in order to obtain the same efficiency as those obtained on lab-scale cells [102]. In yet another publication, the authors concluded that further reduction of the ohmic resistance between the separator plates and the electrode backing layer (current collectors) is necessary to improve the performance [84]. In this sense, it is urgent to develop micro porous layers that could be applied over sintered Ti particle plates in order to smooth the contact between the layers and extinguish those problems.

Hwang et al. attempted to load Ti powder over Ti felt, in order to prepare an MPL over the current collector for PEM electrolysis. The experimental results revealed that a homogenous MPL of Ti was not obtained, and the effect on the performance was therefore insignificant [161]. However, the attempts were made for a reversible fuel cell, and as one can see in Fig. 10, the Ti MPL is not homogenously distributed over the Ti felt, as it is the case for MPL-GDL in fuel cells.

5. Separator plates

Separator plates along with current collectors are responsible for 48% of the stack cost (Fig. 11) and a linear contributor (iR) to the required cell voltage. This is particularly important when operating at higher current densities where the internal ohmic resistance and mass transport become the dominating sources of irreversibility. It is the combination of these factors, ohmic resistance, mass transport and cost that create a difficult set of targets for research and development of the separator plates for a polymer electrolyte membrane (PEM) electrolyzer given the immense list of constraints. The high cost of the separator plates stem from the material, processing costs and limited scales of economy. Currently the PEM electrolyzer employs separator plates with some form of titanium, graphite or a coated stainless steel. None of these offer the benefit of a low cost, and are all plagued a variety of operational drawbacks as well. It is within these drawbacks as well as the ever-important reduction of costs that the research and development of the separator plates face their greatest challenges.

The separator plates must provide structure to the cell, insulation between the reactant gasses and a conductive path for the heat and the electrons. Titanium offers excellent strength, low initial resistivity, high initial thermal conductivity and low permeability, however, especially on the oxygen (anode) side, titanium corrodes and develops a passive oxide

![Fig. 10](image-url) — SEM images of Fig. 10a as-is Ti-felt GDL (Bekinit) and Fig. 10b Ti-powder loaded (300 mg cm⁻³) Ti-felt GDL. Reprinted from ref [161] with permission from Elsevier.
layer that greatly increases the contact resistance and thermal conductivity. Therefore, the performance of the electrolyzer can diminish as the stack ages [159].

To help protect the titanium separator plate’s precious metal, coatings and alloys have been investigated. This drastically reduces the corrosion rate however negates any cost savings over graphite as the platinum and gold coatings add an extra processing step as well as an expensive coating material to the already expensive titanium base.

Graphite has been used quite frequently in the PEM fuel cell field due to its high conductivity, however, its low mechanical strength, high corrosion rates, difficulty of manufacture and its very high cost causes problems within PEM electrolysis. The low strength requires increased thickness, which increase the ohmic resistance, and the high corrosion rates lead to poor contact with the current collectors ultimately increasing the ohmic resistance even further [159].

The high costs of the aforementioned materials have lead to the exploration of less expensive base metals. In most cases these base metal replacements are coated to protect against the harsh environments within a PEM electrolyzer. Stainless steel is one of these less expensive alternatives, however, it is not without drawbacks. The stainless steel components corrode very quickly in the corrosive acidic environment, thus requiring a coating to maintain a reasonable lifespan. The addition of a coating typically increases the ohmic resistance and in many cases minor imperfections in the coatings can expose the base metal and thus fail to prevent corrosion protection.

Coatings can greatly improve the life of the components, however, creating and applying a coating that meets the demands of this environment is not an easy task. The desirable coating must exhibit low resistivity, high corrosion resistance, high thermal conductivity, good durability, good adhesion with the substrate and very low imperfection density. Having a low imperfection density is vitally important as once the base metal is exposed, corrosion will cause the coating to flake off, increasing the ohmic resistance and exposing even more of the base metal to the corrosive environment.

The separator plate must be designed along with the current collectors for best performance. Many electrolyzers, especially those used in early development and testing, have been taken directly from PEM fuel cells. Simply borrowing the design poses a problem as the fuel cell was designed to transport gas phase reactants to the catalyst sites while evacuating the multi-phased products. In a low temperature PEM electrolyzer the reactants are in the liquid phase and the products are in the gas phase altering the flow regimes. The separator plate design depends greatly on the size of the system as well. Systems with relatively small cell areas (<25 cm²) typically employ designs without flow fields and rely on only the current collectors to distribute the water to the catalyst sites.

An example of the codependent design of the current collector and the separator plate was presented in the research by Ojong et al. [162]. Here a bimodal pore distribution current collector was developed and used in the smaller sized electrolyzers to help reduce costs and improve performance [162,163]. The morphology is designed with a porosity gradient in the through plane direction so that the separator plate requires no flow fields. This reduces manufacturing costs, ohmic resistance and increases the durability of a coating on the separator plate, all while still providing an even supply of water to the catalyst sites. However, as the cell area grows, the bimodal current collector cannot supply the water evenly thus limiting the effectiveness of a cell’s full active area and overall capacity.

Balancing the mass transport and ohmic losses in the current collector and separator plates is a delicate act. For every cell configuration, geometry, and operating condition, a morphology exists that will optimize performance. When designing a current collector for optimum performance; the size, shape and operating parameters (current density, temperature and pressure) must all be considered before a morphology can be chosen.

6. Poisoning by foreign ions

Since platinum has the best catalytic activity for the HER (Fig. 6), any other metals deposited on to the platinum surface will consequently decrease its activity. Stucki et al. investigated the poisoning of platinum during H₂ evolution in the presence of metal ions in the electrolyte [164]. The authors found that the presence of Cu, Mo, Ag, Cd, Sn and Pb resulted in considerable poisoning of the cathode.

Poisoning of platinum is expected because the reversible potential is positive of the H₂ evolution potential (under potential deposition (UPD) phenomena). Small amounts of metal ions in solution are sufficient to cover, and thus poison the
platinum surface completely. This can be a serious issue for larger PEM electrolyzers, since the deionized water circulated in the cell stack might become poisoned by metallic cations, due to the slow but steady corrosion of the stack components. This is especially the case if steel piping is used, and/or impurities are contaminating the feeding water. This will consequently result in an increase in cathodic cell overvoltage [66] and loss of performance overtime. Fortunately, it is also demonstrated that the UPD phenomena is negligible on IrO₂ and RuO₂ surfaces [66,165].

Foreign ions in the feeding water can also affect the proton exchange membrane and ionomer layers. The membrane and ionomer will also face a reduction in proton conductivity due to external metallic cations contamination (R–SO₂H⁺ groups going back to R–SO₂M⁺, with M being the foreign metal such as Cu, Ni, and Pb). The resistivity is at least 5 times higher for a Nafion® membrane in Ni²⁺ form than in H⁺ form, thus a dramatic increase of the ohmic drop is observed [66]. Millet et al. pointed out, for example, that while Fe⁶⁺, Ni⁶⁺ and Cr⁶⁺ concentrations in the water feeding remained low, those cationic impurities are still trapped and concentrated in the membranes. This results in an increase of the ohmic drop in the membrane as well as an increase in the electrode overvoltages. According to Millet et al., on-line deionizers could be used and would give more stable cell voltage, but are a limitation for operating at high pressure and high temperature [156].

7. Standard materials and methods

The materials and methods used in PEM electrolysis are crucial to obtain systems operating with satisfactory performance and durability. Since the first investigations, the progress on the development of new materials and methods have not faced considerable refinement. The majority of materials and methods have been obtained from PEM fuel cells R&D. However, the interest in PEM electrolysis has been rekindled, and many research groups started to develop new alternatives with extended interest. Modern techniques for the physical characterization appeared in the last decades and have become combinable with electrochemical tools. The surface and bulk characterization of materials for PEM electrolysis resulted in the appearance promising materials. Advanced structures and methods have become the norm for obtaining high performance and durability.

Nevertheless, PEM water electrolysis has never had the same level of debate or attention as in PEM fuel cells. Furthermore, information on the materials and methods used in PEM electrolysis R&D is scarce. In this section, we will attempt to list the synthesis and methods traditionally used to prepared catalysts, electrodes, and CCMs for PEM electrolysis. The purpose is to compile the information as a standard for future improvements.

7.1. Electrocatalysts synthesis methods

7.1.1. Pechini–Adams method
The polymer precursor (Pechini-Adams) method is among the ways of obtaining catalysts with a high degree of dispersion and uniform component distribution. In this method, electrocatalysts are synthesized by thermal decomposition of polymeric precursors [92,166]. In a classic route, Ru and Ir polymeric precursors are separately prepared, mixing citric acid (CA) in ethylene glycol (EG) at 60–65 °C. The precursor salt RuCl₃xH₂O is then dissolved in an acidic solution (HCl/H₂O 1:1, v/v) then it is added slowly at a molar ratio of 1:4:16 of CA/EG/metal. After total dissolution of the precursor salt, the temperature is raised to 90 °C and kept at this level for 2–3 h, under vigorous stirring. In a similar way, iridium catalyst can be prepared with the same ratios but with IrCl₃xH₂O. Then the different composition of ruthenium and iridium is prepared and calcined until 400 °C in an oven under an oxygen atmosphere in order to obtain the oxide counterparts. The temperature is increased to 250 °C at a rate of 1 °C min⁻¹ and kept for 1 h. Then, the temperature is increased to 350 °C at a rate of 10 °C min⁻¹, and kept for another 1 h. Finally, the temperature is increased up to 400 °C at a rate of 30 °C min⁻¹ and holding for 1 h to recover a material free of organic carbon [68,166].

7.1.2. Adams fusion method
Electrocatalysts for PEM electrolysis can be prepared using a modified version of the Adams fusion method [167]. The suggested chemical reactions Eq. (2) and Eq. (3), corresponding to the Adams fusion are shown below:

\[ \text{H}_2 \text{IrCl}_6 + 6\text{NaNO}_3 \rightarrow \text{NaCl} + \text{Ir(NO}_3)_4 + 2\text{HNO}_3 \]  
\[ \text{Ir(NO}_3)_4 \rightarrow \text{IrO}_2 + 4\text{NO}_2 + \text{O}_2 \]

Alternatively, electrocatalysts supports (such as carbon black, and TiO₂) can be added at this stage to the metal precursor (in this case H₂IrCl₆·4H₂O). The precursor mixture is then added to 10 mL of isopropanol and stirred for 1 h to ensure complete dissolution of the iridium salt. After the addition of finely ground NaNO₃ (16.7 × molar excess), the salt mixture is heated in air to 70 °C and evaporated to dryness. The mixture is placed into a furnace and heated up to 500 °C at a rate of 250 °C h⁻¹ and remains at 500 °C for 1 h before cooling to room temperature overnight. The fused product is washed six times with deionized water and separated on a centrifuge. Finally, the powder is dried in air at 90 °C [70,82,87].

7.1.3. Ethylene glycol colloidal method
In a typical procedure [93], 150 mL of a solution of 0.2 mol L⁻¹ sodium hydroxide in ethylene glycol is added to a round bottom flask together with the catalyst support (TiO₂ for example). The suspension is sonicated for 45 min to homogeneously disperse the support particles in solution. Under N₂ atmosphere, the metal precursor (s) (PtCl₄ and/or IrCl₄ and/or RuCl₃) is (are) added to the mixture in the following amounts: (i) 1:1 bimetallics, 2.04 mmol of each metal precursor; (ii) 2:1 Ir:Ru bimetallic, 2.04 mmol of iridium chloride and 1.02 mmol of ruthenium chloride; (iii) 1:1:1 trimetallic (Pt:Ir:Ru), 1.23 mmol of each metal precursor; and (iv) pure Pt metal, 3.08 mmol of platinum chloride. The complete mixture is stirred for 2 h, and subsequently heated to 175 °C for 3 h. The sample is then mixed with approximately 1000 mL of deionized water, and nitric acid is added until pH reaches 1. The colloidal suspension is mixed for an additional 3 h. After allowing the solution to settle for 5 h, the sample is filtered
and washed with several aliquots of water. The sample is dried at 110 °C for 4 h under vacuum conditions. The resulting material is finally crushed with a pestle and mortar to obtain a fine powder. Unsupported catalysts can also be made following a similar procedure, by excepting the support material in the initial mixture.

7.1.4. Sulfite complex method
To synthesize electrocatalysts using the sulfite complex routine, in a typical procedure [84], IrCl₄.xH₂O is used to prepare the Na₆Ir(SO₃)₄ precursor. In this process, all chlorides are replaced by sulfite anions in the Ir-complex. Iridium tetra-chloride is dissolved in deionized water and the pH of the solution is adjusted to 7 by adding Na₂CO₃. Subsequently, NaHSO₃ is added to the solution to obtain a precipitate of Na₆Ir(SO₃)₄, which is filtered, washed with distilled water up to a complete disappearance of chloride residues, which can then be confirmed by x-ray fluorescence analysis. The precipitate is then dried in an oven at 80 °C. The Ir-sulfite complex is suspended under stirring in distilled water and then decomposed by adding drop-wise a 40% H₂O₂ solution at a temperature of 80 °C, which resulted in a vigorous gas evolution. The colloidal IrOₓ is filtered, washed with distilled water, and dried in an oven at 80 °C. Subsequently, IrOₓ amorphous is calcined in air at 400 °C for 1 h, using a heating ramp of 5 °C min⁻¹.

7.1.5. Magnetron sputtering method
The method of plasma enhanced physical vapor deposition (magnetron sputtering) is a well-know and widely used method for the preparation of thin and low-loading catalyst films for specific applications [115,116,168–170]. Recently, a few authors have introduced this method for the fabrications of low-loading catalysts for PEM electrolysis [116,168,169]. According to Slavcheva et al., opposed to conventional methods such as wet chemical reduction, solgel deposition and thermal decomposition of metal salts, etc. where the catalysts are obtained as powders, the catalysts prepared by magnetron sputtering are deposited as thin compact mono, bi- or polymeric and/or oxide films upon a selected substrate material or also deposited directly onto the membrane or current collector material [168]. It is suggested that the numerous necessary steps to fabricate catalysts or CCMs using those conventional, e.g. preparation of catalyst ink, the following spreading of the ink on the substrate, the hot pressing of the catalytic layers on the polymer electrolyte, etc. can be essentially reduced and/or simplified. Other advantages of the catalysts prepared by sputtering are the excellent homogenous distribution of metal particles on the support and the extremely low metal loadings, which can be achieved (down to 10 μg cm⁻²) [168]. However, sputtering systems are limited to produce small electrodes, batch production, and the cost for those systems could be an issue, limitations that are quite relevant for commercial purposes.

In a typical procedure, sputtered iridium oxide films can be deposited using a Ar/O₂ plasma atmosphere. Before the deposition procedure initiates, the sputtering chamber is evacuated to a high vacuum of 5 × 10⁻⁹ bar. The sputtering process is then performed in a dc mode applying a power of 100 W without heating the substrate (“cold” dc sputtering). Iridium oxide is then sputtered on Toray paper substrates (hydrophobic carbon paper) upon a 50 nm thick Ti sublayer. According to the publication by Slavcheva et al., the function of Ti is firstly, to improve the adherence of the catalytic layer to the substrate and secondly, to prevent the oxidation of the carbon paper at the high anodic potentials where oxygen evolution takes place. The thickness of the oxide film can be varied as desired. The loading is controlling by the exposure time of the used substrate.

7.1.6. Sonochemical method [171]
The sonochemical method (ultrasound) is an alternative and simple technique to develop and prepare catalyst nano-structured materials [171–173]. The physical phenomenon responsible for the sonochemical process is acoustic cavitation, i.e., the creation, growth, and collapse of a bubble that is formed in the sonicated liquid, leading to a very high local temperature, and consequently producing extraordinary high heating and cooling rates (above 10⁹ K s⁻¹). Sonication of the desired metal precursor in the presence of an inorganic support such as silica spheres provides an alternative way of preparing supported catalyst nanoparticles also having different catalyst compositions. This method has the advantage for being inexpensive, simple and various classes of materials can be generated simply by changing the reaction medium. If water is chosen to dissolve the precursors, further treatment of the catalyst to remove the organic additives or surfactants, (which could influence the electrocatalytic activity of the catalysts) is avoided. However, controlling the applied temperature, degree of metal reduction, homogeneity, and particle size remain as challenges aspects.

In a typical procedure, Pt and PtRu nanoparticles are supported on a high surface area Vulcan XC72 carbon (20 wt% metals content) by mixing the support powder with a 50 mL water solution (containing the desired metal precursors with the desired ratio of the metals) placed in a cylindrical vessel (150 mL). H₂PtCl₆ and RuCl₃ in this case is used as precursors. In this sonochemical procedure, the mixture is irradiated with an ultrasound intensity (20 kHz, 80 W cm⁻², 1 cm² titanium horn) by direct immersion of the titanium horn for 1 h at 80 °C under a H₂ atmosphere at 1 bar. The resulting powder is filtered and then dried at 60 °C for 3 h [171].

7.2. Ultra-thin layer electrodes for rotating disk electrodes (RDE) experiments
A great deal of electrochemical characterization work has been done on the rotating disc electrode (RDE). This is a powerful tool employed in electrochemistry, capable of controlling the transport regime of electroactive species toward the electrode. Briefly, catalysts are deposited over a glassy carbon disk and immersed in a liquid electrolyte using a three-electrode cell configuration. In a typical procedure, catalytic inks are prepared using the following method. The catalyst powder is dispersed in a solution of water and 2-propanol then the resulting ink is ultrasonically homogenized. The catalytic ultra-thin-layer is formed on top of the glassy carbon electrode by drying under nitrogen [114]. Subsequently, Nafion™ solution is deposited on top to give mechanical stability to the electrode. More information can be found in the work by Vielstich et al. [114].
7.3. Polymer exchange membranes and ionomers

Perfluorosulfonic acid polymers, such as Nafton® from Dupont are the state-of-the-art membrane solid electrolytes used in PEM electrolysis. In the first studies, sulfonated polystyrene was used as solid electrolytes, but those materials were not chemically stable enough over operation time. After the introduction of Nafton®, the great majority of studies used the 115 version (1/1000 inch × 5 = 127 μm thickness) or the 117 version (1/1000 inch × 7 = 177 μm thickness) of Nafton® membranes, as one can see in appendix A.

In a typical procedure for the protonation of Nafton® membranes (Dupont) or CCMs, the membranes are firstly boiled in deionized water following by 3 wt% H2O2 at 80 °C to remove organic impurities. Subsequently, the membranes are boiled in 0.5 mol L−1 sulfuric acid solution at 80 °C and to protonate the membrane. Finally, the membranes are boiled and stored in deionized water [174].

7.4. CCM preparation methods

A characteristic of PEM electrolysis is the use of catalyst coated membranes (CCMs) where thin (a few μm thick) and porous catalyst layers are preferably deposited on both sides of the membrane, instead of depositing over the current collectors. In this configuration (zero-gap concept or Grubb cell) [24], the catalytic layers are well attached to the membrane, providing optimal mechanical stability to the CCM. The ohmic losses between the catalytic layer and membrane are also attenuated, giving higher current densities.

The polymer electrolyte with high ionic conductivity (typically 0.1 S cm−1 for Nafton® 117 at 80 °C) [26] will also afford a maximum voltage drop of 150 mV at 1 A cm−2. The gas bubbles are not released inside the interpolar area but at the backside of the cells [175]. Other advantages are also present such as (i) the catalytic layer is more adherent (the possibility of continuous operation over 20,000 h has been demonstrated); (ii) CCMs are less prone to dimensional changes when the membrane is dried; (iii) CCMs can be easily removed from the stacks for maintenance operation; (iv) pollution levels due to gas cross-permeation at high operating pressure are significantly lowered (this is because catalyst particles in the sub-surface region of the membrane promote the catalytic re-oxidation of cross permeating hydrogen) [102].

7.4.1. Decal method

CCMs can be prepared using the decal method (also called transfer method) [176, 177], where the catalyst layer is transferred from a PTFE sheet to the membrane by hot pressing. In a typical procedure, Ir black catalyst ink containing 10 wt.% Nafton® from a dispersion in aliphatic alcohol (D-520, 5 wt.%, DuPont) is brushed, sprayed, or blade coated on a PTFE or PTFE coated substrate with controlled loading of the catalytic layers. The coated PTFE sheet is carefully weighed, after drying at 100 °C, and then hot pressed on each side of a pretreated Nafton® 115 membrane at 135 °C at a pressure of 4 MPa. PTFE sheet is removed and again weighed to calculate the final amount of catalyst transferred to the membrane.

7.4.2. Brushing procedure

To prepare the catalyst ink using the brushing procedure for a MEA, the catalyst is typically mixed with glycerol, 5% Nafton® solution, and tetrabutylammonium hydroxide (TBAOH) in 1.0 mol L−1 methanol, then stirred overnight. The dispersion is then brushed onto a decal, teflon coated, fiberglass surface which is then heated and dried at 140 °C for 30 min. The coated PTFE sheet is carefully weighed, and then hot pressed on each side of a pretreated Nafton® 112 membrane at 210 °C for 5 min at a pressure of 454 kg cm−2. The PTFE sheet is finally removed and again weighed to calculate the final amount of catalyst transferred to the membrane [178].

7.4.3. Spray procedure

In a typical procedure to prepare the catalyst ink layer with the spray method [179], commercial PtRuO2 electrocatalyst, Nafton® solution (5 wt%, Dupont), isopropanol, and de-ionized water are mixed (in a weight proportion of 7:2:30-2), and superniciously stirred for 1 h. An air driven spray gun is utilized to spray amounts of anode and cathode inks on the decal substrate. The coated PTFE sheet is carefully weighed, after drying at 100 °C, and then hot pressed on each side of a pretreated Nafton® 115 membrane at 135 °C at a pressure of 4 MPa. PTFE sheet is removed and again weighed to calculate the final amount of catalyst transferred to the membrane.

7.4.4. Blade coat procedure

In a typical procedure to manufacture symmetrical CCMs with a blade coat technique, catalyst powder (60% PtRu/C, HiSPEC 10000, Johnson & Matthey) and various amounts of ionomer solution (15% Nafton®) are dispersed in appropriate mixtures of water, 1-propanol and isopropanol in total volumes of 1–3 mL using cylindrical glass containers [180]. The mixture is agitated for 2 min in an ultrasonic homogenizer (15% of its nominal power with alternating intervals of 0.4 s ultrasound and 0.6 s idle time). The catalyst ink is then coated on an inert decal substrate (PTFE-coated glass-fiber Thomaplast/Thomafluor NRN, purchased from Reichelt Chemietechnik GmbH & Co) in predefined forms by automated bar coating (Coatmaster 509 MCI, Erichsen GmbH & Co. KG, used with a coating speed of 5 mm s−1 and gap clearances between 160 and 420 μm) and dried slowly. Afterward, the catalyst layer is transferred to the opposite sides of a Nafton® 115 membrane (DuPont) by a hot-pressing step at 130 °C [180].

7.5. Stack compression (torque)

During electrolysis, the porous current collectors must be firmly pressed against the catalytic layers to obtain good electrical contacts and prevent leakage. As can be seen from Fig. 12 [175], for the condition obtained in this study, gas evolution does not take place homogeneously over the surface of the catalytic layers. Instead, gas is collected through cracks located in the neighborhood of sintered titanium particles, at contact points with the current collectors, and transferred away from the interface through the porous current collectors. When current collectors are pressed too firmly against
theMEA, the catalytic layer can be locally crushed and even destroyed (direct contact between current collector and membrane), and this can reduce the lifetime and efficiency of the MEA [175]. To the best of our knowledge, a study over the influence of stack compression over the structure of the electrodes and performance is still necessary.

7.6. Electrochemical characterization of the CCMs

The PEM electrolyzer performances are usually evaluated at 80 °C and under atmospheric pressure. In most test results presented in appendix A a single 25 cm² PEM electrolyzer was used with deionized water (<0.1 μS) circulating at a flow rate of around 2 ml min⁻¹ to the anode compartment. The water temperature is maintained at the same temperature of the cell (usually 80 °C – appendix A).

In summary the methods used to synthesize electrocatalysts play a fundamental role in the final performance, durability, and cost of the fabricated catalysts. In theory, the ideal method shall be uncomplicated, scalable, economical, and efficient in producing catalysts with high utilization, high activity, and high durability. The main drawback relies on the fact that catalysts with high surface area tend to have a lower durability or loss of active surface area over time due to nanoparticle agglomeration, dissolution, or corrosion. For the CCM fabrication, the challenges are committed to obtain homogenous catalyst layers over the membranes, with controllable catalyst and ionomer loading. Also important is to develop a scalable CCM method for commercial purposes, and also to prepare CCMs with geometric surface areas higher than 1000 cm². Hence, the optimization of the preparation methods to produce catalysts with optimized particle size, metal loading, and the stabilization of those catalysts systems is necessary. The optimization and verification of those methods for PEM electrolysis is even more relevant since not much research has been demonstrated for this application.

Due to the many variables, research groups essentially choose their method based on their expertise and economical requirements.

8. Modeling PEM water electrolysis

Unlike modeling of the PEM fuel cell, which dates back to the early 1990s [181], the modeling of PEM electrolysis is still early in its development, with the earliest models reported in 2002 [182]. The modeling efforts in the literature is still sparse for PEM electrolysis, however, the PEM fuel cell modeling is close in principal and is vast with several good review papers available [183–192]. Fig. 4 illustrates how the publications, and thus research, in the field of PEM electrolysis is bimodal with an initial interest in the mid 1980s then a renewed research effort in the early 2000s that is continuing to grow through present day. This stagnant interest until the late 1990s is the reason for such a delay in the state of modeling for PEM electrolysis.

In the early modeling studies of PEM electrolysis the primary approach was to apply Faraday’s Law to determine a steady state approximation of a cells polarization curve [182, 193–195]. This one dimensional, steady state approach greatly limits the models ability to predict scenarios required for the optimization of system control strategy and startup/shutdown, thus limiting the ability to examine integration in an intermittent system. The early models were primarily based off of already existing PEM fuel cell, alkaline electrolysis or non-specific electrolysis models (models neglecting mass transport due to varying morphology and proton transport due to varying membranes).

As the modeling progressed, and the need for dynamic modeling grew, in 2005 the first dynamic PEM electrolysis models were introduced [196, 197]. The first dynamic modeling approaches were still only one-dimensional in nature, mimicking the “sandwich” modeling approach employed by the fuel cell community and primarily used as a predictor for the general performance and output of a cell. Due to the greatly varying time scales between the electrical conduction and the mass transport certain aspects of the model are assumed to always be operating at steady state, or are said to occur instanteously, while others are considered to be time dependent.

It wasn’t until recently that a higher dimension model was introduced with the goal of examining the individual components of an electrolyzer with focus ranging from the separator plate flow field design [153, 198, 199] to the electrical resistance of the stack [200]. The early multi-dimension models have however been employed with the goal of designing individual components.

The modeling of PEM water electrolysis has developed quickly, much due to the research efforts in PEM fuel cells. Although computational modeling of PEM electrolysis is still far behind the state of the PEM fuel cell, its progress is developing at a fast pace.

8.1. Modeling cell voltage

The approach to modeling the cell voltage has been consistent through the various different authors. Whether
evaluating a fuel cell or an electrolyzer a similar approach to Eq. (4) is used:

\[ V = E + V_{\text{act}} + V_{\text{trans}} + V_{\text{ohm}} \]  

(4)

The first term \( E \) is the open circuit voltage (OCV) and is sometimes referred to as the reversible cell voltage (\( E^\text{rev} \)), because it is the theoretical voltage required by the electrolyzer, neglecting losses. The activation overvoltage, \( V_{\text{act}} \), is the voltage loss attributed to driving the electrochemical reaction and is necessary to overcome the molecular bonds. The losses due to mass transfer, \( V_{\text{trans}} \) are caused by flow restriction to the catalyst sites such as current collector and separator plate morphology as well as gas bubbles formed from the reaction products. Finally there are the ohmic losses, \( V_{\text{ohm}} \) created by the resistance to the flow of electrons through the current collectors and separator plates as well as the conduction of protons through membrane. What differs between the models in the literature is how these losses are determined, thus each of these terms will be addressed individually in the following sections.

### 8.2. Open circuit voltage

An electrolyzer OCV is typically determined through the use of the Nernst equation, or by evaluating the Gibb’s Free Energy. These two methods are the same in theory; however, different approaches exist in the literature in determining the temperature dependent value of the OCV. For example in the model presented by Awasthi et al. the Nernst equation, Eq. (5), was employed

\[ E = E^\text{rev} + \frac{(RT_{\text{avg}})}{nF} \ln \left( \frac{P_{\text{eq}}}{{P_{\text{eq}}}} \right) \]  

(5)

where \( P_i \) is the partial pressure of species \( i \), \( R \) is the universal gas constant, \( T_{\text{avg}} \) is the average cell temperature, \( F \) is Faraday’s constant and \( E^\text{rev} \) is the reversible cell potential at standard temperature and pressure [201]. To adjust the OCV from standard temperature and pressure Awasthi et al. used the empirical relation shown in Eq. (6) which is then combined with Eq. (5) to calculate the OCV [201].

\[ E^0_{\text{rev}} = 1.229 - 0.9 \times 10^{-3}(T_0 - 298) \]  

(6)

Alternatively, Marangio et al. takes a more fundamental approach with the application of the Gibb’s Free Energy [196,200,202–204], here the OCV is determined by

\[ E = \frac{\Delta G}{nF} \]  

(7)

where \( \Delta G \) is the Gibb’s Free Energy. This can be adjusted for non-standard temperature and pressure by applying Eq. (8) [200].

\[ \Delta G = \Delta G^0 + RT_{\text{avg}} \ln \left( \frac{P_{\text{eq}}}{P_{\text{ref}}} \right) \]  

(8)

For the reaction taking place in the PEM electrolyzer the temperature and pressure adjustment of the Gibb’s Free Energy equation can be performed by

\[ \Delta G^0 = \left[ H_i(T_{\text{cat}}) + \frac{1}{2}H_{O_2}(T_{\text{an}}) - H_i(O_2) \right] - T_{\text{avg}} \left[ S_i(T_{\text{cat}},P_0) + \frac{1}{2}S_{O_2}(T_{\text{an}},P_0) - S_i(O_2,T_{\text{an}},P_0) \right] \]  

(9)

where \( H_i(T) \) and \( S_i(T,P_0) \) is the Enthalpy and Entropy of species \( i \) respectfully evaluated at either the cathode or anode temperature depending on the location of that species reduction reaction. This approach is advantageous due to its ability to evaluate a temperature difference between the cathode and the anode as well as its reliance on the well-established empirical data for Enthalpy and Entropy as opposed to merely using a fitting parameter.

The two basic approaches each have their own advantages and disadvantages. For example through the application of the Nernst equation (Eq. (5)) an empirical relation is employed, this eliminates the use of large thermodynamic lookup tables thus improving computational efficiency. However, when the temperature fluctuations being modeled begin to grow the empirical formulation will introduce error. This can be solved by instead applying the balance of energy with the Gibb’s Free Energy (Eq. (8)) approach.

### 8.3. Activation overpotential

The activation overpotential is an energy loss in a reaction that can be described as the amount of energy require to begin the reaction. This loss is directly affected by the temperature, catalyst material, utilization, and loading. Modeling this phenomenon accurately can be challenging as material processing, temperature, active catalyst areas, utilization, distribution, age, pressure, morphology and many other parameters [205], some very difficult to quantify, all play a role. The electrochemical model used throughout both the fuel cell and electrolyzer communities to describe the activation overpotential is referred to as the Butler–Volmer equation. This can be applied to both the anode and the cathode individually [200,205], or together as in Awasthi et al. [201].

\[ V_{\text{act,an}} = \frac{RT_{\text{an}}}{\alpha_{\text{an}}F} \text{arcsin} \frac{i}{i_{0,\text{an}}} \]  

(10)

\[ V_{\text{act,cat}} = \frac{RT_{\text{cat}}}{\alpha_{\text{cat}}F} \text{arcsin} \frac{i}{i_{0,\text{cat}}} \]  

(11)

In the Butler-Volmer equation, \( \alpha_{\text{an}} = 2 \) and \( \alpha_{\text{cat}} = 0.5 \) are typically values for the charge transfer coefficient, at the anode and cathode respectively [196,200,202,203,205,206]. What tends to vary greatly throughout the literature is the value chosen for the exchange current densities, \( i_{0,\text{an}} \) for the anode and \( i_{0,\text{cat}} \) for the cathode. The exchange current density is determined by many physical parameters of the catalyst that are difficult to quantify. This creates a problem, especially on the anode side, as the overall polarization curves predicted from a model are heavily dependent on the exchange current density, a value known in the literature to fluctuate over seven orders of magnitude [200,202]. Table 6 illustrates what various authors have chosen for the exchange current density.
Due to the large variability of the exchange current density in the literature, many authors have used the exchange current density as a fitting parameter to fit their models to their experimental data. Garcia-Valverde et al. [205] attempted to model the temperature dependence of the exchange current density by applying an Arrhenius expression. This increases the effective range of temperatures of a model, however, does not truly model the exchange current density.

$$i_0 = i_{0,ref} \exp \left[ \frac{-E_{exc}}{R} \left( \frac{1}{T_{avg}} - \frac{1}{T_{ref}} \right) \right]$$ (12)

In the calculation of the exchange current density, Eq. (12), $E_{exc}$ is the activation energy of the electrode and $i_{0,ref}$ is the measured exchange current density at the reference temperature $T_{ref}$. This approach yields a better approximation of the exchange current density for a simulation with a variable temperature, however it still requires the empirically determined $E_{exc}$ and $i_{0,ref}$ in order to approximate the exchange current density.

### 8.4. Mass transport overpotential

The mass transport overpotential is rather well established. Due to the vast number of devices that exist making use of flow through a porous media the modeling of such phenomena has been thoroughly developed. Though other approaches exist in the field of electrolysis the mass flow through the porous current collectors is typically explained as a diffusion phenomenon. Computationally this is achieved through the application of Fick’s Law, which for diffusion in the $x$-axis direction is,

$$J = -D_{eff} \frac{\partial C_i}{\partial x}$$ (13)

where $J$ is the diffusion flux, $D_{eff}$ is the effective diffusivity of the transport media, and $C_i$ is the molar concentration of species $i$. To predict the voltage loss due to a surplus of reactant products at the catalyst sites blocking the reactants the Nernst equation can be combined with Fick’s law to create a diffusion rate that limits the reaction rate at higher current densities. This approach, referred to as the diffusion driven approach herein, can be applied for both the cathode and the anode accounting for the greatly differing diffusion rates of hydrogen and oxygen.

$$V_{trans, an} = \frac{RT_{an}}{nF} \ln \frac{C_{i, mem}}{C_{i, mem, 0}}$$ (14)

$$V_{trans, cat} = \frac{RT_{cat}}{nF} \ln \frac{C_{i, mem}}{C_{i, mem, 0}}$$ (15)

In the calculation of the voltage loss due to mass transport $C_{i, mem}$ is the concentration of species $i$ at the membrane-electrode interface and $C_{i, mem, 0}$ is a working condition taken as a reference. In the work by Marangio et al. the diffusion driven approach is derived in a more in depth manner [200].

Alternatively, a multiphase flow through porous media can be described by assuming a specified pore network or deriving a network through intensive image processing [210] and modeling the flow through the individual pores using the Poiseuille equation. This approach, which is referred to as the momentum driven approach, has been used in fuel cell modeling to capture the effects of morphology on the gas diffusion layers [211,212].

$$Q = \frac{\pi r^4 \Delta P}{8 \mu L}$$ (16)

Where $Q$ is the volumetric flow rate through the pore, $L$ is the length of the pore, $\mu$ is the viscosity of the fluid, and $r$ is the radius of the pore.

Advantages and disadvantages exist between the two approaches. The diffusion driven approach is very computationally efficient, it is still capable of capturing the differences in flow between the oxygen and hydrogen, and can easily be related to the cell voltage as a loss term. On the other hand, when evaluating and developing the design and morphology of the flow field and current collectors the pore network modeling has proven to provide more meaningful results. This is due to the inclusion of the inertial effects of the water and the morphology of the current collector into the model [213].

### 8.5. Ohmic and ionic transport overpotential

The ohmic overpotential for the current collectors and separator plates is typically modeled using a standard Ohm’s Law equivalent resistor model as seen in Fig. 13. In Fig. 13 the resistors $R_{LP}$ and $R_P$ are the through-plane and in-plane resistance of the current collector. $R_L$ and $R_P$ are the land and plate backing resistances, respectively. This type of analysis is very well established and can be predicted very accurately given the material, temperature and in the case of the current collector sintered particle size and porosity [214]. For the sake of combining both conductivities in a single section, electrical conductivity through current collector/separator plate and proton conductivity through the membrane are discussed in this section. This approach is very versatile as it allows for nearly all geometry of an electrolyzer to be modeled for ohmic losses.
The voltage loss due to the conductivities of the separator plate and the current collectors can be large at high current densities, so as the need to run an electrolyzer in an over-voltage scenario grows, this loss becomes more and more prevalent. The modeling approach adopted by nearly all models for this type of loss is the application of Ohm’s Law.

\[ V_{\text{ohm}} = R_{\text{tot}} I + \delta_{\text{mem}} \frac{I}{A \sigma_{\text{mem}}} \] (17)

Here \( R_{\text{tot}} \) is the total resistance of the cell (catalyst side and anode side), \( I \) is the cell current, \( \delta_{\text{mem}} \) is the thickness of the membrane and \( A \) is the surface area of the membrane. To find \( R_{\text{tot}} \) Ohm’s law is applied to a circuit that is similar to that shown in Fig. 13. Many approaches exist to modeling proton conductivity through the membrane, most of which have been developed for the modeling of fuel cells. A very commonly used empirical relation \( \sigma_{\text{mem}} \) for the membrane conductivity is

\[ \sigma_{\text{mem}} = (0.005139 \lambda - 0.00326) \exp \left( \frac{1268}{303} \right) \] (18)

where \( \lambda \) is the water uptake coefficient or degree of hydration [196,200,201,206]. Historically the value for the water uptake coefficient has been in dispute due to the possibility of Schröder’s Paradox for liquid equilibrated membranes [125–127]. A much more detailed model for membrane conductivity was developed by Choi et al. that was based off of the Grotthuss diffusion and ordinary mass diffusion of the hydronium ions [215]. This model is an improvement over the typical empirical relation as it removes the reliance on fitting parameters for proton transport and relies solely on physical parameters of the membrane. The proton transport can then be described by

\[ \sigma_{\text{mem}} = \frac{\epsilon_1}{\tau} \left( \frac{F^2}{RT_{\text{avg}}} \left( D_{\text{S,H}1} C_{\text{H}1} + D_{\text{S,H}1} C_{\text{H}1} + \frac{D_{\text{W}}}{1 + \delta_{\text{c}}} \right) \right) \] (19)

where \( \epsilon_1 \) is the porosity of the membrane, \( \tau \) is the tortuosity factor, \( D_{\text{S,H}1} \) is the surface diffusion coefficient, \( C_{\text{H}1} \) is the concentration of surface protons, \( D_{\text{S,H}1} \) is the Grotthuss diffusion coefficient, \( C_{\text{H}1} \) is the bulk proton concentration, \( D_{\text{W}} \) is the en masse diffusion coefficient, and \( \delta_{\text{c}} \) is the Stefan–Maxwell diffusion ratio. The complete derivation of this method is beyond the scope of this paper, however for more information see the work by Choi et al. [215].

9. Final remarks

This manuscript has extensively reviewed, since its first developments (1960s), the technical state and the progress in the areas of electrocatalysis, essential components, and modeling activities for PEM water electrolysis. After more than 50 years of research, PEM electrolysis units are still dependent on Nafion® membranes, Ir for the anode, Pt for the cathode, sintered Ti for the current collectors, and Ti separator plates. However, this lack of consistent development can be attributed to the fact that not much research was done on PEM water electrolysis until the late 1990s. The rekindled interest on PEM electrolysis that can be coupled to intermittent but renewable power sources, such as wind turbines, can be seen by the exponential growth in recent publications on PEM electrolysis (Fig. 4). Fig. 14 illustrates a compilation of the results obtained from 2010 to 2012. This range can be used as a...
benchmark to maintain performance while improving on the primary challenges of PEM electrolysis. In the past 50 years of research, many challenges were identified, a few were resolved, and many still exist.

The primary challenges presenting PEM electrolysis can be summarized as:

- Reduction (metal loading) and/or substitution of noble (expensive) catalysts
- Increase the catalyst utilization
- Development of low cost and corrosion resistant current collectors and separator plates — Improvement of long term stability/durability of all components
- Improvement of overall membrane characteristics
- Development of both empirically and physically predictive relations for operating parameters
- Developments of stacks concepts (MW range)

Through these individual improvements, the overall performance must at least maintain the same levels as observed in the state-of-the-art of today (Fig. 14), because improving on one area may degrade several others.

Some of the main costs of the CCM are directly affected by a reduction in the catalyst loading and catalyst utilization. For example, a reduction in the catalyst loading from 1.5 to 0.75 mg cm\(^{-2}\) can reduce the cost for the catalyst materials by as much as 60% as can be seen in Fig. 15. The catalyst utilization also plays an important role, and if combined with a catalyst reduction in the loading for both electrodes, the costs can be considerably reduced (Fig. 15).

Concerning the OER, improving the activity and catalyst stability, especially when using non-noble or at least iridium dispersed catalysts, is still the short term research and development priority. When specifically considering noble catalysts, a certain level of performance should first be obtained, then only should durability move to the forefront of investigations.

A very critical point is also the use of expensive titanium materials for the separator plates and current collectors. As can be seen in Fig. 11, the separator plates and current collectors correspond to 48% of the stack cost [29]. The development of alternative low cost materials for these components is very urgent.

Nevertheless, these challenges can stimulate research groups on finding new research directions or perspectives that could be proposed as follows:

- Improve the catalytic activity for HER and OER by using binary, ternary or quaternary alloys with an advanced design, improving the electrochemical active surface area, catalyst utilization, and stability against corrosion.
- In the case of using supported catalysts, development of highly conductive supports that can sustain the corrosion environment and still provide high nanoparticle dispersion and homogeneity.
- Understand and improve the triple-phase-boundary (ionomer-catalyst, ionomer-support, catalyst-support), in order to enhance the nanoparticle dispersion, improve the proton transport across the catalytic layer, decrease nanoparticle hindering, and diminish the electronic resistance provided by the ionomer. Also important is to understand the water transport across the triple-phase-boundary.
- For the anode, find catalyst alternatives to replace scarce iridium or unstable ruthenium will be considered a great achievement. New catalyst configurations or designed structures (e.g.: core-shells, BMGs, NTSFs, nanostructures, tuned alloys) could provide the necessary condition to decrease the amount of iridium or stabilize the ruthenium dissolution over time.
- For the cathode, improve the catalyst stability (especially when supported on carbon materials), explore alternative supports other than carbon and investigate metal-free N-C or N-CNTs catalysts. Also important, is to explore the use of high surface area carbon materials (carbon blacks, CNTs, graphenes) with adjusted pore size, functional groups, grafted polymers and electrical conductivities for the purpose of achieving higher activities and stability.
- Use innovative synthesis methods to produce new support materials, catalysts, and electrode systems.
- Use new advanced physical and electrochemical characterization tools, together with theoretical calculations (molecular/electronic level) to fundamentally and more deeply understand the mechanisms for the water transport and the electrochemical reaction.
splitting reactions (both OER and HER) and their relationship with the cell components and structures in order to tailor the same components and raise performance levels.

- Develop membrane alternatives to Nafion/C210 with advanced membrane synthesis methods, resulting in electrolytes with higher proton transport but providing at the same time lower gas crossover and higher durability. This could be done by; using membrane composites or blends, adding inorganic or organic fillers, or introducing molecular barriers to the electrolyte.

- Develop low cost current collectors with tuned porous structure, high corrosion resistance, low ohmic resistance, and optimized mass transport. The interface between the catalyst layer and the current collector must also be improved by developing a microporous layer that could better integrate the two layers in terms of mass and electron transport. This could be accomplished by using nanostructured fillers or dopers with high conductivity and high corrosion resistance.

- Ti separator plates could be replaced by using lower cost materials (e.g.: copper, graphite, stainless steel) coated with high electronic transport and high corrosion resistance materials.

- Develop a predictive model for the exchange current density for various catalysts. Although this task is very demanding, if successfully accomplished, modeling would prove to be a much more useful design tool capable of aiding in the design of all the individual components.

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A. Historical results in PEM electrolysis

<table>
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<th>Cathode catalyst</th>
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<th>Cathode loading mg cm⁻²</th>
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<th>Ionomer</th>
<th>Anode current collector</th>
<th>Cathode current collector</th>
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Abbreviations: TKK = Tanaka Corp.; JM = Johnson & Matthey; Etek = BASF; N. = Nafion®; c = cathode; a = anode; SPT = sintered porous titanium; C = carbon; ELAT = electrode Los Alamos type; E = electrodeposited catalysts; S = sprayed catalysts; Mem = membrane; CC = current collector; E(V) = cell voltage / 1 A cm⁻².
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<td>[92]</td>
<td>RuO2, IrO2, O2</td>
<td>46%Pt/Cnix</td>
<td>2.5</td>
<td>0.4</td>
<td>N.115</td>
<td>(a20c30)%N.5%</td>
<td>SPT</td>
<td>C Cloth</td>
<td>5</td>
<td>–</td>
<td>25</td>
<td>2.30</td>
</tr>
<tr>
<td>[234]</td>
<td>IrO2</td>
<td>30%Pt/Ccer</td>
<td>2.5</td>
<td>0.5</td>
<td>N.115</td>
<td>33%N.5%</td>
<td>Ti mesh</td>
<td>ELAT</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>1.70</td>
</tr>
<tr>
<td>[179]</td>
<td>Pt/IrO2</td>
<td>40%Pt/Cmem</td>
<td>1.8</td>
<td>0.3</td>
<td>N.117</td>
<td>N.5%</td>
<td>SPT</td>
<td>SPT</td>
<td>20</td>
<td>1</td>
<td>60</td>
<td>1.81</td>
</tr>
<tr>
<td>[179]</td>
<td>RuO2, IrO2, O2, Pt, I15</td>
<td>40%Pt/Cmem</td>
<td>1.8</td>
<td>0.3</td>
<td>N.117</td>
<td>N.5%</td>
<td>SPT</td>
<td>SPT</td>
<td>20</td>
<td>1</td>
<td>60</td>
<td>1.77</td>
</tr>
<tr>
<td>[72]</td>
<td>IrO2</td>
<td>40%Pt/Cmem</td>
<td>1</td>
<td>0.2</td>
<td>N.212</td>
<td>25%N.5%</td>
<td>C Cloth</td>
<td>C Cloth</td>
<td>1</td>
<td>1</td>
<td>80</td>
<td>1.64</td>
</tr>
<tr>
<td>[72]</td>
<td>IrO2, SnO2, 2:1</td>
<td>40%Pt/Cmem</td>
<td>1.2</td>
<td>0.2</td>
<td>N.212</td>
<td>25%N.5%</td>
<td>C Cloth</td>
<td>C Cloth</td>
<td>1</td>
<td>1</td>
<td>80</td>
<td>1.60</td>
</tr>
<tr>
<td>[72]</td>
<td>IrO2, SnO2, 2:1</td>
<td>40%Pt/Cmem</td>
<td>1</td>
<td>0.2</td>
<td>N.212</td>
<td>25%N.5%</td>
<td>C Cloth</td>
<td>C Cloth</td>
<td>1</td>
<td>1</td>
<td>80</td>
<td>1.66</td>
</tr>
</tbody>
</table>

Abbreviations: TKK = Tanaka Corp.; JM = Johnson & Matthey; Etek = BASF; N. = Nafon®; c = cathode; a = anode; SPT = sintered porous titanium; C = carbon; ELAT = electrode Los Alamos type; E = electrodeposited catalysts; S = sprayed catalysts; Mem = membrane; CC = current collector; E(V) = cell voltage @ 1 A cm⁻².
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