Introduction to PEMFC

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Proton Exchange Membrane Fuel Cells (PEMFCs) Operation

Anode (Negative)

Fuels (H₂, CH₃OH) react with the Pt catalyst on the PEM to form protons and release electrons

\[ H^+ + e^- \]

The protons travel across the PEM

Cathode (Positive)

The protons combine with O₂ and electrons to form water

\[ O_2 + H^+ + e^- \rightarrow H_2O \]

Temperaute Range: 60-120°C
Among the PEMFCs, three types can be distinguished:

- direct H$_2$-PEFC,
- direct methanol fuel cell (DMFC),
- indirect reformate PEFC.
**H₂-PEMFC**

### Anode (Negative)
- Hydrogen reacts with the Pt catalyst on the PEM to form protons and release electrons.
- The protons travel across the PEM.

### Cathode (Positive)
- The protons combine with O₂ and electrons to form water.
- This reaction is also catalyzed by Pt.

**Anode:** \( 2H_2(g) \rightarrow 4H^+(aq) + 4e^- \)

\[ E^{0}_{H_2/H^+} = 0.0\text{V} \]

**Cathode:** \( O_2(g) + 4H^+ (aq) + 4e^- \rightarrow 2H_2O(l) \)

\[ E^{0}_{O_2/H_2O} = 1.23\text{V} \]

**Cell Reaction:** \( H_2 (g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \)

\[ E^{0}_{\text{cell}} = 1.23\text{V} \]

**Operation Temperature:** 100°C
The availability of hydrogen especially for portable or mobile use presents a challenge. Hydrogen can be stored as:

- compressed gas in pressure bottles. This option suffers from the low storage density and the resulting high volume. Depending on the storage material the storage system in addition shows a high weight.
- cryogenic (liquid) storage would overcome the disadvantage of the storage density. However, liquefaction consumes roughly 30% of the inherent energy.
- storage in metal hydrides is comparatively simple to implement, but suffers from the heavy weight of the system.
- storage in carbon nanotubes are the subject of much research efforts, but to date usefulness and storage capacity are questionable.

**High safety precautions have to be taken to prevent explosion of hydrogen.**
**DMFC**

**Anode (Negative)**
Methanol reacts with the Pt/Ru catalyst on the PEM to form protons and release electrons

\[ \text{CH}_3\text{OH}(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{CO}_2(g) + 6\text{H}^+(aq) + 6\text{e}^- \]

**Cathode (Positive)**

\[ \frac{3}{2}\text{O}_2(g) + 6\text{H}^+(aq) + 6\text{e}^- \longrightarrow 3\text{H}_2\text{O}(l) \]

The protons combine with \( \text{O}_2 \) and electrons to form water

This reaction is catalyzed by Pt

**Operation Temperature: 120°C**

**Anode:** \( \text{CH}_3\text{OH}(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{CO}_2(g) + 6\text{H}^+(aq) + 6\text{e}^- \) \( E_{\text{Anode}}^0 = 0.046 \text{V} \)

**Cathode:** \( \frac{3}{2}\text{O}_2(g) + 6\text{H}^+(aq) + 6\text{e}^- \longrightarrow 3\text{H}_2\text{O}(l) \) \( E_{\text{Cathode}}^0 = 1.23 \text{ V} \)

**Cell Reaction:** \( \text{CH}_3\text{OH}(aq) + \frac{3}{2} \text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O} (l) \) \( E_{\text{cell}}^0 = 1.18 \text{ V} \)
Slightly higher operating temperature of 100-120°C can be realized due to the high water content at the anode (feeding the anode with a liquid methanol/water mixture), which keeps the membrane in a well-humidified state. However, despite the similar standard cell potential (1.18 V vs. 1.23 V) and the slightly increased temperature, tremendous polarization losses (ç ~ 0.3 V vs. ç ~ 0.05 V for the H2 oxidation) lead to a 0.2 to 0.4 V reduced operation voltage of a DMFC. In addition, methanol shows a high diffusion rate through the state of the art polymer membranes (methanol crossover).* The methanol loss on the anode side (up to 50% methanol crossover) and the decrease of the cathode potential due to the build up of a mixed potential (simultaneous oxygen reduction and methanol oxidation) are responsible for extended efficiency losses. The application of thicker membranes reduces the methanol crossover, but on the other hand increases the ohmic resistance. Thin membranes with a low ohmic resistance, which still act as a methanol barrier, are subject to research.

Suitable chemical processes are steam reforming or partial oxidation of a variety of carbonaceous fuels. One widely considered option is the steam reforming of methanol. Methanol itself is relatively simple to synthesize and shows a high energy density of 5 kWh/kg (4.2 kWh/l).

\[
\text{Methanol Steam Reforming} \quad \text{CH}_3\text{OH (g) + H}_2\text{O} \rightarrow \text{CO}_2\text{(g) + 3H}_2\text{(g)}
\]

\[
\text{Water Gas Shift Reaction} \quad \text{CO + H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
\]

\[
\text{Selective Oxidation of CO} \quad \text{CO + } \frac{1}{2} \text{ O}_2 \rightarrow \text{CO}_2
\]

However, a major problem of utilizing reformate fuel is its CO content. CO decreases the electrocatalytic activity of platinum tremendously. Although several platinum alloys (e.g. Pt-Ru) show an enhanced CO tolerance compared to platinum (100 vs. 10 ppm), gas-cleaning systems are nevertheless required to use reformate fuel without irreversible catalyst degradation. Providing an infrastructure for the liquid methanol fuel is regarded to be less complicated compared to the build up of a hydrogen distribution infrastructure.
Comparison between the $H_2$-PEFC and the DMFC
The reactions which take place at the electrodes in a PEMFC are:

- Hydrogen oxidation
- Methanol oxidation
- Oxygen reduction

The first two reactions, which occur at the anode compartment, correspond to the oxidation of fuel in H2-PEFC and DMFC respectively.

The reduction of oxidation occurs at the cathode side.
The reaction involves the adsorption of the gas onto the catalyst surface, followed by a dissociation of the molecule and electrochemical reaction which gives hydrogen ion

\[
2 \text{Pt}_\text{s} + \text{H}_2 \rightarrow \text{Pt-H}_{\text{ads}} + \text{Pt-H}_{\text{ads}} \\
\text{Pt-H}_{\text{ads}} \rightarrow \text{H}^+ + \text{e}^- + \text{Pt}_\text{s}
\]

where \(\text{Pt}(s)\) is a free surface site and \(\text{Pt-H}_{\text{ads}}\) is an adsorbed H-atom on the Pt active site.

The overall reaction of hydrogen oxidation is:

\[
\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \quad U^0 = 0\text{V}
\]
In most practical systems the fuel stream contains certain traces of elements or compounds such as CO, S, and NH3. All these substances can to a greater or lesser extent poison the anode catalysts. CO is one of the major poisons in low temperature fuel cells. Its poisoning occurs due to adsorption of the species to the active sites of the platinum catalysts.

To avoid CO contamination in the cell different strategy can be applied:

- A gas clean-up can be built in between the reformer and the fuel cell which adds complexity to the system.

- Other methods to remove CO from the fuel cell deal with the mixing of the fuel feed with small amounts of air or oxygen.

- The electrical pulses increase the anode potential to values at which the CO is oxidised to CO2. In this way the catalyst surface is continuously cleaned and the loss of cell voltage is minimised.
Hydrogen oxidation

CO-tolerant catalysts are still being investigated by numerous research groups in order to reduce the importance of the problem. CO-tolerant anodes usually contain a Pt-Ru alloy. The mechanism of CO oxidation and CO tolerance of Pt-Ru catalysts with well-defined surfaces has been investigated and clarified by several groups. *

PtRuW and PtRuMo showed an improved CO tolerance over Pt and PtRu catalysts.


Methanol oxidation

The overall reaction mechanism for methanol oxidation is:

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \]

Very few electrode materials have been shown to be capable of adsorbing methanol in acidic media and of these only Pt-based materials display a high enough stability and activity to be attractive as catalysts. Many studies on the oxidation of organic molecules and specifically on methanol have been carried out. An overview of methanol oxidation and methanol fuel cells has been published in the literature. *

Methanol oxidation

Scheme of methanol oxidation on Pt

It is assumed that the oxidation of methanol on Pt based catalysts proceeds by the adsorption of the molecule followed by several steps of deprotonation.

CO is formed during the oxidation of methanol.

CO species can block the surface of the catalyst and hinder any further reaction.

Co-metals are usually added to the Pt catalyst to facilitate CO removal by oxidation to CO$_2$. This can be achieved by oxidising the CO species using oxygen containing species adsorbed at the surface either from the water in solution or hydroxide ions.
Much research is being rendered on catalysts for methanol oxidation to find a catalyst which can avoid the poisoning effect of the CO species. Several promoters have been found to increase the activity of the Pt catalyst. One of the most important and most investigated promoters is Ru. A bimetallic alloy consisting of Pt and Ru supported on carbon has thus far been one of the major research interests in direct methanol fuel cells. Other promoters such as Sn, Os, W, Mo and other metals have also been investigated for oxidise methanol and reduce CO poisoning.
The oxygen reduction reaction (ORR) can proceed by two overall pathways, either a direct 4-electron pathway or an indirect 2-electron pathway. The direct 4-electron pathway is preferable as it does not involve peroxide species and the Faradaic efficiency of the reaction is greater. This pathway, however, consists of a number of steps in which molecular oxygen has to be dissociated at the surface and recombined with hydrogen ions to form water. The adsorption of an oxygen species on the surface of the metal particles is necessary for electron transfer.

\[
\text{Direct reduction: } \quad O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E_{O_2/H_2O}^0 = 1.23 \text{ V}
\]

\[
\text{Indirect reduction: } \quad O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E_{O_2/H_2O_2}^0 = 0.682 \text{ V}
\]

Followed by a further reduction via

\[
\text{Electrochemical reaction: } \quad H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E_{H_2O_2/H_2O}^0 = 1.77 \text{ V}
\]

or

\[
\text{Chemical decomposition: } \quad 2H_2O_2 \rightarrow 2H_2O + O_2
\]
Pt based catalysts are the superior material for the oxygen reduction reaction. Pt dispersed on carbon or other small Pt particles (such as colloids) exhibit a good performance. Due to the low temperature in PEMFC, the loadings for the oxygen catalysts are significant to compensate for the slow reaction kinetics. Since pure oxygen is seldom available, fuel cells require air for the cathode gas supply. The lower oxygen partial pressure in air leads to a decrease in activity compared to pure oxygen. Research into less expensive materials and better catalysts for the ORR is being carried out by various groups.
PEMFC Components

- Plaque bipolaire
- Anode
- Cathode
- Plaque bipolaire
- Backing
- Membrane
- Backing
MEA
(Membrane Electrode Assembly)

Proton Exchange Membrane ~ 25-200 μm thick

Anode
Pt/Ru catalyst:
XRD crystallite size ~ 3 nm
Surface area ~ 60 m²/g

~ 10 μm thick
10nm-1μm pores

Cathode
Pt catalyst:
XRD crystallite size ~ 1-3 nm
Surface area ~ 30 m²/g

~ 10 μm thick
10nm-1μm pores
The essential requirements of polymer electrolyte membranes include:

- high proton conduction value,
- chemical stability,
- thermal stability,
- mechanical properties (strength, flexibility and processability),
- low gas permeability,
- low water drag,
- low methanol crossover,
- low cost,
- ready availability.

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Per Fluoro sulfonic Acid (PFSA) membrane, where the sulfonic acid groups are attached to a fully fluorinated Teflon-based (PTFE) backbone. Among them the most studied and employed is Nafion (schematic structure compare figure). The perfluorinated backbone structure, being similar to that of Teflon, is strongly hydrophobic. As opposed to the polymer backbone, the short spacer including the proton conducting sulfonic acid group is very hydrophilic and a micro phase separation is obtained, where the sulfonic acid groups are oriented in clusters or inverted micelles surrounded by the hydrophobic backbone. *

However, Nafion suffers from various disadvantages such as conductivity decrease above 90°C and high methanol permeability, which lead to cell potential reduction. The water management is a crucial issue for the system design and a correct water balance must be maintained in order to guarantee an optimal performance. Due to the low operating temperature, liquid water is continuously produced at the cathode compartment. This can cause its flooding which reduces the performance of the cell not permitting the reactant gases to reach the electrocatalyst. On the other hand, as the membrane’s transport properties are often highly water dependent, too little water will cause the drying of the anode side, leading to a dramatic decrease of membrane conductivity.
Examples of such polymers are radiation-grafted membranes

1) PVDF (Poly Vinylidene Fluoride),
2) heterocyclic polymers such as PBI (Polybenzimidazole)
3) sulfonated aromatic hydrocarbons (SAPs).
1) Radiation-grafted membranes.

The radiation grafting approach has the potential to produce membranes with low cost on a large scale. The principle of this approach is based on irradiation of a chemically and mechanically stable polymeric matrix, such as PVDF (Poly Vinylidene Fluoride). During irradiation, radicals are induced in the polymer backbone and grafting is obtained by radical polymerisation when swelling the sample in styrene. Another polymerisation approach is atom transfer radical polymerisation (ATRP), which has been investigated by Holmberg et al. The radiation-grafted membranes show sufficiently good mechanical properties, high proton conductivity and have been successfully demonstrated in PEFC applications. However, there are some major drawbacks related to the weaker oxidation stability of the aliphatic chain.


Electrolyte

2) Heterocyclic Polymers

A reliable way to overcome the problem of oxidative stability is to employ heterocyclic polymers. Their major advantage comes from the opportunity to utilize a solvent different from water as proton carrier, which could increase the conductivity at temperatures above 100 °C. * An example is PBI-based membranes having a thermally and chemically stable polymer backbone. The PBI-based (Polybenzimidazole) membranes are some of the most promising alternatives to Nafion in high temperature PEFC. PBI membranes treated with phosphoric acid show high proton conductivity depending on doping level. **


3) *Sulfonated Aromatic Polymers*

The sulfonated hydrocarbons polymers are also potentially promising for high temperature fuel cells. These polymers can provide a higher oxidation resistance compared to aliphatic polymers due to the aromatic bonds. They exhibit a microstructure composed of two phases as in the case of PFSA polymers; the hydrophobic phase is associated with the polymer backbone, while the hydrophilic one is related to the acidic groups. The differences in performance, between the two systems, can be essentially explained in terms of distinct microstructure features and in different strength of the acidic groups. *

Electrodes for PEM fuel cells are generally porous gas diffusion electrodes to ensure the supply of the reactant gases to the active zones where the noble metal catalyst is in contact with the ionic and electronic conductor. The fabrication of gas diffusion electrodes (GDE) is an intricate procedure in which all details are important. The reason for this is that the function of the electrodes is far more than just catalysing a reaction, which is carried out by the catalyst particles.
The development and implementation of PEMFCs is strongly affected by several technical issues. These include:

- the nature of polymer electrolyte,
- the water management,
- CO poisoning,
- fuels (hydrogen, direct and reformed methanol),
- heat management,
Water management in a PEMFC is one of the most essential issues for obtaining good and reliable performance. The objective of effective water management is to regulate the transport of water in such way that a sufficient amount of water is retained in the proton conductive phases, but excess liquid water is removed from the cathode at the same rate as it is produced, with minimum obstruction of the gas transport paths. Water in a PEM fuel cell can originate from two sources: humidification of the reactant gases and cathode reaction. Water transport across the membrane takes place by three different processes:

- Electro-osmotic drag
- Back diffusion
- Hydraulic permeation
Water Management

When current is drawn from the cell, protons migrate through the membrane from the anode to the cathode and carry water molecules with them. The process is called electro-osmotic drag.

When the amount of water differs across the membrane, its concentration gradient drives the diffusion of water through the membrane from the cathode to the anode. This process usually counters the electro-osmotic drag and is, therefore, often referred to as “back diffusion”.

Related to the continuous water removal and back diffusion at the cathode, a gradient pressure can be generated across the membrane and hydraulic permeation can contribute to the water transport.
Water Management

Water management methods

The proper content of water inside the membrane can be obtained taking into account and controlling all those factors and phenomena, such as electrode flooding and drying out, the rate of water transport processes, membrane thickness. Using humidified reactant gases is necessary when the reaction product water is not sufficient to keep the membrane hydrated. The need for external humidification arises usually from drying out of the anode. That occurs, when the electro-osmotic drag is stronger than water back diffusion, leading into net flux of water from the anode to the cathode side and distorted hydration profile. Thick membranes aggravate the problem, since they require more water to remain hydrated and make the diffusion driving concentration gradient less steep.

The anode can easily be kept humidified by controlling the hydrogen humidification temperature, but water removal conditions on the cathode should be carefully controlled. Water production, together with electro-osmotic drag and humidified cathode gas, leads easily into accumulation of water and flooding of the electrode or the gas diffusion backing.
Another critical aspect, associated with a low operation temperature, is the reduced tolerance to fuel impurities, such as CO, in the hydrogen and methanol steam. This poisoning has been shown to be very temperature-dependent. For example at 80°C, the typical operational temperature of a Nafion polymer membrane, a CO content as low as 20 ppm in the fuel stream will significantly decrease the cell performance. Most of the shortcomings associated with the low temperature PEMFC technology based on PFSA membranes could be solved or avoided by developing alternative membranes operating at higher temperatures than 100°C. Several aromatic polymeric membranes have been studied in the last years: sulphonated polysulfone, sulphonated polyphosphazene, sulphonated polyamides and sulphonated polyether-ether-ketone. However, the methanol permeability is in many cases still relatively high.
This stimulates the oxidation of CO over the catalyst. This method requires an extensive control system since the air content has to be closely monitored. The addition of hydrogen peroxide to the fuel stream has also been investigated as a method to minimise the CO contamination. A new method of operating PEM fuel cells with reformed hydrogen consists in electrically applying pulses to the cell. The electrical pulses increase the anode potential to values at which the CO is oxidised to CO2. In this way the catalyst surface is continuously cleaned and the loss of cell voltage is minimised. CO-tolerant catalysts are still being investigated by numerous research groups in order to reduce the importance of the problem. CO-tolerant anodes usually contain a Pt-Ru alloy. The mechanism of CO oxidation and CO tolerance of Pt-Ru catalysts with well-defined surfaces has been investigated and clarified by several groups. PtRuW and PtRuMo showed an improved CO tolerance over Pt and PtRu catalysts. Alternatives to pure hydrogen are natural sources such as natural gas, propane or alcohols. These substances have to be reformed, however, into hydrogen and even after gas clean up some contaminants such as carbon monoxide can still exist in the fuel feed.
Operating temperature affects the performance of the cell in several aspects. The rates of the electrochemical reactions depend on temperature, the protonic conductivity of membrane materials increases with increasing temperature, and the tolerance of the catalysts against impurities is improved along with it. Increasing temperature also facilitates water removal, thereby enabling higher currents to be drawn from the cell before the onset of flooding. Because the saturation pressure of water increases strongly with increasing temperature, more water transport can take place in vapour form, which is generally more practical than removing water in liquid form. In addition, an increase in temperature increases the diffusivities of gases. If the flow of air on the cathode is driven by natural convection, the flow rate increases with increasing temperature difference to the surroundings.
Methanol Crossover

The cross-over of methanol from the anode to the cathode in a DMFC has serious consequences in reducing coulombic and voltage efficiencies. It is known to be one of the most challenging problems affecting the performance of DMFCs. The overall efficiency of a methanol fuel cell is determined by both voltage and faradaic efficiency for consumption of methanol. The faradaic efficiency is mainly influenced by methanol crossover through the membrane.

Due to the similar properties of water, such as dipole moment, methanol molecules are transported to the cathode by the electro-osmotic drag as well as diffusion. At the cathode, methanol causes a mixed potential due to the interference of its oxidation with the oxygen reduction reaction. As a consequence, cell performances decrease.

Methanol cross-over depends on a number of factors, the most important ones are the membrane permeability/thickness, the concentration of methanol in the fuel feed, the operating temperature, and the performance of the anode itself. The nature of the membrane is a very important factor regarding the methanol cross-over problem. Great efforts have been made to reduce this phenomenon by varying the membranes morphological features in order to reduce the methanol permeability.
Methanol Crossover

A different approach to cope with the methanol cross-over problem is the investigation of methanol-tolerant cathodes. Here, the methanol diffusion is not prevented but cathode catalysts inactive regarding methanol oxidation, are employed. Hence, the establishment of a mixed potential at the cathode is prevented. Different methanol tolerant cathodes have been investigated. Modified composite membranes (Nafion-silica), with SiO2 particles entrapped in the polymeric structure, can serve as physical barrier for methanol crossover, even though the ohmic resistance is increased (depends on the concentration of silica). Low crossover rate have been demonstrated in presence of Nafion-Silica and Nafion compositemembranes.
Applications

Those cells operate at low temperature (less than 120°C), allowing for faster start-up and immediate response to changes in the power demand.