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Hydrogen fuel cells for cars and buses

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Abstract The use of hydrogen fuel cells for cars is strongly promoted by the governments of many countries and by international organizations like the European Community. The electrochemical behaviour of the most promising fuel cell (polymer electrolyte membrane fuel cell, PEMFC) is critically discussed, based on results presented in the literature. Moreover, when some non- electrochemical aspects are taken into consideration, it is concluded that the prospects are not too bright. Moreover, the hydrogen-rich gas generated from small organics contains CO_2 and a small amount of CO, its use easily leads to poisoning of the platinum gas diffusion anode in the fuel cell. Also the hydrogen storage problems are still not solved.

Keywords Hydrogen · Oxygen · Fuel cell · Cars · Poisoning and storage

1 Introduction

To save the environment, to reduce the dependence on fossil fuels and to increase the contribution of renewable energy sources, the use of hydrogen is strongly promoted by the European Commission. Currently 100 M€ of EU funding is being awarded to research and demonstration projects for hydrogen and fuel cells in the 6th Framework Program (FP6). Moreover, it must be taken into account that about half of the project costs are funded by the EU.

Various types of fuel cells are known [1]. For mobile applications only, acidic fuel cells working at temperatures below 400 K are of interest. It is commonly accepted that alkaline fuel cells are not suitable for mobile applications, because of the carbon dioxide absorption intolerance. The acidic polymer electrolyte fuel cell (PEMFC), fed with pure hydrogen and working at about 350 K, is the most promising type. Two stacks of 900 cells of this type-(fed with hydrogen generated electrochemically and loaded with a current density of about 25 mA cm^{-2}) are being tested in buses driving through various European cities within the FP6 (private communication). In 1993, a 9.8 m long bus with hydrogen fuel cells containing proton exchange membranes was already operational.

The electrochemical behaviour of PEMFCs and some important non-electrochemical aspects are discussed in this paper.

2 Electrochemical behaviour of PEMFCs

2.1 Hydrogen platinum anode

Many fundamental studies have been performed to determine the mechanism of hydrogen oxidation on platinum [2–8]. Some investigations [2–5] used rotating platinum discs and others [6–8] used gas diffusion electrodes, loaded with a small quantity of highly dispersed platinum (typically 0.50 mg cm^{-2}).

To reduce the effect of carbon monoxide in poisoning this oxidation reaction, platinum is alloyed with noble metals like ruthenium, palladium and rhodium and even with non-noble metals like tin, molybdenum and iron.

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However, in a very strong acidic medium, the platinum alloys are insufficiently stable and dissolve partly, leaving finely dispersed platinum particles. This strong acidic medium (pH is about zero) is present at the anode surface of the PEMFC cell. Pure platinum has been found to give the best performance and has been selected for use in acidic fuel cells [9].

Generally, it is accepted that hydrogen oxidation on platinum electrodes occurs according to the Volmer–Tafel mechanism consisting of two reactions, viz.: the Tafel reaction $H_2 \leftrightarrow 2H_{ad}$ and the Volmer reaction $H_{ad} \leftrightarrow H^+ + e^-$. The activity of the platinum electrode has a large effect on the kinetic parameters of these reactions [10]. The transfer coefficient of the Volmer reaction $\alpha_V = 0.5$ and the ratio between the exchange current densities of both reactions ($i_{0,V}/i_{0,T}$) is ≤ 0.1 for a very active platinum gas diffusion electrode. This ratio decreases with decreasing catalyst activity. For hydrogen oxidation on an active platinum gas diffusion electrode in 0.5 M H_2SO_4 and at 298 K the overall exchange current density i_0 is 80 mA cm^{-2}, corresponding to an overpotential of 70 mV at 300 mA cm^{-2} [10]. This exchange current density is about a factor of 300 larger than that for an active platinum sheet electrode [11], owing to a large difference in electrochemical surface area per unit geometrical surface area and in the structure of the electrode surface. Unfortunately, no other experimental results are available for platinum gas diffusion anodes with pure hydrogen fed. Mostly, the anode activation overpotential is only a very small part of the potential losses of a well-operated cell.

For very active platinum electrodes, the limiting current density of the hydrogen oxidation is dominated by transport of hydrogen. For a less active platinum electrode the limiting current density is determined by the kinetic parameters of the Tafel reaction. There is a strong relationship between the activity of the electrode and the limiting current density for hydrogen oxidation.

The activity of the platinum electrode is affected by its potential. Adsorbed oxygen species are formed increasingly on the platinum electrode at increasing potential. At an overpotential of about 0.8 V versus SHE, the platinum surface is almost completely covered with an oxide layer. The formation of this oxide layer starts at much lower overpotentials for finely dispersed platinum particles. Adsorbed oxygen strongly inhibits hydrogen oxidation.

Impurities can be adsorbed by, and accumulate on the platinum electrode from the solution and from the hydrogen feed, so the electrode becomes less and less active, as reported by Vermeijlen [10]. He found that for a rotating platinum disc electrode (electrochemically activated) in a hydrogen saturated sulphuric acid solution and loaded with 0.74 mA cm^{-2}, the overpotential was practically zero at the start of the experiment, increased with increasing rate to about 250 mV during the first 15 min; thereafter, the overpotential oscillated strongly with increasing amplitude for 10 min and then the potential jumped into the potential region of oxygen evolution. The time to the potential jump decreased with increasing current density and with increasing transport rate of impurities to the electrode surface. A similar result was obtained with a hydrogen diffusion electrode (0.5 mg platinum loading, E-TEK, USA) in 1 M H_2SO_4 and at 500 mA cm^{-2} and 313 K.

Hydrogen is produced by the electrolyses of water and chemically formed by organic compounds like methanol, methane and ethanol by reforming. The ‘electrochemical’ hydrogen contains no or almost no organic impurities. It is used in the fuel cells of the buses in the EU-demonstration projects. ‘Chemical’ hydrogen from methanol contains small quantities of carbon monoxide, carbon dioxide and water vapour, even after cleaning.

Carbon monoxide, present in the “chemically-derived” hydrogen is a catastrophic poison for platinum electrodes to oxidize hydrogen electrochemically. The carbon concentration in the hydrogen feed must be very low and should not be higher than 10–100 ppm [12]. Methanol and carbon dioxide also affect the fuel cell catalyst, but not as severely as carbon monoxide [13]. New results [14] show that even a carbon monoxide content of 5 ppm causes a strong increase of anode overpotential. It was found that for a PEM cell at 358 K, 1000 mA cm^{-2} and fed with hydrogen gas containing 5 ppm carbon monoxide, the cell voltage and also the anode overpotential was 0.01 V higher than for hydrogen without carbon monoxide. Assuming these experiments are not long-term experiments, it is likely that based on Vermeijlens’ experiments [10], that the negative effect will be much larger in long-term experiments. Moreover, the ageing of platinum catalysts is well-known, leading to increases in the anode overpotential. Based on the results with hydrogen gas with various concentrations of carbon monoxide [14], it is concluded that for platinum electrodes the carbon monoxide content must be much lower than 1 ppm to prevent troublesome poisoning of the platinum catalyst of the anode.

A platinum electrode completely poisoned with carbon monoxide is inactive. It can be reactivated by oxygen bleeding, leading to an unrecoverable performance loss [14]. The lifetime of the electrode will be shortened.

2.2 Oxygen reduction platinum cathode

Considerable effort has been expended to replace platinum in acidic medium using non-precious metal catalysts [9]. On platinum oxygen can be reduced to water and hydrogen peroxide, their molar ratio depending on the ratio between the reaction rate of the first step of the two mechanisms, viz. one leading to water and the other to hydrogen peroxide.

The dissociation of oxygen according to $O_2 \rightarrow 2O_{ad}$ leads to water and the electrochemical one-electron step reduction, viz. $O_2 + e^- \rightarrow O_2^-$ gives hydrogen peroxide; both reaction mechanisms are very complicated. The water/hydroxide peroxide product ratio depends on the electrode potential and in particular on the electrode material.

At platinum, oxygen is reduced predominately to water. The polarization curve for oxygen reduction on sheet platinum shows the existence of two distinct Tafel slopes [15]. At 298 K the Tafel slope is 60 mV decade^{-1} at potentials higher than 0.9 V relative to a hydrogen electrode in the same solution and 120 mV decade^{-1} at lower potentials. The exchange current density is extremely small, viz. 8.5×10^{-6} mA cm^{-2} for a platinum sheet electrode in 1 M H_2SO_4 at 298 K.

For oxygen reduction at a platinum gas diffusion electrode with 0.4 mg platinum per cm^2 (E-TEK, Inc.) it was found that the exchange current density at 323 K is 1.8×10^{-2} mA cm^{-2} [16], corresponding to a cathode overpotential of 0.5 V at 1,000 mA cm^{-2} [16]. The exchange current density is related to the electrochemical active surface area per cm^{-2} of geometric area [16]. From recent results [17], it can be deduced that for a PEM fuel cell with platinum catalyst, the cathode overpotential at 1,000 mA cm^{-2} and at 353 K is about 0.45 V. The slow kinetics of the oxygen reduction reaction is the main cause of efficiency losses in fuel cells that operate at low temperature, e.g. below 473 K [18].

Platinum catalysts lose activity by dissolution into the solution, as well as loss of surface area per unit mass. Platinum has a solubility as Pt^{2+} ions that increases with increasing potential [19]. These ions migrate towards the anode in the cell and deposit as Pt metal by reduction with hydrogen. Platinum catalysts age by three processes: sintering, dissolution-precipitation and crystallite migration. Moreover, platinum cathode catalyst ages faster than platinum anode catalyst. Even a small quantity of hydrogen peroxide formed during oxygen reduction can affect the ageing process.

The platinum catalysts are almost exclusively used, and also have to be stable, under open-circuit conditions. Therefore, it is of utmost importance that whenever the cell is switched off, the oxygen in the cathode lumen is rapidly exchanged by inert gas and that the cell voltage under operation does not exceed 0.8 V [20, 21].

2.3 Membranes

Nafion-type membranes based on perfluorosulfonic acid are used practically exclusively in proton exchange membrane fuel cells (PEMFCs). Perfluorinated membranes are very stable to oxidation, evidenced by more than 10 years use in chlorine-alkali cells and stability against even fluorine/hydrogen mixtures [22]. The remarkably high proton conductivity of Nafion-type membranes makes them very important for fuel cells. The liquid inside the membrane is very acidic (pH is about 0), since the perfluorosulfonic acid is a very strong acid and is almost completely ionized in aqueous media.

To operate well, the membrane must contain a certain quantity of water. In practice, fuel cells with Nafion-type membranes operate mostly at a temperature of 353 K. Probably at higher temperatures, the water content of the membrane becomes too low, resulting in too low a proton conductivity. The problems of pressurization, heat and water management of the PEMFC are related to the membrane type. These problems will be solved only if a new type of proton conductor is found for operation at higher temperatures and low humidity. Preferably, such a polymer should still have the beneficial properties of Nafion-type polymers: cold start capabilities, toughness and good proton conductivity [23]; a very big task.

3 Hydrogen

3.1 Electrochemical hydrogen

Hydrogen is produced by electrolysis of a concentrated KOH solution; usually the electrolysis voltage is 1.85 V and the temperature 363 K. Electrochemical hydrogen is very clean and does not contain carbon monoxide; it is used in the fuel cells on board buses within EU FP6 projects. Taking into account that the hydrogen fuel cell operates at a voltage of 0.6 V at a reasonable loading, this means that the maximum energy efficiency of the whole cycle (electric energy-hydrogen- electric energy cycle) is about 30%. A much higher energy efficiency can be attained with batteries; for instance, the efficiency of the whole cycle for a lead battery (loading and unloading) is 80% [24, 25].

3.2 Chemical hydrogen

3.2.1 On-board production

Since hydrogen storage is a big problem, it is proposed to refuel vehicles with methanol and to convert this methanol into reformate gas (a gas mixture containing typically 65% hydrogen, 20% carbon dioxide, 12% water vapour, 0.6% carbon monoxide and 1% oxygen). Much research has been carried out to reduce dramatically the CO content of the reformate gas by oxidation with oxygen in a specially designed oxidation reactor. It was found that the CO content could be reduced to a minimum value of 10 ppm [26]. This value is much lower than that at 353 K, viz.110 ppm, predicted by thermodynamic data [27] for the enthalpy and entropy of the gaseous compounds of the water-gas shift reaction $CO_2 + H_2 \leftrightarrow CO + H_2O$. The PEFMC usually operates at about 353 K. Similar platinum catalysts are used in the oxidation reactor and the fuel cell. Since each system tends to equilibrium, CO can be reformed at the platinum anode surface of the fuel cell fed with purified reformate gas containing 10 ppm.

This reformation of carbon monoxide is established by experiments with hydrogen–carbon dioxide mixtures fed to PEFMCs with platinum gas diffusion electrodes. It was found that the presence of CO_2 in the anode feed can lead to a significant loss in performance. The negative effect is likely to be caused by the formation of CO via the reverse water-gas shift reaction on platinum which is not covered with Nafion [28].

It is concluded that the formation of sufficiently pure hydrogen from methanol and also for other organic compounds like methane and ethanol on-board of vehicles is practically impossible [29]. By contrast, these organic compounds can be used very successfully as fuels in combustion engines.

3.2.2 Hydrogen from stationary plants

The process conditions of the production of reformate gas can be much better regulated in a big stationary plant than in a reactor on-board a vehicle. Moreover, the removal of carbon dioxide and carbon monoxide can be achieved very efficiently in a stationary plant. In this case, the vehicle is refuelled with hydrogen and the hydrogen storage problem will arise.

4 Hydrogen storage on board vehicles

Today, there are three principle storage technologies available: high-pressure storage, cryogenic storage and hydride storage [30].

Metal hydride contains hydrogen in the form of hydrides. The technical feasibility of hydride storage systems is controlled by the kinetics of the hydrating and dehydrating processes. Hydrides that will readily release their hydrogen at room temperature have reversible gravimetric H-densities no more than about 2 wt% (container not included). This is not sufficient for most fuel cell vehicles, at least in competition with compressed gas storage [31].

Cryogenic storage is also not a realistic option because of the extremely low temperature of 25 K to handle cryogenic hydrogen liquid on board vehicles.

High pressure storage is applied in demonstration projects with buses within the EU-program FP6 and is the most promising storage technology, using steel and all-composite pressure vessels. The latter consist of carbon fibre where a thin plastic or metallic (e.g. aluminium) liner guarantees the leak tightness of the system. The weight and the volume of the vessels determine their usefulness for mobile applications. This high-pressure storage is compared with the petrol storage.

The weight of a steel vessel completely filled with 50 dm^3 petrol is approximately 50 kg [32]. A 200 bar 50 dm^3 composite pressure vessel weighs approximately 25 kg, whereas a 200 bar 50 dm^3 steel vessel weighs 85 kg; both containing 0.7 kg hydrogen (200 bar is the maximum pressure by law in the Netherlands). The amount of energy of 50 dm^3 petrol is equal to 18.6 kg hydrogen [32]. To transport this quantity of 200 bar hydrogen, the weight and the volume of the required steel vessels are 1869 kg and 1,328 dm^3, respectively, and those of the required composite vessels 664 kg and 1,328 dm^3, where the contribution of hydrogen to the weight is neglected. In 1975, it was mentioned [32] that the weight of the required steel vessels including the 200 bar content was equal to 1,000 kg.

The influence of increasing the operating pressure of composite vessels is significant. A pressure increase from 200 to 700 bar needs a weight increase of a composite vessel from 25 to 85 kg (a factor of 3.4), where the stored hydrogen weight increases from 0.7 to 2 kg (a factor of 2.9). This means that a pressure increase has practically no effect on the weight of the total hydrogen storage system with composite vessels, but gives a clear decrease in volume. To make the high-pressure hydrogen acceptable a further reduction in vessel weight and volume is necessary.

5 Conclusions

- Electrochemical hydrogen formed by electrolysis can be used as fuel in fuel cells.
- Chemical hydrogen formed by conversion of methanol, ethanol and methane is not useful, unless after thorough purification; the carbon monoxide content must be lower than 1 ppm.
- Chemical conversion of methanol on board cars and busses to produce hydrogen with sufficient purity is not attainable in practice.
- Hydrogen storage problem for cars and buses has not been solved in a proper sense; the weight and the volume are much too high.
- Use of hydrogen as fuel is a waste of energy; electric vehicles are to be preferred for short distances.

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