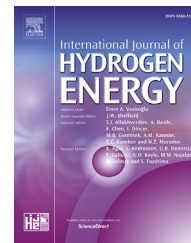


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Electrochemical reforming of dimethoxymethane in a Proton Exchange Membrane Electrolysis Cell: A way to generate clean hydrogen for low temperature fuel cells

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ABSTRACT

The electro-oxidation of dimethoxymethane (DMM), leading to the generation of clean hydrogen, was carried out at a Pt–Ru anode for several concentrations and different temperatures in a Proton Exchange Membrane Electrolysis Cell, based on a Direct Methanol Fuel Cell configuration.

At given concentrations of DMM (0.5–4 M) and cell temperatures (25–85 °C) the quantity of produced hydrogen and the voltage of the electrolysis cell were recorded as a function of time for any current intensity used (from 5 to 800 mA). The cell voltage stabilizes after 15 min and never exceeds 0.50 V corresponding to electrical energy consumption lower than 1.1 kWh (Nm³)⁻¹.

The quantity of hydrogen produced is a linear function of the current density and of the electrolysis time, i.e. of the quantity of electricity consumed in the electro-oxidation reaction. Therefore the quantity of hydrogen produced at a given electrolysis time (15 min here) depends only on the current intensity, regardless of the DMM concentration, the cell voltage and its temperature. On the other hand the electrical energy consumed is proportional to the cell voltage, so that it greatly depends on the kinetics of the anodic reaction at a given current density.

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Introduction

Technological civilization needs more and more energy, particularly in emerging and developing countries. Fossil resources, such as coal, natural gas and hydrocarbons, are the

main primary energy sources, but their amount is limited and will be exhausted in a few decades. Furthermore their combustion in air oxygen is the main contribution to carbon dioxide emission leading to greenhouse effect. An alternative energy source and carrier is hydrogen, which strongly limits the production of greenhouse gases, depending on the

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primary sources used for its fabrication. Using electricity from renewable energy sources, such as hydroelectric power, wind, solar or tidal power, the production of hydrogen by water electrolysis [1] is the cleanest process, leading to high purity hydrogen, containing less than 5–10 ppm of carbon monoxide (CO). Then hydrogen can be electrochemically converted into electricity in a fuel cell, such as the Proton Exchange Membrane Fuel Cell (PEMFC) or the Alkaline Fuel Cell (AFC) [2]. However the production of hydrogen by water electrolysis is still not competitive with the main production processes which are based on steam methane reforming (SMR), or partial oxidation of natural gas or hydrocarbons. This results from the fact that the electrolysis cell voltage is very high (1.6–2.0 V) due to the high overvoltages occurring at the catalytic anode [3]. This leads to production costs much higher than those encountered in the thermal decomposition of hydrocarbons, e.g. SMR, since the energy needed (typically 50 kWh kg⁻¹) is greater than the theoretical value of 33 kWh kg⁻¹ (at a standard cell voltage of 1.23 V), corresponding to an electrical energy efficiency lower than 65%.

Instead of water other hydrogen containing compounds (such as those derived from biomass) can be used as an alternative source of hydrogen, leading to clean molecular hydrogen by their electro-oxidation in the so-called electrochemical reforming process [4–6]. A recent review paper by Sapountzi et al. [7] discussed the electrochemical reforming of C1–C3 alcohols using a PEM electrolyzer leading to the production of high purity hydrogen. This is a very interesting approach, because the theoretical cell voltage for their electro-oxidation is much lower than that of water (1.23 V under standard conditions). Therefore many organic compounds, such as carboxylic acids, e.g. formic acid [8,9], low weight alcohols [7,10], (e.g. methanol [11–18], ethanol [19–21], ethylene-glycol [22], glycerol [23–26]), sugars (glucose [25], etc.), have been considered to produce clean hydrogen by their electrochemical reforming. But if most of their electro-oxidation reactions can occur at a very low cell voltage (close to 0 V under standard conditions) their electrochemical decomposition requires usually higher cell voltages, under working conditions, which comes from the high anodic overvoltages encountered, and which can be reduced only by the right choice of an active and specific electrocatalyst.

Besides, other organic compounds can be conveniently used for producing clean hydrogen by their electrochemical oxidation, particularly those derived from methane (natural gas, shale gases, etc.) or from methanol (mainly produced by the conversion of “syngas”), such as the dimethyl ether DME (CH₃OCH₃), the dimethoxymethane DMM [(CH₃O)₂CH₂] and the trimethoxymethane TMM [(CH₃O)₃CH]. The syngas (mixture of carbon monoxide CO and hydrogen H₂) can be produced by SMR [27], coal gasification and flash pyrolysis or gasification of biomass compounds [28,29].

In particular, DMM, which can be directly synthesized from methanol [30,31], is a very interesting compound which has several applications, e.g. perfume manufacturing, resins, adhesives, paint strippers and protective coatings. Indeed DMM is liquid at room temperature, since its boiling point is 42 °C. DMM is also considered as a potential alternative fuel and fuel additive due to its high oxygen content. Moreover it has also been investigated as a fuel in a Direct Oxidation Fuel Cell

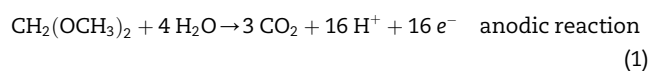
[32–36], since its complete electrooxidation into CO₂ only involves breaking of C–H and C–O bonds, which is easier than breaking C–C bonds in most alcohols (except methanol). Furthermore due to its hydrolysis in acidic medium (see Section Principle of DMM electro-oxidation in a PEMEC) leading to methanol or formaldehyde through a reaction mechanism involving the formation of (–OCH₃)_{ads} adsorbed species, its electrocatalytic oxidation at Pt-based electrodes is easier than that of methanol under similar experimental conditions. Although its electrooxidation can occur with a convenient catalyst (e.g. Pt/C or Pt–Ru/C nanoparticles supported on a carbon powder) [37,38], DMM seems to have never been used as a hydrogen precursor allowing producing clean hydrogen by its electrocatalytic oxidation.

In this work the production of clean hydrogen by the electrochemical reforming of DMM was carried out in a Proton Exchange Membrane Electrolysis Cell (PEMEC) based on Direct Methanol Fuel Cell (DMFC) configuration. The Pt/C oxygen cathode of the DMFC can be used as a reference electrode when the cathodic compartment is filled with gaseous hydrogen under 1 bar pressure. It is thus possible to record cyclic voltammograms and polarization curves of DMM oxidation, which allows investigating its oxidation kinetics at the catalytic Pt–Ru/C anode of the DMFC configuration. The electrolysis of DMM was carried out at a constant current intensity (from 5 mA to 800 mA) with different concentrations of DMM (0.5 M–4 M) at several cell temperatures (25–85 °C). Both the cell voltage of the electrolysis cell and the amount of hydrogen produced were recorded at each current intensity.

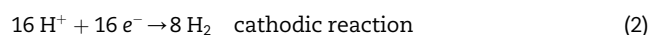
Principle of DMM electro-oxidation in a PEMEC

The electrochemical splitting of DMM for producing clean hydrogen is realized through its oxidation in a PEMEC of configuration similar to water electrolysis (Fig. 1).

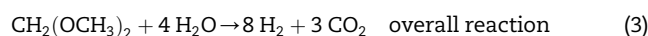
The electro-oxidation of DMM can be carried out at the Pt–Ru/C catalyst of the anodic compartment of the DMFC layout, leading to carbon dioxide and protons [reaction (1)]:



Then the protons produced cross-over the proton exchange membrane and are reduced to molecular hydrogen, at the Pt/C catalyst of the cathodic compartment of the DMFC, by the electrons arriving from the external circuit [reaction (2)]:



The electrical balance between reactions (1) and (2) leads to the following overall reaction:



Reaction (3) corresponds to the electrochemical splitting of DMM producing hydrogen and carbon dioxide.

The electrochemical decomposition of DMM is thus similar to a steam reforming process, but this reaction can occur at relatively low temperatures (25–85 °C) instead of the high temperatures encountered in steam DMM reforming.

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