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In situ hydrogen utilization in an internal reforming methanol fuel cell

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ABSTRACT

In this work, we report on the catalytic properties of a novel ultrathin methanol reformer incorporated into the anode compartment of a High Temperature PEM Fuel Cell (HT-PEMFC). A highly active Cu-based methanol reforming catalyst (HiFuel R120, Johnson Matthey) was deposited on the gas diffusion layer of a carbon paper and the influence of anode flow distribution through the catalytic bed was studied in the temperature range of 160–220 °C. Inhibition by produced H₂ is higher in the case of through plane flow, especially in more concentrated methanol feeds. Higher methanol conversions were achieved with the in-plane flow distribution along the catalytic bed (>98% at 210 °C and without any deactivation for at least 100 h test), with a 50 cm² reformer (total thickness = 600 μm). The corresponding Internal Reforming Methanol Fuel Cell (IRMFC) operated efficiently for more than 72 h at 210 °C with a cell voltage of 642 mV at 0.2 A cm⁻², when 30% CH₃OH/45% H₂O/He (anode feed) and pure O₂ (cathode feed) were supplied.

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Introduction

There are a number of reasons which require the design and development of compact and friendly to the end user, fuel processor–fuel cell energy systems for portable applications. These reasons are briefly the following:

- Simplification of fuel processor–fuel cell unit via (i) high temperature (>200 °C) operation of PEM fuel cell and (ii) incorporation of fuel processor in the fuel cell stack. These are also related to additional advantages concerning steam, heat (the “waste” heat produced by the fuel cell is

in-situ utilized to drive the endothermic reforming reaction) and air management and volume reduction.

- The increasing demands for high energy and high power sources in a variety of portable applications with respect to cost effective long term and safe operation at wide environmental temperatures and any orientation.
- Utilization of methanol as primary hydrogen carrier offers higher energy densities and overcomes technical obstacles associated with the use, storage and transportation of pure hydrogen, while it may be derived from renewable energy sources. In such a case, a full environmental benefit is achieved, because no CO₂ emissions are added to the atmosphere, and fossil energy resources are preserved.

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Aforementioned issues may be technologically approached and satisfied via an Internal Reforming Methanol Fuel Cell (IRMFC) [1–6]. IRMFC is an attractive configuration which takes advantage of the HT-PEMFC features and incorporates the methanol reformer inside the fuel cell, so that methanol reforming takes place inside the fuel cell stack (Internal Reforming). The proposed system does away with conventional fuel processor–fuel cell systems in terms of (i) operation temperature, (ii) reformer utilization, (iii) heat management, (iv) cost–volume–weight effectiveness. The latter factor with respect to the corresponding power density makes IRMFC very attractive for emerging commercial/military portable applications. The functionality of IRMFC concept has been already demonstrated and operational parameters for further improvement and optimization have been identified [1–6]. These are: (i) the activity/stability of the reforming catalyst at temperatures lower than 220 °C, (ii) the phosphoric acid poisoning of the reformer, (iii) the thermal stability of the membrane for operation above 200 °C and (iv) the poisoning effect of unreacted methanol on the electrocatalyst and the proton conductivity of the membrane.

Recent advances in the design and development of polymer electrolyte membranes (e.g. ADVENT cross-linked TPS[®] high-temperature polymer electrolyte) and electrocatalysts allow the efficient operation of PEMFCs at 200–220 °C [7–9]. Beyond their good mechanical and chemical properties the aforementioned membrane type is the only one known to operate with H₃PO₄ doping level even below 200 wt.%. The low acid content of these membranes can result in limited phosphate anions adsorption on the active sites of the methanol reforming catalysts, thus diminishing its poisoning effect. Doping of these membranes with phosphoric acid resulted in materials with ionic conductivity in the range of 0.1 S cm⁻¹. Stable operation at 210 °C of a membrane electrode assembly (MEA) comprising a covalently cross-linked membrane with 500 h continuous operation was achieved, at 0.2 A cm⁻², with H₂/Air feed and an average voltage drop of only 3 μV h⁻¹. The cell voltage was 0.660 V and the corresponding power density was 0.132 W cm⁻².

On the other hand, efficient operation of IRMFC requires the development of highly active, stable and selective methanol reforming catalysts, which will be able to operate at temperatures as low as possible with minimal CO formation. Steam reforming of methanol (CH₃OH + H₂O ⇌ CO₂ + 3H₂, ΔH₀ = 49.4 kJ mol⁻¹) is an endothermic process that provides a product gas with high H₂ content (up to 75%) and low CO concentration (1–2%) at relatively low temperatures (200–300 °C) [10–15]. CO may be produced either as a primary product of direct methanol decomposition reaction, or as a by-product via decomposition of various formates, such as methyl formate, or via the reverse water–gas shift reaction.

In the case of the Internal Reforming Methanol Fuel Cell (IRMFC), the required heat for the reforming process will be supplied by the cell itself. Commercially available copper-based catalysts, typically with composition Cu–ZnO–(Al₂O₃) have been widely used for generating hydrogen from methanol [11–15]. PdZn-based catalysts have also been considered for methanol reforming process [16]. The high selectivity to CO₂, comparable to that reported for the well studied Cu-

based catalysts, was attributed to the strong chemical interaction between the noble metal and the support oxide that leads to the formation of a Pd–Zn alloy. However the cost of a fuel cell-based power system is a critical parameter that currently favors the use of Cu-based catalysts. Even though these catalysts are widely used in H₂ plants, they have not been designed for application in small stationary or portable/mobile fuel processors. Thus, optimization of Cu-based catalysts for the envisaged application is of primary concern. Taking into account the need of the presence of well dispersed metallic (reduced) Cu species as active sites for methanol adsorption and reaction, significant enhancement of copper oxide reducibility – especially under methanol/water feeds – is necessary at the cell operation level of around 200–220 °C. Additionally, improvement of the catalytic activity will allow the reforming catalyst to operate more efficiently at this temperature level.

In the present work, a novel ultrathin reformer based on a commercial catalyst (HiFuel R120) was incorporated into the fuel cell and tested under various methanol/water feedstreams in the temperature range of 160–220 °C. The proposed configuration may offer a significant decrease in the weight and volume of the whole power system, as compared with previous voluminous foam-based cells. The influence of in-plane or through-plane flow distribution through the catalytic bed was studied and the optimum configuration was tested in an integrated single cell, taking advantage of the most recent achievements on the development of Advent high temperature polymer electrolytes and MEAs [7–9].

Experimental

Methanol reformer

Highly active HiFUEL[®] R120 methanol reforming catalyst (CuZnAlOx) was purchased from Johnson Matthey in non-reduced form. The cylindrical pellets of CuZnAlOx were crushed and sieved (fraction <90 μm) and mixed with Vulcan[®] XC-72R (Cabot) in a weight ratio of 9:1, in order to improve contact resistance properties of the reformer during fuel cell operation. The obtained powder mixture was subjected to 1 h ball milling at 300 rpm using a planetary mill (Fritsch Pulverisette 7). A well-dispersed catalyst ink was prepared by mixing and stirring for 1 h at 7000 rpm in a Silverson SL2T stirrer, the CuZnAlOx/C powder with 1 wt.% Teflon binder (60 wt.% PTFE dispersion in water, DuPont) and appropriate amount of isopropanol (Sigma–Aldrich). After adequate stirring, the catalyst ink was added dropwise on the surface of gas diffusion layer (GDL) of carbon paper (Freudenberg H2315 – C2; thickness: 250 μm; hereafter called GDL/CP), using a vacuum table (Nuvant Systems) heated at 100 °C. Following this procedure, high catalyst loadings were successfully applied (42–90 mg cm²) on 25 and 50 cm² GDL/CP supports and ultrathin (thickness of the catalytic layer = 250–500 μm) and lightweight (1–4 g) reformers with good mechanical integrity were produced. The catalytic layer was in-situ activated under MeOH/H₂O reaction mixture at temperatures lower than 220 °C.

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