



Insights on the effective incorporation of a foam-based methanol reformer in a high temperature polymer electrolyte membrane fuel cell



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HIGHLIGHTS

- Highly active Al-doped CuMnO_x low temperature methanol reforming catalysts.
- Scale-up synthesis of catalyst-coated metallic foams via in-situ combustion method.
- Incorporation of the reforming catalyst into the HT-PEM fuel cell.
- Special fuel cell design to avoid undesired reaction of the reformer with H₃PO₄.
- Improved functionality of the unit demonstrated in a single-cell prototype.

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ABSTRACT

Highly active Al-doped CuMnO_x catalyst supported on metallic copper foam was prepared via the combustion method and placed adjacent to the anode electrocatalyst of a high temperature PEM fuel cell operating at 200–210 °C. The addition of aluminum oxide in the catalyst composition enhanced the specific surface area (19.1 vs. 8.6 m² g⁻¹) and the reducibility of the Cu–Mn spinel oxide. Accordingly, the catalytic performance of CuMnO_x was also improved. The doped sample is up to 2.5 times more active than the undoped sample at 200 °C, depending on the methanol concentration at the inlet, while CO selectivity is less than 0.8% in all cases. A membrane-electrode assembly comprising the ADVENT cross-linked TPS[®] high-temperature polymer electrolyte was integrated with the Cu-based methanol reformer in an Internal Reforming Methanol Fuel Cell (IRMFC). In order to avoid extensive poisoning of the reforming catalyst by H₃PO₄, a thin separation plate was placed between the reforming catalyst and the electrooxidation catalyst. Preliminary results obtained from a single-cell laboratory prototype demonstrated the improved functionality of the unit. Indeed, promising electrochemical performance was obtained during the first 24 h, during which the required H₂ for achieving 580 mV at 0.2 A cm⁻², was supplied from the reformer.

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1. Introduction

Methanol may offer considerably higher volumetric energy densities than either batteries or fuel cells operating on compressed H₂, making it an attractive energy carrier for advanced

portable power systems. It can be easily stored, transported and dispensed, and, at the same time, it can be efficiently produced from a wide variety of (renewable) sources [1]. A reformed methanol fuel cell is a type of indirect methanol fuel cell, in which methanol is initially converted to hydrogen in a methanol reformer, and then the hydrogen rich gas is sent to a hydrogen/air fuel cell to generate electricity. The process of methanol reforming must be carried out at 250–300 °C in order to obtain more than 90% fuel conversion efficiency and 50% hydrogen molar fraction [2]. However, the state-of-the-art H₂/air fuel cell in the RMFC can operate

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only between 160 and 180 °C and more recently up to 210 °C [3]. There is a mismatch of the operating temperatures between the fuel cell and the reformer, while many auxiliary balance-of-plant components are needed for each of the subsystems, since they are present as separate components. Furthermore, these components not only consume additional energy, but also increase the total system weight and volume, thus reducing the final energy efficiency to less than 30%. Similarly, low temperature DMFCs, though more compact as they do not include a methanol reformer, they also suffer from low efficiencies (<20%) and low power densities due to slow kinetics.

On the other hand, there are several advantages of integrating the reformer into the fuel cell [2–6]:

- Simplification of design. The reformer is placed into the stack, eliminating the need for a separate fuel processor and heat exchangers thus contributing significantly to the stability of the system.
- Increased overall efficiency. In contrast to a conventional PEM fuel cell fed by reformed fuel, the internal reforming fuel cell does not require burning of fuel to drive the reforming reaction because it uses directly the excess heat created by the fuel cell. In addition, a heat exchanger is not needed because the reforming catalyst is in direct contact with the heat source.
- Minimization of system weight and volume due to elimination of the WGS and PROX reactors.
- The option of in-situ “pumping” of H₂ from the reforming catalyst via its oxidation by the anode electrocatalyst, enhances the reforming reaction kinetics and results in smaller mass of catalyst (a common kinetic aspect of methanol reforming catalysts is H₂ inhibition).

Several attempts have been reported in the past for the construction of compact integrated PEMFC reformers either by the introduction of reforming catalyst in the flow channels of the bipolar plate [2] or with the placement of small reformers in thermal contact with the stack [7]. Non-uniform flow distribution and reforming catalyst deactivation by phosphoric acid leaching were not an issue in the case of the integrated HT-PEM fuel cell – methanol reformer reported by Pan et al. [8]. However, high contact times are required in order to achieve complete methanol conversion at low temperatures since the reformer is not placed into the anode compartment and does not take advantage of in-situ extraction of H₂ by the anode electrocatalyst. Therefore, an integrated system is expected to improve system efficiency and simplify system construction and operation, as compared with conventional fuel cell – reformer systems. Recently, a direct alcohol fuel cell using a solid acid electrolyte and internal reforming catalyst has been reported by Haile and Uda [9]. This fuel cell comprises an anode, a cathode, a solid acid electrolyte and an internal reformer positioned adjacent the anode. Such an integrated configuration resulted in an increased power density and cell voltage compared to direct alcohol fuel cells not using an internal reformer. The electrolytes used in these fuel cells are of the solid acid type (e.g. CsH₂PO₄), which enable operation at high temperatures (200–350 °C) where the Cu–Zn–O reforming catalysts are active.

Recently, we demonstrated the functionality of an Internal Reforming Methanol Fuel Cell (IRMFC), in which methanol is reformed by CuMnO_x catalyst incorporated into the anode compartment of a high temperature PEM fuel cell [3–6]. The catalyst was supported on aluminum or copper foam monolithic structures and was directly attached to the anodic electrode aiming at increased catalyst loadings and good electronic conductivity. Though the catalysts exhibited appreciable catalytic activity, one of the main practical drawbacks is the requirement of an ex-situ

preactivation step (reduction) at temperatures higher than 250 °C. This is followed by a passivation step at room temperature before catalyst exposure to ambient atmosphere and incorporation into the anode compartment of the fuel cell. Additionally, a high amount of catalyst should be loaded within the pores of the metal foams in order to achieve the necessary hydrogen production rates for efficient operation of the fuel cell at 200–210 °C with a current density of 0.2 A cm⁻². Based on this preliminary work, specific parameters influencing the efficiency of the IRMFC have been identified as follows: (i) the activity of the reforming catalyst at temperatures as low as 210 °C, (ii) the enhancement of the catalytic reforming rate by the concomitant removal of H₂ through the membrane-electrode-assembly (MEA) of the fuel cell, (iii) the inhibiting effect of methanol on the MEA's performance and (iv) the thermal stability of the polymer electrolyte membrane for operation above 200 °C. The main drawback of the above configuration is the severe poisoning of the MEA when exposed to methanol partial pressures higher than 3 kPa [10,11]. Based on the polarization curves and the characteristics of the electrochemical impedance spectra of the proposed IRMFC, the poisoning effect was attributed to adsorbed species derived from methanol adsorption on the anode electrocatalyst and the negative effect on the proton conductivity of the membrane [11]. In addition, increased steam partial pressure (>10 kPa) –even under pure H₂ conditions–has a negative effect on the anode's performance [12].

Recently, stable operation of a MEA comprising the ADVENT cross-linked TPS[®] high-temperature polymer electrolyte was achieved at 210 °C and 0.2 A cm⁻² for 500 h with H₂/Air feed and an average voltage drop of only 3 μV h⁻¹ [13–15]. The cell voltage was 0.660 V and the corresponding power density 0.132 W cm⁻². Despite the higher operating temperature of the MEA, the negative effect of unreacted methanol is still an issue and higher methanol conversion should be achieved by the reforming catalytic bed.

An additional drawback arises from the direct contact of methanol reformer with the MEA. As it will be shown below the strong acidic environment prevailing inside the cell and especially the H₃PO₄ vapors cannot be tolerated by the reforming catalyst [16]. These MEAs are based on high-temperature polymer electrolytes imbibed with phosphoric acid at levels of 200 wt.%, thus providing the required proton conductivity [13–15]. Furthermore, phosphoric acid is also added into the electrocatalytic layer creating ionic pathways and effective electrochemical interface. In addition, the metallic foam substrate is also sensitive to phosphoric acid attack and gradual corrosion will result to higher contact electronic resistance and lower power output.

In this work, we report on the enhanced catalytic properties of Al-doped CuMnO_x methanol reforming catalyst supported on metallic copper foam and its deactivation due to H₃PO₄ vapors that originate from the MEA. In addition we analyze the functionality of a modified anode arrangement in order to avoid the negative effect of phosphoric acid.

2. Experimental

2.1. Methanol reformer

Incorporation of the reforming catalyst into the HT-PEM fuel cell (Fig. 1) was carried out with the aid of copper metal foams which offer a wide variety of advantages mainly related to reduced pressure drop, mechanical integrity, improved heat and electron transfer. Synthesis of CuMnAlO_x-coated metallic foams was carried out via an in-situ combustion method [17,18]. Details of the synthesis procedure are given in the [Supplementary Material](#). The CuMnAlO_x foam catalyst was finally coated with a thin layer (~300 μm) of carbon/teflon (70/30) paste in order to minimize

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