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CuMnOx catalysts for internal reforming methanol fuel cells: Application aspects

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ABSTRACT

The Internal Reforming Methanol Fuel Cell (IRMFC) incorporates a methanol reforming catalyst into the anodic compartment of a high temperature, polymer electrolyte membrane fuel cell (HT-PEMFC). The present work examines application aspects of the cell, including the operation temperature, the type of catalyst pretreatment, the effect of phosphoric acid leaching and the time-on-stream behavior of CuMnOx catalysts. Combustion-synthesized structured catalysts can efficiently operate at 200 °C with a 30% decline in MeOH conversion after 350 h on methanol/water stream in the presence of the high temperature polymer electrolyte membrane electrode assembly. Differences observed in the catalytic activity of oxidized versus prerduced samples with respect to phosphoric acid poisoning are negligible after long operation time.

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1. Introduction

The internal reforming alcohol fuel cell (IRAFC) is a type of high temperature polymer electrolyte membrane fuel cell (HT-PEMFC), in which the alcohol reforming catalyst is incorporated into the anode compartment [1–3]. Alcohol (methanol, for example) gets reformed by the catalyst inside the cell (internal reforming). Integration of the reformer into the fuel cell eliminates the need for additional heat exchangers and a separate fuel processor. Especially in the case of methanol as starting fuel, WGS and PrOx reactors are not necessary since (i) high temperature operation (i.e. 180–220 °C) enables utilization of lower quality reformat feeds containing up to 2–3% CO and (ii) the “waste” heat produced by the fuel cell is in-situ

utilized to drive the endothermic reforming reaction. Thus, the design of the fuel processor-fuel cell system offers room for simplification, increase of efficiency and minimization of system weight and volume.

Alcohol fuels and, more specifically methanol, are attractive chemical sources of hydrogen, since they can be easily stored, transported and dispensed, and, at the same time, they can be efficiently produced from a wide variety of sources including fossil fuels, but also agricultural products and municipal waste, wood and biomass, in general [3–7]. More importantly, they can be also made through chemical recycling of carbon dioxide. Methanol has 5–7 times higher energy density than compressed H₂. Moreover, it has low sulfur content and can be reformed to hydrogen rich mixtures with

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low CO byproduct formation at the temperature level of IRAFC.

H₂ can be catalytically produced from methanol via steam reforming (SRM: CH₃OH + H₂O ⇌ CO₂ + 3H₂) at relatively low temperatures (200–300 °C) with high selectivity [1,4,7–10]. In the case of the integrated PEM fuel cell system, the required heat for the SRM 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 [4,5,7]. 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. It is well established that the activity and CO selectivity of Cu-based catalysts is greatly dependent on their morphology (high copper dispersion is desirable) and the redox properties of the catalyst. 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 °C. Additionally, improvement of the catalytic activity will allow the reforming catalyst to operate more efficiently at the target IRAFC temperatures. In addition to catalyst activity, optimization of the catalyst formulation should take into account (i) the CO selectivity, (ii) the stability/deactivation in respect to coke formation or phosphoric acid leaching from polymer electrolyte membrane and (iii) pyrophoricity parameters.

Recently, a single-cell (Internal Reforming Methanol Fuel Cell, IRMFC) incorporating ADVENT TPS[®] phosphoric-acid-doped copolymer membrane and a CuMnOx/Cu foam methanol reforming catalyst in the anode was constructed and tested at 200 °C demonstrating the functionality of the unit (Fig. 1) [1–3]. In view of the IRMFC implementation, important improvements of reforming catalysts are required regarding their efficient operation at temperatures around 200 °C. In order to cope with the above operating framework we have reported on the application of combustion-synthesized CuMnOx catalysts for methanol reforming process. In the present study, CuMnOx catalyst synthesis in powder and monolithic form was carried out via the combustion method. Detailed screening of the catalysts was performed under conditions relevant to the proposed application taking into account the following parameters: temperature (focus at around 200 °C), type of pretreatment, effect of phosphoric acid leaching and time-on-stream. Selected reforming catalysts were introduced in the anode compartment of an IRMFC and tested for their chemical stability.

2. Experimental

2.1. Synthesis of methanol reforming catalysts

The urea–nitrates combustion method (Fig. 2) was used for the synthesis of CuMnOx spinel oxide catalysts [11]. Urea [CH₄N₂O] with manganese nitrate [Mn(NO₃)₂·6H₂O] and copper nitrate [Cu(NO₃)₂·3H₂O] were mixed in an alumina crucible in the appropriate molar ratios (Cu/(Cu + Mn) = 0.30,

75% excess of urea) in a minimum volume of distilled water to obtain a transparent solution. The values for copper loading and initial amount of urea were selected from our previous studies on these catalytic systems prepared with the same technique and tested for the methanol reforming process [11,12]. The mixed solutions were heated for a few minutes at 80 °C, so that excess water was removed. The resulting viscous gel was introduced in an open muffle furnace, preheated at 400–500 °C, in a fuming cupboard. The gel started boiling with frothing and foaming, and in a couple of minutes ignited spontaneously with rapid evolution of a large quantity of gases, yielding a foamy, voluminous powder. In order to burn-off carbon residues and form well-crystalline structure, the powders were further heated at 550 °C for 1 h (CuMn-ox samples). A half portion of the prepared batch was reduced at 350 °C under H₂ flow (CuMn-red samples). All the obtained powders were sieved to obtain the desired size, with diameter between 90 and 180 μm.

CuMnOx catalysts supported on Cu metal foam (Changsha LYRUN New Material Co., Ltd.; 30 ppi (pores per linear inch) porosity; 7 mm thickness; 4000 g m⁻² density) were also prepared via the in-situ combustion method [1,13] in order to test the stability behavior with reaction time in the presence or absence of an ADVENT TPS[®] high temperature polymer electrolyte membrane electrode assembly.

2.2. Treatment of combustion-synthesized CuMnOx catalysts with phosphoric acid vapors

Since the reforming catalyst should be resistant toward deactivation caused by phosphoric acid (i.e. H₃PO₄ leaching from membrane electrode assembly), combustion-synthesized CuMnOx samples (both oxidized and reduced) were exposed to phosphoric acid vapors in a teflon autoclave vessel (Fig. 3). 750 mg of CuMn-ox and CuMn-red samples were placed on the bottom of a pyrex fritted disc assembly and treated hydrothermally in a teflon autoclave containing 15 ml of 85% H₃PO₄. The vessel was heated at a rate of 2 °C min⁻¹ to the desired temperature level (150 or 200 °C) where it was kept for 5 h. Following this treatment, the autoclave was opened and the samples were dried at 120 °C for 12 h. In order to facilitate the presentation of results, the following encoding of catalysts is used: CuMn-ox or red-P150 or 200, denotes the oxidized or reduced sample treated with H₃PO₄ vapors either at 150 or 200 °C. For example, the CuMn-red-P200 sample was prereduced at 350 °C under H₂ flow and treated at 200 °C with H₃PO₄ vapors.

2.3. Redox catalyst properties

In-situ XRD measurements (X-ray powder diffractometer: Bruker D8 Advance using Cu K_α radiation with λ = 0.15418 nm) were carried out on selected CuMnOx catalysts. Temperature programmed reduction (TPR) and oxidation (TPO) experiments were performed under H₂ and O₂ flows. Two different sets of experiments were performed. The applied experimental conditions were the following:

- (A) Isothermal reduction with H₂ at 200 °C
□ heating 30 °C → 200 °C (6 °C min⁻¹), 5% H₂/N₂, 60 ml min⁻¹

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