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Short communication

New, efficient and viable system for ethanol fuel utilization on combined electric/internal combustion engine vehicles

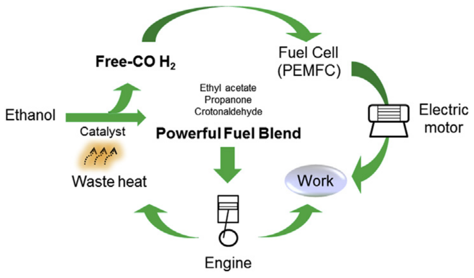
André G. Sato [a], Gabriel C.D. Silva [b], Valdecir A. Paganin [b], Ana L.G. Biancolli [b], Edson A. Ticianelli [b], *

[a] *Department of Chemistry, Universidade Federal de Viçosa, Av. P.H. Rolfs w/n, CEP 36570-000, Viçosa, MG, Brazil*
[b] *Department of Physical Chemistry, IQSC, Universidade de São Paulo, Av. Trabalhador Saocarlense 400, CEP 13560-970, São Carlos, SP, Brazil*

HIGHLIGHTS

- An ethanol dehydrogenation reactor for producing hydrogen is coupled to a PEMFC.
- A liquid effluent of the reactor can be used as fuel for internal combustion engines.
- Power densities near to those of a PEMFC operating with pure hydrogen are attained.
- The hybrid system is feasible and leads to an increase of ethanol energy utilization.

GRAPHICAL ABSTRACT



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ABSTRACT

Although ethanol can be directly employed as fuel on polymer-electrolyte fuel cells (PEMFC), its low oxidation kinetics in the anode and the crossover to the cathode lead to a substantial reduction of energy conversion efficiency. However, when fuel cell driven vehicles are considered, the system may include an on board steam reformer for converting ethanol into hydrogen, but the hydrogen produced contains carbon monoxide, which limits applications in PEMFCs. Here, we present a system consisting of an ethanol dehydrogenation catalytic reactor for producing hydrogen, which is supplied to a PEMFC to generate electricity for electric motors. A liquid by-product effluent from the reactor can be used as fuel for an integrated internal combustion engine, or catalytically recycled to extract more hydrogen molecules. Power densities comparable to those of a PEMFC operating with pure hydrogen are attained by using the hydrogen rich stream produced by the ethanol dehydrogenation reactor.

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1. Introduction

The technical/economical feasibility of fuel cell driven electric and hybrid vehicles should still overcome inherent challenges of the so-called “hydrogen economy”, such as the production of hydrogen and its distribution infrastructure, as well as on issues related to on board hydrogen storage. Methanol has been considered an interesting fuel candidate for fuel cells [1]. However, the usage of biomass-derived ethanol [2] may represent a superior choice since it is a less volatile liquid at room temperature and allows the establishment of a sustainable fuel cycle.

Low-temperature proton-exchange membrane fuel cells (PEMFC) can be directly operated with ethanol, but the kinetics of ethanol oxidation and the problems of its transport from the anode

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* Corresponding author.
E-mail address: edsont@iqsc.usp.br (E.A. Ticianelli).

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to the fuel cell cathode [3,4] lead to much lower performance when compared to devices operated directly with the hydrogen gas [5]. In this way, the direct electrochemical oxidation of ethanol in PEMFC has resulted in very low power densities (<0.100 W cm^{-2}) [6] compared to conventional PEMFC fed with pure hydrogen (~0.700 W cm^{-2}) [5]. Besides the crossover effect, the difficulty of C–C bond cleavage [7] at a low temperature (80–120 °C) and also to oxidize CO at low electrode overpotentials [4], are the main hurdles for the viability of this direct ethanol fuel cell (DEFC) system. Even when operated at 200 °C with polybenzimidazole (PBI) based-DEFC, the performance is smaller than that of the conventional PEMFC fed with pure hydrogen [8], particularly because the proton conductivity of the polymer electrolyte, usually Nafion (E.I DuPont), is much better than PBI [9].

A well-developed method to produce hydrogen from ethanol is the steam reform of ethanol (SRE) process [10], usually operated at high temperatures to minimize coke deposition in the catalyst and to obtain high hydrogen yields. Nevertheless, SRE forms CO due to the occurrence of thermodynamically favored reverse water-gas shift (WGS) process. Even though there are methods of purifying the reformed hydrogen stream (by preferential oxidation of CO [11] or WGS [12], or by filtering devices involving the use of a H_2-selective membrane) [13], the PEMFC can tolerate less than 10 parts per million (ppm) of CO [14]. In addition, formation of CO_2 in the SRE introduce several problems regarding possible utilization of the reformate hydrogen on alkaline fuel cell systems.

Our long term interest in ethanol fuel cells [15], and systems for releasing hydrogen from ethanol [16], led us to identify an active catalyst [17] for hydrogen and ethyl acetate formation from ethanol in one-pot stepwise. In this process, ethanol can be converted to ethyl acetate with selectivity above 80% [18] by an endothermic process;

$$2C_2H_5OH \rightarrow CH_3COOC_2H_5 + 2H_2$$

in a coupling dehydrogenation process (250 °C) facilitated by a copper-based catalyst. It is well known that copper does not promote the C–C bond scission [19], and so the ethanol dehydrogenation generates a H_2 flow free of either CO and CO_2. The catalytic interface properties of copper–ZrO_2 might be optimized to lead ethanol conversion to ethyl acetate in detriment of acetaldehyde.

In this work, we introduce a new, efficient and viable system for ethanol fuel utilization, comprising a catalytic dehydrogenation reactor, coupled to a PEMFC and to an internal combustion engine, as shown in Scheme 1. In this system, a hydrogen rich stream instantaneously produced by ethanol dehydrogenation facilitated by a copper-based catalyst is fed to a PEMFC. The liquid by-product effluent of the reactor (condensed at −1.5 °C) can be used as fuel for internal combustion engines, or recycled catalytically to extract more hydrogen molecules or even added to gasoline or diesel oil. The thermal energy required for the dehydrogenation catalytic reactor unit may be supplied by the heat discharged by the exhaust gas of combustion in a hybrid automobile.

2. Experimental section

Commercial grade monoclinic zirconia (ZrO_2, Saint-Gobain NorPro) was used as support. Cu/ZrO_2 sample was prepared by incipient wetness impregnation of the support with a solution of ($Cu(NO_3)_2 \cdot 2.5H_2O$, 98%; Aldrich) in methanol. The mixture was stirred in a round-bottomed flask under ultrasonic bath coupled with a rotary evaporation. The solid was dried at 100 °C overnight and calcined from room temperature to 400 °C at a heating ramp of 10 °C min^{-1} and a dwell time of 5 h under synthetic air flow (100 mL min^{-1}), so to produce CuO_x deposited ZrO_2 (CuO_x/ZrO_2). The nominal amount of Cu was 10 wt.% with respect of ZrO_2.

PEMFC single cell studies were performed with membrane and electrode assemblies (MEA) prepared with standard gas diffusion electrodes containing Pt/C catalysts (20 wt.% Pt/C, E-TEK) for the anodes and cathode [23]. Both anode and cathode electrodes (1.00 cm^2, each) contained 0.4 mg cm^{-2} of metal loading. The electrocatalyst was dispersed in 2-propanol together with an amount of Nafion solution (Aldrich, 5.5% on aliphatic alcohols) in order to provide 35.5% (w/w) of Nafion with respect to the final catalyst mass. This was left in an ultrasonic bath for 20 min, after which the solvent was evaporated to dryness. The resulting powder was dispersed in 2-propanol to form an ink, which was quantitatively deposited by a brushing procedure in one of the faces of the gas diffusion later (GDL). The electrodes were hot pressed on both sides of a Nafion 115 membrane at 125 °C and 5 MPa for 2 min. The MEA was then placed between graphite plates with serpentine-type channels for the fuel gas circulation. Single cell polarization measurements were conducted at a temperature of 70 °C and by using H_2/O_2 humidified at the cell temperature, under atmospheric pressures. These conditions were employed because of the difficulties of pressurizing the catalytic ethanol reactor, as described below.

The ethanol dehydrogenation reaction was carried out in a continuous-flow, tubular fixed-bed glass reactor (10 mm i.d.) at a temperature of 250 °C, under atmospheric pressure. Prior the reaction, the CuO_x/ZrO_2 sample was reduced *in situ* by heating in pure H_2 flow from room temperature to 250 °C at 10 °C.min^{-1} staying at this temperature for 120 min, resulting the final desired product Cu/ZrO_2. The ethanol reactions were carried out with 1 g of the Cu/ZrO_2 catalyst. The feed was a constant flow in the range of 4, 8, 16 and 20 mL h^{-1} of liquid ethanol (99,9%) introduced into the reactor via a syringe pump, mixed with pure Argon gas (10 mL h^{-1}) resulting in W/F = 19, 9.5 and 4.75 and 3.80 g_{cat} min g^{-1}_{EtOH} (the unit was simplified to min). Additionally, W/F = 1.2 and 38 min were obtained with ethanol in gas phase by passing He flow through a saturator immersed in a water bath at a temperature at 55 °C. The gas effluent was collected periodically and analyzed by on-line gas chromatography (Shimadzu GC-2014) with a Porapak Q column. The liquid effluent leaving the ethanol reactor was trapped by a cold condenser at −1.5 °C, and periodically analyzed by high-performance liquid chromatography (Shimadzu HPLC) with refractive index (RID-10A) and UV–VIS (SPD-20A) detectors in an AMINEX HPX-87H column. Heats of combustions of the liquid effluents were obtained employing a bomb calorimeter IKA (WERKE C2000 Basic), using a weight of liquid samples of about 500 mg. The data were collected at 25 °C and atmospheric pressure.

3. Results and discussion

The effect of contact time of the reactant with the catalyst bed on the ethanol conversion and on the selectivity in terms of products distribution are seen in Table 1. Under the catalytic conditions employed here, ethyl acetate, acetaldehyde, methyl ethyl ketone, crotonaldehyde, propanone were the main formed products. The higher the contact time or W/F (where W is the catalyst weight and F is the flow rate of ethanol in the catalytic reactor; hereafter the unit W/F will be simplified to min), the greater is the ethanol conversion. In the experiment of low contact time, acetaldehyde was preferentially formed as primary product. However, the ethyl acetate (less volatile and toxic) formation predominates at high contact times. Moreover, acetaldehyde is difficult to handle and has lower specific heat of combustion than ethyl acetate. An expected increase in specific heat of combustion is seen as a function of W/F (Table 1), in agreement to the increase in the amount of ethyl acetate in the liquid effluent.

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