



Short communication

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



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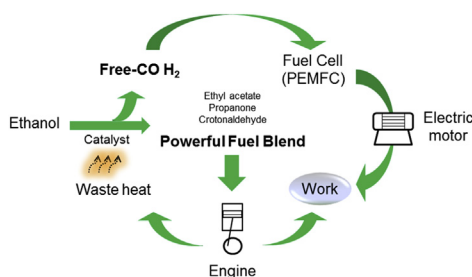
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HIGHLIGHTS

- 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



ARTICLE INFO

Article history:

Received 16 March 2015

Received in revised form

21 May 2015

Accepted 15 June 2015

Available online 1 July 2015

Keywords:

Ethanol

Hydrogen

Fuel cell

Hybrid vehicle

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

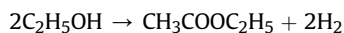
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to the fuel cell cathode [3,4] lead to much lower performance when compared to devices operated directly with the hydrogen gas [5]. In this way, the direct electrochemical oxidation of ethanol in PEMFC has resulted in very low power densities ($<0.100 \text{ W cm}^{-2}$) [6] compared to conventional PEMFC fed with pure hydrogen ($\sim 0.700 \text{ W cm}^{-2}$) [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 H₂-selective membrane) [13], the PEMFC can tolerate less than 10 parts per million (ppm) of CO [14]. In addition, formation of CO₂ in the SRE introduce several problems regarding possible utilization of the reformed 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;



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 H₂ flow free of either CO and CO₂. The catalytic interface properties of copper–ZrO₂ 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 (ZrO₂, Saint-Gobain NorPro) was used as support. Cu/ZrO₂ sample was prepared by incipient wetness impregnation of the support with a solution of (Cu(NO₃)₂·2.5H₂O, 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 ZrO₂ (CuO_x/ZrO₂).

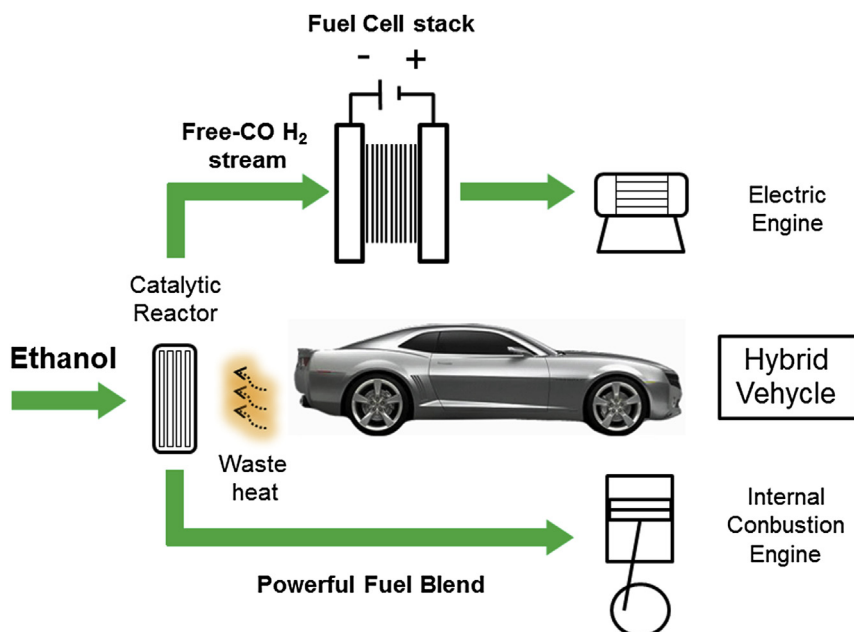
The nominal amount of Cu was 10 wt.% with respect of ZrO₂.

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 cm², 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 H₂/O₂ 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/ZrO₂ sample was reduced *in situ* by heating in pure H₂ 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/ZrO₂. The ethanol reactions were carried out with 1 g of the Cu/ZrO₂ 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.



Scheme 1. Illustration of a hybrid system, which releases electrical energy and a powerful fuel blend from ethanol for a vehicle application.

Table 1
Effect of contact time W/F in the liquid fuel blend composition after cold trap.

W/F (min)	Molar composition (%)							Experimental ΔH_{comb} (kJ mol ⁻¹)	Calculated ΔH_{comb} (kJ mol ⁻¹)
	EtOH	AcH	AcOEt	MEK	CROT	PROP	Others		
–	–	–	100	–	–	–	–	2082.51	–
–	100	–	–	–	–	–	–	1378.92	–
19.0	47.9	21.4	24.0	1.2	1.2	1.0	3.3	1486.43	1513.27
9.5	56.9	23.0	12.9	1.3	1.3	1.2	3.4	1458.43	1429.13
4.75	65.3	20.8	9.5	0.9	0.9	0.6	2.0	1406.66	1403.33

Ethanol (EtOH); Acetaldehyde (AcH); Ethyl Acetate (AcOEt); Methyl Ethyl Ketone (MEK); Crotonaldehyde (CROT); Propanone (PROP); others (diethyl ether, etene, water, CO₂).

Calculations of the flow with respect to the vapor–liquid equilibrium (VLE) for each pure chemical by-product transported by argon (40 mL min⁻¹), obtained according to Antoine's equation [20] leads to the information displayed in Fig. 1. Results show that significant amounts of the liquid effluent can be dragged by the hydrogen flow, thus entering in the PEMFC anode. However, since

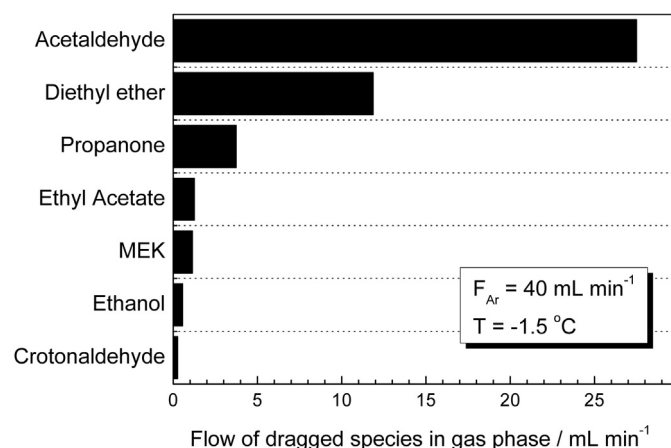


Fig. 1. Flow of dragged species in gas phase by argon at 40 mL min⁻¹. Considering VLE of each pure species at -1.5 °C.

these products are diluted in the liquid effluent, the real dragging flows should be smaller than those in Fig. 1. This is particularly important for acetaldehyde, because of the high vapor pressure and relatively high content in the liquid mixture. Regarding ethyl acetate (the major product expected to be formed, after optimization of the catalytic reactor), the VLE calculation indicates that it is much less dragged by the H₂ stream.

Fig. 2 shows the effect of the contact time on the PEMFC (Pt/C, 0.4 mg cm⁻² in the anode and cathode) voltage vs. current density characteristics at a temperature of 70 °C, when the anode is supplied with H₂ produced from the ethanol reactions and the cathode with pure oxygen, both under atmospheric pressure. For comparison, the result for the same cell fed with pure H₂ at the anode is included. At a constant potential, a downward trend of the current density is noted for shorter contact times, demonstrating the considerable poisoning effect of the dragging product on the Pt/C anodic electrode catalyst. In the case where W/F is equal to 19.0 min, the cell potential decay resulted close to 50 mV, under these experimental conditions and with the Pt/C anode catalyst. This result clearly point to the need of further investigation so to develop more tolerant anode electrocatalysts.

Fig. 3 shows single cell polarization curves obtained for a PEMFCs with Pt/C anode and cathode, operated under H₂ flow coming from the ethanol reaction (W/F = 4.75 min) without gas carrier and for comparison purpose a DEFC with Pt/Sn electrodes [21]. The power densities of PEMFC with Pt/C anodes were calculated for a cell potential of 0.6 V (at which the hydrogen energy

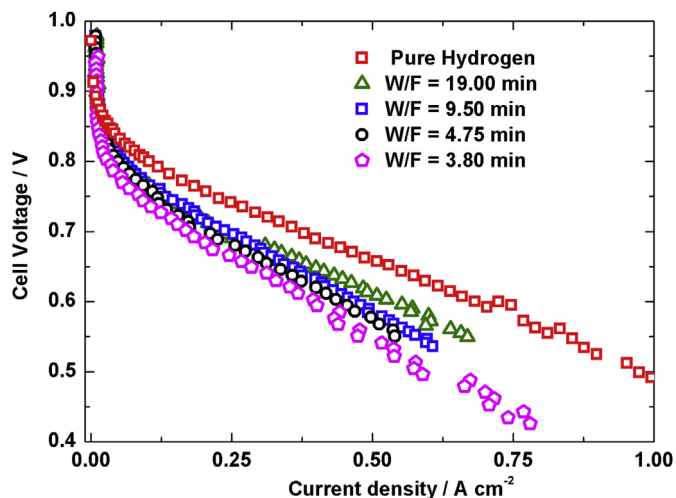


Fig. 2. Cell voltage vs. current density plots of Nafion 115-coated electrodes prepared with $0.4 \text{ mg Pt cm}^{-2}$, operated with H_2 flow due ethanol reaction at different contact times, compared to pure H_2 .

conversion is near to 41%) [22], and these values resulted in 0.12 W cm^{-2} for a cell anode fed with $\text{H}_2/100 \text{ ppm CO}$ [23], 0.055 W cm^{-2} for DEFC [21], 0.30 W cm^{-2} for H_2 coming from the ethanol reactor, and 0.45 W cm^{-2} for pure H_2 . These results indicate that the power generation of the cell coupled with the ethanol reactor represents almost 70% of that of the cell fed with pure hydrogen, and more than 120% higher than that shown by the CO-contaminated system. Moreover, PEMFC fed with H_2 coming from the ethanol reactor showed *ca.* 6 times higher power generation than that observed by DEFC. These data highlight the relevance of the system described in this investigation. It should be remarked that the performance of the PEM single cells in Fig. 3 are lower than those reported previously [23] just because of the lower cell temperature and the use gases at atmospheric pressures employed in these experiments.

Assuming an optimized reactor producing mainly ethyl acetate and hydrogen, the reaction combustion enthalpies (at 25°C),

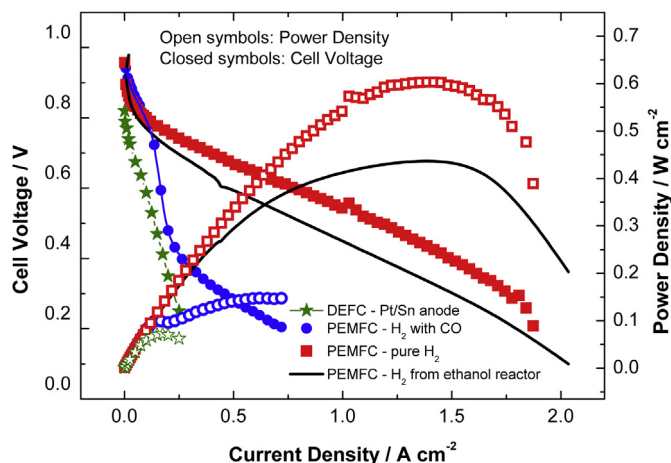
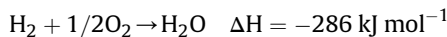
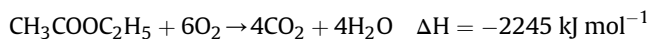
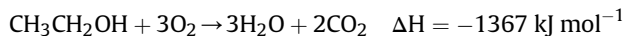


Fig. 3. Stabilized polarization and power density curve of the PEMFC with anode operated under H_2 coming from the ethanol reactor compared to pure H_2 , cell anode fed with $\text{H}_2/100 \text{ ppm CO}$ [23], and a DEFC results from Ref. [21]. Anode: pure H_2 (flow rate = 125 mL min^{-1}) or H_2 from ethanol reactor (obtained at $\text{W/F} = 4.75 \text{ min}$) without gas carrier; Cathode: pure Oxygen.



can be used to estimate the energy conversion efficiencies. In this calculation it is obtained that a heat engine (energy conversion efficiency of *ca.* 22%) fed with ethanol will release -301 kJ per mol of ethanol of mechanical work, while when fed with ethyl acetate the mechanical work is -494 kJ per mol of ethyl acetate or -247 kJ per mol of ethanol. This calculation also show that a system comprising an ethyl acetate combustion engine (-247 kJ per mole of ethanol of mechanical work) integrated to a PEMFC fed with H_2 (working at 0.6 V , 41% efficiency) coming from the ethanol reactor and coupled to an electric engine yields -120 kJ of work per mole of hydrogen (and hence per mole of ethanol), resulting in a total of -367 kJ per mole of ethanol of mechanical work. This represents a 20% increase over the 301 kJ from an ethanol fueled engine. This is a very relevant surplus when the ethanol fuel economy is taken into account. Finally it should be noted that the mechanical work from the ethyl acetate represents 2/3 of the total energy while the electrical work represents 1/3 of the total energy.

As a final remark, it should be mentioned that this is a first report for demonstrating the proof of concept of the hybrid system, including some analysis of the potential use of the liquid effluent as fuel. Further developments on the system should still be made, and these include optimizing the reactor set up and operating conditions to improve ethanol conversion, minimize acetaldehyde production (maximizing ethyl acetate); also, a work in course involves development of new PEMFC anode catalysts with improved tolerance for the contaminants. Together with this, the sensitivity of effluent composition with the cooling temperature and the need and the dimension of a refrigeration system has to be considered.

4. Conclusions

The system described here can help to solve three issues regarding the utilization of PEMFC in electric vehicles and these are related to the production, distribution and on board hydrogen storage, to the extent that this fuel is produced from liquid and renewable ethanol, employing a low cost copper-based catalyst. Based on the results of the electrochemical experiments, it is unequivocally demonstrated that the integrated system is feasible and, after further advances, can positively contribute to the energy scenario related to hybrid vehicles, particularly driven by ethanol.

Acknowledgments

The authors thank the CNPq and FAPESP (PROC. 2012/04112-5 and 2011/50727-9) for financial supports. We express our gratitude to Professor A. M. dos Santos and G. Cruz for their useful contributions for the calorimetric measurements.

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