



Partial oxidation of methane and generation of electricity using a PEMFC

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Abstract

The aim of this work was to produce methanol through partial oxidation of methane. The gas fed in a solid membrane reactor-PEM fuel cell type ($H_2/H_2O_2 + CH_4$) has been used for electrosynthesis of methanol at room temperature, with electricity cogeneration as a benefit. It was observed that the current density measured when injected CH_4 in the cathode decreased about 45%. This occurs due to the conversion of methane in methanol in some ranges of potentials. In the other hand, in lower ranges of cell potential, formaldehyde was found. In this work, methane was injected on the cathode together with H_2O_2 solution, where it was observed that the catalytic layer adsorbed CH_4 and H_2O_2 in active sites, which produced OH^- radicals that reacted with the hydrocarbon.

Keywords Electrosynthesis · Methane · Methanol synthesis · Solid membrane reactor · PEM fuel cell

Introduction

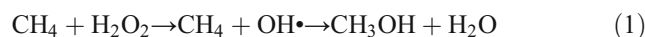
Methane (CH_4) is a component of biogas that can be generated in landfills where waste decomposes [1], and it is considered a promising energy resource as a substitute for crude oil [2]. This hydrocarbon is almost inert, and it has a low solubility in water. For that matter, recent research about partial methane oxidation into other chemicals is gaining significant importance, especially if it is done in a single step [2]. When it is converted into alcohol, a new range of possibilities emerge. For instance, methanol is easy and inexpensive to store and transport; it can be used as solvent, fuel, and chemical feedstock and has other applications [3, 4].

At room temperature, we can transform methane into methanol in applied photoreactors [5–7] or electrochemical reactors [8–10]. In both methods, free radicals are produced, which can react with the hydrocarbon. By electrochemical means, Rocha et al. [10] convert methane into methanol in

an electrolytic process over $TiO_2/RuO_2/V_2O_5$ gas diffusion electrode (GDE) with high efficiency. Lee and Hibino [11] promote anode reaction of methane with water into methanol using fuel cell type reactor over Pt and V_2O_5/SnO_2 operating from galvanic cell to electrolytic cell conditions. It was observed that the higher the current, the lower is the methanol conversion. Nandenha et al. [12] studied Pt/C, Pd/C, Pt/C-ATO, and Pd/C-ATO catalysts in a direct methane fuel cell anode, where it was possible to measure power densities in the order of 0.5 mW cm^{-2} , and in electrochemical in situ experiments, a sign of carboxylic acid and aldehyde was detected.

Tomita et al. [13] used a proton exchange membrane fuel cell (PEMFC) for conversion of methane into methanol with hydrogen in the anode, and oxygen and methane in the cathode, and measured the conversion at open circuit voltage (OCV), which resulted in a maximum current. The explanation for this effect was attributed to water activation and hydroxyl species.

The hydroxyl species also can react with methane, producing methanol. Also, the decomposition or hydrogenation of hydroxyl produces only water [14], and the two ways show that energy is required to potentiate the action of peroxide, due the radical way, as indicated by Eq. 1.



PEMFC can be used as a solid membrane reactor (SMR), maintaining the conditions of operation very similar to the

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ones mentioned in the literature for fuel cells, using the anode as the chamber where the molecule of interest is oxidized. In PEMFC, the anodic reaction normally has the presence of water that acts in the hydration of the membrane, and when a molecule more complex than the H_2 is used, like alcohols, these solutions provide the oxygen for the complete oxidation of the compound. In the cathode of a PEMFC, although not desired, hydrogen peroxide is a product of oxygen reduction reaction (ORR) during its operation [15, 16], thus creating an environment that may favor the partial methane oxidation.

This article has used a Pt/C catalyst in a PEMFC $H_2/H_2O_2 + CH_4$ as a SMR at room temperature to verify how the potential rate in a reaction of electric power generation would affect the production of partially oxidized compounds originated from methane.

Experimental

Solid membrane reactor-PEMFC type (SMR-PEMFC) tests were carried out using Pt/C BASF (20 wt.%) electrocatalyst applied to a carbon cloth treated with PTFE, in the amount of 1 mg cm^{-2} in the anode as well as the cathode, forming the gas diffusion electrodes with total area of 5 cm^2 prepared according to Neto et al. [12, 17–19]. Nafion® 117 was used as a proton exchange membrane. The reactor was fueled with H_2 at 300 ml min^{-1} , went into a humidifier at $85 \text{ }^\circ\text{C}$, and then went into the anode. At the same time, the methane at 75 ml min^{-1} went into a humidifier at $80 \text{ }^\circ\text{C}$. Meanwhile, an aqueous solution of 10% H_2O_2 was pumped from a connector, and both methane and H_2O_2 went into the cathode. The polarization curves were obtained using an Autolab PGSTAT 302N

Potentiostat with a current booster. Figure 1 outlines the experimental development for the acquisition of results.

Products of the cathodic reaction were collected at the cathode output for 300-s increments of 100 mV and analyzed by ATR-FTIR performed in an ATR accessory (MIRacle with a ZnSe Crystal Plate Pike®) installed on a Nicolet® 6700 FT-IR spectrometer equipped with a mercury cadmium telluride (MCT) detector cooled with liquid N_2 . Absorbance spectra were collected in the ratio ($R:R_0$) where R represents a spectrum at a given potential at the cathode and R_0 is the spectrum obtained for H_2O_2 of 10% aqueous solution. Negative and positive bands represent the consumption and production of substances, respectively. The methanol concentration was determined by the method proposed by Boyaci et al. [20] used for alcoholic beverages and validated for other applications such as photocatalysis [21] and sensors [22, 23]. Raman spectroscopy was performed using the MacroRam Raman spectroscopy by Horiba Scientific. The wavelength was set up in 785 nm.

Results and discussion

Figure 2 shows the polarization curve of H_2/H_2O_2 obtained by SMR fuel cell type. When methane together with H_2O_2 flux is added, the curve pattern is modified; this can be an indication of interaction between the gas and the catalytic sites. The polarization curve of $H_2O_2 + CH_4$ conduction shows three losses for concentration; the first loss can indicate the CH_4 adsorption in active sites, reducing the availability of active sites for peroxide reduction reaction, and the other losses show the depletion of species generated during the cathodic reaction. The power curves

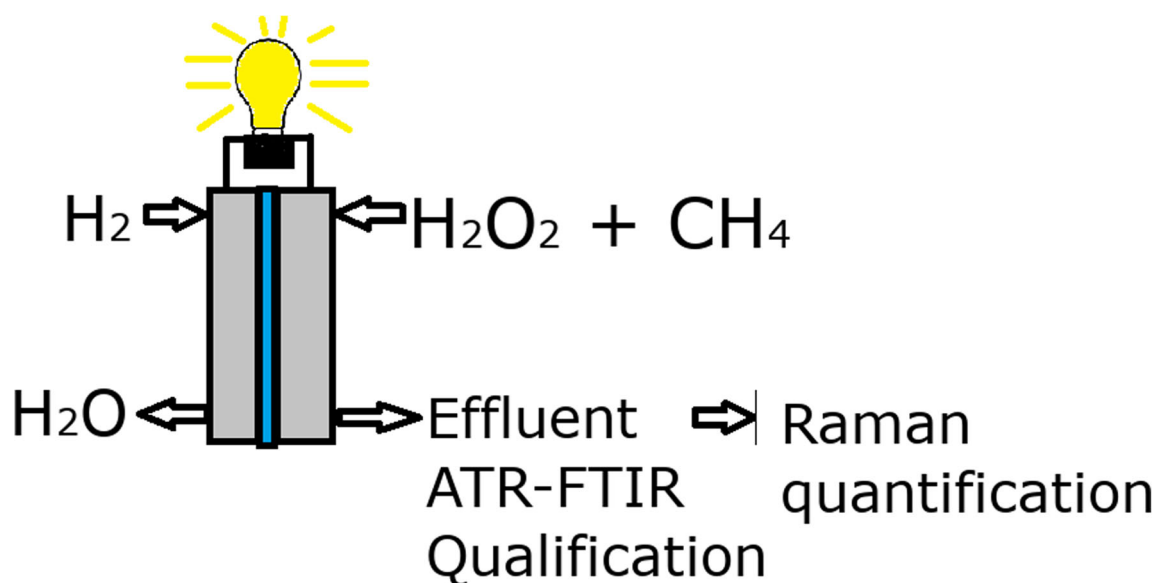
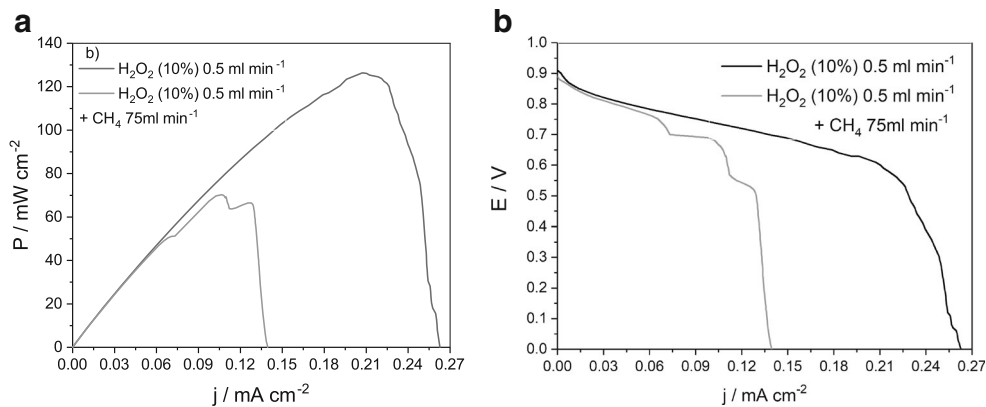


Fig. 1 Outline experimental

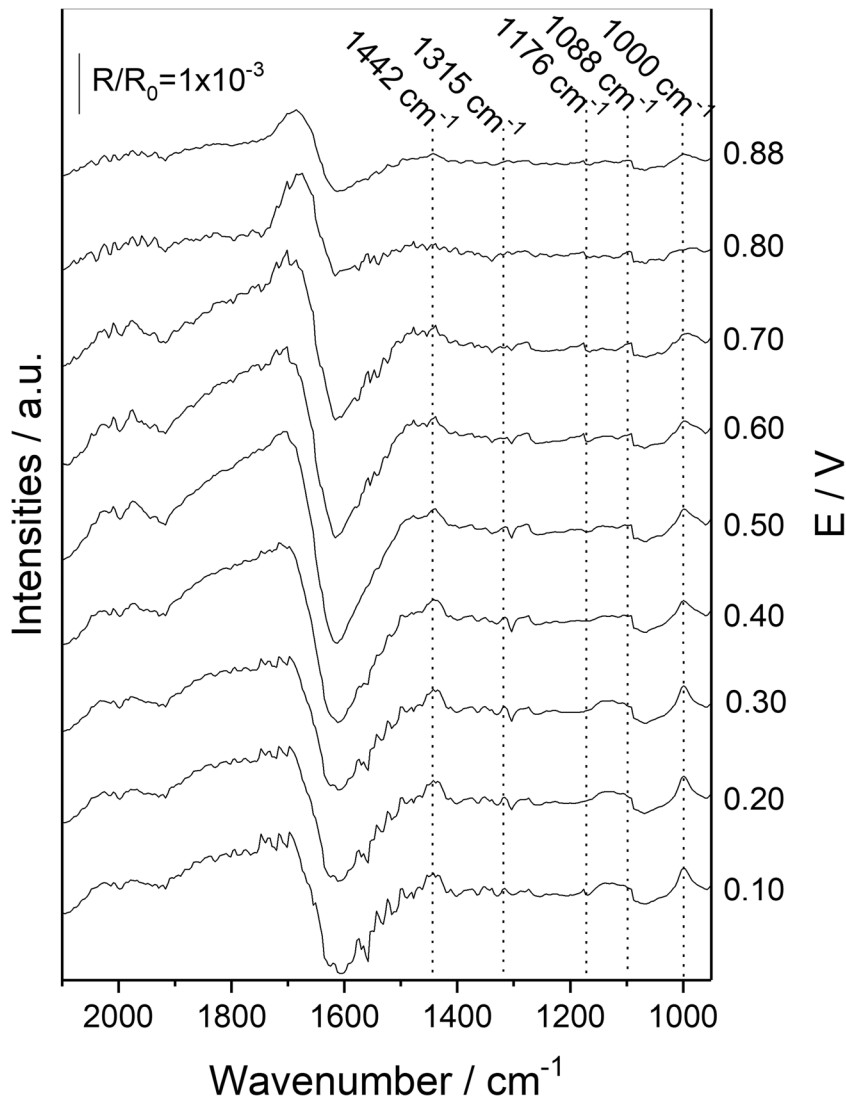
Fig. 2 **a** Polarization and **b** Power curves of H₂/H₂O₂ and H₂/H₂O₂ + CH₄ fuel cell at 25 °C



(Fig. 1b) showed that SMR H₂/H₂O₂ + CH₄ present near half of power presented by SMR H₂/H₂O₂, which the densities of powers measured near the 70 mW cm⁻² and 126 mW cm⁻², respectively.

Figure 3 shows IR spectra of partial methane oxidation in the PEMFC, where it is possible to observe already OCV bands at 1442 cm⁻¹, 1088 cm⁻¹, 1031 cm⁻¹, and 1000 cm⁻¹ corresponding to band of CH₃ s-deform of methanol [24],

Fig. 3 FTIR spectra obtained for samples collected at increments of 100 mV



methanol CH_3 rock [24], C–O bond stretch mode [25], and $\nu(\text{COH})$ vibration of methanol and/or $\nu(\text{COC})$ in oligomers of the formaldehyde in aqueous solution [26], respectively, indicating that the process can occur by H_2O_2 and methane. However, the role of SMR is not clear yet.

On the other hand, the band increases with the current obtained in the polarization curve, indicating that there was a partial oxidation of methane, which can be increased by the potential at which the cell is operated. A band near 1088 cm^{-1} appears in OCV and increases the intensity with the potential decrease until 0.4 V. This band convolved with a band at 1115 cm^{-1} refers to the formic acid [27], and it is possible to note the decrease after 0.3 V, indicating possible methanol consumption.

The formic acid can be reinforced by the band at 1281 cm^{-1} [28]. In potentials lower than 0.6 V, the band at 1315 cm^{-1} corresponding to the deg. deform of methane [29] can be indicated that some methane is solubilized in the aqueous solution due to the increased concentration of small organic molecules produced by the partial oxidation of the hydrocarbon. It is known that this gas is soluble in methanol and formaldehyde [30]. The variation of methanol, formaldehyde, formic acid, and methane in function of potential showed that SMR has an active role in methane partial oxidation.

The amount of methanol produced in fuel cells was analyzed using Raman spectroscopy applied Boyaci method [20]. Figure 4 shows the amount of methanol produced as a function of potential that was collected using an analytical curve constructed in the concentration range of $0.005\text{--}1.000\text{ mol l}^{-1}$ of methanol. For the following analytical curve, an intensity =

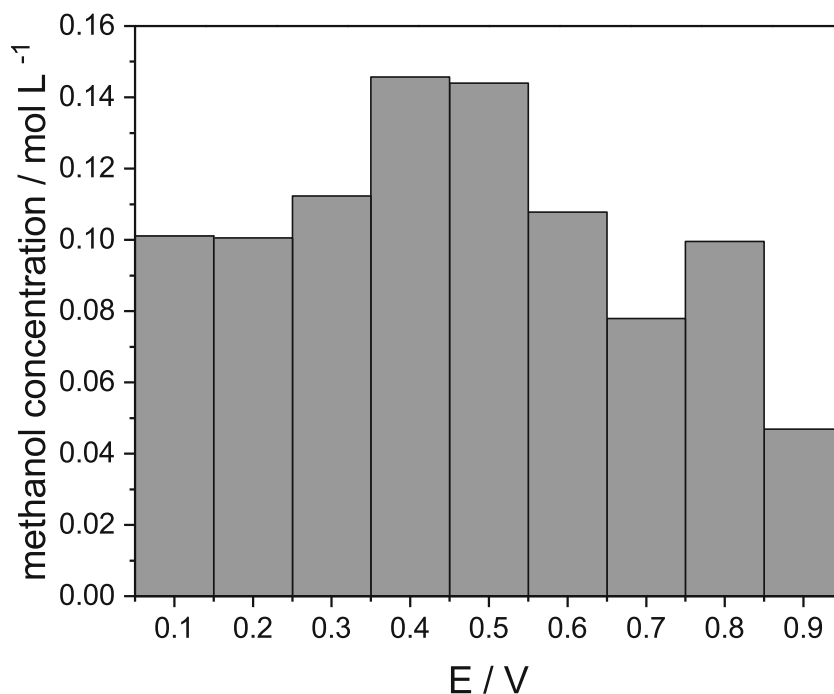
$0.64414 + 1.19027 [\text{CH}_3\text{OH}]$ was obtained and the correlation coefficient was 0.962.

About methanol production as a function of the potential, it is possible to note in higher potentials (880–700 mV) that there is a lower alcohol concentration due to the lower hydrocarbon adsorption so that the currents obtained in the polarization curve $\text{H}_2/\text{H}_2\text{O}_2$ and $\text{H}_2/\text{H}_2\text{O}_2 + \text{CH}_4$ are very close. In the range of 600–400 mV, more methanol is detected, in which $\text{H}_2/\text{H}_2\text{O}_2 + \text{CH}_4$ decreases more in comparison with $\text{H}_2/\text{H}_2\text{O}_2$, probably due to the adsorption of CH_4 in the catalytic layer. And in the third segment of the polarization curve (400–100 mV), the methanol concentration decreases, as it can be seen in Fig. 2, and coincides with the appearance of bands correlated to formaldehyde, indicating that alcohol produced in the reactor is being oxidized due to hydroxyl species formed over Pt during cathodic reaction.

Conclusion

This work showed that the use of the SMR-PEMFC type is promising for the conversion of CH_4 to methanol with cogeneration of electricity. The maximum power loss achieved was higher than 55% for the $\text{H}_2/\text{H}_2\text{O}_2$ system, in addition to producing 0.14 mol l^{-1} methanol. Methanol production is related to the potential for SMR-PEMFC operation; this should not be attributed only to the interaction of $\text{CH}_4 + \text{H}_2\text{O}_2$ in the reactor, as the action of the cell's operation potential was observed. Where there is selectivity of the operation potential of the fuel

Fig. 4 Variation of methanol concentration with E increments



cells, it can favor the oxidation of the hydrocarbon in alcohol and alcohol + aldehyde + carboxylic acid, which means that the most oxidized compounds are derived from the oxidation of alcohol.

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