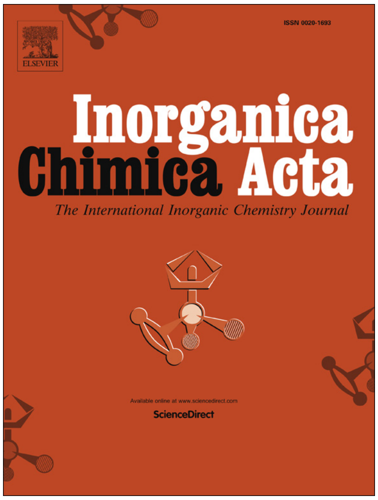

Research paper

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Hydrogen production from the electrooxidation of methanol and potassium formate in alkaline media on carbon supported Rh and Pd nanoparticles

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Abstract

Small organic molecules such as alcohols and formate salts can be readily transformed into hydrogen and carbon dioxide through electrochemical reforming at low energy cost. In this article methanol and potassium formate are studied for hydrogen production in alkaline anion exchange membrane electroreformers using two anode electrocatalysts, nanoparticle Pd and Rh supported on carbon (5 wt%). Firstly, we report a study of the electrochemical activity of both catalysts in electrochemical test cells at 80 °C. Formate oxidation kinetics are found to be fast on both catalysts. Rh/C shows the best performance for methanol electrooxidation with an onset potential 200 mV lower than Pd/C and a specific activity almost double reaching the value of 2600 A g^{-1}_{Rh}. The energy cost and conversion efficiency for hydrogen production was determined in complete electrochemical reforming cells at 80 °C using both anode catalysts. The energy costs are low for both substrates (< 14 KWh Kg^{-1}_{H2}) with Pd/C producing hydrogen from potassium formate at an energy cost of 5 KWh Kg^{-1}_{H2}. Considering both the energy consumption and conversion efficiency (substrate to hydrogen), it is shown that the Rh/C catalyst performs best with methanol as substrate.

1. Introduction

One of the most important challenges for our society is to build a sustainable world economy based on the use of clean and renewable energy. Hydrogen, thanks to its high specific energy density and clean combustion to water, is an attractive alternative to our current dependence on fossil fuels. Although hydrogen is the most abundant element in nature, it mostly exists combined with other elements, so it must be produced using a primary source of energy.[1],[2] Irrespective of how hydrogen is produced, these processes are endothermic and require a large amount of energy, either provided as heat as in steam reforming or through electrochemical or photochemical processes activated with suitable catalysts. [3]–[5] At present hydrogen is principally produced by the steam reforming of hydrocarbons at high temperatures (700-1200 °C) with CO and CO_2 as waste products.[6]

Since the 1960s, hydrogen production by the dehydrogenation of formic acid or methanol, through homogeneous or heterogeneous catalysis, has been widely investigated.[7] Different types of catalysts have been developed, ranging from noble metals (iridium, palladium, platinum, rhodium and ruthenium) to molybdenum and ruthenium complexes with monodentate phosphines as ligands.[8], [9] These materials decompose formic acid to H_2 and CO_2, although in some cases carbon monoxide (and water) is also formed through a side reaction. The presence of CO in the product gas stream is problematic as small quantities can quickly poison fuel cell electrocatalysts.[10]

Another method to produce hydrogen is through electrolysis; electrochemical routes are particularly appealing in terms of sustainability, in fact using appropriate substrates, it is possible to convert electrical energy directly into pure molecular hydrogen. [11]–[15] The most established technology is water electrolysis, although this method has a high energy cost due to the high cell voltages required to produce hydrogen (> 1.23 V RHE at room temperature).

Methanol and formic acid have been widely studied as potential fuels for Direct Fuel Cells (DFCs) thanks to their low molecular weight, ease of transport and storage and high energy densities. [16]–[18] There are only a very few works that report their use in electrolysis cells to produce hydrogen through a technology known as electrochemical reforming.[19]–[21] Electrochemical reforming produces hydrogen as low energy cost by replacing the anodic oxygen evolution reaction with the oxidation of a sacrificial substrate (e.g. alcohol or formate). For example, the electrical energy input for an electroreformer fed with ethanol consumes less than half of that required to produce the same amount of hydrogen from water splitting.[11] In comparison to catalytic reforming technologies where the product gas stream contains a mixture of H_2 and CO_2, electrochemical reforming in alkaline media produces pure hydrogen at the cathode . This is because the anode and cathode are separated by a membrane. Additionally, the CO_2 produced from the oxidation of the anolyte is transformed into carbonate by reaction with the strong base in the electrolyte and hence cannot migrate to the cathode and mix with the hydrogen gas stream.

As alternative to formic acid, which is corrosive and dangerous to human health, formate salts are less toxic, less volatile, and can be easily stored and transported. Moreover, as shown in a number of recent reports, Direct Formate Fuel Cells (DFFCs) produce high power densities as the kinetics of the formate oxidation reaction is very fast in alkaline media.[22]–[24]

In this article, we investigate the electrooxidation of methanol and formate in electrochemical cells as well as in complete electrolysis cells at 80 °C. As electrocatalyst we study two carbon supported nanoparticle based catalysts, Pd/C and Rh/C, each with a 5 wt% metal loading. This study evaluates the energy efficiency and stability of the electrolysis process with methanol and formate, using these two electrocatalysts. We demonstrate that with the use of these anode electrocatalysts, it is possible to obtain high purity hydrogen (CO_2 free) at low energy cost. An energy analysis shows that Rh outperforms Pd both in terms of energy cost as well as conversion efficiency. Considering the yield of hydrogen, methanol is preferable as substrate as more hydrogen is obtained per molecule compared to formate while the energy cost remains the same.

2. Experimental

2.1 Materials and methods

Carbon black (Vulcan XC-72) was purchased from Cabot Corp., USA. The alkaline anion exchange membrane used was A201 obtained from Tokuyama Corp. (Japan). All metal salts and reagents were purchased from Aldrich and used without further purification. All the solutions were freshly prepared with doubly distilled deionized water. All materials preparation, except as stated otherwise, were routinely performed under nitrogen atmosphere using standard airless technique.

The active metal surface area and average nanoparticle size were determined by a CO chemisorption method, adapted to carbon supported materials, at 35°C by the use of an ASAP 2020C Instrument (Micromeritics Corp.). Before the measurements, the samples were treated at 120 °C with H_2 for 12 hours.

The electrochemical measurements were carried out using a Parstat 2273 potentiostat-galvanostat (Princeton Applied Research) equipped with a Model 616 Rotating Disk electrode (PAR-Ametek). A 5 mm ($A = 0.1963$ cm^2) teflon potted glassy-carbon disk electrode tip (PINETM) was used as substrate for the deposition of the catalyst ink. Before the deposition, the glassy-carbon surface was polished with different CT diamond suspensions that had progressively smaller particle size (1 µm, 0.25 µm, 0.1 µm) and finally washed with distilled water. The catalyst ink consisted of Rh/C or Pd/C (14 mg) and water (1.2 g). The resulting suspension was sonicated for 1 h with a FALC sonic bath to reach a uniform suspension. The catalyst film was prepared by dispersing 8 µL of the catalyst ink on the glassy-carbon electrode. The exact amount of ink deposited was determined using an analytical balance. The final metal loading on the electrode is between 5 and 6 µg. Each electrode was dried for 30 min before the addition of 2.5 µL of a Nafion solution (0.5%) and finally it was mounted on the rotating disk electrode shaft and immersed into the electrolyte solution. The reference electrode was a commercial Ag/AgCl/KCl (1M). The counter electrode was a platinum gauze enclosed in a glass tube with porous bottom. All the potentials reported are versus the reversible hydrogen electrode (RHE). The electrochemical experiments were conducted at 80°C. The CV experiments were registered in either 2M aqueous KOH or 2M KOH + 2M methanol or potassium formate. All the solutions were prepared with Millipore water (18MΩcm) provided by a milli-Q labo apparatus (Nihon Millipore Ltd.). Solutions were first treated by bubbling high-purity N_2 before measurements.

The MEAs (membrane electrode assemblies) were composed of a nickel foam support coated with a Rh/C or Pd/C catalyst as anode, a commercial Tokuyama A-201 anion-exchange membrane, and a commercial 40 wt% Pt/C (Aldrich) catalyst supported on carbon cloth as cathode. The anode ink was prepared by mixing Rh/C or Pd/C (C=Vulcan XC-72) with a 5% aqueous suspension of PTFE to form a think catalyst paste which is spread onto a 5 cm^2 Ni-foam support (Heze Tianyu Technology Development Co, China) in order to obtain a catalyst coated electrode with a metal loading of 1 mg cm^{-2}. The cathodic ink was prepared in a 5 mL high density polyethylene vial, mixing 200 mg of the commercial Pt (40 wt.%)/C in 450 mg of distilled water, 790 mg of 1-propanol and 1.56 g of the ionomer Nafion® (5 wt.% in 2-propanol). The mixture was suspended with three pulses of ultrasound, 20 W power at the frequency of 20 kHz (Bandelin Sonor pulse UW 2200 SERIES). Finally this paste was spread onto a carbon cloth W1S1005 (CeTech Co. Ltd.) gas diffusion layer, with a Meyer rod (n°150) obtaining a 0.4 mg cm^{-2} Pt loading.

The active electroreformer cell was purchased from Scribner-Associates (USA). The MEAs were assembled by mechanically pressing together the anode, cathode and membrane within the cell hardware. The cell temperature was regulated at 80 °C using a Scribner 805e fuel cell station. The aqueous fuel solution (2M KOH + 2M methanol or potassium formate) was delivered to the anode at 1 mL min^{-1}. Voltage scans and galvanostatic curves were determined using an ARBIN BT-2000 5A-4 channels instrument. Polarization experiments were recorded by applying a linear voltage ramp with a 10 mV s^{-1} scan rate between 0.2 to 0.8V. Chronopotentiometry experiments were performed applying a constant electrolysis current of 125mA until the cell voltage reached the value of 0.65 V. The fuel solutions after each experiment were quantitatively and qualitatively analyzed by $^{13}C\{^1H\}$ NMR spectroscopy and HPLC. A UFLC Shimadzu Chromatograph equipped with refraction index detector (RID) was used; the column is a GRACE- Alltech OA-1000 Organic Acids (300mm x 6.5 mm), thermostated at 65°C. The eluent is 0.01 N H_2SO_4; and the eluent flow is 0.4 mL min^{-1}. NMR spectra were acquired with a with a Bruker Avance DRX 400 spectrometer. Chemical shifts (δ) are reported in ppm relative to TMS (^1H and ^{13}C NMR spectra). Deuterated solvents (Sigma-Aldrich) used for NMR measurements were dried with activated molecular sieves; 1,4-dioxane was used as internal standard for product quantification.

2.2 Synthesis of electrocatalysts

The detailed synthesis of Rh/C (Rh =5 wt%) and Pd/C (Pd =5 wt%) anode electrocatalysts has been already reported in our previous works[25], [26]. Briefly, as follows:

Rh/C: Vulcan XC-72 (3.8 g) was suspended in 640 mL of ethylene glycol and sonicated for 80 min. Then the suspension was mechanically stirred (400 rpm) for 1 h under a N_2 atmosphere. A solution of 740 mg of $RhCl_3•6H_2O$ in water (160 mL) was added dropwise to the suspension under stirring. Subsequently an alkaline solution of 15.8 g of NaOH in water (80 mL) and ethylene glycol (200 mL) was introduced to the reactor and the resulting mixture was heated at 120 °C for 3 h. After cooling to room temperature the resulting solid product was collected by filtration and washed with water to neutral pH and lastly dried in vacuum oven at 40 °C. Yield of Rh/C: 80%.

Pd/C: Vulcan XC-72 (4.5 g) was suspended in 250 mL ethylene glycol and sonicated for 20 min. Then a solution of 50 mL of H_2O, 50 mL of ethylene glycol and 6 mL of HCl (37%,) with dissolved 445 mg of $PdCl_2$ were added drop by drop to the resulting solution under stirring in a N_2 stream. An alkaline solution of 5 g of NaOH in H_2O (10 mL) and ethylene glycol (35 mL) was introduced into the reactor which then was heated at 125°C for 3 h. After cooling to room temperature the resulting solid product was collected by filtration and washed with water to neutral pH and lastly dried in vacuum oven at 40 °C. Yield of Pd/C: 94 %.

3. Results and discussion

3.1.Chemisorption measurements

The active surface area and the mean nanoparticle size for both the Rh/C and Pd/C electrocatalysts were calculated by a CO chemisorption method; the respective values are reported in Table 1.

Table 1: Chemisorption data.

Electrocatalyst	Mean Nanoparticle Size (nm)	Metal Specific Surface Area ($m^2\ g^{-1}_{Metal}$)
Rh/C	5	76
Pd/C	9	52

These values are consistent with what has been found by the use of other physical and electrochemical characterization techniques in previous reports. For the Rh/C catalyst, an average particle size was estimated from a statistical count using TEM images and gave a value of 2.2 nm. CO stripping voltammetry gave a value for the ECSA of 75 $m^2\ g^{-1}_{Rh}$.[26] A recent TEM investigation of the Pd/C catalyst showed a NP distribution of 2-10 nm.[25]

3.2.Half-cell testing

The electrochemical activity of Pd/C and Rh/C was investigated using cyclic voltammetry (CV) studies in electrochemical three electrode test cells. All the experiments were performed in N_2-saturated aqueous solutions, and using a metal loading on the glassy carbon substrate of 25-35 µg cm^{-2}. Firstly, we studied the electrochemical behavior of both catalysts (without fuel) in 2 M KOH at 80°C (Fig. 1). The potentials reported in the cyclic voltammetry curves reported versus RHE are calculated according to the Ag|AgCl|KCl_{sat} electrode temperature dependence as described in the supplementary of our previous work.[26]

The different transitions observed in each CV can be assigned by comparison with literature data.[25], [26] In the case of Pd/C, starting from the low potential region, on the anodic sweep we first see a large broad peak (A') with a shoulder attributable to the oxidative desorption of hydrogen. Subsequently there is a small peak (A'') at 0.4 V which can be assigned to the formation of Pd(I) hydroxide species (Pd-OH).[27] This is followed by the formation of an oxide layer (A''') on the palladium surface that is associated with a gentle increase in the anodic current density. On the reverse cathodic scan, a well-defined peak (C') at 0.85 V is attributed to the reduction of Pd surface oxides species. At potentials between 0.1 and 0.2 V there is a large cathodic current (C'') associated to the adsorption of hydrogen on the Pd surface and then hydrogen evolution. [22], [25], [28].

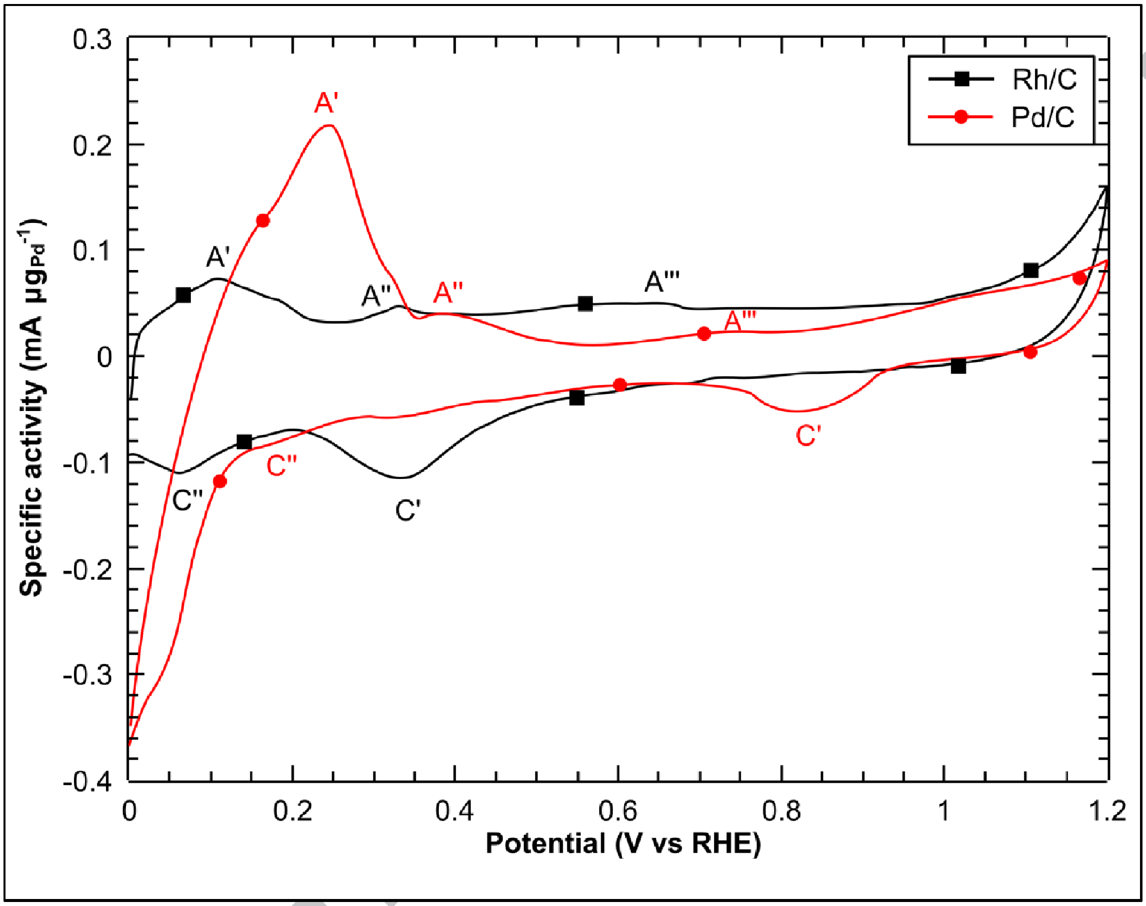


Fig. 1 CVs of Rh/C (■) and Pd/C (•) in N_2 saturated 2M KOH at 80°C and a scan rate of 50 mV s^{-1}.

The CV of Rh/C in KOH 2M at 80 °C corresponds to data recently reported in the literature. [25], [26] The anodic peaks can be assigned to hydrogen desorption (A' at 0.1 V), the formation of Rh_xOH_y (A'' at 0.3 V) and Rh_xO_y (A''' at 0.6 V). In the reverse scan there are peaks for the reduction of the oxide layer (0.35 V) and for hydrogen adsorption (0.05 V).[29]–[31]

We also studied the electrochemical oxidation activity by cyclic voltammetry of both catalysts in 2M KOH + 2M potassium formate (Figure 2, A and B) and 2M KOH + 2M methanol (Figure 2, C and D) in the potential range of 0-1.20 V vs. RHE at the temperature of 80 °C and at a scan rate 50 mV s^{-1}. Fig. 2A shows formate oxidation activity of Pd/C. The onset potential is low at about 0.2 V, and there is a specific activity of 2.1 mA μg$^{-1}_{Pd}$, for the forward going peak (important electrochemical data is also reported in Table 2). We have recently reported a cyclic voltammetry study of a Pd/C electrocatalyst (Pd = 20 wt%) with potassium formate in alkaline media at room temperature.[22] The peak current density for potassium formate oxidation was at least three times lower compared to this work even with a much higher Pd loading. This confirms the positive effect of increased temperature on oxidation kinetics of alcohols in alkaline media. In the case of methanol Fig. 2 C, Pd/C has a higher onset potential representing the more difficult nature of methanol oxidation. In both CVs (A and C) the reverse scan shows an anodic peak corresponding to fresh oxidation of the fuel after reduction of the surface Pd oxides.[32] Regarding the electrochemical activity of rhodium, with both fuels the onset potentials are lower than Pd (see data reported in Table 1). The oxidation peak on the forward scan is much higher for methanol than formate reaching a specific current value of 2.6 mA μg^{-1}_{Rh} (Fig. 2 D).

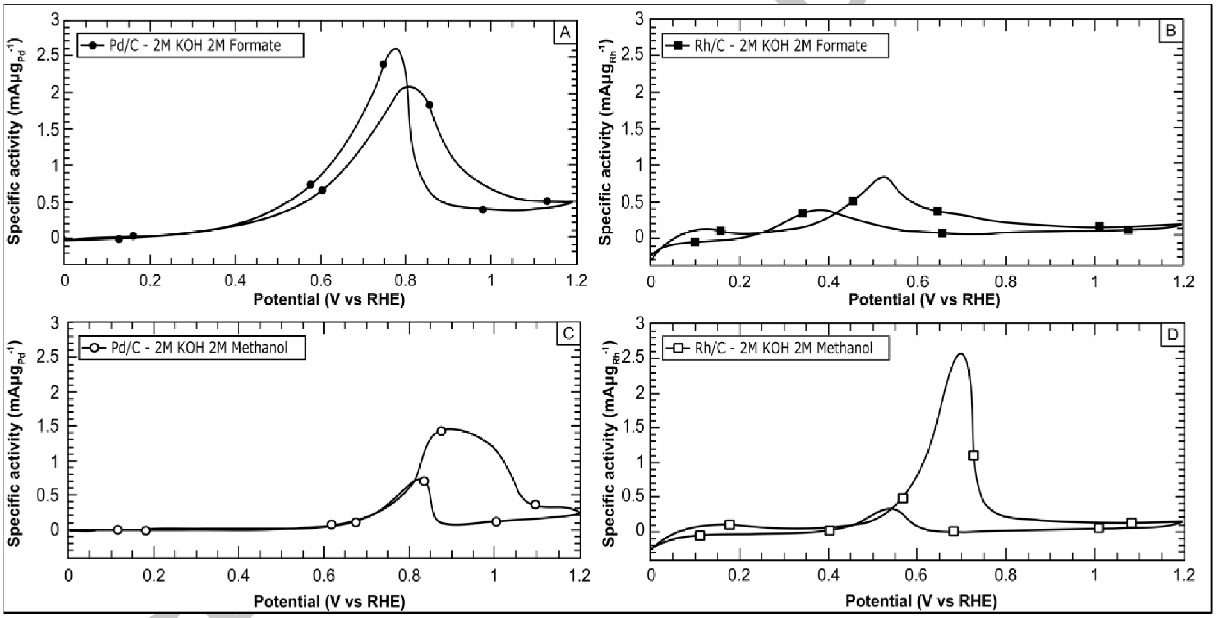


Fig. 2 CVs of Pd/C in 2M KOH + 2M Potassium Formate (A) and 2M KOH + 2M Methanol (C), and Rh/C in 2M KOH + 2M Potassium Formate (B) and 2M KOH + 2M Methanol (D). Scan rate of 50 mV s^{-1}.

Table 2 Relevant electrochemical parameters of CVs of Pd/C and Rh/C with Potassium Formate and Methanol at 80°C and a scan rate of 50 mV s^{-1}. [a] Current density normalized to metal loading

Fuel	Pd/C			Rh/C		
	E_{onset} (V vs. RHE)	$E_{forward\ peak}$ (V vs. RHE)	$J_{peak}{}^{a}$ (mA $\mu g^{-1}{}_{Pd}$)	E_{onset} (V vs. RHE)	$E_{forward\ peak}$ (V vs. RHE)	$J_{peak}{}^{a}$ (mA $\mu g^{-1}{}_{Rh}$)
Formate	0.20	0.81	2.1	0.30	0.52	0.9
Methanol	0.62	0.90	1.5	0.42	0.65	2.6

3.3.Electrolysis cell testing

Nickel foam (4 cm^2) coated with either of the Rh/C or Pd/C catalyst inks was used as anode electrode (1 mg_{metal} cm^2) in the electrolyzer equipped with an anion exchange membrane (Tokuyama A201) and a Pt/C on carbon cloth cathode (0.4 mg_{Pt} cm^{-2}). The fuel, fed to the anode, was an aqueous solution (30 mL) of 2M KOH and 2M potassium formate or 2M KOH and 2M methanol.

The electrolysis cell performance were evaluated using both potentiodynamic scans and galvanostatic experiments at 80°C. The experiments were repeated three times, using the same cell and only changing the fuel with a fresh solution. Every cycle of experiments consisted of a voltage scan, undertaken in the potential range from 0.2 to 0.8V at 10 mV s^{-1}, followed by a galvanostatic experiment (at a costant electrolysis current of 125 mA). The cell potential was monitored and the experiment was stopped when it reached 0.65 V. The first cycle of the voltage scans are reported in Fig. 3. The Rh/C cell reached a higher maximum current density with both methanol and potassium formate compared to Pd/C. The values of peak current density are reported in

Table 3. The electrochemical activity of both Pd/C and Rh/C was stable over all the three cycles confirming the stability of the anode materials during electrooxidation.

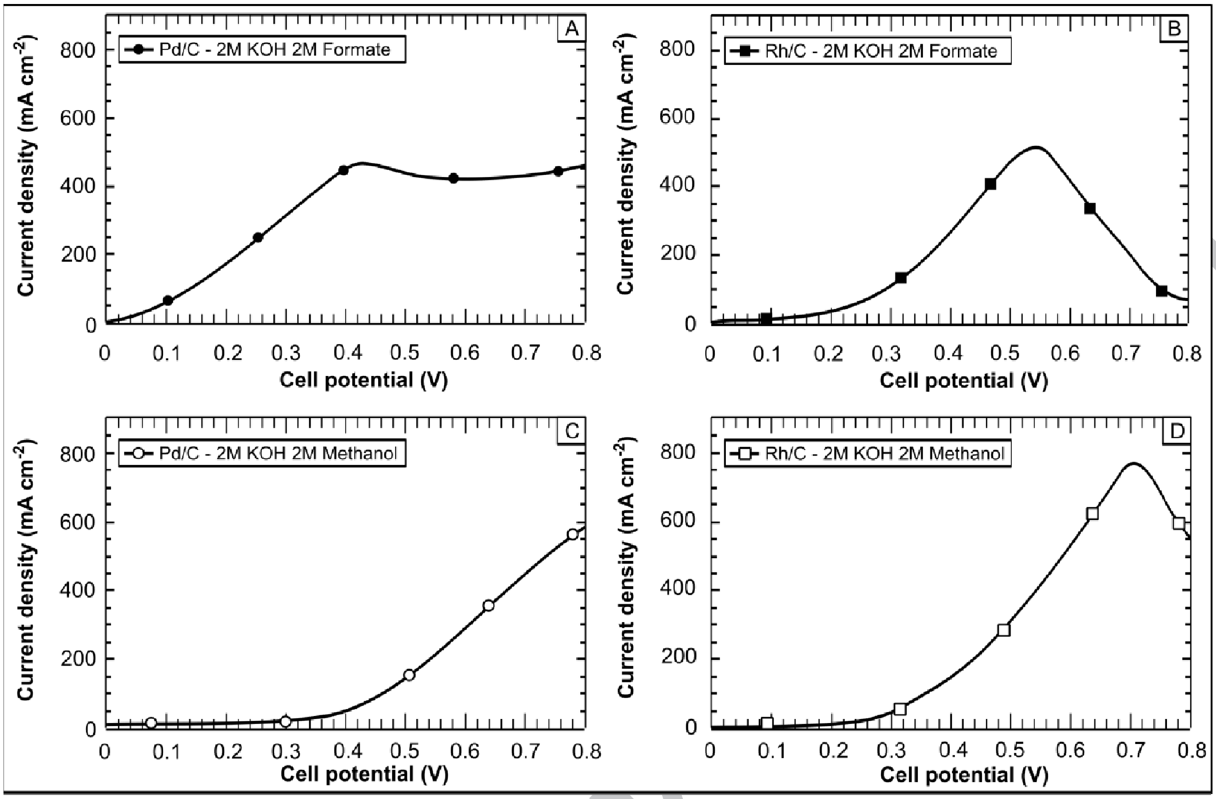


Fig. 3 First cycle of the potentiodynamic experiments of Pd/C with 2M KOH + 2M Formate (A) and 2M KOH + 2M Methanol (C), and of Rh/C 2M KOH + 2M Formate (B) and 2M KOH + 2M Methanol (D). Scan rate of 10 mV s^{-1}. Cell temperature 80 °C.

Table 3 Relevant electrochemical parameters of the cell at 80°C using Pd/C or Rh/C as anode and 2M KOH + 2M Formate or 2M KOH + 2M Methanol as fuel.

Fuel	Pd/C				Rh/C			
	Jmax (mA cm-2)	Conversion (%) [mmol]	H2 produced (Nm3 m-2)	Energy consumption (KWh Kg-1H2)	Jmax (mA cm-2)	Conversion (%)[mmol]	H2 produced (Nm3 m-2)	Energy consumption (KWh Kg-1H2)
Formate	460	75 [45]	2.5	5	510	79 [47]	2.6	8
Methanol	580	38 [23]	3.8	14	780	51 [31]	4.8	12

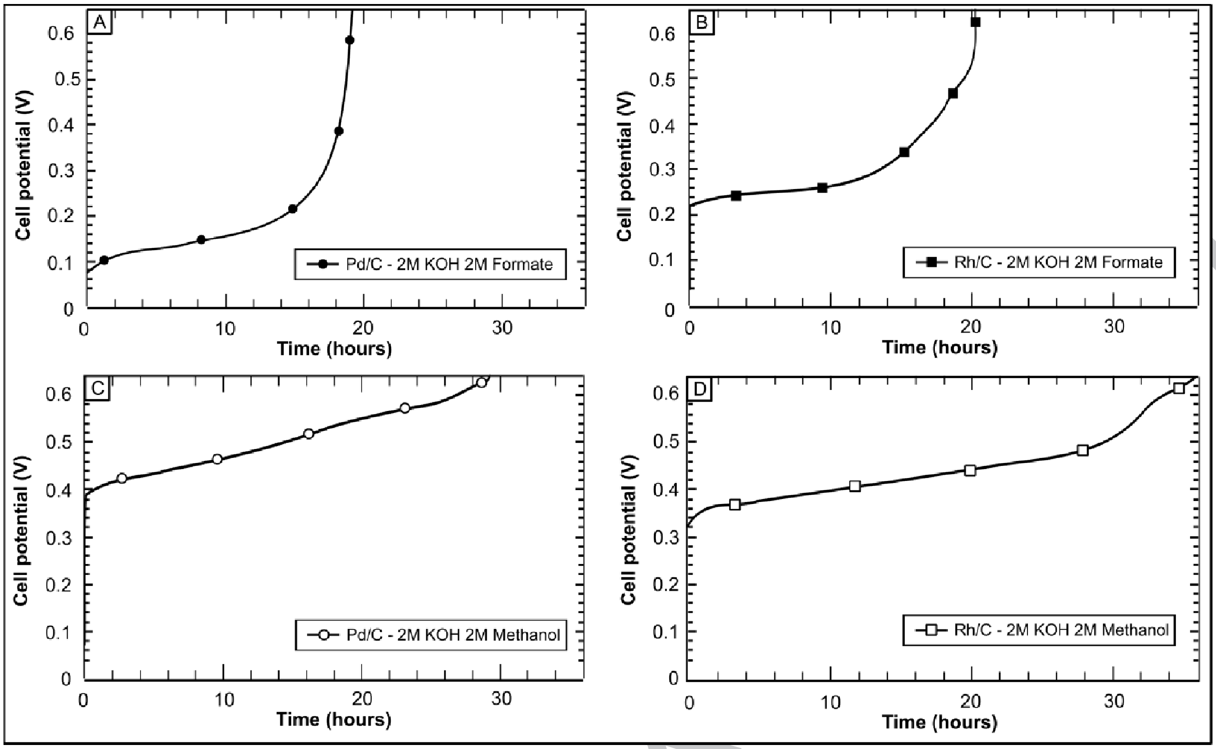


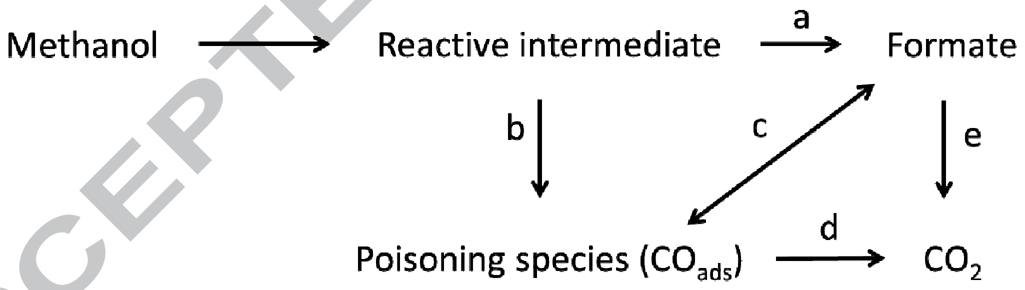
Fig. 4 First cycle of the galvanostatic experiments of Pd/C with 2M KOH + 2M Potassium Formate (A) and 2M KOH + 2M Methanol (C), and of Rh/C 2M KOH + 2M Potassium Formate (B) and 2M KOH + 2M Methanol (D). Constant current of 125 mA. Cell temperature 80 °C.

The galvanostatic experiments, shown in Fig. 4, were performed to determine the energy efficiency and conversion efficiency of the system for hydrogen production. For each cycle, 30 mL of fresh fuel was provided to the anode compartment of the cell. A constant current (125 mA) was set to the cell and the change in potential was recorded over time until it reached a value of 0.65 V. The same experiment was repeated three times changing only the fuel solution. The reproducibility of the experiment during time confirmed the stability of the catalysts (see Figures S1 and S2 in the Supporting information). With potassium formate, the only possible product that can be formed is carbonate; in the case of methanol, from $^{13}C\{^{1}H\}$NMR analysis of the fuel exhausts, we found that with Pd/C 100% of CO_3^{2-} was obtained while Rh/C oxidizes methanol to 85% of CO_3^{2-} and 15% of formate. On the basis of this selectivity, and the number of moles of electrons exchanged during the experiment, we have calculated the conversion % of the fuel and the quantity of hydrogen produced (see

Table 3). The energy consumption was also calculated from the integration of the instantaneous charging power over duration time of the experiment. All the obtained values, reported in

Table 3, are under 14 KWh $Kg^{-1}_{H2.}$ Pd/C presents the best performance with formate as fuel showing a value of 5 KWh Kg^{-1}_{H2}. The Faradic efficiency, defined as the ratio between the discharge capacity and the theoretical discharge capacity, has been calculated from galvanostatic experiments. In the case of formate oxidation to carbonate, it is equal to 74% for Pd/C and 78% for Rh/C; and in the case of methanol oxidation values of 38% for Pd/C and 48% for Rh/C were obtained. The faradaic efficiencies obtained for methanol were lower than formate. We believe this was mostly due to loss of methanol through crossover from the anode solution and evaporation at the cathode as no methanol was found in the fuel solution after the experiments. From the $^{13}C\{^{1}H\}$NMR analysis of the fuel exhausts we have demonstrated that Pd/C and Rh/C have different selectivity for methanol oxidation: Pd/C leads to 100% of carbonate, and Rh/C to 85% of carbonate and 15% of formate. The complete oxidation of methanol to CO_3^{2-} involves six electrons. For both electrocatalysts, there are two possible pathways of electrooxidation of methanol, firstly through the formation of formate (scheme 1 path a and e) and its direct oxidation to carbonate, and an indirect pathway through the formation of poisoning species (CO_{ad}) and finally of carbonate (path b and d).[16] In our study, given the fast kinetics with which formate is oxidized to carbonate and the presence of formate as intermediate, we can assume that the most likely path is the one (path a) that avoids poisoning intermediates. This is in agreement with what is reported in the literature, indeed formate has been identified as an active intermediate for the direct oxidation of methanol on Pt electrodes. [33]

Scheme 1: Methanol oxidation process in alkaline medium.[16]



Conclusions

In this paper, we report a study of the electrooxidation performance of Pd/C and Rh/C catalysts, in alkaline media at 80 °C. The two fuels studied were potassium formate and methanol. The electrochemical measurements show for both metals low onset potentials, and high specific current densities. In particular, Pd/C with formate, exhibits an onset of 200 mV and a specific activity of 2100 A g^{-1}_{Pd}; while Rh/C has an excellent activity for methanol oxidation, showing an onset potential 200 mV lower than Pd/C and a specific activity almost double reaching the value of 2600 A g^{-1}_{Rh}.

In complete electrolysis cells, high current densities for hydrogen production are obtained at low cell potentials. Indeed, the energy costs are very low for both substrates (< 14 KWh Kg^{-1}_{H2}). Pd/C with formate shows 5 KWh Kg^{-1}_{H2}. Taking into account both the energy consumption and conversion efficiency then we can conclude that the Rh/C catalyst performs best with methanol as substrate.

In summary, we report for the first time a complete study of alkaline alcohol electrolyzers fed with methanol and formate. We have evaluated the energy consumption for the production of CO_2-free hydrogen, demonstrating the ability of the Rh/C and Pd/C anode catalysts to perform the complete oxidation of methanol, without being subject to CO poisoning, confirmed by their stability over continued testing.

This technology is an important example of novel strategies for the conversion of waste biomass into valuable biofuels e.g. hydrogen. Today, in fact, there is a need to search for more sustainable fuels to develop a carbon-neutral energy economy, and hydrogen is an excellent candidate for becoming a next-generation bio-fuel.[34] Technologies such as electroreforming can be easily integrated into a future energy system not based upon oil, which are based upon the exploitation of local sources of biomass.

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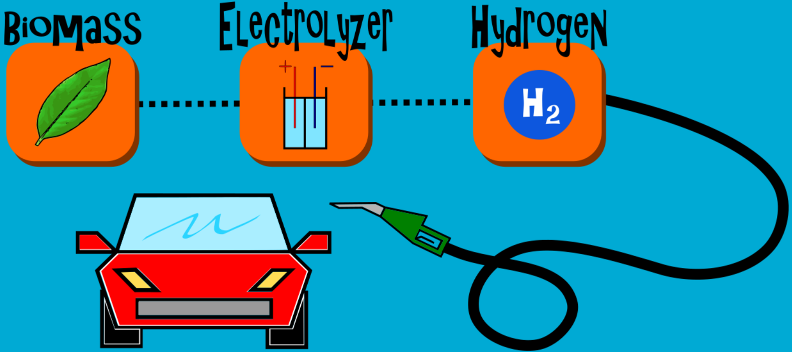
Highlights:

- Rh and Pd nanoparticles supported on carbon were studied for the electrooxidation of formate and methanol
- The electrooxidation of methanol and formate to hydrogen was investigated in complete electrolysis cells
- The energy consumption for the production of CO_2-free hydrogen was determined.


Biomass
Electrolyzer
+
−
Hydrogen
H_2