

Short communication

Development of electrocatalysts for solid alkaline fuel cell (SAFC)

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Abstract

It is now widely accepted that the proton exchange membrane fuel cell (PEMFC) concepts can be applied for a rather large range of power production at low temperature, including ambient conditions for some applications. For small power units, the concept of fuel cell with a solid electrolytic membrane can be extended to the alkaline medium. The main condition is to develop an anionic membrane with a sufficient stability and a good electric conductivity. The aim of this paper is to discuss on the development of electrocatalysts (both anodic and cathodic) suitable with their use in a solid alkaline fuel cell working at room temperature. The fuel cell is conceived around a new kind of anionic membrane developed by an industrial partner.

The catalysts need to be adapted to this new concepts and working conditions. For oxygen reduction, catalysts containing silver have been prepared and gave encouraging results. For the anodic side, fuels such as methanol or ethylene-glycol have been considered. Platinum-based catalysts have been developed and tested in addition with platinum-free electrocatalysts. The electrocatalytic activity of Pt–Pd catalysts was first evaluated in semi-cell in order to optimize the composition of the electrodes. Then, tests in fuel cells working at room temperature were carried out, and confirm the validity of the solid alkaline fuel cell (SAFC). A power density of 18–20 mW cm⁻² was observed with methanol or ethylene-glycol at 20 °C. © 2005 Elsevier B.V. All rights reserved.

Keywords: Alkaline fuel cell; Anionic membrane; Electrocatalysts

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is now widely accepted as a suitable system for a rather large range of power production at low or medium temperature. The use of a polymeric membrane as solid electrolyte allows for example use in fuel cell for applications such as power sources for electronic devices (computer, phone, etc.). Until now, only protonic membranes have been considered (typically Nafion®). If the conductivity of such membranes is convenient, their strong acidic behaviour leads to limitations due to the necessity to use platinum or platinum-based electrocatalyst. If platinum is very efficient for pure hydrogen oxidation or even for oxygen reduction, the presence of adsorbed carbon monoxide, coming from the dissociative adsorption of oxygenated organic compounds, leads to a poisoning effect and a decreasing of the performances. Then, in the case of direct methanol fuel cell (DMFC) [1], as methanol and more generally alcohols are used as fuels for application for electronic devices, the poisoning of Pt and Pt-based electrocatalysts is important [2–5].

On another hand, it is well known that the electrooxidation of organic compound in alkaline medium is much easier in comparison with acid medium. In such a medium, poisoning effect appears very weak and even platinum-based catalysts are not necessary, and cheaper catalyst can be used.

The rather recent development of polymeric membrane presenting a good anionic conductivity opens a new research area to conceive solid fuel cells working with an electrolytic membrane different from the common protonic membrane. This paper concerns a preliminary study of different electrocatalysts for oxygen electroreduction or alcohols oxidation convenient for their use in a solid alkaline fuel cell (SAFC) [6–10]. The anionic membrane is provided by Solvay, and tests of different electrocatalysts (anodic or cathodic), suitable for alkaline medium, were carried out in order to validate the concepts of SAFC working at room temperature.

2. Experimental

2.1. Synthesis of Pt-based and Ag/C electrocatalysts

Pt and Pt-based particles were prepared from colloidal precursors and dispersed on carbon powder (Vulcan XC72). The technique used is based on the well-known “Bönneman” method

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[11]. The colloid precursor is first synthesized under inert atmosphere from anhydrous metallic salts in an organic solvent (THF) in the presence of a surfactant (typically a quaternary ammonium salt). The role of this surfactant is essential as it prevents the agglomeration of the metallic particles during the reduction step and allows the formation of nanoparticles.

The Pt-based nanoparticles are obtained by a similar technique but with the co-reduction of the different metallic salts. The precursors are then adsorbed on the carbon powder and the surfactant is removed by thermal treatment. This step is important and the temperature used is crucial to avoid sintering of the metallic particles. Typically, 300 °C is the optimal temperature for such a process.

Ag nanoparticles were obtained from a silver nitrate solution with Brij[®]30 (tetraethyleneglycoldodecylether) in *n*-heptane under vigorous stirring. Then a solution of sodium borohydride was added, always under stirring conditions. The reduction of Ag⁺ occurs when a hydrogen evolution took place and the solution is darkened.

The precursor colloids were dispersed onto high surface area carbon (Vulcan XC72), preliminary treated at 400 °C under nitrogen during 4 h in order to clean it. The catalytic powder was prepared by thermal treatment of the colloidal solution—carbon mixture at 300 °C under air for 1 h in order to remove the organic surfactant. Catalytic powders were obtained by mixing desired amount of colloid and carbon powder in order to obtain a metal loading from 10 to 30 wt.% on carbon.

Electrodes were prepared from ink made from the supported catalyst and a Nafion[®] solution according to a method described elsewhere [12]. For cyclic voltammetry (CV), this ink is deposited on a vitreous carbon disk and used after evaporation of the solvent at room temperature for several hours. For fuel cell tests, electrodes were prepared according to a technique commonly used and described previously. It consists in painting the ink prepared with the catalysts at the surface of a diffusion layer (E TEK Inc.) and dried. The loading of the anode was 2 mg cm⁻² in metal, with a loading of 40% of Pt-based on carbon powder (Vulcan XC72). The cathodes used are 40% Pt/C electrodes containing 2 mg cm⁻² of platinum.

The dispersed catalysts were deposited on vitreous carbon according to a method proposed previously [12]. The carbon supported catalyst powder is added to a mixture of 25 wt.% (based on the powder content) Nafion[®] solution (5 wt.% from Aldrich) and ultra-pure water (Millipore MilliQ – 18 MΩ cm). After ultrasonic homogenisation of the catalyst/XC72-Nafion[®] ink, a given volume is deposited from a syringe onto a fresh polished glassy carbon substrate.

The catalysts are characterized by transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis using a Philips CM 120 microscope/EDX analyser equipped with a LaB₆ filament. To prepare the sample, a small drop of the solution is put on gold grid and the solvent is evaporated.

2.2. Electrochemical measurements

The electrochemical set-up consists of a Voltalab PGZ 402 potentiostat controlled by a computer, a radiometer speed control unit CTV 101 and a rotating disk electrode (RDE) radiometer BM-EDI 101. The rotating ring disc electrode (RRDE) experiments were performed with a Pine Instrument Company equipment AFRDE4 bipotentiostat and AFMSRX modulator speed rotator mounted with an AFDT22 electrode including a Pt ring and a GC ring disc leading to a collection efficiency of 20%.

The solutions were prepared from NaOH (Suprapur, Merck), high purity grade methanol or ethylene-glycol (Merck) and ultra-pure water (MilliQ, Millipore 18 MΩ). The electrochemical experiments were carried out at 20 °C in either N₂-purged or O₂ saturated 0.1 M NaOH + X M MeOH (X=0; 0.1; 0.5) using a conventional thermostated standard three-electrode electrochemical cell. The working electrode was a glassy carbon plate, the counter electrode was also a glassy carbon plate and the reference electrode was a mercury mercurous sulphate electrode (MSE), but all potentials are related to the reversible hydrogen electrode (RHE).

Finally, electrical tests in a single solid alkaline fuel cell (SAFC) were performed using a Globe-Tech test bench. The effects of the composition of the anodes and/or of the working temperature were evaluated with this test bench. The membrane

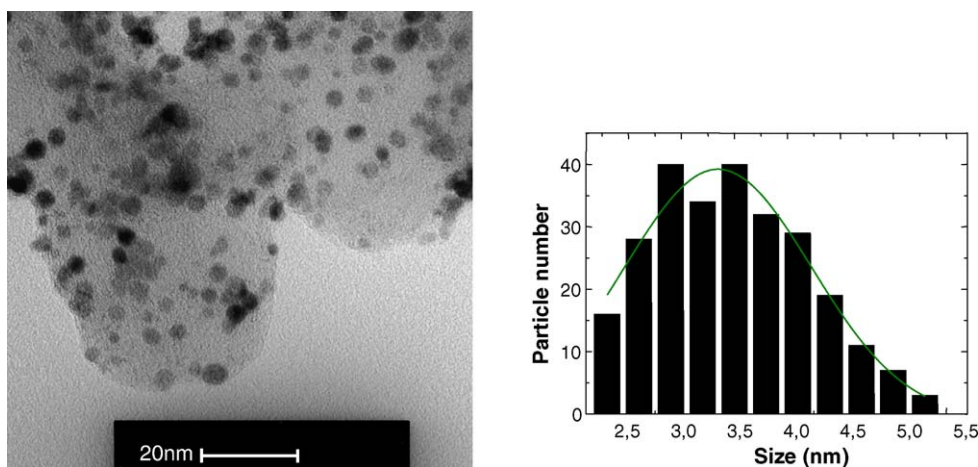


Fig. 1. Characterization of Pt–Pd (1:1) 20% prepared in the laboratory. TEM image, and particle size distribution estimated from TEM.

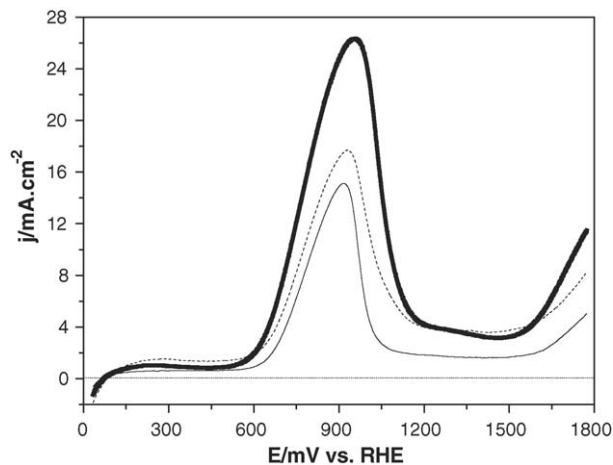


Fig. 2. Electrooxidation of 0.1 M of ethylene-glycol in 0.2 M NaOH on Pt–Pd (1:1) with different metal loadings. (—) Pt–Pd (1:1) 10%; (---) Pt–Pd (1:1) 20%; (· · ·) Pt–Pd (1:1) 40%.

electrode assemblies were realized by pressing directly in the cell the electrodes against a commercial ADP-type membrane from Solvay. The ADP membrane used in this work was described elsewhere [13].

3. Oxidation of alcohols

Platinum is known to be a good electrocatalyst for alcohols oxidation in alkaline medium. Among the different possibilities to use bimetallic platinum-based catalysts, we tested the case of Pt–Pd nanoparticles for the electrooxidation of ethylene-glycol. The choice of palladium was taken after preliminary tests showing best performances in alkaline medium when added to platinum. Particles aspect can be seen by transmission electronic microscopy (Fig. 1). The particles size distribution was also estimated from the TEM images and an average size of 3.2 nm was observed with a distribution size rather narrow. Fig. 2 represents the activity of different Pt–Pd/C electrodes prepared with

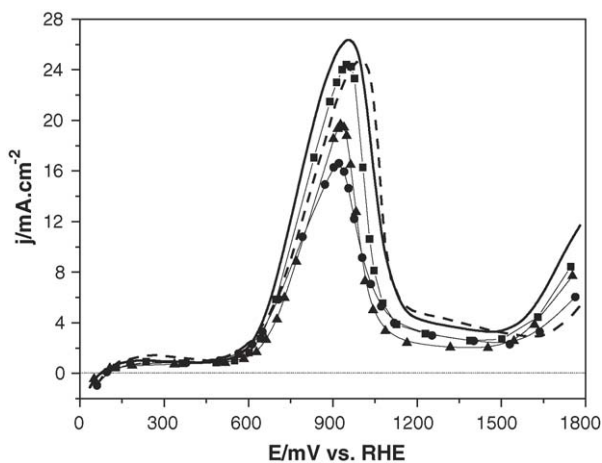


Fig. 3. Electrooxidation of 0.1 M of ethylene-glycol in 0.2 M NaOH on different Pt–Pd (20%) of different compositions compared to Pt: (—) Pt–Pd (1:1) 20%; (---) Pt 20%; (■) Pt–Pd (1:1) 20% E TEK; (▲) Pt–Pd (1:3) 20% E TEK; (●) Pt–Pd (3:1) 20% E TEK.

nanoparticles synthesized according to the Bönnerman method. The effect of metal loading (with Vulcan XC72 as conducting support) is shown.

The maximum of activity was observed with the Pt–Pd/C catalyst with 20% metal loading. The behaviour of these home-made catalysts were also compared to commercial nanosized bimetallic catalysts provided by E TEK.

This comparison is given in Fig. 3. All the catalysts were with 20% metal loading. In terms of maximum activity, our catalyst appears as the most active one. But the most interesting fact is the negative potential shift observed in comparison to pure platinum which confirms that the Pt–Pd is less poisoned than pure platinum.

4. Reduction of oxygen

As noted in the introduction, one of the advantages to use alkaline medium and anionic membrane is the possibility to limit or even avoid platinum as component for the electrodes. For the electroreduction of oxygen several metals different from platinum can be considered. In the present work, we evaluate the activity of silver particles for the reduction of oxygen, which was proposed in a few works [14,15]. Ag particles were prepared according to the chemical procedure described in the experimental section. These particles were supported on Vulcan XC72.

In Fig. 4 are shown the reduction currents obtained for different silver loadings and a comparison, with the behaviour of platinum under the same experimental conditions, is also given. The influence of the metal loading is obvious and it seems that the optimum loading in silver is around 20%. The activity with platinum is better than with silver, with a potential shift of 50 mV towards more negative values for silver in comparison to platinum. However, the value of current observed with silver for oxygen reduction, mainly for Ag/C 20 or 30%, suggests a number of exchanged electrons close to four corresponding to a complete reduction of oxygen into water. This value of the number of exchanged electrons during the oxygen reduction reaction was determined by analysing the curves obtained

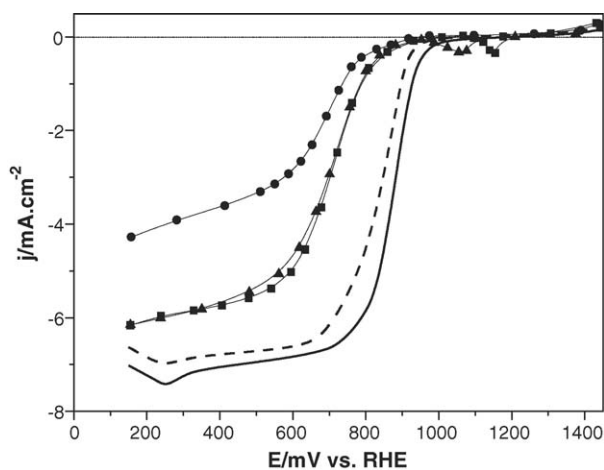


Fig. 4. Oxygen electroreduction in 0.1 M NaOH with Pt/C or Ag/C particles ($\Omega = 2500$ rpm). (—) Pt 40%; (---) Pt 20%; (■) Ag 20%; (▲) Ag 30%; (●) Ag 40%.

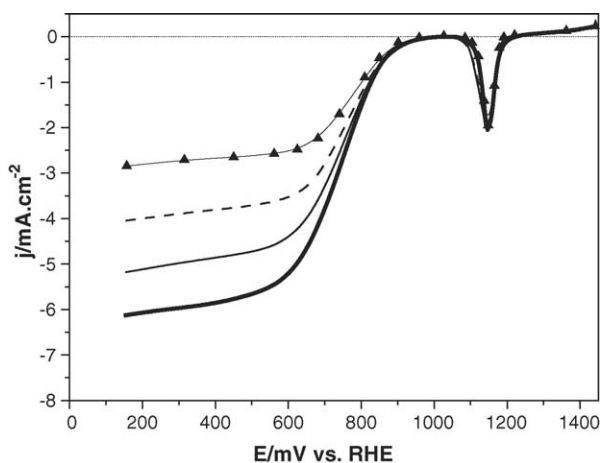


Fig. 5. Oxygen electroreduction in 0.1 M NaOH. Influence of the rotation rate of a silver electrode. (—) 2500 rpm; (---) 1600 rpm; (· · ·) 900 rpm; (▲) 400 rpm.

at different rotation rates (Fig. 5). From an analysis using the Koutecký–Levich equation [16–18], the number of exchanged electrons during the oxygen electroreduction was estimated as 3.6. This value shows that the main reaction product formed is water. This result is close to that obtained from rotating ring-disk electrode experiment ($3.8 e^-$). A remark should be done concerning the peak visible in Fig. 4 at 1150 mV versus RHE. This peak is related to the reduction of silver oxides formed at more positive potential at the beginning of the experiment (curves are recorded from high to low potentials).

An important point in relation with the fuel cell application is the tolerance to the presence of methanol. This is important due to the cross-over of methanol generally observed in membrane fuel cell. When this cross-over exists, the presence of methanol in the cathodic compartment leads to the depolarisation of the cathode when the electrocatalyst used is not selective to oxygen reduction. Fig. 6 represents the electroreduction of oxygen in the presence of methanol (0.5 M). It is obvious that the reduction wave is modified by the presence of methanol. The less tolerant electrocatalyst is Pt/C 40%, which exhibits methanol

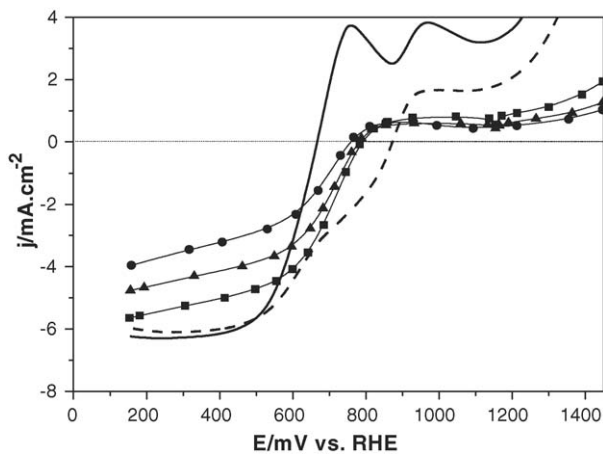


Fig. 6. Oxygen electroreduction in 0.1 M NaOH on platinum and silver in the presence of 0.5 M of methanol ($\Omega = 2500$ rpm). (—) Pt 40%; (---) Pt 20%; (■) Ag 20%; (▲) Ag 30%; (●) Ag 40%.

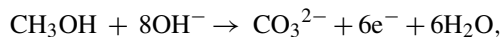
oxidation current for high potentials. However, it is clear that the three Ag/C catalysts tested present a very good tolerance to the presence of methanol. As expected, Ag/C 20% appears as the most selective to oxygen reduction and then presents the best methanol tolerance.

5. Fuel cell test

Preliminary tests were carried out in solid alkaline fuel cell based on an anionic membrane and different kinds of electrode.

5.1. Methanol

First tests are performed with methanol as fuel (Fig. 7) in a SAFC. Both electrodes are Pt/C 40% (2 mg cm^{-2}) with a 5 cm^2 geometric area. In this figure is demonstrated the necessity to add sodium hydroxide to methanol aqueous solution in order to obtain significant performance. With only an aqueous solution of methanol, the performances obtained are very weak. Thus, without a sufficient amount of OH^- added, the reaction of oxidation of methanol is impossible and the conductivity of the membrane, based on the presence of hydroxyl ions, decreases rapidly. This is the consequence of the alkaline medium where the reaction of electrocatalytic oxidation of methanol can be written as:



Due to alkaline medium, the final product of oxidation of methanol is transformed in carbonate ions. Then eight OH^- are necessary to oxidize one molecule of methanol. Taking into account that the anionic membrane used in SAFC is an ionic conductor needing a constant concentration of OH^- to maintain its conductivity, the amount of added sodium hydroxide is a critical point. If it is not sufficient, some hydroxyl species would be taken from the membrane to form carbonate and the conductivity of the membrane will drop rapidly. However, if the concentration of NaOH is too high, working conditions of the SAFC become difficult to stabilize and the observed performances decrease rapidly with time. Then, with 4 M of NaOH added which seems to be an optimum value, a maximum of 18 mW cm^{-2} was observed at room temperature (Fig. 8).

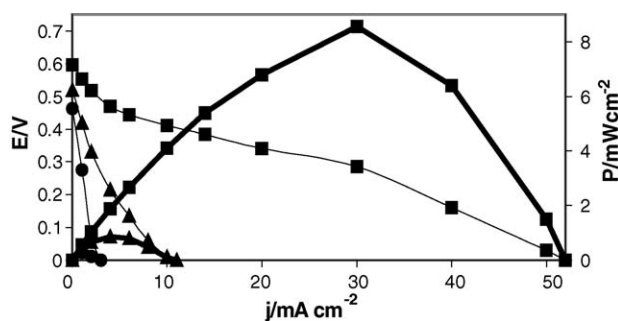


Fig. 7. Cell voltage and power density vs. current density curves for 1 M methanol in (■) 1 M NaOH; (▲) with an increasing concentration of NaOH (until 0.25 M); (●) without NaOH. Anode and cathode Pt/C 40% 2 mg cm^{-2} homemade. Anionic membrane 20°C .

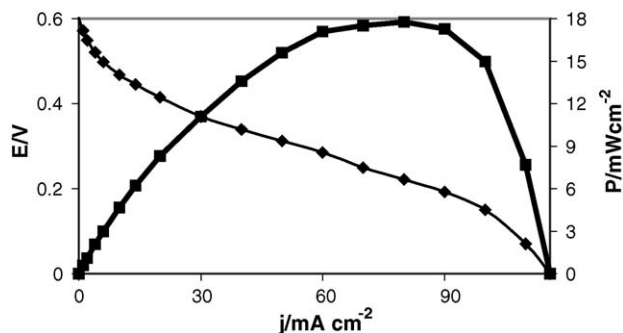


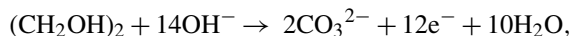
Fig. 8. Cell voltage and power density vs. current density curves for 2 M methanol with 4 M NaOH. Anode and cathode Pt/C 40% 2 mg cm⁻² homemade. Anionic membrane 20 °C.

5.2. Ethylene-glycol

Among the other candidates as fuels suitable for fuel cell application in alkaline environment, ethylene-glycol seems to be a good candidate. This diol is no toxic and presents a boiling point, which leads to easy handling and storage. Its electrocatalytic reactivity is good and the final product can be either carbonate or oxalate.

We realized preliminary tests in a fuel cell under the same experimental conditions as with methanol described above.

Again in this case, addition of sodium hydroxide is necessary to form the final product of oxidation. With ethylene-glycol this final product can be carbonate through the following equation:



However, as the cleavage of the C–C bond is generally difficult, final product can be oxalate:

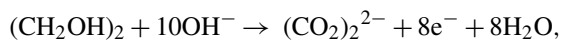


Fig. 9 shows the cell voltage and the power density versus the current density for a SAFC fed with ethylene-glycol. As for the previous tests with methanol, both electrodes are Pt/C 40% (2 mg cm⁻²) with a 5 cm² area.

Under such conditions, with a concentration of 2 M ethylene-glycol and 4 M sodium hydroxide, a maximum of 19 mW cm⁻² of power density was obtained at 20 °C, a value very closed to the maximum observed for methanol.

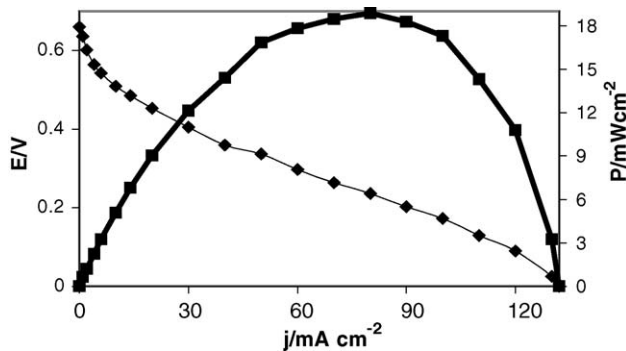


Fig. 9. Cell voltage and power density vs. current density curves for 2 M ethylene-glycol with 4 M NaOH. Anode and cathode Pt/C 40% 2 mg cm⁻² homemade. Anionic membrane 20 °C.

6. Conclusion

Fuel cells seem to be a suitable power source for portable electronic devices. As the storage of hydrogen limits drastically the use of such a fuel for a wide public utilization, the case of liquid fuel needs to be evaluated. Until now, only PEMFC are generally considered for this purpose, but the performances for the direct oxidation of liquid fuel (such as alcohol) are limited mainly at ambient temperature. This preliminary study is a contribution to an evaluation of solid alkaline fuel cell (SAFC) constructed with an anionic membrane. The alkaline medium opens new possibilities for the composition of the electrodes, as platinum is not the only possible catalyst.

In this work we tested Pt–Pd/C electrocatalysts for the oxidation of ethylene-glycol. This fuel, due to its physical properties, is a convenient fuel for portable applications. It was demonstrated that, if sodium hydroxide is added to the ethylene-glycol aqueous solution, significant performances could be reached. A non-platinum cathodic catalyst was also tested for the oxygen reduction. Silver particles are suitable for this purpose, and it was confirmed that the reduction of oxygen into water is quite complete (3.6 to 3.8 exchanged electrons).

After this preliminary study, it is clear that more work is necessary to optimize the electrodes and more generally the electrode membrane assembly. But the concept of SAFC appears to be valid, with significant performances obtained at room temperature.

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