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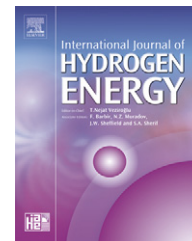
Methanol/air fuel cells: catalytic aspects and experimental diagnostics

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ABSTRACT

Methanol/air fuel cell with direct feed of methanol has received growing attention due to the possibility of using a liquid fuel of simple storing. This work comments studies on the preparation of PtRu catalysts for methanol oxidation and on the influence of different operative parameter on the performance of a lab scale fuel cell.
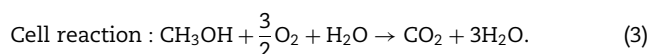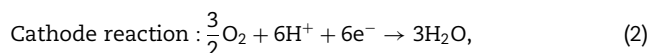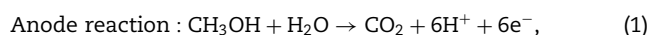
The best conditions for PtRu catalysts preparation using metal electrodeposition techniques were found. Different carbon materials were used, such as glassy carbon, carbon paper and graphite fiber cloths and felts . The more active materials were found to be graphite felts after being preoxidized electrochemically to obtain a higher surface oxide concentration.

Acceptable performance of the fuel cell was obtained working at $90\,^\circ C$ and low methanol concentration, because in these conditions the potential, the transport process rates and the electrode reaction kinetics increase.

1. Introduction

Direct methanol fuel cells (DMFC) have advantages over other fuel cells because methanol is easily prepared, handled and stored [1–4]. The key component of a DMFC is the membrane electrode assembly (MEA), which comprises a polymer electrolyte membrane, and catalyst coated porous electrodes for methanol oxidation (reaction 1), and oxygen reduction (reaction 2).

$$\text{Anode reaction}: CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-, \qquad (1)$$

$$\text{Cathode reaction}: \frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O, \qquad (2)$$

$$\text{Cell reaction}: CH_3OH + \frac{3}{2}O_2 + H_2O \rightarrow CO_2 + 3H_2O. \qquad (3)$$

In a DMFC many processes and phenomena occur simultaneously, such as

- methanol distribution and CO_2 removal in flow channels in the anodic compartment,
- the electrochemical oxidation of methanol in the anode catalytic layer,
- transport of reactant and products through the polymeric electrolyte,
- methanol oxidation in the cathode, due to the crossover process,
- distribution, transport and reaction of oxygen in the cathode.

Not all these phenomena are assigned the same importance in the current fuel cell research. In general, the development

of a fuel cell covers three basic fields: electrode reactions catalysis, MEA components and the influence of the different operative variables in the cell performance [5,6].

As it is known, methanol oxidation kinetic is slow and at the actual stage of development, more effective catalysts are required to obtain higher current densities. The most efficient catalysts for methanol oxidation are based on platinum combined with ruthenium [7–9]. There are many preparation methods [10–12], but electrodeposition was chosen because it has the advantage of placing selectively the deposits in zones accessible to the electrolyte, with the consequent more efficient employ of the catalyst [13].

Moreover, the actual operation of a cell also depends on the adequate balance between the different factors such as temperature, methanol concentration, transport processes, etc. [14–16]. Methanol and water readily diffuse through the polymeric membrane electrolytes and significant quantities of methanol and particularly water pass from the anode to the cathode. This reduces the cathode efficiency in two ways. First, any methanol that comes in contact with the cathode electrocatalyst will reduce the efficiency of the oxygen reduction reaction by a competing electrochemical process known as the mixed potential effect. Second, the cathode structure becomes waterlogged or flooded, and is no longer an efficient structure for gas diffusion (mass transport loss). Both these effects can reduce the cell voltage by a further 0.2–0.3 V, particularly when practical air flow is used [17].

In this work some results obtained with PtRu catalysts prepared by electrodeposition on different carbon substrates and their activities for methanol oxidation are discussed. Simultaneously, tests of a methanol/air lab fuel cell for finding diagnostic criteria that help to identify the origin of the problems that arise during this system operation are reported.

2. Experimental

PtRu electrodes were prepared using different substrates such as graphite fiber cloths (GC-10) and felts (GF-S2), carbon paper (CFP) and glassy carbon (GC). Electrochemical measurements were carried out in a conventional glass half-cell arrangement at room temperature. The counter electrode was a platinum sheet, separated from the working electrode compartment by a porous glass diaphragm. A saturated calomel electrode located in a Luggin capillary served as the reference electrode (+0.241 V vs.SHE). Pt and Ru catalysts were electrodeposited simultaneously from 2 mM H_2PtCl_6 + xmM $RuCl_3(x = 2, 5, 10)$ + 0.5 M H_2SO_4 solutions. Different combinations of potential pulses were used, modifying the positive (0.5 and 1.0 V (SCE)) and negative potentials, and the number of cycles applied. Carbon substrates were oxidized in 0.5 M H_2SO_4, at 2.0 V during 300 s and then reduced by a potential linear sweep at 1 mV s^{-1} down to −0.8 V [18]. Hereafter, we will refer to these oxidized electrodes with the subindex ox (i.e. PtRu/GC$_{ox}$). The supported catalysts were characterized using scanning electronic microscopy (SEM) with an associated EDX analyzer, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and electrochemical tech-

niques. The electrodes were tested for methanol oxidation in acid media (1 M MeOH + 0.5 M H_2SO_4), and the catalyst activity was determined comparing the peak current in a voltammogram obtained at 50 mV s^{-1} expressed in function of the real surface area. The real surface area of the supported catalysts was determined using underpotential deposition of copper [19].

Complete fuel cell tests were carried out in a PEM fuel cell with 25 cm^2 electrodes. The MEA was composed by a Nafion$^{®}$ 117 membrane, a Pt/C cathode (1 mg Pt cm^{-2}, 20 wt% Pt/C), and a PtRu/C anode (1 mg Pt + 0.5 mg Ru cm^{-2}, 20 wt% Pt/C and 10 wt% Ru/C).

The anode compartment was fed with an aqueous solution of methanol (MeOH) with concentrations raging from 0.1 to 1.0 M, and different flow velocities (2−10 ml min^{-1}). The cathodic compartment was fed with air or oxygen, at atmospheric pressure, with flow velocities between 60 and 500 ml min^{-1}. The influence of different operative parameters on fuel cell performance was evaluated discharging the cell through a resistor and determining the polarization curve.

3. Results and discussion

3.1. Preparation of PtRu catalysts

Simultaneous electrodeposition of platinum and ruthenium in the conditions described previously permits to obtain bimetallic alloys with ruthenium content between 7 and 30 at%. The catalyst active surface area, determined with an error minor than 10% has been found to depend positively on the number of cathodic potential pulses at −0.5 V, and on the potential of the anodic pulse. At −0.5 V a great quantity of nuclei are formed, whereas at 0.0 V the metals tend to deposit over the preexistent particles, giving rise to fewer new nuclei. The effect of the positive pulse at 1.0 V is the rapid oxidation of the hydrogen formed during the negative pulse and probably the oxidation of the particles previously produced, facilitating the formation of new nuclei.

Better dispersion and uniformity of the catalyst particles can be obtained when the carbon substrate is modified by electrooxidation at high positive potentials. The SEM images in Fig. 1 show that the metal deposits prepared on the oxidized substrate appear as 50 nm agglomerates, while the same system with unoxidized substrate exhibits particles of 70 nm or bigger. The agglomerates are constituted by particles of 5 and 8 nm, respectively, as determined by XRD.

The electrochemical oxidation of the different carbon substrates influences on the electrodeposition of the PtRu binary catalyst due to the modification of metal/substrate interactions and to the increase of active sites available to the formation of metal nuclei. The catalysts prepared under the above conditions present higher active surface area, and when they are used as catalysts for methanol oxidation they show an interesting activity.

From Table 1 it can be concluded that the most active catalyst for methanol oxidation is PtRu deposited on oxidized graphite felt. The difference in activity between the various materials can be attributed to their dissimilar macroscopic
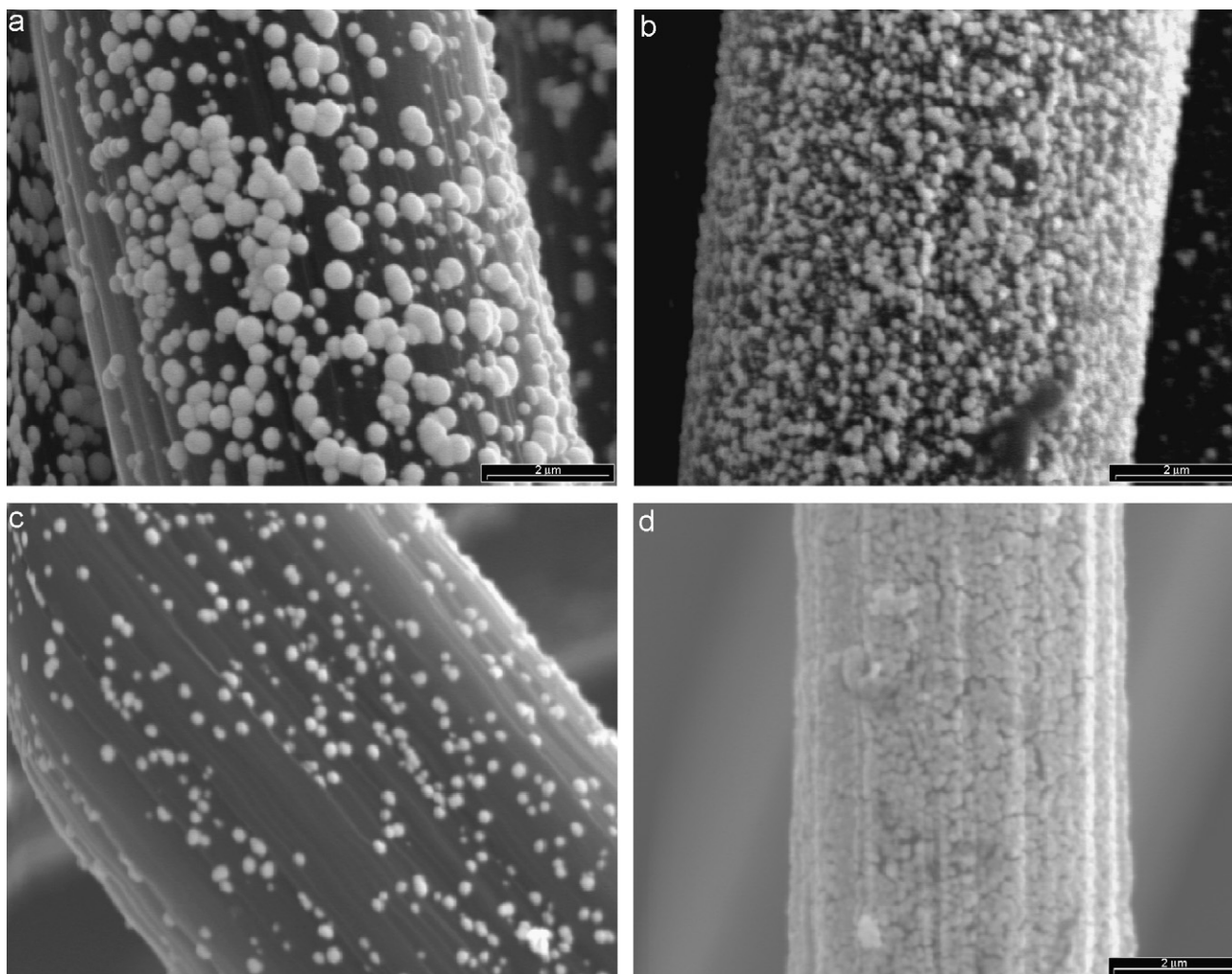
Fig. 1 – SEM micrographs showing the influence of the substrate oxidation in the electrodeposition of PtRu catalysts: (a) GC-10; (b) GC-10$_{ox}$; (c) GF-S2; (d) GF-S2$_{ox}$. Magnification $10,000\times$.

Table 1 – Effect of substrate material and oxidation pretreatment on the surface area of the supported PtRu catalysts and their activity for methanol oxidation in acid media

Electrode	A	i_p (mA cm^{-2})	i_p^* (mA cm^{-2})
GC	7.2	0.7	0.100
GC$_{ox}$	10.6	1.2	0.113
GC-10	24.6	1.6	0.070
GC-10$_{ox}$	45.4	2.4	0.080
GF-S2	24.0	3.5	0.150
GF-S2$_{ox}$	28.1	4.0	0.190
CFP	4.6	0.25	0.054

A: real surface area per geometric area unit; i_p: peak current of methanol oxidation in acid media per geometric area unit; i_p^*: peak current per real area unit.

structures that affect the reaction kinetics and to different active site concentrations over the carbon surface, which depends on the materials previous history.

3.2. Influence of the operative parameters on the operation of a DMFC

The effects of methanol concentration, anodic and cathodic feed flow velocities and operation temperature were studied to evaluate their influence on the fuel cell performance and to find the experimental conditions to minimize the energy losses in this system.

Cell behavior depends only slightly on the reactant feed flow velocities, because both oxygen and methanol transport through the catalytic layer is predominantly by diffusion in the pores. In the cathode, the use of pure oxygen produces a little improvement in the cell performance.

Methanol concentration in the anolyte flow is one of the parameters that most affects the performance of these cells as can be seen in Fig. 2, where the variation of the cell potential with the current is shown. The cell potential decreases when methanol concentration rises and the reduction is close to 100 mV when the concentration increases in an order of magnitude. The best operation of the cell happens at low concentrations of methanol [20].
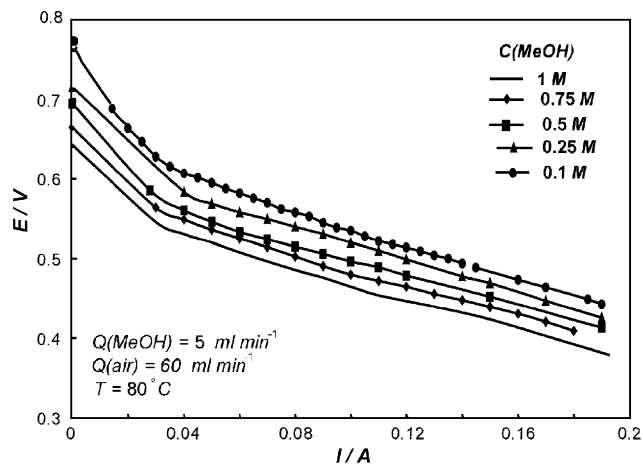
Fig. 2 – Steady-state polarization curves showing the influence of methanol concentration in the performance of a methanol/air fuel cell.
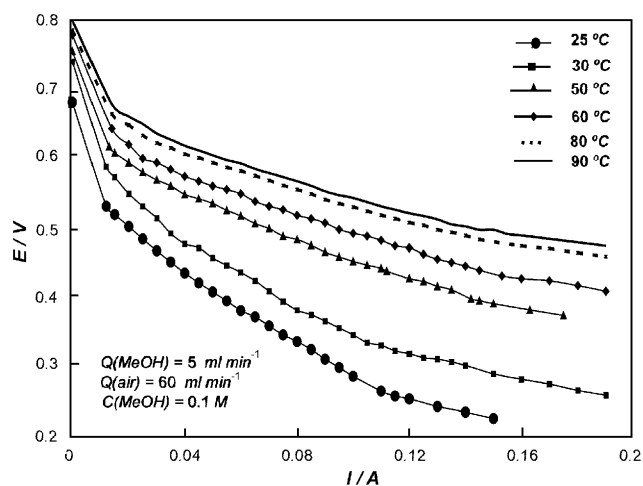

Fig. 3 – Steady-state polarization curves showing the influence of temperature.

When the anolyte methanol concentration is higher, the concentration gradient between anodic and cathodic compartment is more important and the methanol crossover rate increases. This leads to higher cathode overpotential and poisoning of the cathode catalyst with reduction of cell performance.

The effect of temperature on the cell behavior is shown in Fig. 3, where polarization curves for different temperatures can be seen. Rising the temperature from 25 to 90 °C results in higher cell potentials over all the range of current analyzed. For example, at 0.1 A increases of 0.2 V have been measured. This behavior is attributed to different effects of the temperature, such as higher mass transfer rate, higher reaction rates in the electrode reactions and a lower cell internal ohmic resistance [21]. At low temperatures cathode flooding may occur because water evaporation rate is insufficient to ensure a rapid removal from the pores.

4.   Conclusions

PtRu electrodeposited on different graphite fiber based materials such as cloths and felts, carbon paper and glassy carbon by electrodeposition exhibits differences that can be attributed to the geometry and the surface properties of the carbonaceous supports. The more active electrodes for methanol oxidation were prepared from preoxidized graphite fiber felts, using a sequence of negative and positive pulses between −0.5 and 1.0 V potential. The effect of the substrate changes significantly when the material undergoes an electrochemical pretreatment to generate higher concentrations of surface oxides. Catalyst composition depends primarily on the ratio between platinum and ruthenium concentration in the electrodeposition solution. Particle size and catalyst specific surface area are influenced by the substrate and the combination of pulses used in the deposition process. Both composition and morphology of supported PtRu catalysts are controlled by an adequate combination of potential pulses.

The tests carried out with the methanol/air fuel cell show the complexity of the interactions between the different simultaneous processes and phenomena that occur during the fuel cell discharge. Rising methanol concentration produces a reduction of the cell potential, which is associated to the increase of the methanol crossover through the proton exchange membrane. In consequence, on the cathode side a mixed potential is established that reduces the cell potential. The behavior of the cell depends in less measure on the cathodic reactant flow velocity. An acceptable operation of the tested fuel cell was obtained working at 90 °C, since under these conditions the potential increases. The velocity of several important processes rises, for example, mass transport processes rate, principally proton migration through the membrane, electrode reaction kinetics and water evaporation that reduce flooding in cathode pores.

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