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Short communication

Investigation of Pt–Fe catalysts for oxygen reduction in low temperature direct methanol fuel cells[☆]

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Abstract

High surface area carbon supported bimetallic Pt–Fe catalysts have been investigated for the oxygen electro-reduction process in low temperature direct methanol fuel cells (30–60 °C). The electrocatalysts have been prepared by using a combination of colloidal and incipient wetness methods allowing of synthesis carbon supported bimetallic nanoparticles with a particle size of about 2–3 nm. These materials were studied in terms of structure, morphology and composition using XRD, XRF and TEM techniques. Oxygen reduction properties of these bimetallic catalysts were investigated in single cell DMFC polarizations. The electrochemical data were compared with those obtained in the presence of a Pt/C catalyst prepared by the same procedure and characterised by the same concentration of active phase on the carbon support and a similar particle size. An improvement of the DMFC single cell performance was observed in the activation controlled region in the presence of the bimetallic catalysts. Moreover, the influence of the ionomer loading on the performance of the DMFC was investigated. The highest power density was recorded with electrodes containing 25% Nafion loading (87 mW cm^{-2}).

Keywords: Direct methanol fuel cells; Oxygen reduction reaction; Pt–Fe catalyst; Nafion loading

1. Introduction

Direct methanol fuel cells (DMFCs) have recently attracted interest for portable applications due to their superior specific energy density compared to the best rechargeable battery and their potentiatary of instantaneous refueling [1–3]. It is well known that one of the problems affecting DMFCs is the poisoning of the cathode surface in the presence of methanol cross-over [4,5].

Although a Pt/C electrocatalyst is the most widely used cathode material, there is a great interest in the development of more active and more methanol tolerant electrocatalysts for the ORR. Promising results have been achieved by alloying Pt with non noble metals [6]. A relationship between the electrocatalytic activity and the adsorbate bond length has been envisaged [7,8]. Thus, a lattice contraction due to alloying would result in a more favorable Pt–Pt distance for the dissociative adsorption of O_2. Besides this, an interplay between electronic and geometric factors (Pt-d vacancy and Pt-coordination numbers) and its relative effect on the OH chemisorption from the electrolyte occurs [9]. The increase of d-band vacancies on Pt by alloying produces a strong metal–O_2 interaction. Such interaction weakens the O–O bonds resulting in bond cleavage and bond formation between O and H^+ of the electrolyte, thus improving the ORR [10].

The synthesis of a highly dispersed electrocatalyst phase in conjunction with a high metal loading on a carbon support is one of the present goals in DMFCs. One of the main requirements for an optimal electrocatalyst is its high dispersion. The mass activity (A g^{-1}) of the catalyst for an electrochemical reaction is directly related to the degree of dispersion since the reaction rate is generally proportional to the active surface area. However, for the oxygen reduction process, it has been found that there is an optimum particle size of ca. 30 Å for Pt electrocatalysts, that corresponds to a maximum in mass activity [11]. For this reaction, it was found that the specific activity (A cm^{-2} real area) increases with the particle size and thus decreases with the active

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surface area. Another significant aspect concerns the loading of the metal phase on the carbon support. A high Pt concentration on the carbon substrate will reduce the anode thickness for the same Pt loading for geometric electrode area. Thus, it is possible to enhance the mass transport through the electrode and at the same time reduce the ohmic drop. The aim of the present work is to increase the catalytic activity for the oxygen reduction reaction by alloying Pt with Fe. The oxygen reduction properties of these bimetallic catalysts were investigated by half-cell and single cell DMFC polarizations. The electrochemical data were compared with those obtained in the presence of a Pt/C catalyst prepared by the same procedure and characterised by the same concentration of active phase on the carbon support and similar particle size. Moreover, the influence of the ionomer loading on the performance of the DMFC was investigated.

2. Experimental

Platinized carbon was prepared by using the sulfite-complex route [12]. A $Na_6Pt(SO_3)_4$ precursor, obtained from chloroplatinic acid, was impregnated on Vulcan XC-72R carbon black and decomposed by adding H_2O_2 to form a Pt-oxide. Metallic platinum supported on carbon (60% Pt/C) was obtained by reducing the PtOx/C in a H_2 stream. The Pt/C catalyst was characterized by recording the powders X-ray diffraction (XRD) pattern on a Philips X-pert 3710 X-ray diffractometer using Cu Kα radiation operating at 40 kV and 30 mA. The peak profile of the (2 2 0) reflection in the face centered cubic structure was obtained by using the Marquardt algorithm. The Pt/C showed a particle size of 28 Å. A 60 wt.% PtFe/C with a catalyst atomic composition Pt_3Fe_1 was prepared starting from PtOx/C and employing an impregnation procedure. The bimetallic catalyst was reduced in a H_2 stream at room temperature. TEM analysis of the catalysts was carried out with a Philips CM12 microscope.

The electrodes were prepared according to the procedure described in a previous paper [13]; they consisted of carbon cloth, diffusion and catalytic layers. An in-house prepared 85% Pt–Ru alloy (1:1)/C catalyst was employed at the anode [14]; whereas, the 60% Pt/C and Pt–Fe/C catalysts were utilized for cathode fabrication. All catalysts were intimately mixed with Nafion ionomer (15, 25 or 33 wt.% Nafion ionomer on a dry basis) by ultrasonic treatment. A Pt loading of 5 mg cm^{-2} was used for both anode and cathode. A Nafion 117 membrane was used as electrolyte. Membrane-electrode assemblies (MEAs) were formed by a hot-pressing procedure [13] and subsequently installed in a fuel cell test fixture of 5 cm^2 active area. This latter was connected to a test station including an HP6060B electronic load or to an EG&G electrochemical apparatus consisting of a PAR 273A Potentiostat/Galvanostat and a 20A Current Booster.

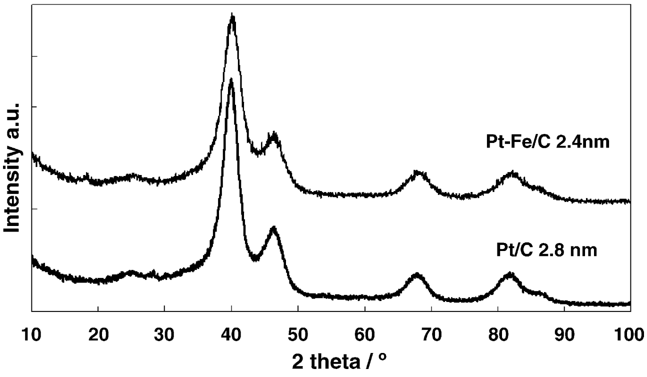

Fig. 1. XRD patterns of Pt/C and Pt–Fe/C catalysts.

For single cell polarization experiments, aqueous methanol (1 M) was pre-heated at the same temperature of the cell and fed to the anode chamber of the DMFC through a peristaltic pump; dry air, pre-heated at the same temperature of the cell, was fed to the cathode. Atmospheric pressure in the anode and cathode compartments was used in most experiments; whereas, 2 atm. rel. was applied to the cathode side in a few experiments to study the influence of cathode pressure in counteracting methanol cross-over effects. Reactant flow rates were 2 and 350 ml min^{-1} for the methanol/water mixture and air stream, respectively. Single cell performances were investigated by steady-state galvanostatic polarization measurements. In half-cell polarization studies a three-electrode configuration was used. Hydrogen was fed to the cathode that was used as both counter and reference electrode. The anode polarization measurements were carried out by potentiodynamic sweeps at a scan rate of 5 mV s^{-1}. The data have not been corrected for the IR-drop. The cathode potential was deduced by adding the anode potential to the cell voltage.

3. Results and discussion

XRD patterns of Pt/C and Pt–Fe/C catalysts are reported in Fig. 1. They show the typical fcc crystallographic structure of

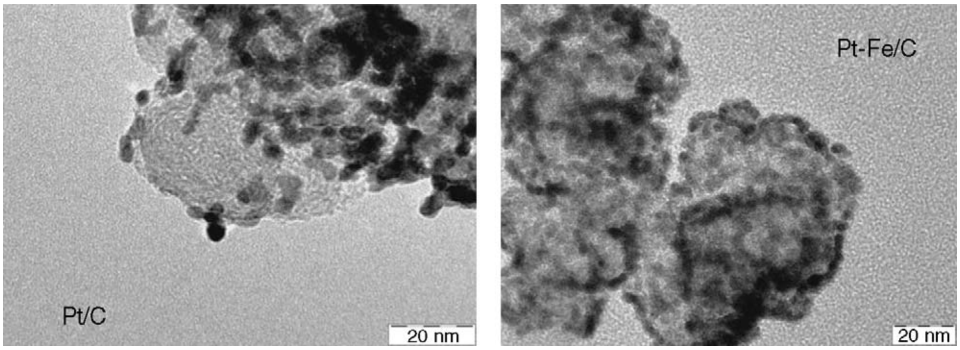

Fig. 2. TEM micrographs of 60% Pt/C and 60% Pt–Fe/C catalysts.

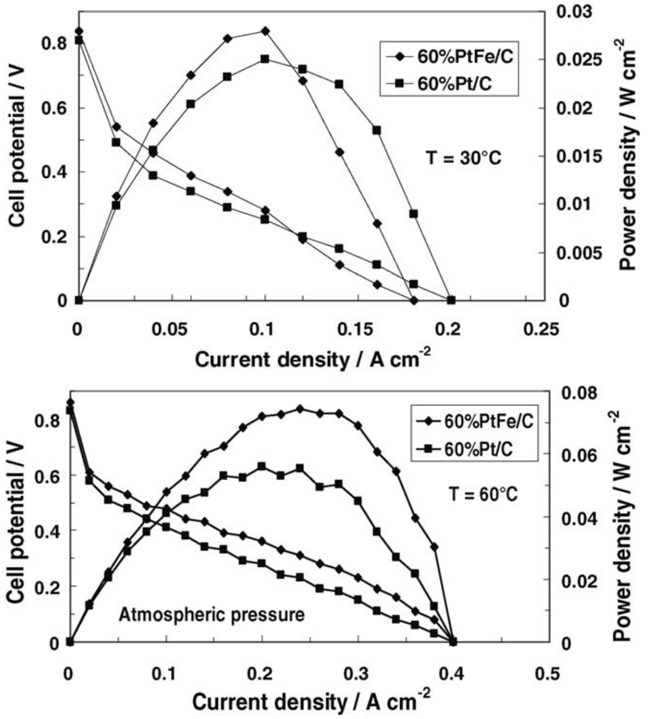

Fig. 3. Polarization and power density curves at 30 and 60 °C for DMFCs equipped with the various cathode catalysts.

Pt and its alloys. A moderate degree of alloying was found for the Pt–Fe catalyst, as indicated by a slight shift of the X-ray diffraction peaks to higher Bragg angles. The crystallite size was calculated for the two catalysts by using the Sherrer equation. Particle dimensions of 24 and 28 Å were obtained for the Pt–Fe alloy and Pt catalyst, respectively. TEM analysis of the catalysts shows a homogeneous distribution of fine metal particles on the support (Fig. 2).

The cathode catalysts were electrochemically investigated in a DMFC, by using at the anode the same Pt–Ru/C catalyst. The Pt loading was 5 mg cm^{-2} for both electrodes. A Nafion loading of 15 wt.% (on a dry basis) with respect to the catalyst was initially used on both electrodes to compare the electrochemical behaviour of the cathodic formulations. Afterwards, the ionomer loading was optimized for the PtFe-based cell. The polarization behaviour in these conditions was investigated in the temperature range from 30 to 60 °C. From the cell polarization curves at 30 and 60 °C (Fig. 3), it appears that the Pt–Fe/C presently performs better than the Pt/C catalyst with similar particle size as cathode catalyst. Higher Open Circuit Voltage (OCV) and potential values at low current densities (in the activation region) for the PtFe-based cell compared to the cell equipped with the pure Pt/C cathode catalyst indicate a higher electro-catalytic activity of the bimetallic phase towards the oxygen reduction reaction and a larger tolerance towards the poisoning effects of methanol cross-over. In particular at 60 °C, this enhanced activity is evident in the whole polarization curve. This is also confirmed by the cathode polarization curves (Fig. 4) that show almost the same trend of the cell polarizations, since the same anode was used in both experiments.

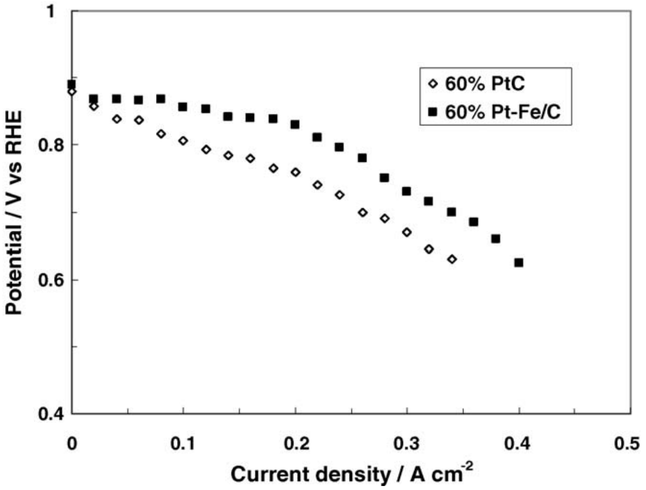

Fig. 4. Cathodic polarization curves for DMFCs based on Pt/C and Pt–Fe/C cathode catalysts recorded at 60 °C under atmospheric pressure.

An investigation of the influence of the ionomer loading on the performance of the DMFC was carried out for the PtFe-based cell. A comparison of DMFC performance at 30 °C for MEAs equipped with electrodes containing 15, 25 and 33% Nafion loading is presented in Fig. 5. OCV and performance in the activation controlled region were larger for the cells based on electrodes containing a Nafion loading of 15%; however, the highest maximum power density was recorded for the 25% Nafion based electrodes. At 60 °C, the performance increased due to the enhanced methanol oxidation and oxygen reduction kinetics (Fig. 6). Still OCV and performance in the activation controlled region are slightly higher for the electrodes containing 15% Nafion than 25%, but the highest maximum power density is again observed with the 25% Nafion loading. A maximum power density of 87 mW cm^{-2} was obtained in these latter conditions. The peak power density reaches a maximum at 25% Nafion loading at both 30 and 60 °C (Fig. 7). This is probably due to a good compromise in terms of cell resistance, extension of the three-phase reaction zone and transport properties through the electrodes.

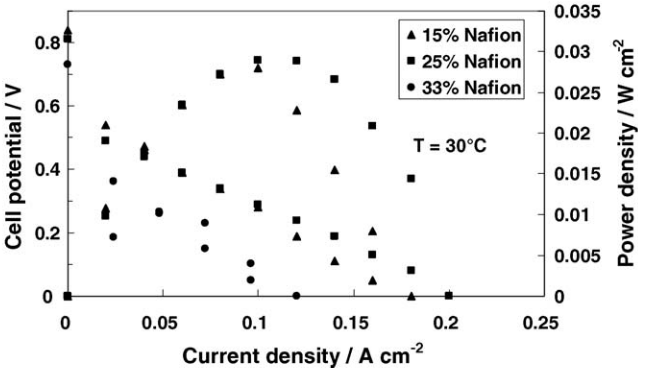

Fig. 5. Polarization and power density curves at 30 °C for the DMFCs equipped with the 85% Pt–Ru (1:1)/C catalyst and the 60% Pt–Fe/C catalyst, containing different Nafion loadings on both electrodes, 5 mg Pt cm^{-2}. Dry air, atmospheric pressure.

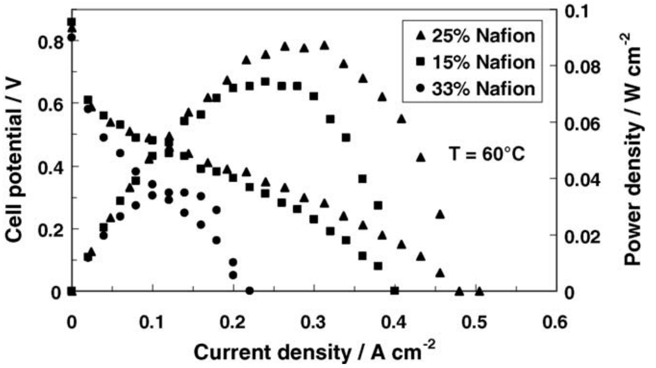

Fig. 6. Polarization and power density curves at 60 °C for the DMFCs equipped with the 85% Pt–Ru (1:1)/C catalyst and the 60% Pt–Fe/C catalyst, containing different Nafion loadings on both electrodes, 5 mg Pt cm^{-2}. Dry air, atmospheric pressure.

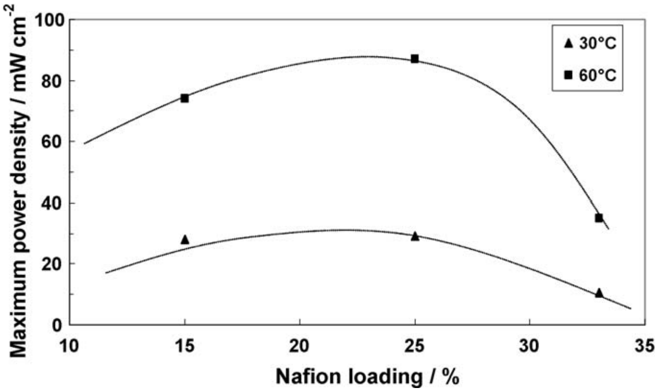

Fig. 7. Variation of maximum power density as a function of Nafion loading in the electrodes.

Fig. 8 shows an increase of cell resistance as the Nafion loading in the electrodes is increased to 33 wt.%. This, in part, explains the poor performance recorded by the cell containing a high amount of ionomer.

Upon increasing the cathode pressure at 2 atm. rel., the performance increased for all the MEAs equipped with the different Nafion loadings (Fig. 9), also due to the influence of the oxygen partial pressure in counteracting the poisoning effects by the cross-over of methanol. Under these conditions, the maximum power density was again achieved with the 25% Nafion loading and approached 100 mW cm^{-2} (Fig. 9).

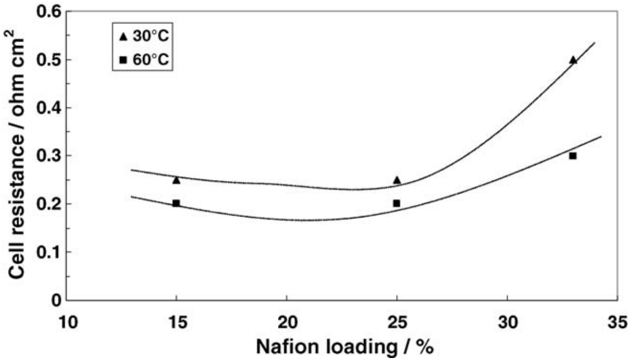

Fig. 8. Variation of cell resistance as a function of Nafion loading in the electrodes.

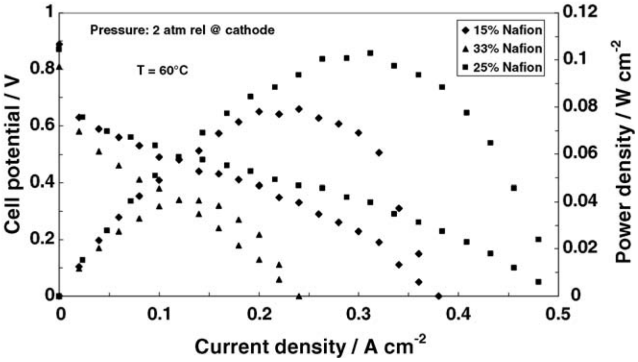

Fig. 9. Polarization and power density curves at 60 °C for the DMFCs equipped with the 85% Pt–Ru (1:1)/C catalyst and the 60% Pt–Fe/C catalyst, containing different Nafion loadings on both electrodes, 5 mg Pt cm^{-2}. Dry air, 2 atm. rel. pressure at the cathode.

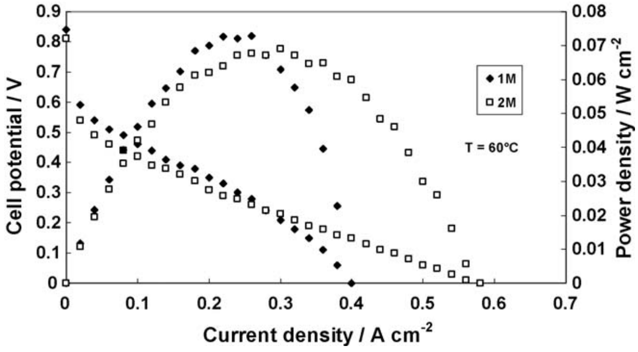

Fig. 10. Polarization and power density curves at 60 °C for the DMFC equipped with the 85% Pt–Ru (1:1)/C catalyst and the 60% Pt–Fe/C catalyst containing 25% Nafion loading in the presence of 1 and 2 M methanol at the anode.

The influence of methanol concentration on the performance of a DMFC equipped with the 85% Pt–Ru (1:1)/C catalyst and the 60% Pt–Fe/C catalyst containing 25% Nafion loading was also investigated. Fig. 10 shows the polarization and power density curves recorded at 60 °C feeding 1 and 2 M methanol solutions to the anode. The OCV and the potential at low current densities are higher in the presence of 1 M methanol, whereas at high current densities the potential losses are lower with 2 M methanol. A slightly higher performance, in terms of maximum power density, was obtained with 1 M MeOH (87 mW cm^{-2} versus 80 mW cm^{-2}).

4. Conclusions

A high surface area carbon supported bimetallic Pt–Fe catalyst has been investigated for the oxygen electro-reduction process in low temperature direct methanol fuel cells (30–60 °C) and compared to a Pt/C catalyst. An improvement of the DMFC single cell performance was observed in the presence of the Pt–Fe catalyst, due to an enhancement of the oxygen reduction kinetics. Moreover, the influence of the ionomer loading on the performance of the DMFC was investigated. The highest power density was recorded with electrodes containing 25% Nafion loading (87 mW cm^{-2}).

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