



Short communication

## Dependence on composition of electronic properties and stability of Pt–Fe/C catalysts for oxygen reduction

A.R. Malheiro<sup>1</sup>, J. Perez<sup>2</sup>, H.M. Villullas\*

Departamento de Físico-Química, Instituto de Química, Universidade Estadual Paulista – UNESP, Caixa Postal 355, R. Francisco Degni, s/n, CEP 14801-970, Araraquara, SP, Brazil

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### ABSTRACT

This work presents studies of electronic characteristics and alloy stability carried out for Pt–Fe/C catalysts of different compositions (10–50% Fe, in atoms) and same particle size. The electronic properties are characterized by *in situ* dispersive X-ray absorption spectroscopy (DXAS). The results show a steady decrease in Pt d-band occupancy as the amount of Fe in the alloy increases. The alloy stability is evaluated by prolonged potential cycling up to 1.0 V. Catalysts with Fe content up to 30% show good stabilities and keep their activities for oxygen reduction after prolonged cycling. In contrast, catalysts with Fe content above 30% suffer pronounced Fe leaching.

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### 1. Introduction

The slow kinetics of the oxygen reduction reaction (ORR) still remains one of the key problems affecting the performance of proton exchange membrane fuel cells (PEMFC), causing overpotential losses of ~0.3 to 0.4 V under typical operation conditions [1]. The most common approach to enhancing activity has been the development of binary and/or ternary alloys with Pt. Pt-based bimetallic materials have been considerably studied and a number of Pt–M/C catalysts (M = 3d transition metals) were prepared using a variety of methodologies. In general, Pt–M/C catalysts are more efficient for ORR than Pt/C and, in many cases, have a superior alcohol tolerance [2].

Pt–Fe catalysts are among the materials which generally show ORR activities larger than that of Pt/C and a number of studies of their catalytic activity for the ORR were published [3–14]. However, to the best of our knowledge, our recent work on the dependence of ORR activity on Fe concentration is the only systematic study carried out in the absence of particle size effects or second metal segregation [13]. In that study, we found that well-alloyed Pt–Fe/C catalysts with the same particle sizes exhibit maximum ORR activities for Fe contents around 20–30% (in atoms).

Evaluating the extent in which different properties might affect activity and assessing stability of electrocatalysts for ORR are still among the key issues for improving the performance of PEMFC. A study of electronic characteristics and stability of well-alloyed Pt–Fe/C catalysts of the same particle size is presented in this work. The electronic properties of Pt–Fe/C catalysts were characterized by *in situ* dispersive X-ray absorption spectroscopy (DXAS) to assess their dependence on Fe content and to analyze its correlation with ORR activity. Also, because leaching of the second metal can have a detrimental effect on the activity of the catalysts, extensive potential cycling up to 1.0 V in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solutions was used to analyze alloy stability and its effects on ORR activity.

### 2. Experimental

#### 2.1. Synthesis of Pt–Fe/C catalysts

Pt–Fe nanoparticles were synthesized by a reverse microemulsion method using sodium bis(2-ethylhexyl)sulfosuccinate (AOT) as the surfactant and n-heptane as oil phase, with n-butanol as co-surfactant, as described in detail elsewhere [15]. Catalysts with different compositions (Pt:Fe = 90:10; 80:20; 70:30; 60:40 and 50:50, in atoms) were prepared varying the atomic ratio of metal precursors in the aqueous phase of the microemulsion, while keeping constant the water/surfactant molar ratio to obtain catalysts with the same particle size [13]. The metal loading (Pt + Fe) was 20 wt% on carbon (Vulcan XC-72, Cabot).

\* Corresponding author. Tel.: +55 16 33016653; fax: +55 16 33016692.

E-mail address: [mercedes@iq.unesp.br](mailto:mercedes@iq.unesp.br) (H.M. Villullas).<sup>1</sup> Present address: Rhodia Poliamida e Especialidades LTDA, CEP 13140-000, Paulínia (SP), Brazil.<sup>2</sup> Present address: Instituto de Química de São Carlos, USP, São Carlos (SP), Brazil.

**Table 1**  
Results of XRD and TEM characterization of Pt–Fe/C nanocatalysts and ORR kinetic current densities at 0.90 V [13].

Pt:Fe (nominal)	Lattice parameter (Å)	TEM particle size (nm)	Polydispersity coefficient	ORR kinetic current density ( $\mu\text{A cm}^{-2}$ )
90:10	3.906	3.3	0.13	167
80:20	3.901	3.3	0.11	290
70:30	3.892	3.0	0.14	235
60:40	3.884	3.3	0.11	154
50:50	3.889	2.9	0.13	154

## 2.2. Electronic properties

DXAS experiments were performed around the Pt  $L_3$  edge (11,564.25 eV) in the Brazilian Synchrotron Light Laboratory (LNLS) [16]. The operation conditions were similar to those reported elsewhere [17,18]. The exposure time for each measured spectrum was 150 ms. A full spectrum involved 100 accumulations (frames) with 1.5 s of total acquisition time. Conversion of data, pixel to energy, was performed by comparing measurements in conventional mode with those in dispersive mode from standard foils (Pt metal). The measurements were taken in a spectroelectrochemical cell [19] and the catalysts were used in the form of pellets that were prepared by pressing a mixture of Nafion<sup>®</sup> solution and the catalyst powder (Pt load was  $6 \text{ mg cm}^{-2}$ ). Measurements were done at constant applied potentials (0.4–1.0 V) in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ .

## 2.3. Electrochemical measurements

Cyclic voltammetry (CV) measurements were done in  $\text{N}_2$  saturated  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solutions in a conventional electrochemical cell, with a Pt wire counter-electrode placed in a separate compartment and a reversible hydrogen reference electrode. Experiments were done at  $25^\circ\text{C}$ . The Pt–Fe/C electrocatalysts were used as ultra-thin layers [20] on a glassy carbon disk ( $0.196 \text{ cm}^2$ ) previously polished down to  $0.3 \mu\text{m}$  alumina. In all cases, the electrode metal load (Pt + Fe) was  $28 \mu\text{g cm}^{-2}$ . ORR polarization curves were obtained in  $\text{O}_2$  saturated  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  using the rotating disk electrode (RDE) technique.

## 3. Results and discussion

### 3.1. Summary of previous studies of ORR activity of Pt–Fe/C catalysts of same particle size

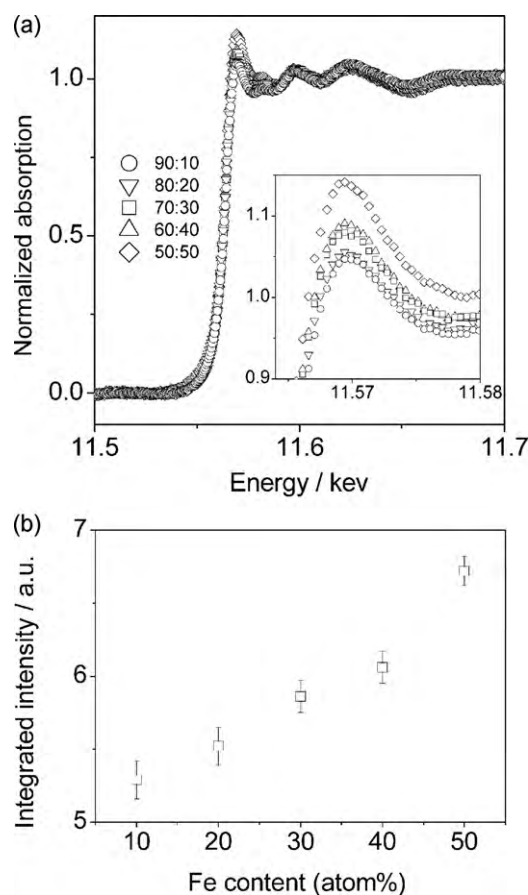
The main findings of our previous study [13] regarding the physical properties of the Pt–Fe/C catalysts of different compositions can be summarized as follows. The average compositions of the Pt–Fe/C catalysts were determined by energy dispersive X-ray analysis (EDX) and were very close to the nominal values attempted in the preparation. X-ray diffraction (XRD) studies showed diffraction signals associated to the fcc Pt structure (PDF 4–802) shifted toward higher  $2\theta$  values compared to those of Pt/C, indicating alloy formation. The lattice parameter and the Pt–Pt distance decreased for increasing Fe content. Moreover, the values of lattice constant decreased linearly for increasing Fe content following Vegard's law, and were nearly identical to those expected for the corresponding solid solutions indicating that catalysts were well-alloyed. For all Pt–Fe/C catalysts, transmission electron microscopy (TEM) studies showed that Pt–Fe nanoparticles were homogeneously distributed on the carbon support and have nearly the same particle size (around 3 nm), as expected from the fact that all samples were prepared in microemulsions with the same water/surfactant molar ratio [15]. Low values of polydispersity index ( $\sigma = \text{standard deviation}/\text{mean value}$ ) were also obtained.

The studies of the ORR carried out using the rotating disk electrode technique showed that activities of Pt–Fe/C catalysts having

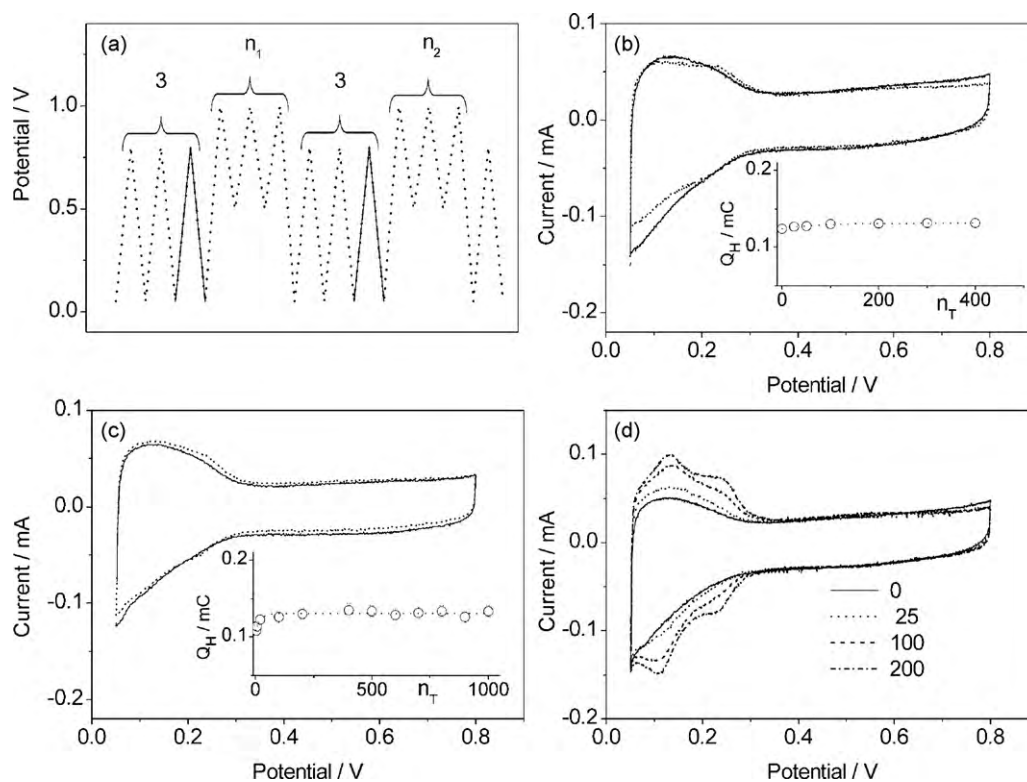
the same particle size depend on composition, and that alloys with 20 and 30% of Fe (in atoms) exhibit the highest catalytic activities [13]. A summary of the most relevant results is given in Table 1.

### 3.2. Electronic properties

DXAS was used to probe the electronic characteristics of electrocatalysts under *in situ* electrochemical conditions. The analysis of white lines was performed by using the method of Shukla et al. [5,21]. The absorption spectra were fitted by an arc tangent function which was subtracted from the experimental data, and the result was fitted by a Lorentzian function. As expected, all samples showed an increase of the white line intensity for increasing applied potential, resulting from the adsorption of oxygenated species on the Pt surface. Fig. 1 shows normalized Pt  $L_3$  absorption edges and integrated intensities for the different Pt–Fe/C catalysts. The white line intensity increases for larger Fe contents, as well as the integrated intensity of the Lorentzian. The same trend was observed for all applied potentials (0.4–1.0 V). The results are consistent with a lesser occupancy of the Pt d-band caused by the increase of the Fe amount in the alloy that would further facilitate the hybridization



**Fig. 1.** (a) Normalized Pt  $L_3$  absorption edges for the different Pt–Fe/C catalysts, as indicated. (b) Integrated intensities of the Lorentzian. Applied potential: 0.90 V.



**Fig. 2.** (a) Potential program for accelerated stability test. The solid lines represent recorded cycles. (b and c) CV curves before (—) and after (---) 400 cycles up to 1.0 V for the Pt–Fe/C catalysts 80:20 and 70:30, respectively. Insets: hydrogen desorption charge against the total number of cycles up to 1.0 V. (d) CV curves for the Pt–Fe/C 50:50 catalyst varying the total number of cycles up to 1.0 V, as indicated.

of the Pt d-band with empty states above the Fermi level reducing the d-electron number.

Previous studies have pointed out that variations in particle size can affect the hybridization of the Pt d-band with empty states above the Fermi level [22,23]. It was suggested that the Pt d-band vacancy would tend to decrease with the increase of particle size. In other words, hybridization will become less favorable when the particle size is increased. Then, it is essential to note that our Pt–Fe/C catalysts had nearly the same particle size and polydispersity index [13]. To the best of our knowledge, results like those shown in Fig. 1, which reflect effects due solely to the variation of Fe content, have not been previously reported.

Because the effects of the Fe content on the Pt d-band vacancy seem to be significant, they might be responsible, at least partially, for the dependence of electrocatalytic activity for the ORR on Fe concentration. It is generally accepted that the rate-determining step of the ORR is the first electron transfer that occurs either after or simultaneously with the adsorption of  $O_2$  [24]. Wang and Balbuena investigated the thermodynamics of key steps of ORR using density functional theory and concluded that the d-orbital coupling effect can significantly decrease the Gibbs energy for the electron transfer steps in the ORR, resulting in enhanced ORR kinetics [25]. Results of Fig. 1 show that as the Fe content of the catalysts is gradually increased the Pt d-band shows a progressively lesser occupancy, while the ORR activity shows a maximum catalytic effect around 20–30% Fe (Table 1). The breaking of the O–O bond after  $O_2$  adsorption is considered by other authors a more likely rate-determining step. According to Toda et al. [3], the increased d-vacancy of the Pt in the alloy will cause a strong metal–oxygen interaction accompanied by weakening of the O–O bond of adsorbed  $O_2$  molecules. Thus, a maximum enhancement would result when an excessive d-vacancy would make insufficient the back-donation of electrons from a Pt atom to an adsorbed  $O_2$  molecule.

### 3.3. Accelerated alloy stability tests

All Pt–Fe/C catalysts were submitted to prolonged cycling between 0.5 and 1.0 V in order to assess the alloy stability. That kind of accelerated test, evaluating the degree of leaching of the second metal through the increase of the Pt electrochemical surface area upon cycling, has been used by other authors for PtCu alloys [26]. Our experiments were done as follows: after recording the three initial cycles between 0.05 and 0.80 V, the lower and upper potential limits were set at 0.5 and 1.0 V, respectively. After a number  $n_i$  of cycles in the 0.5–1.0 V potential range, the potential limits were set back to 0.05 and 0.8 V for three cycles. That procedure was repeated several times. The total number of cycles in the 0.5–1.0 V potential range ( $n_T = \sum n_i$ ) was typically 400, but some experiments were done up to 1000 cycles. The potential program is illustrated in Fig. 2a.

Fig. 2b–d illustrate the behavior of Pt–Fe/C catalysts. No significant changes were observed during extended cycling in the CV curves for catalysts with up to 30% Fe. Hydrogen desorption charges showed slight variations only during the initial 25–50 cycles, as shown in the insets of Fig. 2. In contrast, catalysts with Fe contents of 40 and 50% show significant variations of charge while the shape of the curves progressed noticeably to a more Pt-like profile, indicating that Fe was progressively leached out from the catalysts surface. For catalysts with up to 30% Fe, extended cycling did not affect the ORR activity as shown in Fig. 3. It is noteworthy that Pt–Fe/C nanocatalysts with 20 and 30% Fe, which exhibited the best ORR performances (see Table 1), are quite stable.

Density functional theory calculations [27] performed to estimate trends in the thermodynamics of surface alloy dissolution in acidic media indicated that Fe would be stabilized on various substrates, including Pt. While data for catalysts with up to 30% Fe are in good agreement with theoretical predictions, the two Pt–Fe/C catalysts with the largest amounts of Fe exhibit a clear lack of sta-

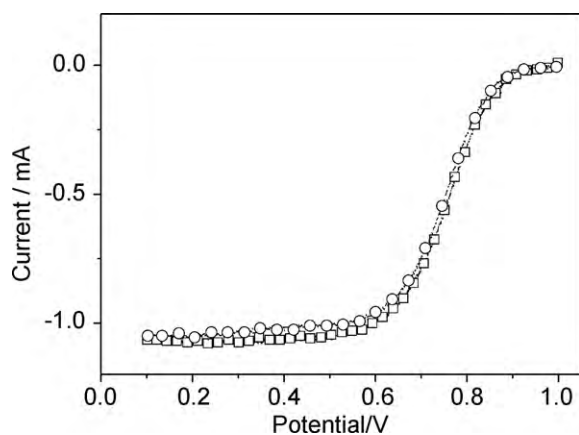


Fig. 3. ORR polarization curves for the Pt–Fe/C catalysts 70:30 before (□) and after (○) 1000 cycles up to 1.0 V.  $\omega = 2500$  rpm.

bility which can be taken as evidence of the existence of a limit in the amount of Fe that can be stabilized in a Pt–Fe solid solution. The lack of agreement between experimental data and theoretical predictions [27] for catalysts with large Fe contents may lay on the differences between the model used for the calculations, i.e., dissolution of a solute metal embedded in the surface layer of a host, and the actual properties of bimetallic alloys in the nanometer scale.

#### 4. Conclusions

The electronic properties of well-alloyed Pt–Fe/C nanocatalysts with different compositions were studied under polarization conditions and in the absence of particle size effects. A steady decrease in the Pt d-band occupancy was verified as the amount of Fe in the alloy increased, indicating that electronic effects are significant. Thus, an insufficient back-donation of electrons from Pt to adsorbed  $O_2$  might be one of the effects causing the decrease in ORR activity for Pt–Fe/C catalysts with Fe content above 30%. When submitted to accelerated stability tests, alloys containing up to 30% Fe exhibited good stability without loss of ORR activity. Catalysts with 40 and 50% Fe showed a pronounced increase of the Pt electrochemical surface area as result of Fe leaching.

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