

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/229391120>

Effect of platinum particle size on the performance of PAFC O₂ reduction electrocatalysts

ARTICLE *in* INTERNATIONAL JOURNAL OF HYDROGEN ENERGY · FEBRUARY 1994

Impact Factor: 3.31 · DOI: 10.1016/0360-3199(94)90122-8

CITATIONS

3

READS

19

8 AUTHORS, INCLUDING:



[Enza Passalacqua](#)

Italian National Research Council

117 PUBLICATIONS 3,244 CITATIONS

[SEE PROFILE](#)



[Lidia Pino](#)

Italian National Research Council

53 PUBLICATIONS 1,053 CITATIONS

[SEE PROFILE](#)



[Vincenzo Antonucci](#)

Italian National Research Council

254 PUBLICATIONS 7,678 CITATIONS

[SEE PROFILE](#)

EFFECT OF PLATINUM PARTICLE SIZE ON THE PERFORMANCE OF PAFC O₂ REDUCTION ELECTROCATALYSTS

N. GIORDANO,* P. L. ANTONUCCI,† E. PASSALACQUA,* L. PINO,* A. S. ARICÒ,* V. ANTONUCCI,*
V. ALDERUCCI* and V. RECUPERO*

*Institute CNR-TAE, Via S. Lucia 39, I-98126 S. Lucia, Messina, Italy

†University of Reggio Calabria, Faculty of Engineering, via E. Cuzzocrea 48, I-89100 Reggio Calabria, Italy

(Received for publication 30 March 1993)

Abstract—The influence of the electrocatalyst characteristics upon activity and stability for the oxygen reduction reaction in phosphoric acid fuel cell (PAFC) systems is widely established. The initial catalytic performance progressively decreases, even on a short-term basis, under operational conditions, due to several factors such as Pt dissolution, sintering and carbon corrosion. The performance of catalysts depends upon the morphological characteristics of the electrodes. The proper tailoring of the Pt/C catalyst plays a fundamental role in obtaining high overall performance in such electrochemical devices. A high mass activity (mA mg^{-1}) and low voltage decay are found, in the present investigation, for catalysts having Pt surface area above $80 \text{ m}^2 \text{ g}^{-1}$. Such results have been tentatively interpreted in terms of the acid-base properties of the surface, as determined by a potentiometric titration technique.

1. INTRODUCTION

The influence of the electrocatalyst characteristics upon activity and stability for the oxygen reduction reaction in phosphoric acid fuel cell (PAFC) systems has been greatly discussed in the literature [1–4].

As is well known, the initial catalytic performance progressively decreases, even on a short-term basis, under the PAFC operating conditions, due to several factors such as Pt dissolution, sintering, and carbon corrosion [5, 6]. The main role played by the proper tailoring of the Pt/C catalyst in obtaining high overall performances in such electrochemical devices is widely established.

In this regard, electronic interactions and synergistic effects between the metal and the support in said electrocatalytic systems have been demonstrated to be of primary importance in a fashion similar to heterogeneous catalysis [7]. Changes in the electronic state of the supported Pt, induced by differences in work function between the metal and the support, have been found to account for the observed variations in electrocatalytic activity in several studies [8–10]; in this respect, the particle size of the crystallites strongly influences the level of the metal-support interaction due to structural sensitivity effects.

In a previous paper [11] we have shown that both the mass and specific activity of Pt change with particle size in a manner which corresponds to the change in the relative fraction of Pt surface atoms on the (111) and

(100) faces of the Pt particle; moreover, the acid-base characteristics of the electrocatalysts were found to be correlated with the Pt particle size and specific activity, i.e. both were found to increase with the zero point of charge (ZPC) of the catalyst.

In this paper, the effect of mass activity on Pt surface area and the behaviour of some catalysts in short-term endurance tests under controlled simulated conditions (i.e. the galvanostatic measurement of the voltage decay of cathodic activity) are reported.

2. EXPERIMENTAL

The electrocatalyst, consisting of Pt supported on carbon black (Ketjenblack EC by Akzo Chemie, BET surface area $950 \text{ m}^2 \text{ g}^{-1}$), is prepared according to two different procedures. In the first method, the H_2PtCl_6 is stabilized with H_2O_2 and reduced with $\text{Na}_2\text{S}_2\text{O}_4$. This colloidal suspension is added to a homogeneous slurry of carbon black to form the supported electrocatalyst. In another method, i.e. the so-called *in situ* method, the carbon black is mixed with water and $\text{C}_2\text{H}_5\text{OH}$ to form a suspension. Then, the H_2PtCl_6 solution stabilized with H_2O_2 and the reductant $\text{Na}_2\text{S}_2\text{SO}_4$ are added. In both methods the supported electrocatalysts are washed, filtered and dried at 70°C . Thermal activation is performed in a quartz tube furnace under a flowing N_2 atmosphere at 900° or 600°C for times ranging from 1 to 4 h [11]. Generally, the catalysts prepared according to the first

procedure are characterized by larger Pt particle dimensions if compared with the other method.

The acid-base properties were evaluated by potentiometric titrations in aqueous suspension according to Parks *et al.* [12]. The apparatus consisted of a Pyrex glass cell with an external jacket for circulation of the thermostatic liquid, a glass electrode for pH measurements (Orion model 91-02) and a probe for temperature control (Orion ATC probe 917002), the latter two connected to an Orion model 311 pH/mV meter. The cell is covered with a Teflon cap provided with an inlet for CO_2 removal by the N_2 flux. Titration was carried out in 500 ml 0.1M KNO_3 electrolytic solution, containing the catalyst powder (5 g), under continuous stirring. The pH of the electrolytic solution before addition of the powder samples was 7 ± 0.2 . A 0.1N HNO_3 solution was introduced (in increments of 5 ml up to 20 ml) to the suspension in the electrolytic solution; the titrant, 0.1N KOH , was added with an automatic burette (Analytical Control Metrohm). After immersion, complete equilibration of the samples required from 5 to 150 min; pH values were recorded after 3 min of stabilization [i.e. after which the pH value displayed by the instrument was stable (± 0.02 pH units) for almost 3 min].

The concentration (c_a , c_b) and strength (pK_a , pK_b) of surface sites were calculated from the difference at the equivalent points of the titration curves, in the presence and absence of the sample powder, by considering that at halfway to each equivalent point $\text{pH} = \text{pK}_a$ or $\text{pH} = \text{pK}_w - \text{pK}_b$ for acidic and basic sites, respectively.

The electrocatalysts prepared following the two methods are formed in gas diffusion electrodes by a screen printing procedure, described elsewhere [11]. The final Pt loading was 0.5 mg cm^{-2} .

The Pt surface area was determined by cyclic voltammetry (CV) on flooded electrodes (10% PTFE) at room temperature in 50% H_3PO_4 at a sweep rate of 50 mV s^{-1} . The arithmetical mean Pt particle size varied from 1.8 to 13 nm, corresponding to surface areas of $153\text{--}22 \text{ m}^2 \text{ g}^{-1}$ (Pt), respectively.

The electrochemical measurements were carried out in a half-cell at 170°C in purified 98% H_3PO_4 . The polarization curves were obtained in a large range of current density ($0\text{--}1000 \text{ mA cm}^{-2}$) in air and O_2 .

The decay of potential (ΔV) was measured in the same cell used for the polarization curves. The measurements were carried out in air at 180°C in purified 98% H_3PO_4 for 24 h at a constant current of 200 mA cm^{-2} . The potential was continuously monitored during the 24 h and the decay was derived from the difference between the potential before and after aging.

3. RESULTS

Figures 1a and b show the effect of the electrocatalytic activity (expressed as potential values in air at 200 mA cm^{-2} and mass activity at 0.9 V in O_2 , respectively) on Pt surface area. The trend of the data shows an increase in O_2 reduction activity as the Pt surface area of the catalyst increases from 25 to $150 \text{ m}^2 \text{ g}^{-1}$. This is in

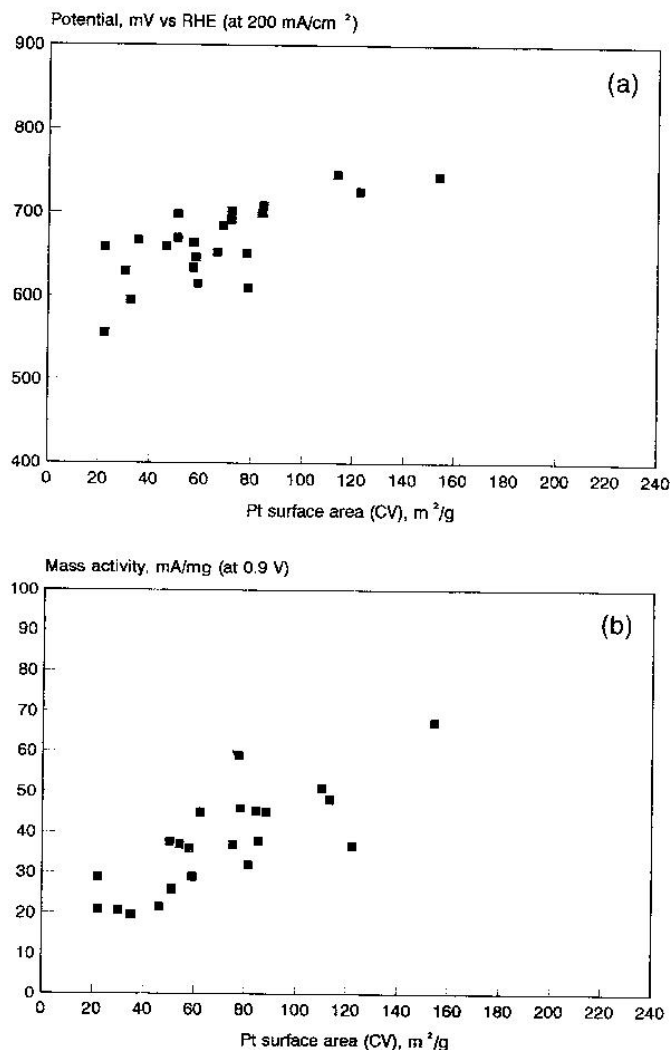


Fig. 1. (a) Potential at 200 mA cm^{-2} and (b) mass activity at 0.9 V as a function of Pt surface area in 98% H_3PO_4 at 170°C .

agreement with the other results reported elsewhere [1, 13].

The relationship between ΔV values and Pt surface area of the catalysts (as obtained by CV) is shown in Fig. 2; lower voltage decays are observed for Pt metal surface areas above $80 \text{ m}^2 \text{ g}^{-1}$.

As the Pt particle size is also expected to influence the metal-support synergism [7], information related to the acid-base properties of the catalyst (ensuing from the peculiar characteristics of Ketjenblack itself and from its interaction with the Pt species as a result of the preparation procedure adopted) were thought to be important in order to identify some distinguishing parameters to be possibly related to the observed decay, and therefore ΔV was tentatively interpreted in such terms.

As outlined in a previous work [14], the "as-received" Ketjenblack (KB), used as support for the present catalyst formulations, is characterized by a significant basicity (0.1 meq g^{-1}); interaction with the Pt precursor and heat treatment have been found to modify the acid-base behaviour of the material [15].

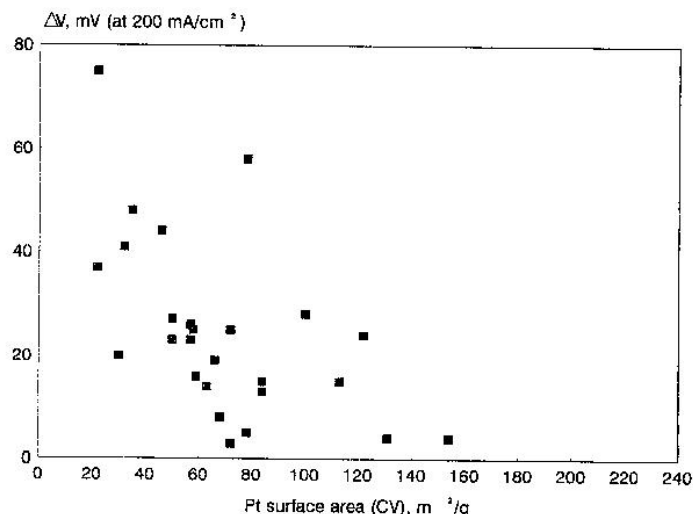


Fig. 2. Influence of Pt surface area on the short-term (24 h) decay of the potential in 98% H_3PO_4 at 180°C.

As the presence of different surface functionalities is expected to have some effect on the behaviour of the catalyst under the activity decay test conditions, we have plotted ΔV values vs the amount of acidic surface functional groups (Fig. 3) of different strength, as resulting from the potentiometric titration data. The plot seems to account for a positive role of acidic surface functionalities towards electrocatalytic stability. No relationship was found for basic surface groups.

4. DISCUSSION

Several investigations have dealt in the past with the influence of Pt particle dimensions on catalyst efficiency, both on a weight and a specific surface basis.

Accordingly, Bregoli [1] reported that the mass activity of different Vulcan XC-72 supported Pt catalysts,

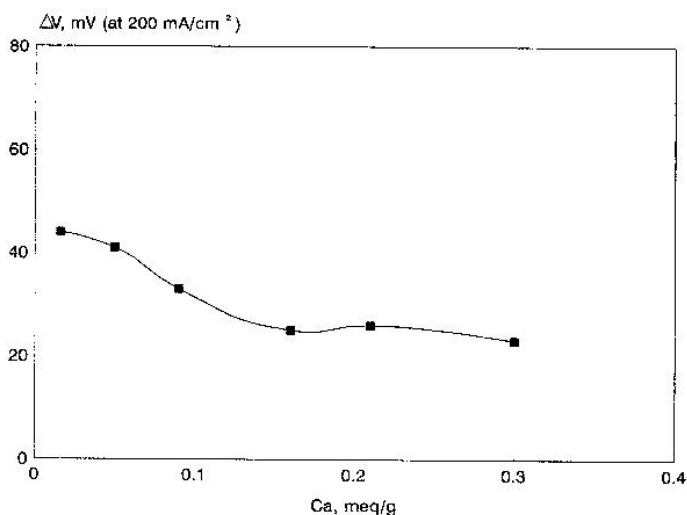


Fig. 3. Influence of acidic groups concentration (c_a) on short-term stability in 98% H_3PO_4 at 180°C.

ranging in metal surface area from 25 to 92 $\text{m}^2 \text{g}^{-1}$, increased with the Pt dispersion.

Peuckert *et al.* [2] reported a maximum in catalyst activity for a Pt crystallite diameter of about 3 nm; according to those authors, as metal dispersion is increased, an increasingly larger fraction of Pt atoms can participate in the surface reactions. On the other hand, the activity for Pt surface atoms decreases with decreasing crystallite size; these two counteracting effects result in a maximum in the activity for a unit weight of Pt.

Buchanan [3] found a mass activity/metal surface area relationship similar to that of Bregoli, in the range 10–100 $\text{m}^2 \text{g}^{-1}$ (Pt).

The crystallite size effect for O_2 reduction was rationalized by Watanabe [13] in terms of intercrystallite distance; provided that a crystallite separation of greater than 20 nm is maintained, a linear dependence of mass activity on Pt surface area was found, up to values of 200 $\text{m}^2 \text{g}^{-1}$.

Kinoshita [4] attributed the maximum in mass activity that was observed at ≈ 3 nm in several studies to the maximum in the surface fraction of Pt atoms on the (100) and (111) crystal faces, which results from the change in surface coordination number with a change in the average particle size. Our present results, referred to Pt sizes not lower than 1.8 nm, seem to be not in contradiction with previous literature data. The shape of the $\Delta V/\text{Pt}$ metal surface area (MSA) plot (Fig. 2) suggests some considerations as to the role exerted by the crystallites' dimensions in determining the observed decay behaviour. A tentative rationalization of the evidence according to which large metal particles display, besides low O_2 reduction activity, high short-term decay, takes into consideration the decrease of interaction energy between the metal and the support of increasingly larger crystallites, as reported by Arai [16].

From the above, it appears that Pt particles having $\text{MSA} > 80 \text{ m}^2 \text{g}^{-1}$ display at the same time high electrocatalytic activity and stability under practical cell conditions. As previously reported [11], the acid-base characteristics of the electrocatalysts were found to be correlated with the Pt particles' dimensions and activity. Now, the plot reported in Fig. 3 seems to account for a positive influence of said properties also on the short-term stability of the catalysts.

Such evidence can be explained by the existence of the so-called anchoring effect exerted by the oxygenated surface groups on the supported particles. Accordingly, the metal and/or its precursor interacts with the support through its surface groups, which thus act as anchorage centres, probably through the formation of platinum-oxygen complexes; it has been previously reported that sintering of Pt particles is significantly less for carbons containing oxygen functionalities [17]. As for the nature of such surface groups, a direct and unequivocal identification of such species is not feasible by the potentiometric technique employed here. Nevertheless, as for the acidic ones, the measured pK_a values (not reported) seem to account for a prevailing presence of mild acidic groups, thus confirming previous findings [18] according

to which phenolic and/or ketone complexes are the most effective in preventing the migration of Pt particles and hence the observed decay.

Pt size effects on the activity (both mass and specific) of electrocatalysts under cell running conditions have been previously reported by Giordano and coworkers [19–22]. The influence of heat treatment temperature on Pt dispersion appears to be concomitant with the evolution from acidic to basic properties of the electrocatalysts. The results have pointed to a sharp correlation between particle size and electrocatalytic activity, which unifies the behaviour of other sources of information in the literature including that for alloyed catalysts.

The picture coming from the present investigation strongly supports, in our opinion, the evidence that strictly controlled preparative procedures and conditioning of Pt/carbon materials (including functionalization of the support) appear to be a prerequisite for good activity and stability characteristics; although no conclusive rules can be drawn from the above evidences as to the mechanisms driving the decay phenomena observed, the present information seems to provide additional insight on the primary role of the metal-support synergism in determining the overall electrocatalyst performance.

In all, the above results show that the electrocatalytic activity increases as the Pt particle size decreases; in addition the concentration of acidic groups of the support appears to exert a favourable influence on the electrocatalytic stability.

REFERENCES

1. L. J. Bregoli, *Electrochim. Acta* **23**, 489 (1978).
2. M. Peuckert, T. Yoneda, R. A. Dalla Betta and M. Boudart, *J. Electrochem. Soc.* **133**, 944 (1986).
3. J. S. Buchanan, L. Keck, J. Lee, G. A. Hards and H. Scholey, in M. Watanabe, P. Stonehart and K. Ota (Eds) *Proc. 1st Int. Fuel Cell Workshop on Fuel Cell Technology Research and Development*, p. 29, Tokyo (1989).
4. K. Kinoshita, *J. Electrochem. Soc.* **137**, 845 (1990).
5. J. A. S. Bett, K. Kinoshita and P. Stonehart, *J. Catal.* **41**, 124 (1976).
6. P. Stonehart and J. P. MacDonald, Stability of acid fuel cell cathode material. EPRI Report EM-1664 (1981).
7. S. Mukerjee, *J. appl. Electrochem.* **20**, 537 (1990).
8. L. J. Hillebrand and J. W. Lacksonen, *J. Electrochem. Soc.* **112**, 249 (1965).
9. J. Escard, C. Leclerc and J. P. Contour, *J. Catal.* **29**, 31 (1973).
10. V. S. Bogotski and A. M. Snudkin, *Electrochim. Acta* **29**, 757 (1984).
11. N. Giordano, E. Passalacqua, L. Pino, A. S. Aricò, V. Antonucci, M. Vivaldi and K. Kinoshita, *Electrochim. Acta* **36**, 1979 (1991).
12. G. A. Parks, *Chem. Rev.* **65**, 177 (1965); G. A. Parks and P. L. de Bruyn, *J. Phys. Chem.* **66**, 967 (1962).
13. M. Watanabe, H. Sei and P. Stonehart, *J. electroanal. Chem.* **261**, 375 (1989).
14. A. S. Aricò, V. Antonucci, M. Minutoli and N. Giordano, *Carbon* **27**, 337 (1989).
15. A. S. Aricò, V. Antonucci, L. Pino, P. L. Antonucci and N. Giordano, *Carbon* **28**, 599 (1990).
16. M. Arai, T. Ishikawa, T. Nakajama and Y. Mishiyama, *J. Colloid Interface Sci.* **97**, 254 (1984).
17. P. Ehrburger, *Adv. Colloidal Interface Sci.* **21**, 275 (1984).
18. C. Prado-Burguete, A. Linares-Solano, F. Rodriguez-Reinoso and C. Salinas-Martines De Lecea, *J. Catal.* **115**, 95 (1989).
19. N. Giordano, E. Passalacqua, L. Pino, M. Vivaldi and M. Scagliotti, Particle size effect upon oxygen reduction on PAFC's cathodes: an unifying approach. *Proc. 25th Intersociety Energy Conversion Engng Conf.*, Extended Abstract Vol. 3, pp. 281–286, Reno, NV (1990).
20. N. Giordano, Catalysis and electrochemistry in PAFC: an unifying approach. *Symp. N.1, 42nd Meeting ISE*, p. IL 1–3, Montreux (1991).
21. E. Passalacqua, L. Pino, M. Vivaldi, N. Giordano, M. Scagliotti and N. Ricci, Influence of particle size of platinum catalysts supported on carbon upon electrochemical O₂-reduction in PAFC. *1990 Fuel Cell Seminar*. Extended Abstract, pp. 351–354, Phoenix, AZ (1990).
22. N. Giordano, E. Passalacqua, L. Pino, V. Alderucci and P. L. Antonucci, Catalysis and electrochemistry in PAFC: a unifying approach. *Proc. Int. Fuel Cell Conf.*, Vol. II-A-3, pp. 25–28, Makuhari (1992).