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Thermogravimetric way to test the oxidation resistance of Pt/C catalysts for fuel cells

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Carbon supported platinum catalysts for fuel cell applications were subjected to linearly programmed heating in air atmosphere under thermogravimetric control. Relative to pure supporting carbon, the carbons composing the Pt/C catalysts were significantly less resistant toward oxidation. Moreover, the Pt/C catalyst samples differed mutually in their oxidation resistances depending on platinum content, carbon texture and presence of additive. Thus, besides of both in-situ and cyclic voltammetric methods, thermogravimetric method was proposed as a fast supplementary way to test the resistance of Pt/C catalyst against oxidation degradation.

Key words: carbon oxidation, fuel cell, Pt/C catalysts, thermogravimetry.

INTRODUCTION

The nanodispersed, carbon supported, Pt catalysts are widely used to catalyse both cathodic and anodic electrode reactions in polymer electrolyte membrane fuel cells (PEMFC). Apart of being current collector, the carbon support prevents the Pt nanoparticles of agglomeration. Under working regime, the cathode catalyst layer is permanently exposed to gaseous oxygen, to provide the electrode potential through the oxygen reduction reaction:

$O_2 + 4H^+ + 4e^- = 2H_2O$ ($E^o = 1.23$ V vs. SHE)...(1)

Thus the carbon support undergoes oxidation, and the loss in its mass enables the loss in active surface area of Pt catalyst through agglomeration. Apart of this, positive potential causes slow anodic dissolution of platinum, being an additional reason of catalyst deterioration.

Searching for an acceptable mechanism, the model of carbon oxidation by ozone reported by Donnet [1], was adapted by Kinoshita et al [2], and followed by other authors [3-5], in description of carbon oxidation in fuel cells. According to these reports, CO_2 is formed in two independent and parallel paths:

$C \rightarrow CO_2$ (2)

$C \rightarrow CO_{surf} \rightarrow CO_2$ (3)

where oxidation by mediation of surface carbon oxides (CO_{surf}) is much slower than the direct oxidation. In fuel cells, the overall reaction (2) may be presented as a part of the following electrochemical reaction [2]:

$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$,
($E^o = 0.207$ V vs.SHE) (4)

Although the potentials of oxygen reduction reaction (1) is typically well above the standard potential of the reaction (4), low kinetic parameters of oxidation make carbon black relatively stable. In addition, the growth of surface oxides (2) may either protect corrosion sites or make a barrier for diffusion of the reactants [2].

The durability of Pt/C composite catalyst manifest itself through the stability of the power of the fuel cell. Usually, it is tested ex-situ, by a persistent cyclic voltammetry and a subsequent observation by electron microscope [6,7]. For example, Wang et al. [6], for a commercial Pt/C catalyst with 20% Pt, provided by Johnson – Matthey, evidenced the decrease of active surface area in function of number of polarization cycles in nitrogen purged perchloric acid solution after 4000 polarization cycles. The TEM pictures taken before and after the cyclo-voltammetric test, unveiled that the agglomeration of Pt particles appeared obviously to be one of the reasons of catalyst collapse. In cyclic voltammetry, the fastest degradation takes place when the potential passes the vertex anodic value, since the concentration of adsorbed oxygen species then passes maximum. This way of testing of catalyst durability is very time consuming. Platinum dissolution and deposition under potentiodynamic condition may cause regrouping of platinum particles resulting in coarsening on account of disappearing of smaller particles. The cyclic voltammetry test does not allow to observe the contribution of carbon oxidation separately from the contribution of

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platinum dissolution/deposition, in an overall catalyst degradation. Therefore it would be useful to dispose with the testing procedure which can characterize carbon resistance to oxidation separately from the other factors of catalyst durability.

The present authors applied the thermogravimetric analysis for accurate determination of platinum content in Pt/C catalysts. In these experiments, the catalysts were subjected to a progressively rising temperature in air atmosphere up to complete combustion of carbon, and the residual mass presented the mass of pure platinum [8, 9]. These experiments indicated that the Pt/C catalyst, obtained from various sources, differ in respect of initial temperature of carbon oxidation. Since the thermogravimetric curves reflect also the kinetics of the observed chemical process, we suggest that the thermogravimetric measurements of Pt/C catalysts in air may be used as an efficient method to characterize their durability, supplementary to a usual cyclic voltammetry method.

EXPERIMENTAL

The device

The device used in the experiments was the thermobalance TA Instruments Model 2960. The air flow rate of 70 $cm^3\ s^{-1}$, and heating rate of 10 $^oC\ min^{-1}$, were constant in all experiments.

The samples

A commercial nanodispersed carbon provided by Cabot Corp., trade mark Vulcan XC 72, used as a support of commercial Pt/C catalyst of Johnson Matthey Co., was used in this study as a reference sample. According to the product specifications, its BET specific surface area 220 $m^2\ g^{-1}$, and according to the TEM picture shown in the reference [10], the mean particle diameter is close to 50 nm.

The second sample was a commercial Pt/C catalyst sample HiSpecTM 4000, provided by Alfa Aesar (with 40 wt% Pt nanoparticles dispersed on Vulcan XC 72). The TEM picture of this sample one may see in the reference [11].

The third, homemade sample Pt/C catalyst sample, contained Vulcan support modified by thin layer of Ta_2O_5 in quantity 20%, overlayered by 10% of nanodispersed Pt. The oxide layer was applied first, by drying the suspension of Vulcan in ethanol + tantalum isopropoxide solution, and then Pt nanoparticles were deposited by polyol method [12].

The fourth of investigated samples was a Degussa Pt/C catalyst, trade mark F 105 R/W, with 10% nanodispersed platinum deposited over nanodispersed activated carbon with high surface area of nearly 1000 $m^2\ g^{-1}$.

RESULTTS AND DISCUSSION

Fig 1, shows the thermogravimetric curves of the three carbon supported platinum catalyst samples described in the experimental section, compared to the the thermogravimetric curve of Vulcan XC R2 used as a reference sample. The F105 R/W (Degussa) sample, thanks to a developed surface area of supporting carbon black (CB), contains a lot of adsorbed water, which caused an initial mass drop of almost 15% on heating up to 100 ^oC. The Vulcan based catalysts do not absorb significant amount of moisture, as visible from a negligible mass change up to at least 200 ^oC. The main mass drop observed in Fig. 1 is due to the combustion of the carbon material. According to the position of the TG curves along the temperature axis, there is an obvious difference between the observed samples in the resistance toward oxidation. The final residual mass in Fig. 1., manifesting itself as a plateau, corresponded precisely to an actual fraction of non-combustible matter, Pt or Pt+Ta_2O_5.

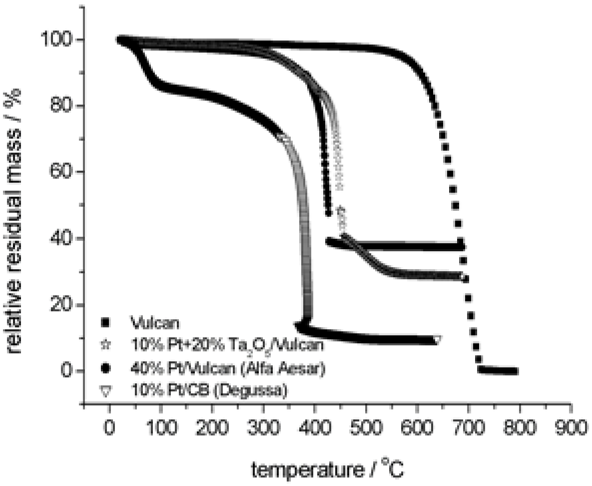

Fig. 1. TG curves of Vulcan XC R2, (10% Pt +20% Ta_2O_5)/Vulcan, 40% Pt/Vulcan (HiSpecTM 4000, Alfa Aesar) and 10% Pt/CB (F105 R/W, Degussa) recorded in air stream at a heating rate 10 $^oC\ min^{-1}$.

For the purpose of more efficient comparison of oxidation resistance of investigated materials, in Fig. 2, the thermogravimetric data from Fig. 1 were expressed in a form of absolute reaction rate in function of temperature. To do this, the fraction reacted (α) was calculated:

$$\alpha = (m_i - m_t)/(m_i - m_f) \qquad (5)$$

where m_i, m_t and m_f are initial, actual and final mass, respectively; for a linearly rising temperature T, time is t = T/b, where b is heating rate. In relation to pure Vulcan, for any of the Pt/C samples, the combustion process was shifted markedly toward lower temperatures. The combustion of Pt/C samples was self-accelerated reaction, since, as Fig. 1 shows, for $\alpha > 0.4$, overheating happened relative to the programmed temperature rise. The overheating might be prevented by dilution of the sample with inert substance, for instance with corund or silica, however this was not performed in this study. Therefore, only initial parts of the TG curves, where overheating was negligible, were used to compare the observed samples. As already expected from Fig. 1, Fig. 2 confirms clearly that the resistance toward oxidation, in average, decreases in the series 10% Pt/CB (F105 R/W, Degussa) < 40% Pt/Vulcan (HiSpecTM 4000, Alfa Aesar) < (10% Pt +20% Ta_2O_5)/Vulcan (homemade) < Vulcan (XC72, Cabot Corp.).

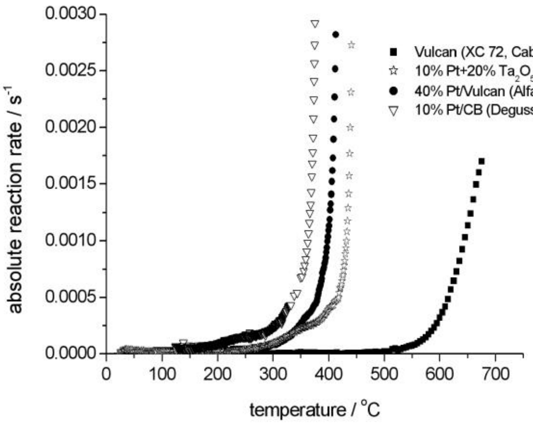

Fig 2. Absolute oxidation rates in function of temperature for Vulcan XC R2, (10% Pt +20% Ta_2O_5)/Vulcan, 40% Pt/Vulcan (HiSpecTM 4000, Alfa Aesar) and 10%Pt/CB (F105 R/W, Degussa); air atmosphere; heating rate 10 ^oC min^{-1}.

There is the possibility to use thermogravimetric data to express the reactivity in more quantitative manner. Namely, first derivation of α vs. t gives the dependence of absolute reaction rate (dα/dt) on time. Absolute reaction rate as a function of temperature, generally, obeys the equation [13, 14]:

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}} f(\alpha) \qquad (6)$$

Here A and E are preexponential factor and activation energy, respectively, and f(α) is a function, the form of which depends on the nature and morphology of the sample, and involves the reaction order, n. The list of available theoretically derived functions for various predicted limiting steps and for particles of variable geometry, one may find in the corresponding literature [13, 14]. The determination of reaction parameters and most suitable function f(α) is the matter of regression analysis, which may be relatively simple by means of a suitable software, some of which are published elsewhere [15, 16].

The rate of oxidation of pure Vulcan XC 72, may be compared with the literature data for non-catalysed oxidation of various carbon materials. As shown in a recent review published by Neff et al [17] and Stanmore et al. [18], the kinetic of carbon combustion is studied mostly with the aim to remove the soot emitted from diesel engines. The detailed study of carbon oxidation is provided by Marsh et al. [19]. They proposed that the combustion involves free carbon sites, chemisorbed both localised and mobile molecular oxygen, and chemisorbed both localised and mobile atoms of oxygen. Moulijn et al. [20] proposed a relatively simple carbon surface during combustion, involving three types of carbon–oxygen complex, carbonyl, semiquinone and pyrone groups, ordered according the increased stability. According to these authors [21], only less stable fraction of the oxygen-containing surface complexes take part in oxidation reactions. One can expect that for different carbons obtained in a similar way, these with higher specific surface area show higher sensitivity toward oxidation, on account of higher number of reactive surface groups. Accordingly, comparing to the results published by López-Fonseca et al. [22], the initial temperature of combustion of Vulcan XC 72 visible in Fig 1, lies between that of Degussa carbons Flammruss 101 (30 m^2 g^{-1}) (combustion started at 600 ^oC) and Printex XE-2B (1170 m^2 g^{-1}) (combustion started at 400 ^oC). By means of two isoconversional methods, averaged value of activation energy of 150 kJ mol^{-1} for Flammruss 101, and 132 kJ mol^{-1} for Printex XE-2B was estimated, while the pre-exponential factors amounted to $2.0 \cdot 10^6$ and $2.9 \cdot 10^6$ min^{-1}, respectively [22]. Therefore, one may expect intermediate values of these parameters for Vulcan CX 72.

Many literature data evidence that the combustion of carbon may be accelerated by means of various catalysts [17, 23-33]. On the basis of results of TPO experiments, Fe_2O_3, γ-Al_2O_3, V_2O_5, CuO, TiO, as well as Pt/γ-Al_2O_3 , may accelerate shoot oxidation [17]. This was investigated and evidenced in the reactors were the shoot was mixed with the catalysts [23-30]. To explain catalytic activity of nanodispersed Pt supported by γ-$A1_2O_3$ in the oxidation of coke, oxygen spillover has been postulated by several authors [29, 30]. The same hypothesis has been suggested to explain higher activity of alumina or copper oxide containing low amounts of platinum in shoot combustion [31, 32, 33]. This hypothesis is in agreement with the report that the oxygen ions of alumina are more mobile when located in vicinity of Pt particles [34]. Moreover, platinum is known to enable the exchange gaseous $^{18}O_2$ with the ^{16}O of the alumina [35]. On this basis, it can be suggested that oxygen is first adsorbed dissociatively on the surface of the noble metal, and then activated oxygen spills over on the supporting surface, where it is able to react with carbon particles at a temperature lower than in the absence of platinum. The experimental arrangement for coke and shoot oxidation in references [23-33], where carbon particles were mechanically mixed with catalyst particles, differ from that used for oxidation of Pt/C catalysts studied here. Namely, in the last case, Pt nanoparticles are applied directly through chemical processes on carbon particles. The suggestion of concentration of adsorbed oxygen on platinum surface [29-35] as a factor of higher corrosion rate of supporting carbon is applicable here, even without any need of oxygen spillover, thanks to a direct contact of platinum and carbon as the reactant.

Between (10% Pt +20% Ta_2O_5)/Vulcan (homemade) and 40% Pt/Vulcan (Alfa Aesar) samples, one might reasonably expect higher oxidation resistance of the first one, based on the lower content of platinum. It appears to be actually so at higher α values (i.e. higher temperatures), as Fig. 2. shows. However, in initial oxidation stages, the oxidation rate is almost identical for both samples, indicating synergistic effect of the Pt/Ta_2O_5 combination in oxidation catalysis. The disappearance of this effect at higher temperatures may indicate the gradual disappearance of the three/phase boundaries Pt/Ta_2O_5/C with the progress of carbon oxidation.

The comparison between two Pt/C catalyst with high and low surface area of supporting carbon (i.e., the Degussa and Alfa Aesar samples), respectively, indicate higher oxidation resistance of Alfa Aesar sample, in spite of its higher platinum content. This emphasizes the importance of surface area effect, connected reasonably with the content of reactive C atoms [19,20].

After the experiments described in this contribution, one may conclude that thermogravimetric analysis under air flow is well capable of detect fine differences in the resistance of different carbon materials and Pt/carbon catalysts towards oxidation. On the basis of similarity of oxidation mechanism of carbons in gaseous and aqueous media [2], the reactivity order of Pt/C catalyst toward oxidation in air established by thermogravimetry, may be expected to reflect the reactivity order in fuel cells, too.

CONCLUSION

Thermogravimetric analysis under air flow is capable of detect fine differences in the resistance of different carbon materials and Pt/carbon catalysts towards oxidation. Among investigated samples, the resistance toward oxidation, decreases in the series 10% Pt/CB (F105 R/W, Degussa)<40% Pt/Vulcan (HiSpecTM 4000, Alfa Aesar) < (10% Pt + 20% Ta_2O_5)/Vulcan (homemade) < Vulcan (XC72, Cabot Corp.). Having in mind similar mechanism of oxidation of carbon in gaseous and aqueous media, one may expect similar order of oxidation resistances in electrolyte media of fuel cells, too.

The thermogravimetric experiments confirmed that

- Pt nanoparticles in Pt/C catalyst cause a significant increase of the oxidation rate of supporting carbon;
- the transition metal oxides used as additives to Pt/C catalyst may influence the rate of carbon oxidation, Ta_2O_5 being the catalyst of oxidation;
- the specific surface area of supporting carbon competes to the platinum content in determination of oxidation resistance of carbon.

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REFERENCES

1. J.-B. Donnet, P. Ehrburger, A. Voet, *Carbon*, **10**, 737 (1972).
2. K. Kinoshita, J. Bett, *Carbon*, **11**, 237 (1973).
3. J. Willsau, J. Heitbaum, *J. Electroanal. Chem*., **161**, 93 (1984).
4. S. Maass, F. Finsterwalder, G. Frank, R. Hartmann, C. Merten, *J. Power Sources*, **176**, 444 (2008).

5. A. M. Chaparro, N. Mueller, C. Atienza, L. Daza, *J. Electroanal.Chem*., **591**, 69 (2006).
6. R. Wang, C. Xu, X. Bi, Y. Ding, *Energ. Environ. Sci*., **5,** 5281 (2012).
7. B. Avasarala, R. Moore, P. Haldar, *Electrochim. Acta*, **55**, 4765 (2010).
8. N. M. Gavrilov, I. A. Pašti, G. Ćirić-Marjanović, V. M. Nikolić, M. P. Marčeta Kaninski, Š. Miljanić, S. V. Mentus, *Int. J. Electrochem. Sci*., **7**, 6666 (2012).
9. N. Gavrilov, M. Dašić-Tomić, I. Pašti, G. Ćirić-Marjanović, S. Mentus, *Mater. Lett*., **65**, 962 (2011).
10. F. Si, L. Ma, C. Liu, X. Zhang, W. Xing, *RSC Adv*., **2**, 401 (2012).
11. J. Parrondo, R. Santhanam, F. Mijangos, B. Rambabu, *Int. J. Electrochem. Sci*., **5**, 1342 (2010).
12. H.-S. Oh, J.-G. Oh, Y.-G. Hong, H. Kim, *Electrochim. Acta*, **52**, 7278 (2007).
13. H. Tanaka, *Thermochim. Acta*, **267**, 29 (1995).
14. B. Janković, S. Mentus, *Metall. Mater. Trans. A*, **40**, 609 (2009).
15. A. K. Burnham, R. L. Braun, *Energy & Fuels*, **13**, 1 (1999).
16. A. Rotaru, M. Gosa, *J. Therm. Anal. Calorim*., **97**, 421 (2009).
17. G. Neff , L. Bonaccorsi, A. Donato, C. Milone, M. Grazia Musolino, A. Maria Visco, *Appl. Catal. B*, **11**, 217 (1997).
18. B. R. Stanmore, J. F. Brilhac, P. Gilot, *Carbon*, **39**, 2247 (2001).
19. H. Marsh, K. Kuo, Kinetics and catalysis of carbon gasification. In: H. Marsh, editor, Introduction to carbon science, carbon active sites in the gasification of coal chars. Fuel, London: Butterworths, 1989, p. 107.
20. J. A. Moulijn, F. Kapteijn, *Carbon*, **33**, 1155 (1995).
21. F. Kapteijn, R. Meijer, J.A. Moulijn, D. Cazorla-Amorós. *Carbon*, **32**, 1223 (1994).
22. R. López-Fonseca, I. Landa, M. A. Gutiérrez-Ortiz, J. R. González-Velasco, *J. Therm. Anal. Cal*., **80**, 65 (2005).
23. J. O. Uchisawa, A. Obuchi, Z. Zhao, S. Kushiyama, *Appl. Catal. B*, **18,** L183 (1998).
24. G. Neri, L. Bonaccorsi, A. Donato, C. Milone, L. M. Grazia Musolino, A. Maria Visco, *Appl. Catal. B*, **11**, 217 (1997).
25. C. Chien, T. Huang, *Ind. Eng. Chem. Res*., **34**, 1952 (1995).
26. R.J. Farrauto, K.E. Voss, *Appl. Catal. B*, **10**, 29 (1996).
27. H.J. Stein, *Appl. Catal. B*, **10**, 69 (1996).
28. M. Hosoya, M. Shimoda, *Appl. Catal. B*, **10**, 83 (1996).
29. E. Baumgarten, A. Schuck, *Appl. Catal*., **37**, 247 (1988).
30. J. Parera, E. Traffano, J. Masso, C. Pieck, *Stud. Surf. Sci. Catal.*, **17**, 101 (1983).
31. A. F. Ahlstrism, C. U. I. Odenbrand, *Appl. Catal*., **60**, 157 (1990).
32. C. C. Chien, T. J. Huang, *Ind. Eng. Chem. Res*., **34**, 1952 (1995).
33. R. E. Marinangeli, E. H. Homeier, F. S. Molinaro, *Stud. Surf. Sci. Catal*., **30**, 457 (1987).
34. V. Ducarme, J.C. Vedrine, *J. Chem. Soc. Faraday Trans.* 1, **74**, 506 (1978)
35. H. Abderrahim, D. Duprez, *Stud. Surf. Sci. Catal*., **30**, 359 (1987)

ТЕРМОГРАВИМЕТРИЧЕН МЕТОД ЗА ТЕСТВАНЕ НА УСТОЙЧИВОСТТА НА ОКИСЛЕНИЕ НА Pt/C КАТАЛИЗАТОРИ ЗА ГОРИВНИ КЛЕТКИ

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(Резюме)

Платинови катализатори, отложени върху въглеродни носители за горивни клетки са подложени на линейно програмируемо нагряване във въздушна атмосфера под термогравиметричен контрол. Установено е, че спрямо чистия въглероден носител, катализаторът Pt/C е значително по-устойчив към окисление. Устойчивостта към окисление за различните Pt/C – композиции е различна в зависимост от съдържанието на платина в тях, въглеродната им текстура и наличието на добавки. В работата освен in-situ методът и методът на цикличната волтаметрометрия, е използван термогравиметричният метод като бърз начин за допълнителна проверка на устойчивостта на Pt/C катализатор към окисление.