CHEMICAL ENGINEERING TRANSACTIONS

VOL. 41, 2014

Guest Editors: Simonetta Palmas, Michele Mascia, Annalisa Vacca

ISBN 978-88-95608-32-7; **ISSN** 2283-9216

A publication of

AIDIC

The Italian Association
of Chemical Engineering
www.aidic.it/cet

DOI: 10.3303/CET1441031

Durability of Pt and Pt-Co Electrocatalysts for Application in a PEM Fuel Cell

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1. Abstract

Efforts for reduction of catalysts loads in PEM fuel cells, are caused by high price of platinum metals and limited sources of this elements. Exist many possible ways, how to reduce load of platinum metals. One is preparing particles with lower diameter, but we are limited minimal diameter for catalytic properties. Second way is preparing catalyst form alloys of platinum with some other metal. This work is focused to alloy Pt with Co. Important parameters of catalyst are activity, stability, sensibility to poisoning and etc. This work compares stability of catalysts based on pure platinum and alloy platinum and cobalt. Although catalyst based on Pt-Co alloy assign approximately half initial electrocatalytic surface in compare with catalyst based on pure platinum, after 10 000 cycles assign catalyst based on alloy higher stability.

2. Introduction

Within the last years are many mobile applications limited by suitable source of electric energy. Increasing number of functions smartphones and notebooks has negative influence to energy consumption. Automotive companies develop cars that produced any pollution during operation, one way is classical electric car with battery, other way is using fuel cells like source of electric energy. Exist six base groups of fuel cells, but for mobile applications are suitable just only proton exchange fuel cells (PEM) and direct methanol fuel cells (DMFC).

Efforts for mass production of PEM fuel cells are limited by many problems [1,2]. One of the most important problem is high investment cost. Relatively high price is caused by necessity used expensive membrane and catalyst based on platinum or platinum metals [3,4,5]. Price of catalyst can be reduced by a lot of different possibilities. One possible way is preparation of particles with diameter 2-3 nm, other suitable way is using alloy platinum with some noble metal [6]. Very important parameter is stability of catalyst during whole operational lifetime of fuel cell.

Catalysts particles with low diameter have high surface energy [7]. This system is very unstable and particles decrease surface energy by agglomeration [8] or sintering [9]. By this two processes increase the particles diameter and we lose electrocatalytic surface. All electrochemical reactions are proceed on the catalyst surface and with decreasing surface decrease intensity of process. Alloys are constituted from minimal two compounds with different red/ox potential [10]. During cyclic voltammetry can be one of compounds dissolved and transported from particles to inter-particles space.

3. Experimental

3.1 Cyclic voltammetry (CV)

An BioLogic Multi-Chanell Potentiostat (Model VMP 3) was used to perform the cyclic voltammetry. When the CV of the cathode (or anode) was measured, it was taken as a working electrode, and was fed with argon. For the activation, the electrode was cycled in potential range 60-1200 mV versus hydrogen

Please cite this article as: Malis J., Colmenares L., Sunde S., Bouzek K., 2014, Durability of pt and pt-co electrocatalysts for application in a pem fuel cell, Chemical Engineering Transactions, 41, 181-186 DOI: 10.3303/CET1441031

electrode. The potential was scan 10, 20, 50, 100 and 200 mV.s^{-1}. 0,5 mol.dm^{-3} solution of sulfuric acid was used as working solution, which was temperate at defined temperature.

3.2 CO-stripping

CO was feed into working solution for 10 minutes. This time was sufficient for adsorption of CO monolayer on the catalyst. Than was argon feed into working solution for minimal 60 minutes, this time was necessary for elimination CO included in working solution. Later was sample minimal two-times cycled in range 60 and 1200 mV versus hydrogen electrode. First cycle was for oxidation CO to CO_2. Second cycle was for determination of CO oxidation peak [11].

3.3 Electrochemical impedance spectroscopy (EIS)

Resist of catalyst for the reactions oxidation/reduction of hydrogen (on anodic or cathodic site) was measured by EIS in a four-electrode arrangement in open circuit potential. A VMP 3 16 Multi-Chanell Potentionstat/Galvanostat/EIS was used.

3.4 Transmission electron microscopy (TEM)

Transmission electron microscopy was used for determination of particles diameter. All samples of catalysts were dissolved in ultrasonic bath into demineralized water and this solution was used for samples for TEM preparation. INCA method was used for determination of particles composition in case of alloy.

4. Results and discussion

In this work was investigated two commercially available catalyst produced by Tanaka company. One was based by pure platinum (TEC10F60TPM) and second by alloy platinum-cobalt (TEC36F62). Activated samples prepared by thin-film method were investigated by cyclic voltammetry in first step. Surface was measured by CO-stripping and catalyst layer was investigated by electrochemical impedance spectroscopy. Samples were subjected by standardized accelerated ageing tests which simulated typical conditions car running [12]. Within ageing tests was recorded current catalytic activity of investigated catalyst and changes in electrochemical active surface. Typical results are represents at graph at figure 1.

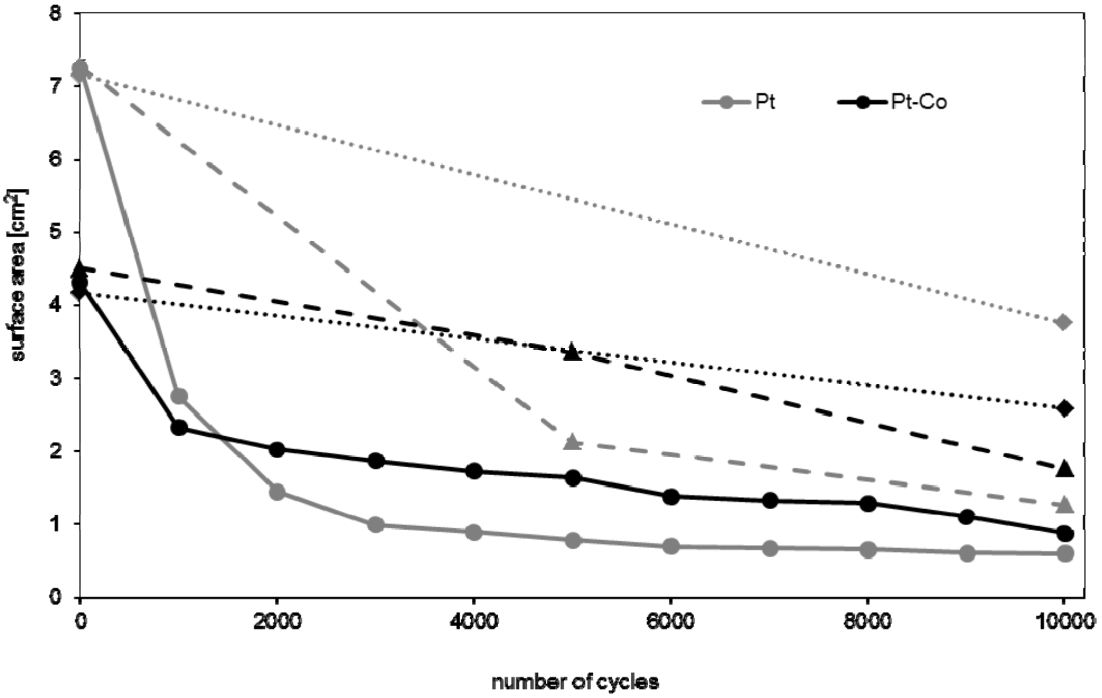

Figure 1: decrease of electro-catalytic surface, during simulated automotive regime: potential range 600-1200 mV versus hydrogen electrode, sweep rate 20 mV.s^{-1}, total number of cycles 10 000, ● 10 x 1000 cycles, ▲ 2 x 5000 cycles, ♦ 1 x 10 000 cycles

Catalyst based on pure platinum (black) assign two-times higher initial surface than catalyst based on platinum-cobalt alloy (dark gray). Decrease of catalytic surface was more significant in case catalyst based on pure platinum. Most aggressive was ageing by ten blocks, each with 1000 cycles. Significant decrease of catalytic surface can be observed during first 1000 cycles. Subsequent decrease was less significant. In case of catalyst based on pure platinum was decrease from 7,28 cm^2 to 0,60 cm^2, 8,24 % initial value. In case of catalyst based on platinum-cobalt alloy was decrease from 4,30 cm^2 to 0,87 cm^2, 20,23 % initial value. Less aggressive was applying only two blocks each with 5000 cycles. In this case decrease of surface pure platinum catalyst from 7,26 cm^2 to 1,27 cm^2, 17,49 % of initial surface. Surface of catalyst based on platinum-cobalt alloy decrease from 4,50 cm^2 to 1,75 cm^2, 38,88 % of initial surface. Lower decrease was record by applying one block with 10 000 cycles. In this case decrease surface of catalyst based on pure platinum from 7,15 cm^2 to 3,74 cm^2, 52,31 % of initial value and surface based on platinum-cobalt alloy from 4,16 cm^2 to 2,59 cm^2, 62,26 % of initial surface.

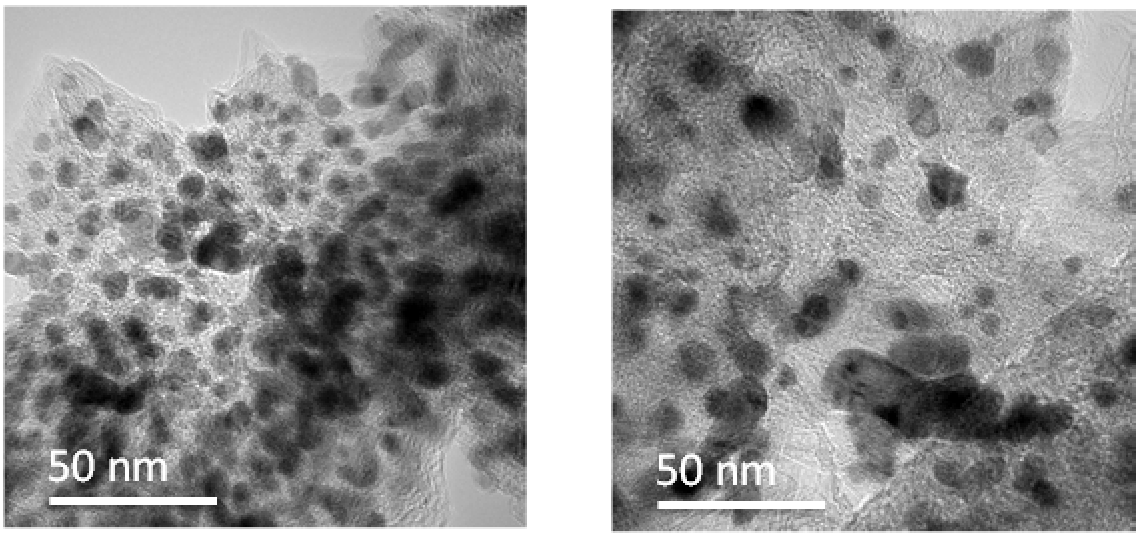

Figure 2: pictures from high resolution transmission electron microscope of catalyst based on pure platinum before ageing (left) and after applying ten blocks each with 1000 cycles (right) at sweep rate 20 mV.s^{-1}

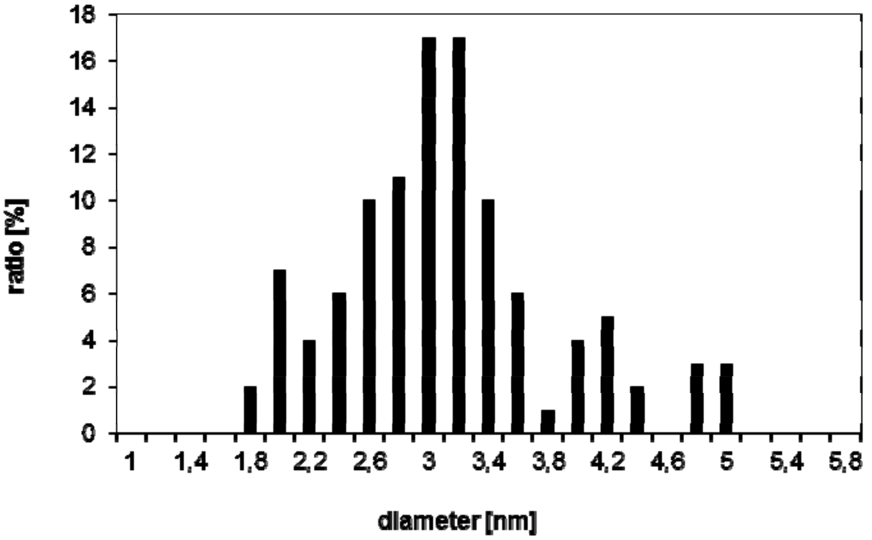

Figure 3: histogram of distribution of particles diameter of catalyst based on pure platinum before ageing

Although catalyst based on pure platinum assign higher initial surface, catalyst based on platinum-cobalt alloy assign higher stability in all type of ageing. Reason of this effect is growing of catalytic particles, which is in case of catalyst based on pure platinum more significant. This theory was supported by changes of capacity of samples. By EIS was measured capacity of interface between catalyst and working solution. Double-layer capacity decreases with decreasing surface of catalyst.

Applying of higher sweep rate was more aggressive, than applying low sweep rate. Decrease of surface was more significant at sweep rate 200 mV.s^{-1} in all cases.

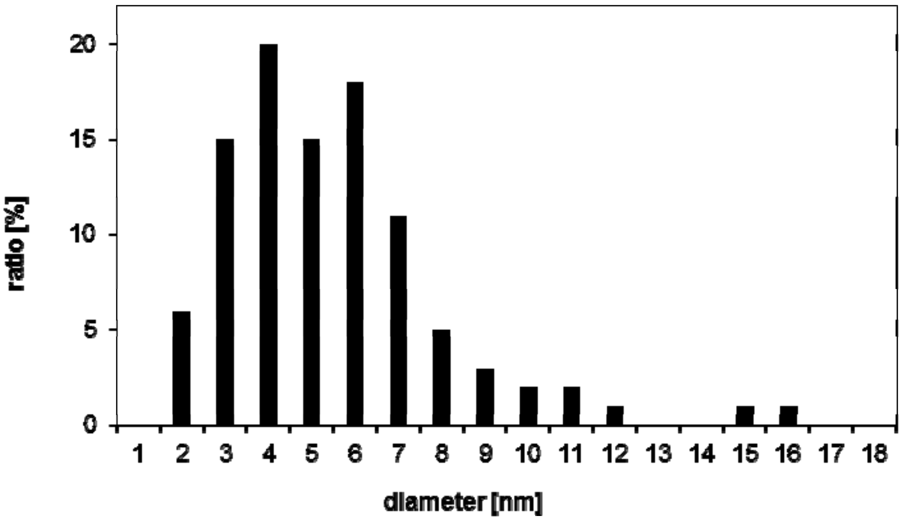

Figure 4: histogram of distribution of particles diameter of catalyst based on pure platinum and after applying ten blocks each with 1000 cycles at sweep rate 20 mV.s^{-1}

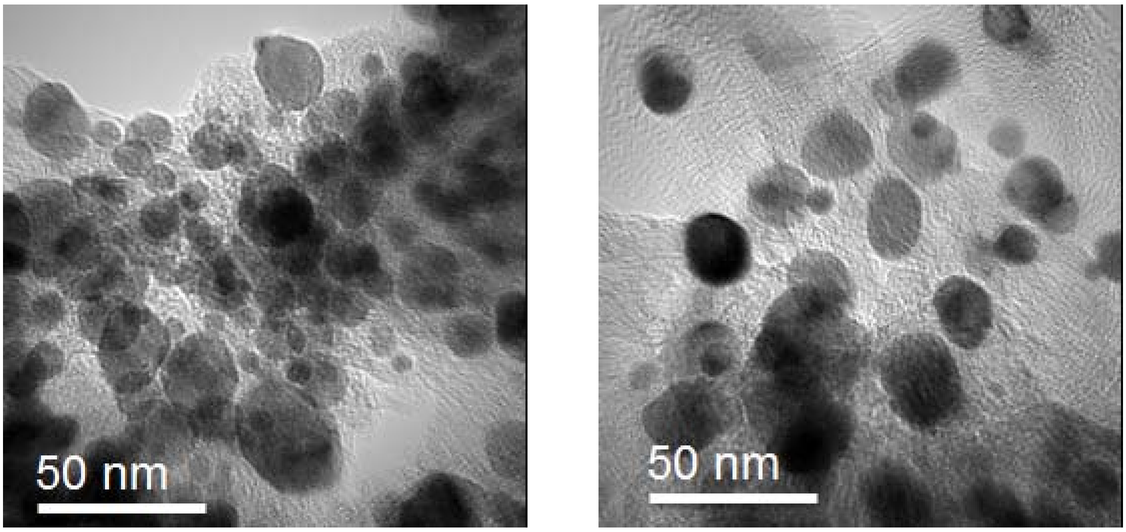

Figure 5: pictures from high resolution transmission electron microscope of catalyst based on alloy platinum with cobalt before ageing (left) and after applying ten blocks each with 1000 cycles (right) at sweep rate 20 mV.s^{-1}

After ageing were samples investigated by high resolution transmission electron microscopy for particles size and distribution. Particles of fresh catalyst (figure 2, left) have main diameter between 3 and 3,2 nm, it is possible to see on the picture 3. After ageing by 10 blocks with 1000 cycles (figure 2, right) increase main diameter to 4 – 6 nm, which is possible to see at picture 4. Loosing of surface was caused by increasing on particles diameter. In case of catalyst based on platinum-cobalt alloy increase main diameter of particles from 3 – 3,5 nm of fresh sample (figure 5, left) to 7 – 9 nm (figure 5, right) after ageing. Particle diameter was strongly dependent on cobalt content in alloy. With increasing particle diameter the cobalt content in alloy increases.

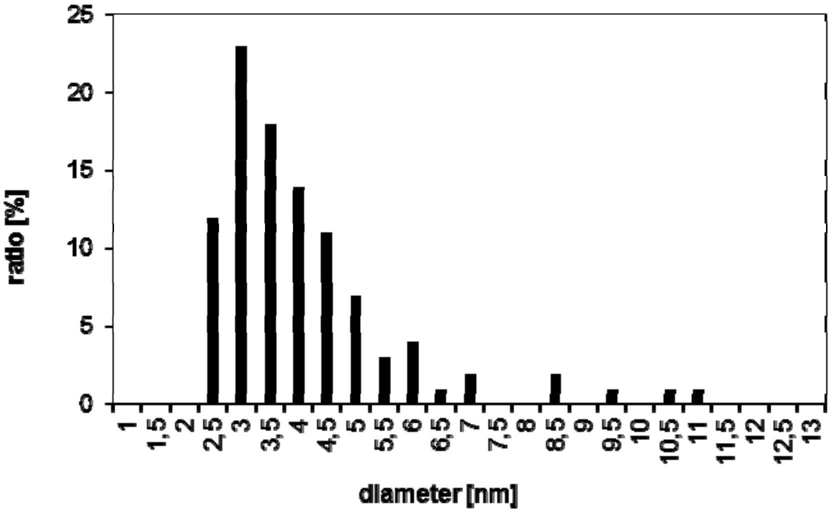

Figure 6: histogram of distribution of particles diameter of catalyst based on alloy platinum with cobalt before ageing

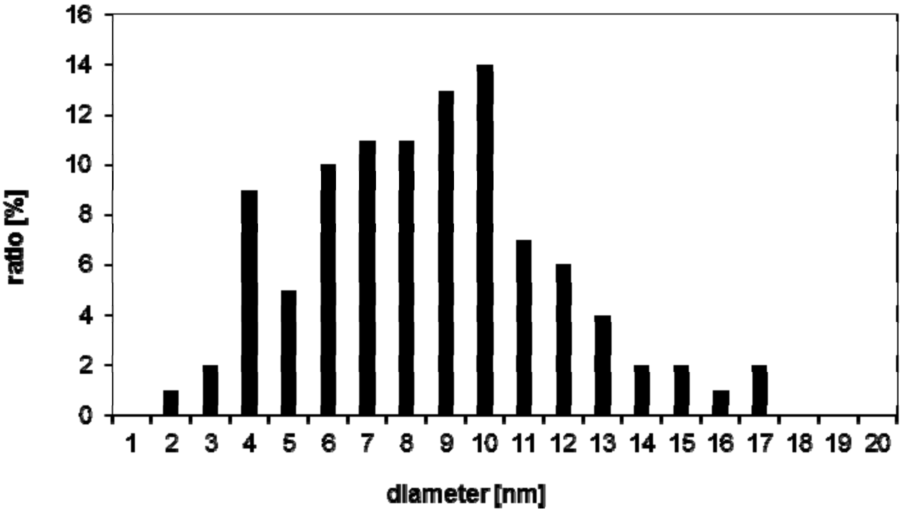

Figure 7: histogram of distribution of particles diameter of catalyst based on alloy platinum with cobalt after applying ten blocks each with 1000 cycles at sweep rate 20 mV.s^{-1}

5. Conclusions

Catalyst based on pure platinum assign approximately two-times higher initial surface, than catalyst based on platinum alloy. During ageing decrease of surface of catalyst based on pure platinum was more significant. Long blocks of cycles are less stress full for catalyst than short blocks. High sweep rate is more aggressive, than slow sweep rate. Reason of decrease of catalyst surface is agglomeration and Ostwald ripening, when small particles reduce own surface energy by the agglomeration and thus increasing particles diameter. Increase of particles diameter is significant and more obvious in case of catalyst based on pure platinum. Content of cobalt in alloy is dependent on particle diameter, with increasing diameter increase content of cobalt.

Acknowledgement

This project was financed from project KEEPEMALIVE (FCH JU # 245113)

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