



On the influence of the Pt to carbon ratio on the degradation of high surface area carbon supported PEM fuel cell electrocatalysts



Jozsef Speder^{a,*}, Alessandro Zana^a, Ioannis Spanos^a, Jacob J.K. Kirkensgaard^b, Kell Mortensen^b, Matthias Arenz^{a,**}

^a Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

^b Niels Bohr Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

ARTICLE INFO

Article history:

Received 30 April 2013

Received in revised form 3 June 2013

Accepted 3 June 2013

Available online 14 June 2013

Keywords:

Polymer electrolyte fuel cells

Electrocatalyst durability

Carbon corrosion

ABSTRACT

In the presented work we investigate the influence of the Pt to carbon ratio on the degradation behavior of Pt based proton exchange membrane fuel cell (PEMFC) catalysts. In order to enable a systematic investigation, we utilized a recently developed colloidal synthesis approach for preparing catalysts with identical Pt nanoparticles (NPs), but varying Pt loadings. Two different commercially available, standard carbon supports were used, Vulcan XC72 and Ketjenblack EC-300. We evaluated the influence of the platinum loading on the electrochemical surface area (ECSA) loss by applying accelerated stress tests simulating a load-cycle in a PEMFC and start-up/shutdown conditions. Simulating load cycles, no clear influence of the Pt loading on the ECSA loss is observed, whereas the ECSA loss significantly increases with increasing Pt loading when simulating start-up/shutdown conditions.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

A significant challenge for the application of proton exchange membrane fuel cells (PEMFCs) is the loss of performance during extended operation, which is in large part caused by the degradation of the catalyst. Several catalyst degradation mechanisms have been identified for PEMFC catalysts, i.e. Pt based nanoparticles (NPs) attached to a high surface area (HSA) carbon support. The most studied phenomenon is platinum dissolution that leads to a reduction in electrochemical surface area (ECSA) via direct loss and growth of particles [1]. Furthermore, particle migration and coalescence as well as electrochemical oxidation of the carbon support have been identified. All phenomena are highly dependent on temperature and electrode potential and often the observed ECSA loss is due to a combination of these degradation mechanisms. Very recently, however, we showed that when applying two different degradation treatments in accordance with the recommendations of the Fuel Cell Commercialization Conference of Japan (FCCJ) [2,3], i.e. a treatment (I) simulating load-cycle conditions and a treatment (II) simulating start-up/shutdown conditions of a PEMFC, the main ECSA loss mechanism can be identified as Pt dissolution and particle migration and coalescence (treatment I) and carbon corrosion and induced particle loss (treatment II), respectively [4].

In the present work we continue our work on carbon corrosion [5,6] and focus on the influence of the ratio between Pt and carbon. Even though carbon corrosion is an extensively studied phenomenon, the mechanism of carbon corrosion is still not fully understood. A controversially discussed aspect of carbon corrosion reaction is a possible catalytic role of platinum. Some studies found no catalytic effect of platinum on the carbon corrosion process [7,8], while others reported a corrosion rate acceleration with an increase in Pt content [9–11]. One main drawback of these studies, however, is that mainly commercial catalyst samples were used, which are prepared by precipitation techniques inhibiting systematic studies by keeping all parameters, e.g. the particle size, constant while only changing the Pt loading. Thus in the present work we studied the catalytic role of Pt systematic by using recommended [2] accelerated stress test (AST) treatments and a well suited catalyst synthesis approach [12].

2. Experimental details

2.1. Catalyst synthesis

The investigated catalysts, hereafter called Pt/C, were synthesized in-house according to [12]. The synthesis consists of two steps. First, a solution of colloidal Pt NPs with narrow size distribution of around 2 nm is prepared, then the NPs are deposited in varying amounts onto the HSA carbon support, i.e. Ketjenblack EC-300 (AkzoNobel, Brunauer–Emmett–Teller (BET) surface area: 795 m² g⁻¹) or Vulcan XC72R (Cabot Corporation, BET area: 235 m² g⁻¹). Catalyst samples

* Corresponding author. Tel.: +45 353 20002; fax: +45 35320214.

** Corresponding author.

E-mail addresses: jozsef@chem.ku.dk (J. Speder), m.arenz@chem.ku.dk (M. Arenz).

were prepared with three different Pt loadings, i.e. 10, 30, and 45 wt.%. The nominal Pt loading of the catalysts was confirmed by inductively coupled plasma mass spectrometry (ICP-MS) measurements.

2.2. Physical characterization

The electrocatalysts were characterized by transmission electron microscopy (TEM) using a Tecnai T20 G2 (Philips FEI, Oregon, USA) equipped with a thermionic electron gun operated at 200 kV. The platinum particle size distribution was determined by small angle X-ray scattering (SAXS) using a SAXSLab instrument (JJ X-ray, Denmark). For more information, see Ref. [12].

2.3. Electrochemical characterization

The electrochemical measurements were performed in an all-Teflon three-compartment electrochemical cell [13], using a home-built multi-electrode setup with eight glassy carbon (GC) tips used as working electrodes (WE). The counter (auxiliary) electrode was a carbon rod, and the reference electrode a Schott Ag/AgCl/KCl (sat.) electrode was located in a separated compartment [14]. All potentials, however, are referred to the reversible hydrogen electrode (RHE) potential, which was experimentally determined for each measurement series. All acid solutions were prepared from Millipore® water ($>18.3 \text{ M}\Omega \text{ cm}$, total oxidizable carbon, TOC $< 5 \text{ ppb}$) and Suprapur acids (Merck). The measurements were performed in de-aerated electrolyte with a Pt loading of $14 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ on the tips. The electrochemically accessible surface area (ECSA) of the catalysts was determined from the CO stripping charge.

2.4. Accelerated stress test (AST) protocols

The degradation behavior of the catalyst was evaluated by employing two degradation treatments in accordance with the FCCJ recommendations [2,3]. Treatment-I simulates load-cycle conditions and consisted of applying square-wave potential steps between 0.6

and $1.0 \text{ V}_{\text{RHE}}$ with a rest time of 3 s at each potential. The total treatment lasted 9000 cycles (15 h). Treatment-II simulates start-up/shutdown conditions and consisted of potential cycling between 1 and $1.5 \text{ V}_{\text{RHE}}$ with a sweep rate of 500 mV s^{-1} . The total treatment lasted 27,000 potential cycles (15 h). All the measurements were conducted at room temperature and without rotation.

3. Results and discussion

In the following we discuss the initial characterization of our Pt/C samples with varying Pt loading. Representative TEM images and a particle size analysis by small angle X-ray scattering of the catalysts (30 wt.% Pt) are shown in Fig. 1 demonstrating well dispersed Pt NPs with an average size of around 2 nm for both carbon supports. For Pt/Vulcan the particle size is $1.7 \pm 1.2 \text{ nm}$ (FWHM as error), whereas for Pt/Ketjenblack it is $2.0 \pm 1.6 \text{ nm}$ in good agreement with the ECSA data obtained in CO stripping. It is seen that the Pt NPs can be efficiently attached to both supports and that the particle size of the Pt NPs does not increase with increasing loading as confirmed by the ECSA values (inset of Fig. 1C).

Furthermore, it is seen that the ECSA is slightly higher in the case of the Vulcan support as compared to the Ketjenblack support. Only at the lowest Pt loading are the ECSAs more or less the same. In other words despite its considerable lower BET surface area the degree of dispersion and utilization of Pt NPs on Vulcan is higher than on Ketjenblack. As the same colloidal suspension of Pt NPs was used to prepare all catalysts, a higher Pt utilization is only possible if less particle–particle agglomeration occurs during synthesis, which is a sign of an improved interaction between Pt NPs and the carbon surface in the case of Vulcan. This can probably be explained best by a larger number of oxygen groups and defects on the Vulcan. For a conventional impregnation synthesis of Pt/C catalysts it has been reported that the metal dispersion on carbon blacks strongly depends on the chemical species present on the carbon surface. Oxygen based functional groups such as quinones ($>\text{C}=\text{O}$), hydroxyl and/or phenols ($-\text{OH}$), and carboxyl ($-\text{COOH}$) increased the Pt NP dispersion by

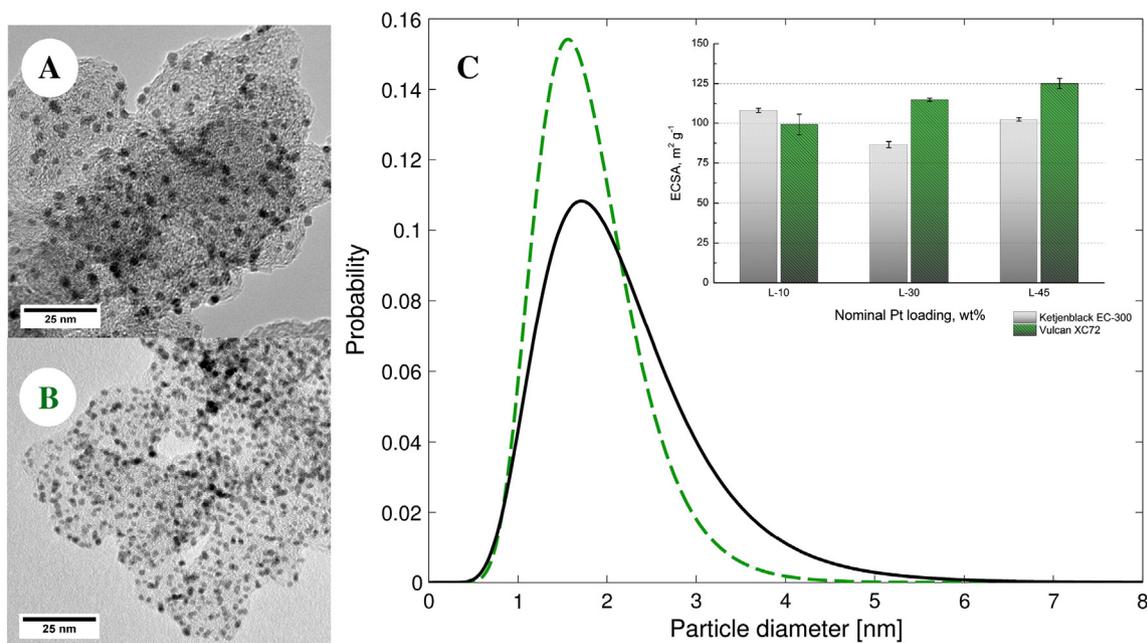


Fig. 1. TEM micrographs of synthesized catalysts: 30 wt.% Pt/Ketjenblack (A) and Pt/Vulcan (B) catalysts. Particle size distribution determined by SAXS (C): 30 wt.% Pt/Ketjenblack (black) and Pt/Vulcan (green) in combination with the ECSA as a function of the nominal Pt loading. The ECSA is calculated from the Pt surface area determined in CO stripping experiments. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

serving as adsorption sites [15]. Such a hypothesis is in line with the reported properties of Ketjenblack and Vulcan as well as with the observed double layer capacitance in our electrochemical measurements, which is higher for Vulcan as compared to Ketjenblack, despite lower BET area (see Fig. 2). Further investigations are under way to substantiate this interpretation.

In the investigation of electrocatalysts using FCCJ recommended AST, it has been proposed [16] and recently confirmed [4] that when simulating load-cycles Pt dissolution as well as NP agglomeration occurs whereas when simulating start-up/shutdown conditions carbon corrosion is predominant. Fig. 2 shows a comparison of the initial (BOT: beginning of treatment; black curve) and final (EOT: end of treatment; red dotted curve) cyclic voltammograms (CVs) of the catalysts under such treatment. When simulating load-cycle conditions (Fig. 2A, C) no change in the double layer region (0.3–0.6 V_{RHE}) is observed and we can conclude that no massive carbon corrosion has taken place. More pronounced changes in the CVs are observed between 0.6 and 0.9 V_{RHE} where Pt oxide reduction occurs. As a result of the AST, the Pt reduction peak shifts towards a higher potential indicating Pt particle growth [4]. The corresponding ECSA losses (Fig. 3) are more or less independent of the carbon support and no significant increase in ECSA loss is observed when increasing the Pt loading.

Simulating start-up/shutdown conditions by comparison, the Pt surface is covered by oxide during the whole test and the CVs recorded after the AST (Fig. 2B,D) exhibit clear signs of carbon oxidation. The double layer capacitance in the potential window between 0.4 and 0.8 V_{RHE} is increased and a hydroquinone–quinone redox

couple is observed [17]. The increase in interfacial double layer capacitance indicates a more hydrophilic surface or an increase in the roughness of the carbon surface [18]. Most likely there are various oxygen containing surface groups formed on the carbon surface and currently we conduct detailed surface studies in order to identify them. In contrast to the load-cycles, in the simulation of start-up/shutdown conditions the ECSA losses (Fig. 3) strongly depend on the carbon support and in both cases significantly increase when increasing the Pt loading. The results clearly show that the Pt to carbon ratio influences the carbon oxidation, which is a sign for a catalytic role of Pt in the oxidation process. Furthermore, it is observed that Pt/Vulcan is less stable than the Pt/Ketjenblack under the applied conditions, which is in contrast to reports claiming that the corrosion rate is proportional to the BET area of the carbon [19].

4. Conclusions

We present a systematic study evaluating the influence of the Pt to carbon ratio on the degradation of PEMFC catalysts. It is seen that the results strongly depend on the treatment conditions. Under conditions mainly inducing Pt dissolution and NP agglomeration, the Pt to carbon ratio only has a minor influence on the ECSA loss – most likely due to an enhanced probability of agglomeration. By contrast, under conditions inducing carbon corrosion increasing the Pt to carbon ratio significantly increases the ECSA loss. Furthermore, it is shown that a lower BET area of the support is no indication of a higher stability.

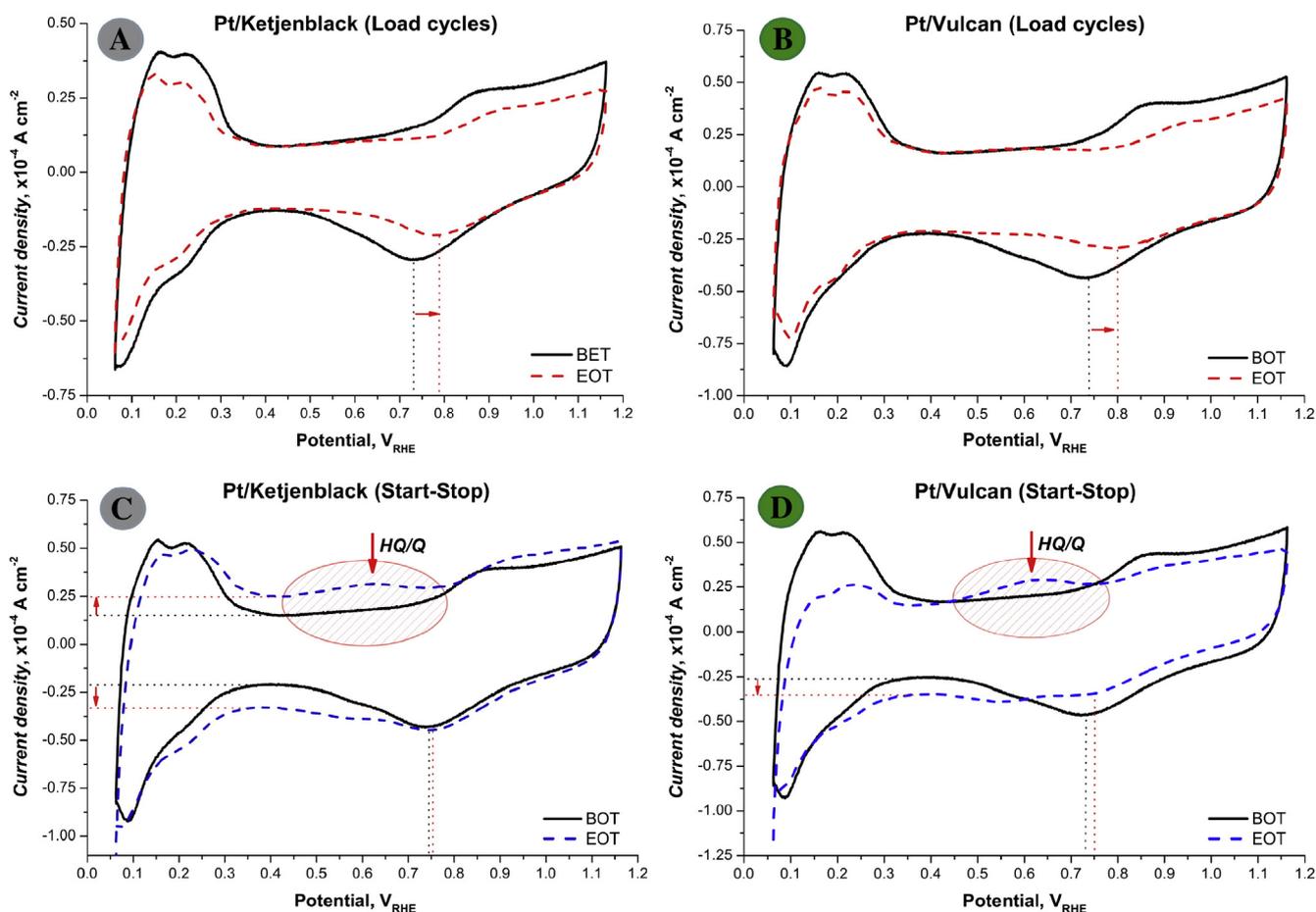


Fig. 2. Effect of AST test on the voltammogram of 30 wt.% Pt/Ketjenblack (left hand side) and 30 wt.% Pt/Vulcan (right hand side) recorded in 0.1 M HClO₄ with a sweep rate of 50 mV s⁻¹. AST test conditions: (A, B) square wave with a holding time of 3 s at 0.6 and 3 s at 1.0 V_{RHE} (15 h), (C, D) triangular wave with a sweep rate of 500 mV s⁻¹ between 1.0 and 1.5 V_{RHE} (15 h). The shaded ellipses indicate the formation of hydroquinone/quinone (HQ/Q) redox peaks in the voltammograms. BOT: beginning of treatment; EOT: end of treatment. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

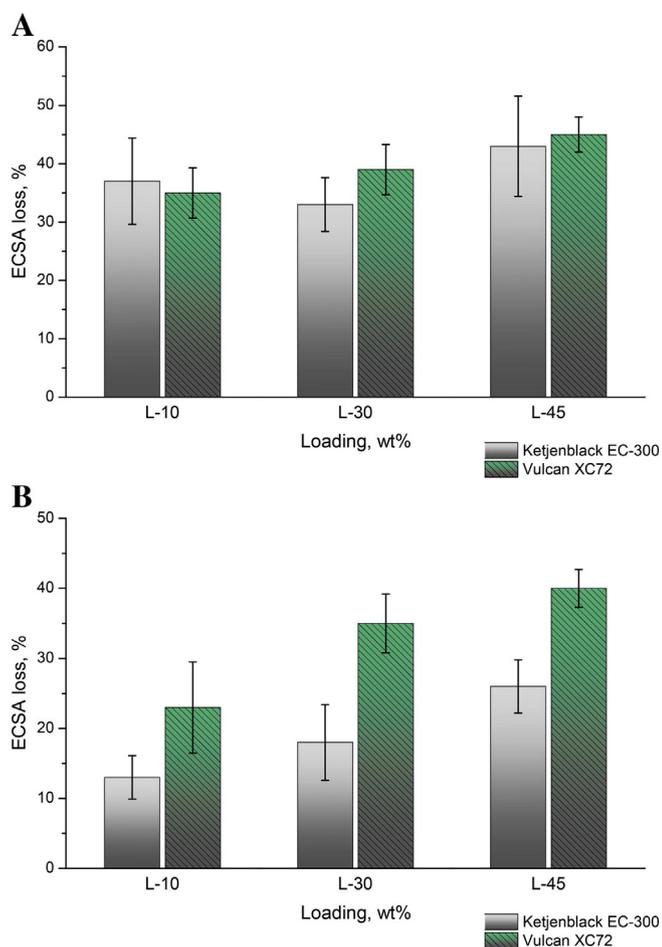


Fig. 3. Summary of the ECSA loss as a function of Pt loading for Pt/Ketjenblack and Pt/Vulcan upon square wave treatment I (upper part) and triangular wave treatment II (lower part).

Acknowledgments

This work was supported by the Danish DFF through grant no. 10-081337. We acknowledge the group of Dr Karl J.J. Mayrhofer at the MPIE for the ICP-MS analysis. We acknowledge the group of Prof. M. Bäumer (University of Bremen) for the collaboration concerning the NP synthesis.

References

- [1] Y. Shao-Horn, W.C. Sheng, S. Chen, P.J. Ferreira, E.F. Holby, D. Morgan, *Topics in Catalysis* 46 (2007) 285–305.
- [2] A. Ohma, K. Shinohara, A. Iiyama, T. Yoshida, A. Daimaru, *ECS Transactions* 41 (2011) 775–784.
- [3] Y.-C. Park, K. Kakinuma, M. Uchida, D.A. Tryk, T. Kamino, H. Uchida, M. Watanabe, *Electrochimica Acta* 91 (2013) 195–207.
- [4] A. Zana, J. Speder, M. Roefzaad, L. Altmann, M. Bäumer, M. Arenz, *Journal of the Electrochemical Society* 160 (2013) F608–F615.
- [5] S.J. Ashton, M. Arenz, *Electrochemistry Communications* 13 (2011) 1473–1475.
- [6] S.J. Ashton, M. Arenz, *Journal of Power Sources* 217 (2012) 392–399.
- [7] P. Stonehart, J.P. MacDonald, *Stability of acid fuel cell cathode materials*, EPRI Report EM-1664, Research Project 1200-2, 1981.
- [8] K. Kinoshita, J.A.S. Bett, *Carbon* 12 (1974) 525–533.
- [9] N. Linse, L. Gubler, G.G. Scherer, A. Wokaun, *Electrochimica Acta* 56 (2011) 7541–7549.
- [10] L.M. Roen, C.H. Paik, T.D. Jarvi, *Electrochemical and Solid-State Letters* 7 (2004) A19–A22.
- [11] D.A. Stevens, J.R. Dahn, *Carbon* 43 (2005) 179–188.
- [12] J. Speder, L. Altmann, M. Roefzaad, M. Baumer, J.J.K. Kirkensgaard, K. Mortensen, M. Arenz, *Physical Chemistry Chemical Physics* 15 (2013) 3602–3608.
- [13] K.J.J. Mayrhofer, G.K.H. Wiberg, M. Arenz, *Journal of the Electrochemical Society* 155 (2008) P1–P5.
- [14] K.J.J. Mayrhofer, S.J. Ashton, J. Kreuzer, M. Arenz, *International Journal of Electrochemical Science* 4 (2009) 1–8.
- [15] C. Prado-Burguete, A. Linares-Solano, F. Rodríguez-Reinoso, C.S.-M. de Lecea, *Journal of Catalysis* 115 (1989) 98–106.
- [16] M. Inaba, *ECS Transactions* 25 (2009) 573–581.
- [17] K.H. Kangasniemi, D.A. Condit, T.D. Jarvi, *Journal of the Electrochemical Society* 151 (2004) E125–E132.
- [18] V. Alderucci, V. Recupero, L. Pino, R. Dileonardo, D.L. Cocke, N. Giordano, F. Parmigiani, *Journal of Applied Electrochemistry* 20 (1990) 811–817.
- [19] M. Cai, M.S. Ruthkosky, B. Merzougui, S. Swathirajan, M.P. Balogh, S.H. Oh, *Journal of Power Sources* 160 (2006) 977–986.