Stability of Commercial Pt/C Low Temperature Fuel Cell Catalyst: Electrochemical IL-SEM Study

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Abstract

Platinum catalyst stability has been investigated under potentiostatic and potentiodynamic conditions with and without the presence of chloride anions. The combination of rotating disc electrode (RDE) and identical location scanning electron microscopy (IL-SEM) methods reveals that potentiodynamic degradation is much more severe compared to the potentiostatic and that chloride enhances platinum dissolution thus catalyst degradation. IL-SEM method nicely shows the platinum dissolution and redeposition on the top of a catalyst film.

Keywords: Platinum, fuel cells, catalyst stability, platinum dissolution, IL-SEM, chloride

1. Introduction

Low temperature or proton exchange membrane fuel cell (PEM-FC) technology is close to pre-commercial viability.[1] In 2015 the Japanese infrastructure will be ready to sell fuel cell powered cars to masses. This is also planned in California whereas in other countries the same will happen in the near future. Since the activity is not an major catalyst issue anymore the main remaining problem besides cost seems to be its stability.[1] It is known that PEM-FC loses its electrochemical surface area (ECSA) and with that its performance with time of operation.[2] Especially damaging are start-stop conditions where potential jumps to 1.4 V were recorded.[3] However the most damaging is the presence of chloride impurities which accelerate the ECSA loss when cycling; that is simulating the start-stop conditions.[4,5] It was shown that chlorides increase the platinum dissolution in acidic media due to the complexing between dissolved Pt and chloride anions.[6] Primary degradation mechanisms are platinum dissolution[7,8] and carbon corrosion.[9,10] Additionally also Ostwald ripening,[9] platinum segregation (dissolution and subsequent redeposition),[11] particle detachment[12] and agglomeration were recognized.[2] However these phenomena are probably just a result of platinum dissolution or carbon

corrosion therefore referred as secondary degradation mechanisms. More studies are needed to better understand platinum degradation processes.

Recently we developed a new electrochemical method for monitoring degradation of the platinum catalyst on the same location (particle). It is called identical location scanning electron microscopy or IL-SEM.[13] The principle is similar to IL-TEM,[14] with one major difference which is that it is done on a graphite SEM holder whereas IL-TEM is done on TEM grid. This enables us to have thicker catalysts loading thus more realistically simulating the real PEM-FC conditions. One of the important finding was that platinum is dissolving form the catalyst layer and is redepositing on the top of a catalyst film.[11] This is similar to PEM-FC where platinum is dissolving from the catalyst and recrystallizing in the membrane.[2]

In this study we simulated the degradation of PEM-FC commercial Pt electrocatalyst under potentiostatic and potentiodynamic conditions with potentials up to 1.4 V. We utilized the rotating disc electrode (RDE) and thin film IL-SEM methods. We report on four important findings. First, ECSA is drastically decreasing with cycling number. Second, interestingly, under constant potential even as high as 1.4 V, the ECSA is not changing as drastically. Thirdly, the rate of degradation is severely accelera-

ted when chloride ions are added. And finally, with IL-SEM we clearly show that the main degradation mechanism under potentiodynamic conditions (even in the presence of chlorides) is platinum dissolution with subsequent redeposition on the top of a catalyst film.

2. Experimental

We chose a commercial state-of-the-art benchmark platinum catalyst shown in Figure 1, because it is the most common catalyst used in the fuel cell studies (usually also taken as a reference material). It has 3–4 nm Pt particles deposited on Vulcan XC72 with a metal loading of 28.6 wt.%; Supplier: De Nora Tecnologie Elettrochomiche S.p.A. (DNTE) (IT). All the measurement were done in 0.1 M HClO$_4$ (70% pro analysis, Merck). RDE and IL-SEM setups were already explained in our previous publication.[11,13] Shortly, the reference electrode (a silver/silver chloride BASi) was separated from the main compartment with an electrolytic bridge. The loading on the RDE glassy carbon electrode (Pine) was 30 μg$_{Pt}$/cm^2. We must note that in this study no rotating was performed. In potentiodynamic tests the potential was cycled between 0.4 V and 1.4 V vs. RHE with 1 V/s, whereas in the potentiostatic test the potential was held at 1.4 V vs. RHE for chosen amount of time. After each treatment a representative cyclic voltammogram was recorded (100 mV/s) in order to assess the catalyst ECSA. SEM with feld-emission scanning electron microscope (Supra 35 VP Carl Zeiss, Germany) was used.
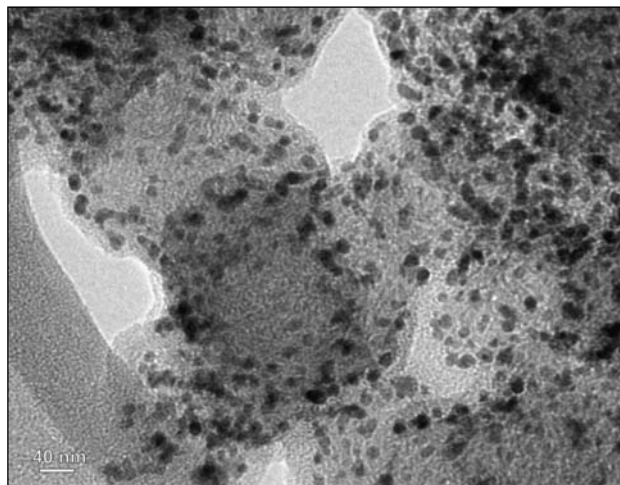

Figure 1: TEM image of Pt/C commercial electrocatalyst.

3. Results and Discussion

It has been only recently shown how cycling affects platinum dissolution. With the coupling of electrochemical flow cell and ICP-MS Topalov et. al. measured the precise Pt dissolution profile.[8] They report that the plati-

num mainly dissolves thru platinum cathodic dissolution (in the negative sweep) when potential is raised above 1.1 V and that the dissolution upon potentiostatic treatments is almost negligible.[15] Similar was also shown on platinum nano-particulate systems.[7] We chose our degradation conditions according to these two studies. We wanted to see how they affect the catalyst in a thin film for which the use of IL-SEM is very appropriate.

In the Figure 2a it can be seen that after cycling ECSA is dropping. ECSA is proportional to the integrated area under hydrogen underpotential desorption peak (between 0 V and 0.4 V).[16] ECSA is also proportional to integrated area under Pt oxidation region and reduction peak (above 0.7 V) at a fixed upper potentialand scan rate. We can see that ESCA is constantly decreasing. Interestingly, the IL-SEM sequential images (Figure 2b, c, d and e) show platinum deposition. This effect was already shown in our recent publication.[11] It is basically redeposition of the dissolved platinum from the solution on the top of a catalyst film. What we can additionally notice in Figure 2a that double layer region (between 0.4 V and 0.7 V) which is
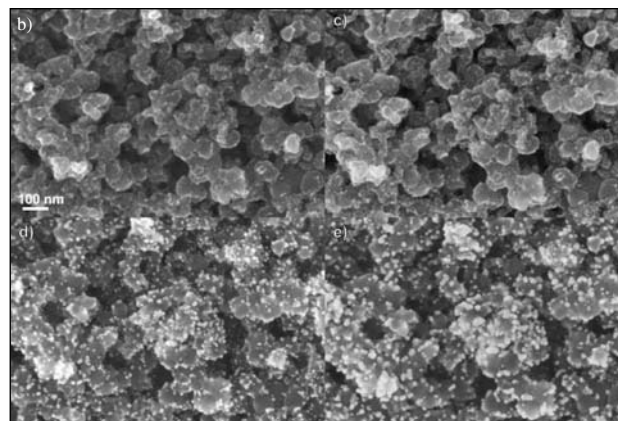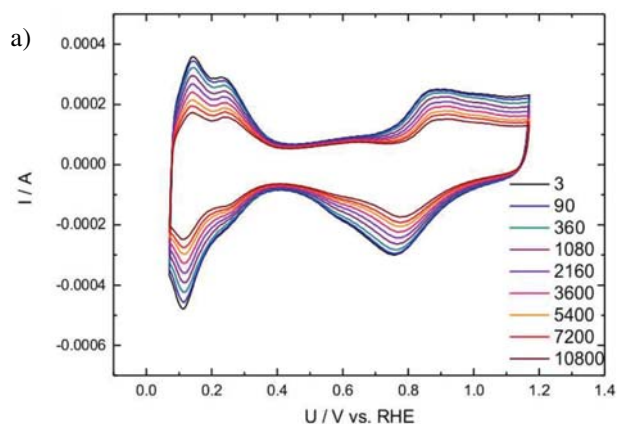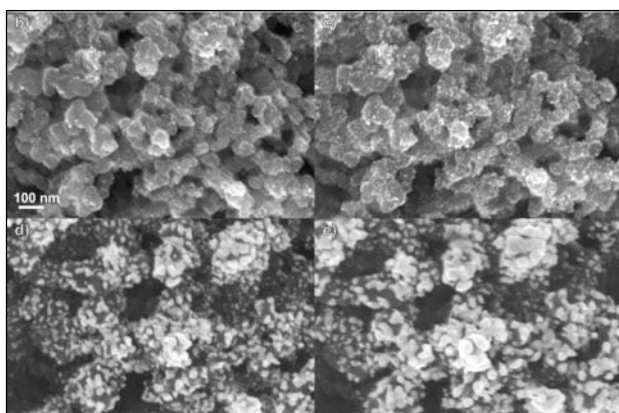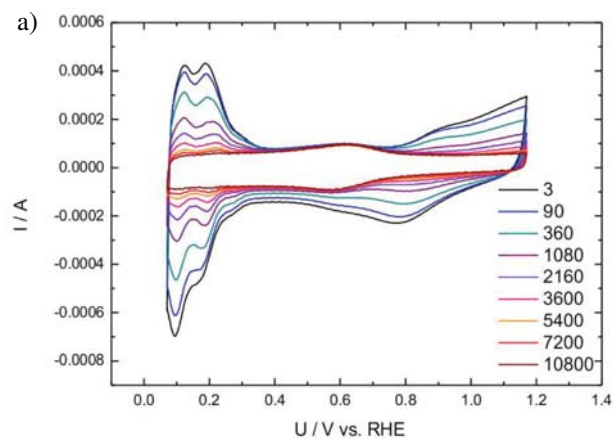

Figure 2: a) Cyclic voltammograms recorded (100 mV/s) after potentiodynamic treatments (number of cycles in the graph). IL-SEM images of potentiodynamically treated Pt catalyst: b) pristine, c) after 500, d) after 5000 and e) after 10000 cycles from 0.4 V to 1.4 V vs. RHE with 1 V/s in 0.1 M HClO$_4$.

just charging of the support and Pt particles remains almost unaffected. This means that the carbon did not change and that there was no carbon corrosion. This is also evident from the IL-SEM (Figure 2).
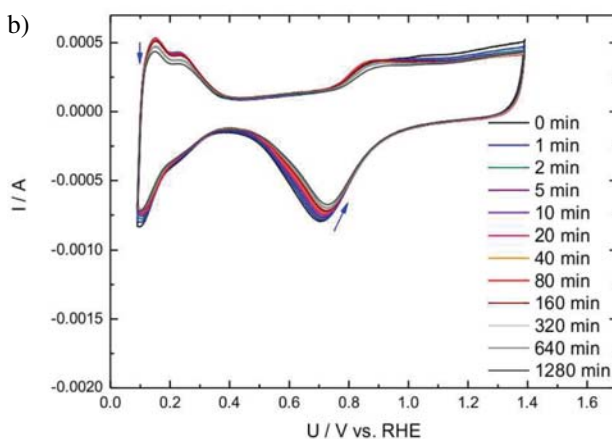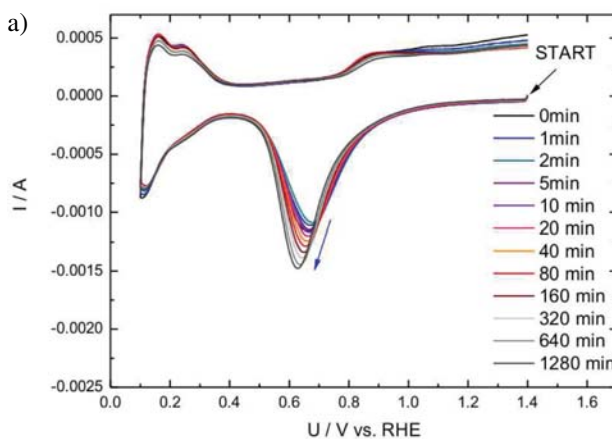
In Figure 3 it can be clearly seen that the addition of chloride increases the rate of ECSA loss. This is in accordance with the fact that chloride increases the platinum dissolution in acidic media[6] and with the studies done by Yadav et. al.[4] and Pavlišič et. al.[5] Interestingly, in consecutive IL-SEM figures it can be seen that platinum deposition is greater than in chloride-free experiment (Figure 2). In our opinion greater deposition can be explained by larger platinum concentration in the electrolyte. Therefore there is more platinum available for the redeposition. From the lack of Pt signature peaks (HUPD and Pt-oxide) in the 10800th cycle in the Figure 3a we can say that almost all the platinum was dissolved from the catalyst film. The only remaining platinum is on the top of a catalyst film, as can be seen in the IL-SEM figure (Figure 3 b, c, d and e). However it is not seen in the cyclic voltammogram because Pt features are masked by large capacitive current

of carbon supporting material. Again we do not see any significant change in double layer region and no noticeable carbon corrosion form SEM images.

In Figure 4 we can see no drastic changes after potentiostatic experiment, meaning the catalyst did not degrade drastically. Probably this is because we did not perform the degradation at higher temperatures (at least above 60 °C) that would induce corrosion of carbon.[10] And we were not changing the potential at the Pt oxide region that would induce cathodic dissolution of Pt.[7,8] Close inspection of Figure 4 a reveals that Pt-oxide reduction peak (at 0.7 V) is increasing (marked by arrow). This is contra-intuitive since the HUPD (ECSA) is decreasing. However, this is because we are holding at 1.4 V for different length of time we therefore make different amounts of Pt-oxide which finally results in different heights of Pt-oxide reduction peak. In the Figure 4b we show the second cycle where HUPD region and Pt-oxide peak are both decreasing (marked by arrows). The duration of the potentiostatic treatment was much longer than potentiodynamic treatment (21 h > 6 h) however the decrease was still modest compared to the potentiodynamic treatment.

Figure 3: a) Cyclic voltammograms recorded (100 mV/s) after potentiodynamic treatments with the addition of 0.1 M NaCl (number of cycles in the graph). IL-SEM images of potentiodynamically treated Pt catalyst. b) pristine, c) 500, d) 5000 and e) 10000 cycles from 0.4 V to 1.4 V vs. RHE with 1 V/s in 0.1 M HClO$_4$.

Figure 4: Cyclic voltmmograms of potentiostatically (1.4 V vs. RHE) treated Pt catalyst recorded with 100 mV/s. a) first cycle after the treatment and b) the second cycle 0.1 M HClO$_4$.

4. Conclusion

We report on four important findings. First, ECSA is drastically decreasing with cycling number. Second, interestingly, under constant potential even as high as 1.4 V, the ECSA is not changing as drastically. Thirdly, that the rate of degradation is severely accelerated when chloride ions are present. And finally, with IL-SEM we clearly show that the main degradation mechanism under potentiodynamic conditions (even in presence of chloride) is platinum dissolution with subsequent redeposition on the top of a catalyst film.

The question whether high potentials or start-stop cycles delivers more damage to the commercial Pt/C low temperature fuel cell catalyst is now answered. It is start-stop conditions that are more severe due to the cathodic platinum dissolution.[7–8]

The IL-SEM method is very convenient method to study any electrochemically induced change on a sample of interest like for instance degradation of RuO_2 type materials that are used for oxygen or chlorine evolution reactions.

5. Acknowledgements

6. References

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Povzetek

Stabilnost platinskega katalizatorja je bila testirana s potenciostatsko in potenciodinamično kontrolo brez in v prisotnosti kloridnih ionov. Z uporabo metode rotirajoče disk elektrode (ang. rotating disc electrode, RDE) in SEM elektrokemične metode identične lokacije (ang. identical location scanning electron microscopy, IL-SEM) se je izkazalo, da je potenciodinamična degradacija veliko bolj agresivna kot potenciostatska. Izkazalo se je tudi, da kloridi pohitrijo raztapljanje platine in s tem degradacijo katalizatorja. Z IL-SEM metodo se lepo vidi raztapljanje in nalaganje platine na vrh katalizatorskega filma.