On the need of improved Accelerated Degradation Protocols (ADPs) examination of platinum dissolution and carbon corrosion in half-cell tests

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On the Need of Improved Accelerated Degradation Protocols (ADPs): Examination of Platinum Dissolution and Carbon Corrosion in Half-Cell Tests


A high surface area commercial Pt/C catalyst (TEC10E50E, loading 46 wt%) produced by Tanaka Kikinzoku Kogyo (TKK) is used for the present study as a benchmark material. The initial particle size distribution is narrow around 3 nm. The catalyst powder is dispersed in few ml of ultrapure water (UPW, 18 MΩ cm, Millipore) by means of a high shear and thensonicated for 30 min. Half-cell thin-film rotating disk electrode (TF-RDE) was used to explore the electrochemical performance of the benchmark Pt/C catalyst. The electrochemical performances of the benchmark catalyst were compared with those of the dual metal catalysts that were investigated in a previous study [2]. The performance of the benchmark catalyst in the half-cell test was found to be similar to that of the dual metal catalysts.

In this work, in addition to traditional ECSA evaluation by half-cell rotating disk electrode (RDE) configuration, a high-fidelity simulation of the degradation processes occurring in PEMFCs was carried out using advanced scanning flow cell based analytical techniques, viz. inductively coupled plasma mass spectrometry (SFC-ICP-MS) and on-line electrochemical mass spectrometry (SFC-OLEMS) for a clear differentiation between carbon corrosion and platinum dissolution. Besides the traditional load cycle and start-stop conditions in proton exchange membrane fuel cells (PEMFCs), we use scanning flow cell thin-film rotating disk electrode (TF-RDE), we use scanning flow cell (SFC) based techniques, viz. inductively coupled plasma mass spectrometry (SFC-ICP-MS) and on-line electrochemical mass spectrometry (SFC-OLEMS) for a clear differentiation between carbon corrosion and platinum dissolution. The degradation mechanisms, especially critical is the avoidance of transitions from start-stop conditions to load cycles and back, i.e. potential transitions between 0.6 and 1.5 VRHE, can occur after the introduction of gases at the cathode side of the fuel cell. Therefore, a drive cycle test up to 0.95 VRHE was suggested recently. At the same time, as all mitigation approaches increase the complexity and price of the system, highly stable catalysts and supports are still the most desirable goal.

In this work, in addition to traditional ECSA evaluation by half-cell thin-film rotating disk electrode (TF-RDE), we use scanning flow cell (SFC) based techniques, viz. inductively coupled plasma mass spectrometry (SFC-ICP-MS) and on-line electrochemical mass spectrometry (SFC-OLEMS) for a clear differentiation between carbon corrosion and platinum dissolution. Besides the traditional load cycle and start-stop protocols we investigate a protocol concentrating on potential transitions between 0.6 and 1.5 VRHE, which we call here a "combined cycles" test. It is shown that in contrast to previous assumptions in both traditional protocols simultaneous platinum dissolution and carbon corrosion occurs. Furthermore, it is demonstrated that both degradation mechanisms are significantly accelerated when employing potential transitions between 0.6 and 1.5 VRHE.

Experimental

A high surface area commercial Pt/C catalyst (TEC10E50E, loading 46 wt%) produced by Tanaka Kikinzoku Kogyo (TKK) is used for the present study as a benchmark material. The initial particle size distribution is narrow around 3 nm. The catalyst powder is dispersed in few ml of ultrapure water (UPW, 18 MΩ cm, Millipore) by means of a high shear and then sonicated for 30 min. Half-cell thin-film rotating disk electrode (TF-RDE) was used to explore the electrochemical performance of the benchmark Pt/C catalyst. The performance of the benchmark catalyst in the half-cell test was found to be similar to that of the dual metal catalysts.
The Pt dissolution and the carbon corrosion are monitored online during the following protocol: 10 activation CVs [0.05–1.5] V_RHE, 0.2 V s\(^{-1}\), 300 load cycles [0.6–1.0] V_RHE, 0.5 V s\(^{-1}\), 500 start-stop cycles [1.0–1.5] V_RHE, 0.5 V s\(^{-1}\), 200 combined cycles [0.6–1.5] V_RHE, 0.5 V s\(^{-1}\) and 200 extended combined cycles [0.05–1.5] V_RHE, 0.5 V s\(^{-1}\).

The SFC-ICP-MS is used to characterize the Pt dissolution. A small amount of Pt/C ink is pipetted and deposited on a glassy carbon (GC) substrate forming homogeneous circular spots of approximately 1 mm in diameter (loading 0.12 μgPt). Such spots can be easily approached by the SFC, whose aperture is around 2 mm in diameter. The electrolyte flowing in the cell is Ar saturated 0.1M H\(_2\)SO\(_4\) prepared from the dilution of concentrated sulfuric acid in UPW. The described protocols are carried out with the SFC. Downstream the electrolyte is then mixed with an internal standard (\(^{186}\)Re) and flows into the ICP-MS where the dissolved ions are detected. Thanks to a daily calibration it is possible to precisely evaluate the quantitative Pt dissolution. As a comparison the measurement is done on a bulk polycrystalline Pt substrate (5 mm Platinum RDE Tip, PINE research) as well.

The SFC-OLEMS is used to characterize the carbon corrosion. The SFC coupled with OLEMS is slightly bigger than the previous one (3 mm in diameter). Therefore also the loading used is higher: 0.48 μgPt and 0.56 μg carbon. The volatile species evolved during the electrochemical measurements (i.e. CO\(_2\)) are collected through a hydrophobic Teflon membrane and flow into the mass spectrometer where they are detected (down to ppb levels). In this case no calibration and therefore no quantitative evaluation have been carried out and only the intensity in arbitrary units is shown. As a comparison, pure Vulcan carbon (Vulcan XC72R) with the same carbon loading is used as well.

Results and Discussion

Indirectly, catalyst degradation can be quantified by tracking the ECSA change. One of the most elegant ways to measure the ECSA with the TF-RDE is the so-called CO-stripping method, in which the Pt surface area is estimated from the oxidation charge of a CO monolayer. As highlighted in the introduction, the PEMFC community accepted as standard the two well-known ADPs for half-cell configuration with potential cycling (square-wave and/or triangular) in the range [0.6–1.0] and [1.0–1.5] V_RHE for simulating load-cycles and start-stop conditions, respectively. The two half-cell durability tests proposed by the FCCJ consist of triangular-wave “start-stop” cycles (0.5 V s\(^{-1}\) scan rate) and of rectangular-wave “load” cycle (3–1.8). Concerning the latter, the DOE proposed instead to use triangular-wave cycles (0.05 V s\(^{-1}\)).\(^{22}\) While the degradation depends only slightly on the form of the potential profile,\(^{18}\) the time of potential transitions by the scan rate can have a significant impact on the dissolution as well on the ECSA losses.\(^{9,24–26}\) For the sake of simplicity only triangular cycles with a scan rate of 0.5 V s\(^{-1}\) are employed in this work. In this context, the room temperature performances of a commercial Pt/C PEMFC catalyst are monitored with 8 consecutive CO-stripping during three selected ADPs: the mentioned load-cycle and start-stop protocols, as well as their combination [0.6–1.5] V_RHE named here “combined cycles” protocol (Figure 1). Note that the CO oxidation was shown to increase the Pt dissolution and thereafter the ECSA losses;\(^{27,28}\) however, the impact of 8 CO-stripping is negligible compared to the total dissolution during 10000 cycles.

The initial ECSA for Pt/C, whose average size is 3 nm, is approximately \(109 \pm 13\) m\(^2\) g\(_{\text{Pt}}\)\(^{-1}\). The evolution of the ECSA under the first two protocols is similar and the percentage losses after 10000 cycles (scan rate 0.5 V s\(^{-1}\)) are quite comparable: \(\sim 14 \pm 2\%\) and \(\sim 15 \pm 5\%\) losses for [0.6–1.0] and [1.0–1.5] V_RHE, respectively. The initial faster decrease and the successive plateau observed for the first protocol, might suggest a diverse impact of the degradation mechanisms. Nevertheless, our data shows that the difference after 10000 cycles is not significant when considering the intrinsic error of the
measurement. Furthermore, even for longer measurements (up to 15h) only small differences in the ECSA losses between load square wave cycles and start-stop cycles were reported in the literature for a Pt/Vulcan catalyst with a similar loading (45 wt%). In any case, an investigation on the different on the catalyst nanoscale degradation behavior, which is out of the scope of the present communication, should be addressed in future works.

The “picture” changes drastically under the third protocol, which can be defined as an ADP that covers the potential range of start-stop and load cycles – “combined cycles” test. Indeed, the ECSA decreases dramatically: already after 5000 cycles it drops below 20% of the initial ECSA to stabilize around 15% after the 10000 cycles. These results already give us an idea of how, compared to the first two traditional protocols, the degradation is accelerated when using a protocol that simulates the transition between the potential regions. Note however, that such a dramatic ECSA decrement is not usually observed in a fuel cell system under real operative condition. In order to gain a better insight on the underlying degradation mechanisms the dissolution and the carbon corrosion are studied separately (see the profiles in Figure 2 and the amount of CO₂ evolved and Pt dissolved per cycle in Figure 3). The catalysts are investigated with the protocol reported in Figure 2a consisting of 300 CVs [0.6–1.0] ŔHE, 500 CVs [1.0–1.5] ŔHE, 200 CVs [0.6–1.5] ŔHE and 200 CVs [0.05–1.5] ŔHE. Prior to any measurement the catalyst is activated with 10 CVs [0.05–1.5] ŔHE 0.2 V s⁻¹, at the end of which reproducible cyclic voltammograms are obtained. The electrochemical measurements are performed in the SFC, whose flexible design allows the online combination with other useful techniques. For example, the CO₂ evolution (shown in Figure 2b), corresponding directly to the CO₂ signal is significantly higher once Pt is present on the carbon surface (blue line in Figure 2b). This catalytic effect is in accordance to earlier reports that showed increase in CO₂ evolution and a shift in its onset potential of up to 0.5 V for the carbon supported Pt. Furthermore, whereas the signal for pure Vulcan exhibits almost negligible deviations from the background signal during the transition between protocols, for the Pt/C sample a large peak was observed that is quickly decaying back close to the background level or to a constant value ("steady-state" regime) depending on the applied protocol. Such decay of CO₂ signal with continuing cycling has been previously observed elsewhere and has been attributed to catalyst layer degradation and/or to the growth of a protective oxide and thus the inhibition of the corrosion process. In the case of load cycles ([0.6–1.0] ŔHE) the relatively low upper potential limit (UPL) as well the high lower potential limit (LPL) can be at the origin of such quick decrease of the CO₂ signal. At the same time the prolonged exposure to high potentials can lead to strong Pt oxidation, which consequently becomes much less active for the catalysis of carbon corrosion, as here for the start-stop cycles ([1.0–1.5] ŔHE). The observed peak in the CO₂ signal at the beginning of this protocol is much higher than the previous and it can be tentatively attributed to the transition from low potential regime to high potential regime. After a fast decay the signal reaches values slightly higher than that observed for the load cycles (see Figure 3). On the other hand, during combined cycles ([0.6–1.5] ŔHE) with the same UPL, the lower potential limit (LPL) is low enough to reduce Pt. Nevertheless, a similar transient behavior is observed, i.e. a strong initial CO₂ signal is followed by a slow decay to values higher than both the aforementioned protocols. Interestingly decreasing the LPL even further

![Figure 2](image-url)

**Figure 2.** Collection of carbon corrosion and Pt dissolution results in Ar saturated electrolyte at room temperature. (a) The applied measurement protocol consisting of 10 activation CVs [0.05–1.5] ŔHE 0.2 V s⁻¹, 300 CVs [0.6–1.0] ŔHE 0.5 V s⁻¹, 500 CVs [1.0–1.5] ŔHE 0.5 V s⁻¹, 200 CVs [0.6–1.5] ŔHE 0.5 V s⁻¹ and 200 CVs [0.05–1.5] ŔHE 0.5 V s⁻¹. (b) Corresponding online CO₂ signal (arbitrary units) for the Pt/C (red) compared to pure Vulcan (gray). (c) Corresponding online Pt dissolution profile for the Pt/C (red) and bulk polycrystalline Pt (black).
(to 0.05 V<sub>RHE</sub>), the CO<sub>2</sub> signal increases dramatically and a significant, almost constant CO<sub>2</sub> signal is observed even at the end of the test cycle. A similar effect was observed independently by Ashton et al. and Linse et al. Linse et al. suggested that below 0.6 V<sub>RHE</sub> the changes in carbon corrosion behavior cannot be attributed to the catalytic effect of Pt, which is already reduced. Both authors agree that it can originate from modifications in carbon surface oxide composition. In particular it has been attributed to the destruction of the passivating functional groups on the carbon support, which are formed during initial carbon oxidation. For such process potentials below the standard redox potential of the complete carbon oxidation reaction (<0.207 V<sub>RHE</sub>) have to be applied. Thanks to the low LPL, the results obtained for this last protocol are of particular interest for the PEM-FCs anode side, where carbon supported Pt catalysts are as well considered the state-of-the-art catalysts. To conclude it is important to stress that carbon corrosion occurring during the considered ADPs strongly depends on the LPL and UPL as confirmed by other studies on MEAs.

Besides carbon corrosion, the dissolution rate of Pt/C (normalized with the surface area estimated from the last activation cycle) is studied with the online ICP-MS (Figure 2c). As comparison also the dissolution of bulk polycrystalline Pt is measured. Comparing two electrodes, the total amount of dissolved Pt is well in agreement for all the applied protocols but the load cycles ([0.6–1.0] V<sub>RHE</sub>) for which the Pt/C dissolution is almost one order of magnitude higher than that of polycrystalline Pt. Despite the difference in both cases the dissolution rate is relatively low in this potential range. Indeed, raising the UPL to 1.5 V (“combined cycles” test [0.6–1.5] V<sub>RHE</sub>) the amount of dissolved Pt per cycle increases from 0.3×10<sup>−3</sup> to 0.14 ng cm<sup>−2</sup> cv<sup>−1</sup>, in accordance with previous studies on Pt polycrystalline. Interestingly, a reduction of the LPL (to 0.05 V<sub>RHE</sub>) in this case does not correspond to an increase in dissolution, which instead even decreases to 0.07 ng cm<sup>−2</sup> cv<sup>−1</sup>. This difference could be due to the re-deposition of Pt that takes place at lower potentials. Recently, Topalov et al. reported that the dissolution increases steeply by decreasing the LPL from 1.0 to 0.6 V<sub>RHE</sub>, whereas only a small dissolution increase was observed upon a further decrease of LPL, apparently in contrast with our results. Nevertheless, in our measurement a much higher scan rate was employed, which could lead to a higher redeposition rate as the Pt-ion diffusion is unfavored. The LPL was also reported to accelerate the ECSA losses. This is due to the changes with the LPL in the degradation mechanisms, such as carbon corrosion and Pt dissolution as evidenced by our results. During these three protocols the dissolution is constant for Pt poly, whereas it is slightly decreasing in the case of Pt/C due probably to a change in the ECSA expected during the measurement. Conversely, during the start-stop protocol ([1.0–1.5] V<sub>RHE</sub>) the dissolution profiles decrease for both Pt poly and Pt/C. After 500 cycles values close to those obtained during load cycles ([0.6–1.0] V<sub>RHE</sub>) are observed. Indeed, under such conditions, despite the high UPL, the LPL is not low enough for Pt to be reduced. Thus the Pt surface passivates protecting Pt from dissolution. The low dissolution amount during both load and start-stop cycles explains the similar time dependency in ECSA decrease shown in Figure 1, even though the influence of other degradation mechanisms such as agglomeration and detachment should be as well taken into consideration.

The comparison of the CO<sub>2</sub> evolved and Pt dissolved (the latter normalized by the number of cycles) during the different protocols, are shown in the following Figure 3. This graph summarizes the previously discussed trends in a clear picture: during the classic load and start-stop cycles, the amount of CO<sub>2</sub> evolution is relatively low, whereas during “combined cycles” tests it increases significantly, especially when decreasing the LPL to 0.05 V<sub>RHE</sub>. Simultaneously, Pt dissolution is approximately two orders of magnitude higher during “combined cycles” test cycles.

**Conclusions**

In this study we investigate the degradation of a Pt/C ORR catalyst in the standard ADPs aiming to simulate the load and start-stop cycles. In literature it is assumed that employing such ADPs in traditional TF-RDE studies it is possible to separate between Pt dissolution and carbon corrosion triggered degradation mechanisms. Following this approach it is found that in both the ADPs the ECSA losses after 10000 cycles are comparable and are around 15%. Significantly higher degradation is observed in a protocol combining both load and start-stop cycling. In order to elucidate the Pt/C degradation mechanisms in the studied protocols, advanced SFC-ICP-MS and SFC-OLEMS analytical techniques, allowing direct detection (and, hence, differentiation) of Pt dissolution and CO<sub>2</sub> evolution, are employed. It is shown that independent of the protocol Pt dissolution and CO<sub>2</sub> evolution are present, questioning the idea of the separation between the two degradation processes on the basis of applied potential window. As an alternative, direct detection of Pt dissolution (e.g. a post-analysis of electrolyte) and/or CO<sub>2</sub> evolution can be suggested. Moreover, the obtained rates of both processes are comparatively low in the standard protocols, whereas both (especially carbon corrosion) are accelerated in a transition to a new potential region, here simulated also by combined cycles. As an example, the rate of Pt dissolution is two
orders of magnitude higher, explaining well the TF-RDE results. These new findings suggest that for comparative tests of catalyst stability, ADPs switching between different conditions, as the combined cycles applied here, should be considered as an important addition to the discussed standard ADPs.

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