Activity, stability and degradation of multi walled carbon nanotube (MWCNT) supported Pt fuel cell electrocatalysts†‡

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Understanding and improving durability of fuel cell catalysts are currently one of the major goals in fuel cell research. Here, we present a comparative stability study of multi walled carbon nanotube (MWCNT) and conventional carbon supported platinum nanoparticle electrocatalysts for the oxygen reduction reaction (ORR). The aim of this study was to obtain insight into the mechanisms controlling degradation, in particular the role of nanoparticle coarsening and support corrosion effects. A MWCNT-supported 20 wt.% Pt catalyst and a Vulcan XC 72R-supported 20 wt.% Pt catalyst with a BET surface area of around 150 m² g⁻¹ and with a comparable Pt mean particle size were subjected to electrode potential cycling in a “lifetime” stability regime (voltage cycles between 0.5 to 1.0 V vs. RHE) and a “start-up” stability regime (cycles between 0.5 to 1.5 V vs. RHE). Before, during and after potential cycling, the ORR activity and structural/morphological (XRD, TEM) characteristics were recorded and analyzed. Our results did not indicate any activity benefit of MWCNT support for the kinetic rate of ORR. In the “lifetime” regime, the MWCNT supported Pt catalyst showed clearly smaller electrochemically active surface area (ECSA) and mass activity losses compared to the Vulcan XC 72R supported Pt catalyst. In the “start-up” regime, Pt on MWCNT exhibited a reduced relative ECSA loss compared to Pt on Vulcan XC 72R. We directly imaged the trace of a migrating platinum particle inside a MWCNT suggesting enhanced adhesion between Pt atoms and the graphene tube walls. Our data suggests that the ECSA loss differences between the two catalysts are not controlled by particle growth. We rather conclude that over the time scale of our stability tests (10 000 potential cycles and beyond), the macroscopic ECSA loss is primarily controlled by carbon corrosion associated with Pt particle detachment and loss of electrical contact.

1. Introduction

The oxygen reduction reaction (ORR) is a key reaction in proton exchange membrane fuel cell (PEMFC) catalysis research. The ORR is the cathode reaction and limits the overall performance of a PEMFC. One goal in fuel cell electrocatalysts research is to increase the catalytic mass activity from currently 0.12 A mg⁻¹Pt to at least 0.44 A mg⁻¹Pt at 900 mV (ir-free) cell voltage.² Pt monolayer, Pt skin, as well as dealloyed Pt alloy nanoparticle catalysts have shown promise to achieve this activity goal.²–⁵

Another goal is the durability of fuel cell cathode electrocatalysts up to 5000 h.⁶ Operating potential ranges of a PEMFC cathode can be split into a “lifetime” regime with potentials at and below 1.0 V vs. RHE. During start-up and shut-down, cathode potentials can temporarily rise up to 1.5 V cell voltage (“start-up” regime).⁶ On the macroscopic scale, catalyst degradation is associated with a loss of electrochemical active surface area (ECSA) at the fuel cell cathode during the potential cycling. On the microscopic scale, the loss of surface area has been linked to (i) metal coarsening,⁷–⁹ that is, particle growth based on a free energy driven dissolution/precipitation process (Ostwald ripening), (ii) metal cluster migration and coalescence (Smoluchowski ripening),¹⁰ (iii) metal loss by dissolution into the electrolyte⁸ and (iv) support corrosion associated with a loss of electrical contact of metal nanoparticle.¹¹,¹² Particle coalescence degradation is the growth of nanoparticles upon coalescence while moving along the support surface. This depends on the mobility of the metal particles and their mutual distance. Particle dissolution based degradation (possibly with subsequent redeposition, that is, Ostwald ripening) depends on electrode potential and particle morphology.¹³–¹⁵ The relation of particle size and dissolution potential is given in the combination of Nernst and Gibbs-Thomson equation (eqn (1)).⁸,¹⁶

\[
E = E(0) - \left( \frac{R T}{n F} \right) \ln K - (2 \gamma \Omega)/(r n F) \tag{1}
\]

With E denoting the particle dissolution potential, E(0) the dissolution potential of flat metal surface, and n, Ω, γ, r being number of transferred electrons, the molar volume, the surface energy, particle radius, and T, F and R having their usual meaning. Based on eqn (1), ECSA loss due to
Pt dissolution/redeposit should be significant at large electrode potentials and very small particles. Carbon corrosion degradation, finally, is facilitated by undersaturated 'dangling' carbon bonds. Amorphous carbon blacks exhibit much dangling sp³ bonds and are hence more prone to corrosion degradation than ordered sp² carbon structure elements. As a result of this, lower surface area graphitized carbons and carbon nanotubes (CNT) promise enhanced corrosion stability.

In this study we compare the electrochemical active surface area, electrocatalytic performance, and morphological stability of a MWCNT (Bayer Materials Science, Baytubes) supported Pt nanoparticle cathode electrocatalyst with that of a conventional furnace black carbon supported Pt catalyst (BASF Fuel Cell). We directly find microscopic evidence for Pt particle migration over relatively long distance, at room temperature. However, our findings suggests that particle growth and coarsening are not controlling the loss of electrochemical active surface area for long potential cycling (thousands of cycles). We rather conclude that carbon corrosion associated with Pt particle detachment from the conductive support are more likely to account for ECSA losses for long-term cycling. Our study highlights that MWCNT supports do not enhance the ORR activity of Pt nanoparticles, however offer significant carbon durability advantages.

2. Experimental

2.1 Synthesis of Pt/MWCNT

The synthesis of 20 wt.% Pt/MWCNT was prepared via an impregnation, freeze drying route followed by annealing step. A commercial multi walled carbon nanotube (MWCNT) powder (Baytubes C150HP, Lot#E0006AAD08, BET surface area of 193 m² g⁻¹) provided by Bayer Material Science was impregnated with H₂PtCl₆ Hexachloroplatinic acid (20 wt.% platinum, Alfa Aesar, CAS#16941-12-1; Lot#G19S028) precursor. After the sonification, the well dispersed suspension was frozen in liquid N₂ and freeze-dried under vacuum. After freeze drying the treated powder was annealed in a tube furnace under reductive H₂ atmosphere (6 Vol.% H₂, 94 Vol.% Ar, quality 5.0) (AirLiquide). The temperature program sequences started with two hours at 250 °C for precursor decomposition followed by 7 h at 300 °C for platinum reduction with a heating rate of 10 K min⁻¹. In the following electrochemical experiments of this self made Pt/MWCNT catalyst (BET surface area of 153 m² g⁻¹) was compared with a commercial Pt/Vulcan XC 72R catalyst (BET surface area of 151 m² g⁻¹, pure Vulcan XC 72R as support 205 m² g⁻¹) provided by BASF Fuel Cell Inc. All chemicals weren’t pretreated and stored according to manufacturer’s data from delivery companies.

2.2 X-Ray diffraction measurement

The characterization of electrocatalysts was carried out with a D8 Advanced X-ray Diffractometer from Bruker AXS equipped with a position sensitive LynxEye detector (PSD). The Cu-Kα tube is operated at a potential of 40 kV and current of 40 mA. Followed scanning parameters were used: 2θ range from 15° to 80°, step size of 0.01°, holding time of 7 s per step, variable divergence slit of 4 mm, PSD Iris from 13 and sample rotation of 15 rpm. The X-ray diffraction (XRD) sample holder was a custom made plexiglas disk. In the center of the disk is a 1 mm depth well with a diameter of 1 cm to position the catalyst powder sample. The catalyst powder was given into the well and carefully flattened and flushed to form a smooth surface. All XRD profiles were analyzed with using TOPAS (Bruker AXS, Version 4-2).

2.3 Electrochemical stability testing

Rotating disk electrode (RDE) experiments were carried out for all electrochemical stability testing. A custom made, three compartment electrochemical cell was used in a three electrode setup. The counter electrode was a Pt mesh and as reference a mercury-mercury sulfate electrode. The working electrode was a commercial glassy carbon rotating disk electrode (GC electrode) of 5 mm diameter (PINE Instrument). A 0.1 M HClO₄ solution prepared by diluting of 70% redistilled HClO₄ (Sigma-Aldrich, #311421) with de-ionized water (18 MOhm at room temperature) was used as electrolyte. All measurements were operated at room temperature. The disk potential was controlled with a potentiostat, VSP-5 (BioLogic, France).

A catalyst ink was prepared by mixing about 5 mg catalyst powder, 2.50 ml de-ionized water and 2.50 ml isopropanol. The mixture was then horn sonicated for 30 min. (Branson Sonifier W150). A 10 µl aliquot of catalyst ink was pipette onto the polished and cleaned 5 mm working GC electrode and dried at 60 °C for 10 min in air. Afterwards, the resulting catalyst film for both catalysts obtained a typical calculated Pt loading between 10 and 12 µg cm⁻² geo. We observed no influence on different Pt mass loading at this range. Activity of catalysts for oxygen reduction reaction (ORR) was obtained through linear sweep voltammetry (LSV) experiments before and after electrochemical stability testing procedure. LSV measurements were conducted in oxygenated 0.1 M HClO₄ electrolyte, under oxygen atmosphere, by sweeping the potential from 0.06 V vs. RHE anodically to the open circuit potential (around 1.0 V vs. RHE) at a scan rate of 5 mV s⁻¹ and a rotation speed of 1600 rpm. The ORR activity of catalysts was corrected for mass transport limitation. Mass and specific activity were then determined at 0.9 V vs. RHE at room temperature. Two different cycling voltammetry (CV) test modes were used for electrochemical stability testing. All cyclic voltammetry were carried out in deaerated electrolyte with nitrogen under nitrogen atmosphere. For the “lifetime” stability testing with 10000 voltage cycles was performed from 0.5 to 1.0 V vs. RHE at the scan rate of 50 mV s⁻¹. During the run-time three CVs from 0.06 to 1.0 V vs. RHE at a scan rate of 100 mV s⁻¹ were measured in each case after 500, 1000, 1500, 2000, 4000, 6000, 8000 and 10 000 voltage cycles to determine the platinum electrochemical active surface area (ECSA). For the “start-up” stability testing with 2000 voltage cycles it was performed from 0.5 to 1.5 V vs. RHE at a scan rate of 50 mV s⁻¹. Thereby, during the run-time three CVs from 0.06 to 1.0 V vs. RHE at a scan rate of 100 mV s⁻¹ were also carried out in each case after 250, 500, 750, 1000, 1250, 1500, 1750 and 2000 voltage cycles to generate the platinum ECSA. The platinum
ECSA of catalyst was calculated using the mean integral charge of the hydrogen adsorption and desorption area with double layer current corrected at 0.4 V vs. RHE and with 210 μC cm⁻² (Pt), assuming one hydrogen atom observed to one platinum atom.

All electrode potentials were converted into and are reported to the reversible hydrogen electrode (RHE) scale. Note that all RDE experiments were realized without Nafion to exclude all other effects. To determine our experimental error of the RDE technique we used multiple independently prepared inks and obtained up to six independent electrochemical active surface area and activity data points for each catalyst. The origin of the error based in the limited reproducibility of the catalyst film preparation on the glassy carbon electrode. This is an intrinsic error of this RDE technique but at this time it is the best and accepted method for ORR catalyst testing.

2.4 Transmission electron microscopy (TEM) measurements

The morphology of platinum nanoparticles was observed through the transmission electron microscopy (TEM), FEI TECNAI G² 20 S-TWIN equipped with energy dispersive X-ray spectroscopy (EDS) and GATAN MS794 P CCD-Camera. TEM was operated by the accelerating voltage of 200 kV. The optimal resolution of this microscopy is 0.24 nm in Bright field. Further, the initial catalyst powders and saved catalyst film after the electrochemical testing were sonicated in a mixture of isopropanol and water. An aliquot was pipette onto a Cu or Au grid with holey carbon film and dried in air. The analysis of the TEM images was occurred with analySIS FIVE software (SIS, Soft Imaging Systems, Olympus) to determine the particle size distribution (around 400 particles) of carbon supported platinum nanoparticle.

3. Results and discussion

3.1 Structural characterization of carbon supported Pt nanoparticles

The X-ray diffraction (XRD) profiles of synthesized Pt/MWCNT and Pt/Vulcan XC 72R are shown in Fig. 1. The pertinent results are consistent to crystallite size from the XRD data. TEM technique was used for further determination of particle size distribution after electrochemical experiments, respectively.

3.2 Stability of Pt/MWCNT in the “lifetime” and “start-up” potential cycling regimes

Fig. 3 combined with Tables 1 and 2 (columns 8–13) report the evolution of the electrochemical active surface area (ECSA) versus the accumulated potential cycle numbers for the two Pt nanoparticle catalysts in two potential regimes. Fig. 3 highlights the normalized N-ECSA values that were calculated according N-ECSA (cycle #) = ECSA (cycle #)/ECSA (initial cycle)* 100%. Tables 1 and 2 present the absolute initial and final ECSA values of each catalyst.

Despite the fact that both carbon supports and catalysts started out with comparable BET surface area (Pt/MWCNT 153 m² g⁻¹ and Pt/Vulcan XC 72R 151 m² g⁻¹) respectively, Pt/MWCNT catalyst exhibited a significant smaller drop in N-ECSA compared to the commercial Pt/Vulcan XC 72R, suggesting an enhanced improvement in cathode catalyst stability using MWCNT support. Under “lifetime” conditions, N-ECSA values of the Pt/MWCNT dropped a mere 12% compared to 25% for Pt/Vulcan XC 72R. Under the...
more severe “start-up” cycling conditions, the N-ECSA value of Pt/MWCNT dropped off by 48%, while Pt/Vulcan XC 72R exhibited 68% decrease. These experimental results are consistent with earlier results and confirm the detrimental nature of electrode potentials above 1.0 V vs. RHE under start/stop and partial fuel starvation conditions.\textsuperscript{24–29} During the first 500 cycles of the “lifetime” testing regime, both Pt/MWCNT and Pt/Vulcan XC 72R catalysts exhibited a characteristic break-in type increase in ECSA and is consistent with earlier reports.\textsuperscript{9,30,31} This gain in ECSA can be linked to a temporary enhancement in Pt dispersion by Pt surface atoms or Pt particle rearrangement. The initial ECSA increase was not observed during “start-up” cycling. This can be account for by the extreme corrosive conditions during the “start-up” regime, where an initial increase in Pt dispersion is impossible due to immediate massive dissolution of the smaller Pt nanoparticles. Thus, they highlight the ECSA benefits of the ordered MWCNT support compared to less ordered carbon black support such as Vulcan XC 72R.

3.3 Activity of Pt/MWCNT in “lifetime” and “start-up” potential cycling regimes

The mass transport corrected oxygen reduction reaction (ORR) activities were established with linear sweep voltammetry (LSV) at 0.90 V vs. RHE at room temperature. The resulting Pt mass and Pt surface area specific activities of Pt/MWCNT and Pt/Vulcan XC 72R catalysts before and after
consistent with literature values. Our study suggested that ORR activities of both catalysts were around 0.1 A mg$^{-1}$ (square) and commercial Pt/Vulcan XC 72R (circular). MWCNT supports do not enhance the initial Pt mass or Pt specific activity of Pt nanoparticles. After 10 000 “lifetime” potential cycles, the mass activity of Pt/Vulcan XC 72R dropped by 34%, while that of the Pt/MWCNT only decreased by 10% to a value of 0.11 A mg$^{-1}$ at 0.90 V vs. RHE. The Tafel plot revealed that Pt/Vulcan XC 72R exhibited a near-constant shift in the logarithmic activity over the 0.96 V–0.80 V potential range. MWCNT supports clearly maintain an improved ORR activity over the durability of catalyst electrodes. The Pt mass and Pt surface area specific activities of Pt/MWCNT and Pt/Vulcan XC 72R catalysts before and after testing under “start-up” cycling conditions are shown in Table 2. The activity data in Table 2 were obtained from cyclic voltammetry and linear sweep voltammetry measurements (Fig. S2†). Detailed mass activity Tafel plots are derived from Fig. S2† and provided in Fig. 5. Here, the mass activities decreased by 59% and by 66% for Pt/MWCNT and Pt/Vulcan XC 72R after 2000 cycles between 0.5–1.5 V vs. RHE, respectively, evidencing a superior

Table 1 Catalyst performance—10 000 voltage cycles from 0.5 to 1.0 V vs. RHE

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>j$^{\text{mass.}, 0.9 \text{ V [RHE]}}$ [A mg$^{-1}$(Pt)]</th>
<th>j$^{\text{spec.}, 0.9 \text{ V [RHE]}}$ [μA cm$^{-2}$(Pt)]</th>
<th>ECSA/m$^2$ g$^{-1}$</th>
<th>N-ECSA$^c$ [%]</th>
<th>Particle size/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/MWCNT</td>
<td>Initial$^a$ 0.12 ± 0.02 0.11 ± 0.01 –10</td>
<td>Final$^b$ 263 ± 63 219 ± 13 –17</td>
<td>47 ± 12 49 7 5 7.5 100</td>
<td>88 ± 2 –12 2.9 ± 1.1 3.9 ± 1.2 34</td>
<td></td>
</tr>
<tr>
<td>Pt/Vulcan XC</td>
<td>Initial$^a$ 0.15 ± 0.02 0.10 ± 0.03 –34</td>
<td>Final$^b$ 291 ± 40 263 ± 82 –9</td>
<td>53 ± 4 39 4 426 100</td>
<td>75 ± 2 –25 2.5 ± 0.6 3.6 ± 0.9 44</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Mean value determined from 6 (= 3 start-up + 3 lifetime) independent measurements. $^b$ Mean value determined from the 3 independent (lifetime) measurement. $^c$ N-ECSA = ECSA (final)/ECSA (initial) *100%.

Table 2 Catalyst performance—2000 voltage cycles from 0.5 to 1.5 V vs. RHE

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>j$^{\text{mass.}, 0.9 \text{ V [RHE]}}$ [A mg$^{-1}$(Pt)]</th>
<th>j$^{\text{spec.}, 0.9 \text{ V [RHE]}}$ [μA cm$^{-2}$(Pt)]</th>
<th>ECSA/m$^2$ g$^{-1}$</th>
<th>N-ECSA$^c$ [%]</th>
<th>Particle size/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/MWCNT</td>
<td>Initial$^a$ 0.12 ± 0.02 0.05 ± 0.01 –59</td>
<td>Final$^b$ 263 ± 63 272 ± 109 4</td>
<td>47 ± 12 18 3 –61 100</td>
<td>52 ± 4 –48 2.9 ± 1.1 5.3 ± 1.4 83</td>
<td></td>
</tr>
<tr>
<td>Pt/Vulcan XC</td>
<td>Initial$^a$ 0.15 ± 0.02 0.05 ± 0.01 –66</td>
<td>Final$^b$ 291 ± 40 294 ± 52 1</td>
<td>53 ± 4 18 1 –67 100</td>
<td>32 ± 1 –68 2.5 ± 0.6 5.2 ± 1.5 108</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Mean value determined from 6 (= 3 start-up + 3 lifetime) independent measurements. $^b$ Mean value determined from the 3 independent (start-up) measurement. $^c$ N-ECSA = ECSA (final)/ECSA (initial) *100%.

Fig. 4 Tafel Plot before (solid symbols) and after (hollow symbols) 10 000 cycles from 0.5–1.0 V vs. RHE with 50 mV s$^{-1}$ for Pt/MWCNT (square) and commercial Pt/Vulcan XC 72R (circular).

Fig. 5 Tafel Plot before (solid symbols) and after (hollow symbols) 2000 cycles from 0.5–1.5 V vs. RHE with 50 mV s$^{-1}$ for Pt/MWCNT (square) and commercial Pt/Vulcan XC 72R (circular).
durability of MWCNT supports even under extremely corrosive cycling conditions. However, the Pt surface area specific ORR activities were essentially constant for both catalysts. The activity analysis clearly revealed that ordered MWCNT supports do not offer initial activity benefits, yet maintain a higher ORR activity even under in extremely corrosive long-time potential cycling.

3.4 Correlation of particle growth and ECSA loss mechanisms

Particle size growth mechanisms. Both Pt/carbon catalysts were prepared with virtually identical initial mean particle size of 2.9 ± 1.1 nm and 2.5 ± 0.6 nm for Pt/MWCNT and Pt/Vulcan XC 72R. After the two potential cycling protocols, the particle size distributions and the mean particle size of Pt were established from TEM images. Fig. 6 and 7 show the detailed histograms of the two cycling protocols compared to the particle size distribution before cycling for Pt/Vulcan XC 72R and Pt/MWCNT, respectively. Over the course of the 10 000 “lifetime” cycles, Pt/Vulcan XC 72R particles grew from 2.5 ± 0.6 to 3.6 ± 0.9 nm, while the MWCNT supported particles coarsened over the same cycling treatment from 2.9 ± 1.1 nm to 3.9 ± 1.2 nm. Under “start-up” conditions Pt/Vulcan XC 72R mean particle size grew to 5.2 ± 1.5 nm, while the Pt/MWCNT particles finally reached 5.3 ± 1.4 nm.

From the thermodynamic relation between particle dissolution potential E and particle size (eqn (1)) a critical particle size (estimate $D_{\text{critical}} = 2r_{\text{critical}}$) can be obtained, at which Pt particles remain essentially stable under the chosen potential protocol. In contrast, there is no thermodynamically dictated slowdown in growth for coalescence of diffusing neutral metal clusters,10 atoms or particles9 on a surface. Particle coalescence results in particle growth through collisions when particles are moving along the support surface. Under “lifetime” conditions, $D_{\text{critical}}$ was computationally predicted to be in the range of 3–4 nm,8,33 consistent with our results here. This lends credibility to the model and parameter used in ref. 8 and highlights a general dominant role of Ostwald ripening (dissolution of Pt followed by ion migration and redeposition on larger particles) compared to neutral atom/particles migration and coalescence. The experimentally observed final particle size also makes it less likely that a Pt mass loss mechanism8 is significantly affecting our measurement. For the “start-up” regime no estimate of $D_{\text{critical}}$ was reported in literature, yet our results indicate a value of about 5–6 nm. If migration/ coalescence of neutral Pt nanoparticles are assumed to be independent of electrode potential, the experimental fact that $D_{\text{critical}}$ “start-up” > $D_{\text{critical}}$ “lifetime” (see Tables 1 and 2) further corroborates a controlling role of a potential-dependent dissolution/reprecipitation mechanism to account for particle growth. Previous reports8 and our own upcoming results33 obtained under very similar conditions showed that Pt particle attains their near-stable critical diameter over the course of 1200 cycles or less. We conclude from this that the growth of carbon-supported Pt nanoparticles had approached a critical near-stable mean diameter prior to the completion of the 10 000 cycles of the “lifetime” and the 2000 cycles of the “start-up” regime. We note that in a degradation regime that is based Ostwald ripening (dissolution/reprecipitation) of ions, ion transport processes may also become growth rate controlling, especially at low loadings and high surface areas of the support.8,34

Even though the electrode potential dependence of the final particle size highlights Ostwald ripening of Pt as the key particle growth mechanism, we propose that under our conditions mobility and coalescence of neutral particle do contribute. We base our proposition on experimental observations presented in Fig. 8. Fig. 8a (bright field) and 8b (dark field) present a direct TEM observation of a migrating neutral Pt particle during potential cycling on Pt/MWCNT. An individual Pt particle, likely inside a carbon nanotubes, migrated over a distance of almost 35 nm, about 10 times its own size, during the cycling protocol. The diffracting electrons of crystalline platinum imaging reveal that during its journey the particle left a atomically thin “sliding” trace of Pt behind,
which appears to be coated on the inside of MWCNT. This image evidences a significant mobility of Pt nanoparticles on electrified carbon supports. It further shows that Pt atoms possess a fairly strong interaction with the graphitic carbon sheets. The formation of atomically thin Pt surface layers in the path of migrating Pt nanoparticles constitutes a new mechanism towards highly dispersed Pt, and could, if occurring on a larger scale, at least contribute to a reduced ECSA loss of the MWCNT supported catalysts. In Fig. 9, TEM images of Pt/Vulcan XC 72R after electrochemical “lifetime” and “start-up” potential cycling evidence severe particle coarsening.

**Long-term ECSA loss mechanism.** We now turn to the experimental ECSA trends in view of the particle size changes. ECSA loss can originate from increases in Pt mean particle size or from a decrease in the number of electrochemically accessible Pt nanoparticles, which, in turn, is controlled by carbon corrosion under particle detachment or, thirdly, from a net dissolution of Pt and loss (mass loss mechanism). Considering our conclusions above, the trends in ECSA losses and particle size changes suggests that, in the short term (first few thousand cycles), ECSA losses are related to growth of particles on the carbon support; however, in the longer term, that is, toward the end of the stability test under our conditions, they do not seem to be controlled by particle size. We rather conclude that ECSA losses under our conditions are based on the loss of electrochemically accessible Pt particles via carbon corrosion and detachment, that is mainly a function of the carbon stability. A significant influence of net Pt metal loss can be excluded for the “lifetime” regime based on the upper electrode potential of 1.0 V vs. RHE. A somewhat different picture of catalyst degradation emerges for the “start-up” potential cycling regime (0.5–1.5 V vs. RHE). The severely corrosive upper turning potential of 1.5 V vs. RHE resulted in immediate massive carbon corrosion and concomitant Pt dissolution of particles of virtually all sizes. Immediate ECSA loss is the consequence. This could be the reason why no break-in period was present in the experiments. ECSA losses are now likely controlled by Pt dissolution losses into the electrolyte as well as by carbon

![Figure 8](image1.png)

Fig. 8  Pt migration within multi walled carbon nanotube—TEM image for Pt/MWCNT after electrochemical “lifetime” potential cycling (0.5–1.0 V vs. RHE, 10 000 cycles). (a) bright field TEM (10 nm scale), (b) dark field TEM (20 nm scale).

![Figure 9](image2.png)

Fig. 9  TEM image for commercial Pt/Vulcan XC 72R after electrochemical (a) “lifetime” potential cycling (0.5–1.0 V vs. RHE, 10 000 cycles, 10 nm scale) and (b) “start-up” potential cycling (0.5–1.5 V vs. RHE, 2000 cycles, 10 nm scale).
support corrosion. A quantitative comparison between N-ECSA losses in Tables 1 and 2 and Fig. 3 (48% for Pt/MWCNT and 68% for Pt/Vulcan XC 72R under “start-up” conditions) demonstrates the stability benefits the ordered, rolled graphene sheets of MWCNT offer under these severe conditions. Here, the enhanced stability of Pt atoms on the rolled graphene sheets may play a significant part in explaining the stability differences.

4. Conclusions

In this study, we have compared the cycling stability (ECSA, particle size) along with the ORR activity of MWCNT and Vulcan XC 72R supported platinum nanoparticle electrocatalysts. We distinguished “lifetime” (0.5–1.0 V vs. RHE with 10 000 cycles) conditions and more severe “start-up” cycling conditions (0.5–1.5 V vs. RHE with 2000 cycles). From our experimental correlations of particle size, ECSA loss and activity change we concluded that

- MWCNT support (BET surface area without Pt 192 m² g⁻¹, with Pt 153 m² g⁻¹) do not enhance nor are detrimental to the Pt mass or Pt specific ORR activity of Pt nanoparticles in comparison to a commercial Pt/Vulcan XC 72R catalyst with comparable BET surface area.
- MWCNT support exhibit a significantly enhanced cycling durability compared to the Vulcan XC 72R support of comparable BET surface area in both potential regimes.
- Pt particle growth is controlled by Pt dissolution/redeposition (Ostwald ripening) and a critical mean particle diameter D_critical is attained over the stability protocol (D_critical “lifetime” < D_critical “start-up”). Particle growth becomes negligible at D_critical for the relevant time scale.
- Carbon corrosion associated with Pt particle detachment controls the ECSA loss of Pt/carbon electrocatalysts for long cycling times after particles have attained D_critical. Despite the absence of a Pt ion sink, such as the hydrogen crossover of fuel cell MEA, a net Pt loss mechanism by dissolution of Pt (from essentially all particles) into the electrolyte can not entirely excluded in the “start-up” regime with potentials up to 1.5 V/RHE. In the latter case, the experimental quasi-stable mean particle size D_critical “start-up” (Table 2) is expected to be smaller than the theoretically predicted value.

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