Surface Area Loss Mechanisms of Pt₃Co Nanocatalysts in Proton Exchange Membrane Fuel Cells

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Abstract

Pt₃Co catalyst nanoparticles of 4.9 nm size present on the cathode side of a PEMFC membrane-electrode assembly (MEA) were analyzed by transmission electron microscopy after 10K voltage cycles under different operating conditions. The operating conditions include baseline (0.4-0.95 V, 80°C, 100% Relative Humidity (RH)), high potential (0.4-1.05 V, 80°C, 100% RH), high temperature (0.4-0.95 V, 90°C, 100% RH), and low humidity (0.4-0.95 V, 80°C, 30% RH). Particle growth and particle loss to the membrane is more severe in the high potential sample than in the high temperature and baseline MEAs, while no significant particle growth and particle precipitation in the membrane can be observed in the low humidity sample. Particles with different morphologies were seen in the cathode including: 1-Spherical individual particles resulting from modified electro-chemical Ostwald ripening and 2-aggregated and coalesced particles resulting from either necking of two or more particles or preferential deposition of Pt between particles with consequent bridging. The difference in the composition of these morphologies results in composition variations through the cathode from cathode/diffusion media (DM) to the cathode/membrane interface.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising energy conversion devices for transportation and stationary applications. For the most part, Pt nanoparticles are currently used as the catalyst to promote the kinetics of hydrogen oxidation and oxygen reduction reactions (ORR) in the anode and cathode of the fuel cell, respectively. However, Pt-based alloys are being investigated to replace Pt on the cathode as a way to improve the efficiency of the fuel cell and reduce cost [1, 2, 3, 4].

With the development of Pt-based alloy catalysts, there have been significant experimental and computational research efforts focusing on the enhanced ORR activity of these materials, compared to pure Pt [5, 6, 7, 8]. The volcano-type activity of Pt-based alloys was correlated with shifts in the d-band center relative to the Fermi level, and attributed to changes in the Pt–Pt bond distance, leading to a weaker Pt–OH_{ads} interaction [9]. This weaker interaction between the catalyst surface and OH species results in a reduction in OH coverage on the catalyst surface at a given potential, which provides a greater number of sites needed for oxygen adsorption, dissociation, and reduction [9, 10, 11, 12, 13]. The ORR activity of Pt alloys can be increased by 2-10 times relative to that of pure Pt by developing Pt enriched surfaces via acid leaching of less noble alloying elements and high temperature annealing [5, 6, 7, 8, 14, 15, 16].

Although the enhancement in the ORR activity of Pt alloys is well established, the durability of the catalysts remains one of the main issues for their commercialization. Dubau et al. have studied the decay characteristic of Pt₃Co alloy in a 16 cells-stack, showing a continuous dissolution of Co in the ionomer phase during operation, which resulted in a core shell structure with a Pt enriched surface. The increase in thickness of the Pt shell results from surface segregation and Ostwald ripening, decreases the ligand effect of the alloying element and thus decreases the specific activity of the catalyst particles [17]. In addition to the change in the atomic structure and composition distribu-

tion of the catalyst nanoparticles during fuel cell operation, loss of active surface area is another source of catalyst degradation. Ferreira et al. proposed four mechanisms describing the loss of electrochemical active surface area of Pt nanoparticles in the cathode of the PEMFC during cycling operation, namely (1) dissolution and re-deposition of Pt on large particles on the nanometer scale or Ostwald ripening, (2) Particle migration on the carbon support and coalescence, (3) Particle detachment from carbon support, (4) Particle dissolution and re-precipitation in the ionomer phase or/and membrane by chemical reduction of soluble Pt with permeated hydrogen from the anode side [18, 19, 20].

Borup et al. demonstrated that potential, temperature, and humidity affect the catalyst degradation during fuel cell operation [21]. Higher upper potential limit of cycling can occur at high fuel utilization conditions and/or during start up or shutdown. Darling and Meyers used a simple model to describe the rate of platinum dissolution as a function of potential [22, 23]. They showed that platinum can dissolve at rapid rates by increasing the cathode potential, until a passivating oxide layer is formed. Humidity, on the other hand, does not have a significant effect on solubility but on the ion mobility according to Bi et al [24]. Accordingly, high potential and low humidity conditions are extreme conditions that impact the Pt dissolution kinetics and migration to the membrane, while high temperature will affect the Brownian motion and thus particle mobility on the carbon support. Thus, each of these parameters during operation affects the catalyst degradation in a different way. **Therefore, the parametric gives us an insight into the mechanisms of electrochemical active surface area loss in the fuel cell and helps us find out how we can mitigate the degradation of the catalyst on the cathode of the MEA. In our previous work, the effect of operating condition on the performance decay and ECA loss of the MEAs was discussed. However the degradation mechanisms of the nanocatalysts were not addressed. In this work, a new set of experiments was conducted, to understand the mechanism of surface area loss in Pt_3Co nanocatalysts by analyzing the cathode of the PEMFC membrane-electrode assembly (MEA) at different distances to the membrane, during potential cycling under different operating**

conditions. The operating conditions include 1) baseline condition, 2) high upper potential limit (1.05 V), 3) high temperature (90°C) and 4) low humidity (30% RH). To our best knowledge this is the first time that a systematic transmission electron microscopy (TEM) analysis has been performed to establish a fundamental correlation between the various operation conditions and the degradation mechanisms in the cathode of PEMFC containing Pt₃Co nanocatalysts.

2. Experimental

2.1. Materials

Catalyst Preparation and Membrane Electrode Assembly (MEA): The catalysts for the cathode were prepared by deposition of 40 wt % Pt and Co (3:1 atomic ratio) onto Akzo Nobel Ketjen EC300J via proprietary methods, then annealed to achieve alloying and produce Pt₃Co catalysts of specific particle size. MEAs were fabricated via a developmental process, with 35.6 wt% Pt/C (~ 2 nm Pt particle size) on the anode and a 25 μ m thickness perfluorosulfonic acid (PFSA) membrane. All the cathode electrodes had the same Pt loading of $0.2\text{mg} \pm 0.02\text{mgPt}/\text{cm}^2$, while the anode electrodes had a similar loading of $0.22\text{mg} \pm 0.05\text{mgPt}/\text{cm}^2$.

2.2. Decay protocol for parametric studies

The accelerated cell degradation test conditions (Table 1), were carried out by potential cycling using a potentiostat (EG&G 273A, Princeton Applied Research Inc., Oak Ridge, TN). A square-wave potential cycle with 20s/cycle was imposed on cells with different temperature, RH, and voltage window conditions for 10K cycles. A fixed gas flow of 0.5 SLPM 4% H₂ balanced with N₂ on the anode and 0.5 SLPM N₂ on the cathode were used. A new MEA with 4.9 nm Pt₃Co particle size in the cathode was used for each test to evaluate the impact of various parametric conditions, namely high temperature, low RH, and high upper potential limit on cell decay behavior. During the potential cycling, the cathode served as the working electrode, while the anode served as both the reference and counter electrodes. The electrochemically active surface area (ECA)

Cell	Potential cycle
Baseline	<i>Square wave potential cycle:</i> 10s at 0.4V, 10s at 0.95V (20s/cycle) <i>Cell Temperature:</i> 80°C <i>Humidity:</i> Anode = Cathode = 100% RH <i>Fuel/Oxidant :</i> 0.5 SPLM 4% H ₂ /0.5 SPLM N ₂ <i>Pressure:</i> Atmospheric pressure
Low RH	<i>Humidity:</i> Anode = Cathode = 30% RH All other parameters as baseline
High Upper Potential	<i>Square wave potential cycle:</i> 10s at 0.4V, 10s at 1.05V (20s/cycle) All other parameters as baseline
High Temperature	<i>Cell Temperature:</i> 90°C All other parameters as baseline

Table 1: Operating conditions used for testing the electrochemical stability of the 4.9 nm Pt₃Co catalysts.

of Pt and Pt₃Co cathode catalysts at different stages of potential cycling was measured using a cyclic voltammogram at 10 mV/s between 0.03 and 1.0 V (vs anode) with nitrogen flowing on the cathode, 4% hydrogen (balance nitrogen) on the anode. The ECA values (m²/g-Pt) were calculated by integrating the hydrogen adsorption charge in the cathodic-going sweep of the voltammogram, multiplying by the cell area, and dividing by 210 $\mu\text{C}/\text{cm}^2$ (theoretical hydrogen monolayer adsorption on Pt) and the cathode Pt loading.

2.3. Transmission electron microscopy

First, the Pt₃Co powder was dispersed in ethanol, ultrasonicated and deposited on a carbon/copper grid for TEM characterization. Subsequently, MEA samples for TEM analysis were prepared by cutting a 1mm wide strip of the

cycled MEAs. Previously heated Hard Plus Resin 812 epoxy is poured into a mold containing the MEA sections, which is cured in a vacuum oven at 60°C for a minimum time of 72 hours. The cured molds were microtomed at room temperature, and subsequently, electron transparent MEA sections of about 70 nm thick were obtained.

The morphology and size of nanoparticles present on the cathode side of the membranes were observed using a JEOL 2010F transmission electron microscope operated at 200kV. For this study, the cathode region was divided into three areas, each approximately $3\mu\text{m}$ wide and thereby covering the cathode width of approximately $10\mu\text{m}$. Two hundred particles were analyzed from each of the regions to give a total of six hundred particles for a cathode section in a used MEA. Energy dispersive X-ray spectroscopy (EDS) coupled to the TEM was used to analyze the composition of the cathode. The Pt/Co composition ratio of different particles was determined from the intensity ratio of the Pt L-line and the Co K-line, using the EDS spectra.

3. Results

The electrochemically active surface area of the cathode was measured in our previous work by Gummala et al [25] through hydrogen adsorption in a cyclic voltamogram and is reproduced in Figure 1. According to ECA decay rates, the degradation of the MEAs as a function of number of cycles is substantially higher for the MEAs operated at higher upper potential limit compared to the ones operated at low humidity. The ECA losses under high temperature and baseline conditions occur at lower rates than high voltage but higher rates than low humidity conditions. As shown in Figure 1, the cathode of the MEA operated at low humidity exhibited very good stability with only 5% loss of surface area within 10K cycles while the ECA of the high potential sample decreased by 65% up to 10K cycles.

Figure 1: ECA loss of Pt_3Co cathode nanocatalysts as a function of number of potential cycles under different operating conditions [25]

3.1. Particle Size Distribution

The particle size distribution (PSD) of the powder sample used to fabricate the MEAs is shown in Figure 2. The mean equivalent diameter d_{eq} is 4.9 ± 0.2 nm with sizes ranging from 2 to 11 nm, while the majority of particles lie between 3 to 7 nm.

Figure 3 and Figures S1-S3 in the supporting information contain the results of the TEM analysis of the cycled cathodes operated at different conditions, namely baseline, 30% RH, high upper potential limit, and high temperature. Images from three separate regions, $3\mu\text{m}$ in length, were acquired across the $10\mu\text{m}$ width of the cathode. As illustrated in Figure 3 and Figures S1-S3, Regions A, B, and C represent regions of the cathode located at distances $0-3\mu\text{m}$, $3-6\mu\text{m}$ and $6-9\mu\text{m}$ from the cathode/membrane interface, respectively. A sample size of 200 nanoparticles was chosen for each region of the cathode, leading to a total 600 nanoparticles for each sample.

Particle size distributions of the baseline sample show that the Pt_3Co nanoparticles in the cathode area grow from 4.9 nm to about 8.3 nm (mean particle size in Regions A, B, and C, combined) after 10K cycles (Figure 3) and the distribution has broadened significantly. The PSDs exhibit a tail to larger sizes of up

Figure 2: Bright field TEM image (a) and particle size distribution (b) of the Pt₃Co nanoparticles

to 33 nm. There is no significant difference in the mean particle size of regions A, B and C to 95% confidence.

In the case of the 30% RH sample (Figure S1), a mean particle size of approximately 7.1 nm was obtained after 10K cycles. In comparison with the PSD of the powder sample (Figure 2), it can be seen that the particle size distribution did not change significantly after 10K cycles of operation under 30% RH. Compared to the baseline sample, no tail toward larger particles is seen in the PSDs of the low humidity sample. The difference in the mean particle size of the three different regions is negligible to 95% confidence.

On the other hand, under a high upper potential limit, Pt₃Co nanoparti-

Figure 3: TEM Characterization of the cathode area of the baseline MEA after 10K cycling

cles in the cathode area show a dramatic increase in size after 10K cycles of operation (Figure S2). PSDs at the three different regions within the cathode area illustrate that the high potential sample reaches a mean particle size of approximately **10.5 nm** after 10K cycles. Compared to the powder sample, the PSD of the MEA operated at high potential has broadened significantly with the majority of particles having sizes greater than 7 nm. Large particles of up to **40 nm** were observed in the TEM images of the cathode area after cycling under high potential. **Unlike baseline and low humidity samples, there is a significant difference between the mean particle size of region A, B, and C. In region A, which is the closest part in the cathode to the membrane, the particles' diameter grew to 11.8 nm while the ones in regions B and C increased their size to 10.5 and 9.1 nm respectively.**

As for the case of the baseline and high potential samples, the MEAs subjected to high temperature also resulted in the growth of particles after cycling. The PSDs in Figure S3 illustrate that for this sample a mean particle size of 8.2 nm was achieved. Beyond approximately 10 nm, the PSDs exhibit a tail to larger sizes. Similar to the high potential sample but to a smaller degree the mean particle size is larger in regions closer to the membrane. Regions A, B, and C have particles with the average size of about 9.5, 8.6, and 7.5 nm, respectively.

Figure 4a compares the mean particle size in the cycled cathodes (Regions A, B and C combined) operated at different conditions to that of the catalyst powders from which they were fabricated. The change in the mean particle size is found to be more significant for the samples cycled in the higher upper potential limit than the baseline and high temperature, whereas operating at low humidity does not have a significant impact. Cycling to a higher upper potential limit results in about 100% increase in mean particle size, whereas cycling under low humidity conditions leads to only 15% increase in mean particle size. The high temperature and baseline samples show a 65% increase in their mean particle sizes.

3.2. Particle loss to the membrane

The area percentage of the particles, which is the projected area of the Pt_3Co nanoparticles divided by the total area of the substrate multiplied by 100 is shown in Figure 4b. It is clear that the high potential sample results in higher particle loss from the cathode than the baseline and high temperature, while the least amount of particle loss occurs in the low humidity MEA. A decrease in the area density of particles represents particle loss from the cathode to the membrane which is confirmed by the TEM images of the cathode-membrane interface of the MEAs exposed to different operating conditions (Figure 5). As for particle loss from the cathode, the precipitation of new particles in the membrane is more severe in the high potential sample than the baseline and high temperature samples, while no significant particle precipitation in the membrane can

be observed in the low humidity sample. This is confirmed by the SEM analysis performed by Gummalla et al [25]. Please note that the particle precipitation occurs across the membrane up to 10 μ m away from the cathode/membrane interface.

4. Discussion

Let us now discuss the trends in mean particle size, particle loss from the cathode, and particle precipitation in the membrane under different operating condition. The largest particle size, the highest amount of particle loss from the cathode and the largest particle precipitation in the membrane occur under high potential operating condition, while the contrary is true for the low humidity condition. The baseline and high temperature operating conditions remain somewhere in the middle. Since both high potential and humidity affect particle dissolution and/or ion diffusion, the fact that potential and humidity have the highest impact on the mean particle size and particle loss from the cathode to the membrane indicates the critical role of particle dissolution and ion mobility on the surface area loss mechanisms of the NPs. Indeed, large particles in the membrane are indicative of Pt₃Co dissolution and re-precipitation in the membrane by chemical reduction of dissoluble Pt due to hydrogen crossover molecules, which results in Pt loss from the cathode area. The fact that Pt loss to the membrane is more severe in the high upper potential limit than for the other conditions is explained by the accelerated dissolution rate at potentials higher than 0.95 V [20, 22, 23]. The effect of the humidity on Pt dissolution and Pt ion transport in the ionomer has been studied by Bi et al [24]. Under high humidity conditions, the polymer electrolyte exhibits large and abundant water channel networks. This is analogous to the effect of humidity on the proton conductivity of the Nafion electrolyte, as the higher water content in the Nafion electrolyte results in higher mobility of protons in the membrane. Accordingly, low humidity conditions limit the Pt and Co ion diffusion, which consequently restricts Ostwald ripening in the cathode area, as well as re-precipitation of Pt

Figure 4: a) Mean particle size after 10K cycling under varied operating conditions b) Area percentage of the particles in three different regions in the cathode after 10K cycles

crystals in the membrane. On this basis, we can conclude that to restrict the degradation of catalysts on the cathode of the MEAs, it is critical to control the Pt dissolution and Pt ion diffusion to minimize Ostwald ripening, as this is a critical mechanism of particle growth and surface area loss inside the cathode.

Another important observation is the inhomogeneity inside the cathode in terms of particle size and particle loss from the cathode. In the case of particle size, although the differences in the mean particle size of regions A, B, and C are negligible for the baseline and low humidity samples, the situation is different for the high potential and high temperature samples. In the last two cases, the increase in particle size is greater in regions closer to the cathode-membrane interface than that of areas far from the interface. Specifically, the mean particle size in region A is about 2.7 ± 0.7 and 1.9 ± 0.5 nm larger than that of region C for the high potential and high temperature samples, respectively. Since particle mobility should be the same in each region of the cathode [20], particle migration and coalescence should not be responsible for the larger particle size in the areas closer to the cathode-membrane interface. This inhomogeneity can be explained by considering the particle dissolution and re-deposition as the dominant mechanism for the nanocatalysts growth inside the cathode. The Pt ion concentration gradient and potential difference between the cathode and anode results in Pt ion transport in the cathode toward the membrane [19]. Among these Pt ions, a fraction will deposit on nearby particles, while the

Figure 5: TEM bright-field images of the nanoparticles in the cathode, and the cathode-membrane interface after 10K cycling under a) baseline; b) 30% RH; c) 1.05 V d) 90 °C.

remainder will move longer distances toward the membrane and re-deposit on particles in regions near the membrane.

This inhomogeneity is also observed in the amount of particle loss from different regions of the cathode toward the membrane. Under all operating conditions, the amount of particles remaining in the cathode decreases as the distance to the membrane-cathode interface decreases (Figure 4b). As shown in the SEM analysis of these samples [25], the particles precipitated at the center part of the membrane show that the soluble Pt species move half way through the membrane, where they are reduced by the hydrogen crossover permeated

through the membrane from the anode to the cathode. The concentration of soluble Pt in the cathode decreases from the cathode/DM interface to the center part of the membrane where the crossover hydrogen chemically reduces Pt soluble ions to platinum particles. **Fickian diffusion law can explain the reason why the amount of particle loss increases in regions closer to the membrane.** By assuming that there are no Pt^{2+} ions at the center part of the membrane, next to the Pt band, the flux of soluble Pt species from the cathode toward the anode (N_{Pt}) can be estimated by means of a Fickian semi-infinite one dimensional diffusion, according to the expression

$$N_{\text{Pt}} = D_{\text{eff}} \cdot \frac{C_{\text{Pt}}^{2+}}{L} \quad (1)$$

where D_{eff} is the effective diffusivity of Pt ions in the membrane, C_{Pt}^{2+} is the equilibrium Pt^{2+} concentration in the cathode and L is the distance from each region in the cathode to the last Pt band in the membrane. The Pt flux from different regions in the cathode to the membrane at the micrometer scale is inversely proportional to the distance between the region and the last Pt band in the center of the membrane. Thus, the Pt loss is more severe in the regions closer to the cathode-membrane interface in the cathode.

4.1. Compositional and morphological analysis of the particles in the cathode

To study the composition changes in the cathode, two types of EDS measurements were performed. First, we measured the variation of Co across the cathode in nine different areas of $1\mu\text{m}$ diameter each. For this purpose, the electron beam was spread to $1\mu\text{m}$ diameter to cover a wide area of the sample. Second, a more detailed compositional analysis of individual and coalesced particles was performed with the electron beam matching the size of each particle to cover the entire particle. Figure 6a shows the Co atomic percentage along the different areas in the cathode of the Low RH, high upper potential and high temperature MEAs, as a function of distance from the cathode-membrane interface. **The atomic percentage of Co in all MEAs is bellow the Pt:Co 3:1 ratio of the initial Pt_3Co particles. The Co concentration in Low RH and base-**

Figure 6: Cobalt atomic percentage a) in different areas of the cathode of the MEAs and b) of individual spherical particles vs particle size after 10K voltage cycles under different operation conditions.

line MEAs is almost constant throughout the cathode with small variations. However, a higher variation of Co concentration is identified in the MEAs subjected to high voltage and high temperature operating conditions. In the last two cases, The highest amount of Co loss is seen in the areas very close to the membrane (Region A), while away from the membrane (Region B), the amount of Co in the cathode is increased. Moving farther toward the cathode-DM interface (Region C), results in a decrease in the amount of remaining Co in the cathode. To understand this Co variation, we should consider the two types of particles, based on their morphology, present in the cathode, namely individual spherical particles and aggregated non-spherical particles.

In terms of individual spherical particles, this morphology is the result of either growth via electrochemical Ostwald ripening or shrinkage due to the dissolution of Pt and Co into the ionomer phase, as both are isotropic processes. Figure 6b shows the Co concentration of individual spherical particles vs particle size in the powder sample as well as low humidity, high temperature, and high voltage MEAs obtained from EDS. All of the cycled MEAs show lower Co contents than the starting powder sample at any given particle diameter. For the Co at% we can observe a clear trend in the experimental conditions,

with 1.05 V > 90°C > baseline $\approx$ 30% RH. This is a result of the particle dissolution rate, which follows the same trend. Even though this is not measured directly, we can infer this from the observations of the particle loss and particle precipitation in the membrane, which is also supported by the literature. The effect of particle size on the Co concentration is similar for all the operating conditions. The Co atomic percentage of the spherical particles increases with increasing the particle equivalent diameter. As it has been observed in previous studies, Co leaching from the Pt₃Co particles occurs preferentially from the outermost layers of the particles, resulting in the formation of Pt enriched surfaces [26, 27, 28]. Thus, decreasing the fraction of atoms present on the surface for the larger particle sizes results in less Co leaching for these particles. In addition, re-deposition of Pt atoms on the surface of larger particles through Ostwald ripening during voltage cycling is expected to increase the thickness of the Pt enriched surface thus reducing the Co leaching to the ionomer. However, in high potential sample, the lower fitting (R-square value) especially for the particles with intermediate sizes might be related to the severe dissolution of Co and Pt which occurs under potentials higher than 0.95 V. This, in turn, might prevent the passivating Pt rich layer on these particles from protecting the particles from Co leaching.

Regarding the non-spherical particles, these arise from the aggregation and coalescence of various particles. The particles are considered to be non-spherical aggregated coalesced if their roundness, R , are smaller than 0.8. The parameter R is defined in terms of its projected area A and the major axis (a) of an ellipse fitted to the particle outline, according to the expression

$$R = \frac{4A}{\pi a^2} \quad (2)$$

The projected area percentage of non-spherical aggregated-coalesced particles was calculated from the ratio of the projected area of non-spherical coalesced particles ($A_{\text{coalesced}}$) to the total projected area of all particles ($A_{\text{individual}} + A_{\text{coalesced}}$) in the cathode. The data set used in the particle size analysis, i.e. 200 particles from each region and a total of 600 particles for each MEA, was also

used for the quantification of the amount of coalescence. Note, that we cannot simply count the number of coalesced particles, as this approach ignores the amount of particles participating in coalescence. Thus, even though there is a small bias towards large particles, the introduced error is much smaller than the error we would get by considering the number fraction of particles. The trend in this value is almost the same as the trend in particle size growth (1.05V > 90°C > baseline > 30% humidity). Operating under the high upper potential limit results in the most severe surface area loss due to aggregation-coalescence with about 38% coalesced particles in the cathode. Coalescence also occurs in the cathode operated at high temperature with about 31% of coalesced particles, compared to the baseline with 23%. However, the low humidity sample contains only 8% of aggregated coalesced particles. Under all operating conditions, the coalescence of particles inside the cathode happens more severely in the regions closer to the membrane, except for the low humidity sample which shows a constant trend across the cathode (see Figure S4 in the supporting information). The highest and lowest percentage of coalesced particles in the high potential and low humidity samples, respectively, in addition to an increased amount of coalescence inside the cathode closer to the membrane, shows the critical role of particle dissolution and diffusion in the formation of such morphology. Accordingly, besides particle migration, which might also occur, two mechanisms can be suggested for particle coalescence:

Deposition of dissoluble Pt between two particles with consequent bridging

This mechanism is supported by the work of Carlton et al. who observed some evidences of preferential deposition of Pt on the particles surface close to nearby particles [29]. This preferential deposition can finally lead to bridging between two particles and coalescence of those particles. Moreover, Asoro et al. [30, 31] provided some evidences of coalescence via deposition of Pt clusters between two or more adjacent particles in their in-situ heating TEM experiments. Figure 7 shows bright-field TEM images of coalesced particles in the baseline, low RH, high voltage, and high-temperature cathode samples showing

Figure 7: TEM images and corresponding Co at% of the coalesced particles formed by deposition of Pt between particles with consequent bridging after 10K voltage cycles under a) baseline, b) low humidity c) high voltage and d) high temperature, as well as TEM images and corresponding Co at% of the coalesced particles formed by necking of the spherical particles after 10 K voltage cycles under e) baseline, f) low humidity g) high voltage and h) high temperature

Co concentrations of less than 3 at%. Due to the low Co/Co^{2+} redox potential and low enthalpy of mixing of Pt-Co, re-deposition of Co ions on the particles is not thermodynamically favorable [28, 32]. Accordingly, the low Co concentration in the particles shown in Figure 7a-d seems to confirm the proposed mechanism of coalescence by preferential deposition of Pt between two or more adjacent particles. As shown in the TEM images, the low Co concentration (less than 3 at%) is characteristic of this mechanism.

Modified electrochemical Ostwald ripening until adjacent particles make contact with each other and coalesce

These particles are formed by necking between spherical particles, which had already grown by Ostwald ripening. Hence, the Co concentration in these particles is the average of the particles before necking. For example, consider the coalesced particle in Figure 7f, which is the result of necking between two spherical particles of about 27 nm and 23 nm under baseline operating condi-

tion. According to Figure 6b) the average Co at% of particles of that size is roughly between 30% and 35%. This is remarkably close to the composition of the coalesced particle shown in Figure 7f, which is 30.1 Co at%. In other words, the fact that the Co concentration in these particles is similar to the Co concentration of individual spherical particles with the same size validates this proposed mechanism. Note, that the argument about Co at% does not hold true for particles formed through the former proposed mechanism (preferential deposition and particle bridging), So we can use the Co concentration to differentiate between these two mechanisms. Figure 7e-h are examples of coalescence via this mechanism.

With this information we can now explain the reason for the variations of Co through the cathode from the cathode/membrane to the cathode/DM interface in the high potential and high temperature samples (Figure 6a). The amount of Co in the cathode is associated with the Co present in individual spherical particles, as well as the Co in aggregated particles, which results from the aforementioned mechanisms. As we discussed before, for these two conditions, the mean particle size as well as the amount of coalesced particles inside the cathode increase as the distance to the membrane decreases. In order to understand if an increase in the mean particle size is merely due to the increase in the amount of coalesced particles, which are typically larger particles, the mean diameter of the spherical particles (with $R > 0.8$) in regions A, B and C of the high potential and high temperature samples were quantified. This figure for the high potential sample is 9.4, 10.0 and 8.1 nm, and for the high temperature sample is 7.8, 8.1, and 7.1 nm in regions A, B, and C, respectively. Thus, the reason for the increase in the Co at% from region C to region B seems to be due to the presence of larger spherical particles which contain more Co according to Figure 6b). Inside region A however, the amount of Co declines significantly due to the proximity of the membrane. Since the mean diameter of the individual spherical particles in region A is not statistically different from that of region B, and considering the fact that more than 50% of the particles in this region are non-spherical coalesced ones (Figure S4), the coalesced particles seem

to be responsible for the decline in Co at% inside region A. One can infer that most the coalesced particles in this region result from deposition of dissoluble Pt between two or more particles and consequent bridging (the second proposed mechanism), which contain considerably low amount of Co. Considering the fact that the highest amount of particle loss occurs in this region (Figure 4b), it seems that Co and Pt diffuse to the membrane, but only Pt species, coming from regions B and C, deposit between particles. This, in turn, results in the dramatic decline in Co concentration inside region A.

4.2. Compositional and morphological analysis of the particles in the membrane

To better understand the precipitation of particles in the membrane, a more careful TEM observation of those particle was made in the high potential MEAs. Figure S5 in the supporting information illustrates the particles precipitated in the membrane which includes larger particles close to the cathode-membrane interface and smaller ones far from the interface. It seems that the larger particles, located in the areas close to the cathode/membrane interface, are dendritic and polycrystalline in nature (Figure 8a), while the smaller ones formed far from the interface are single crystals (Figure 8b). This can be explained by the inhomogeneity in driving force (supersaturation). In the region nearby the cathode/membrane interface, the concentration of Pt ions is relatively high and non-uniform along the growing surfaces. In this case, interfacial kinetics of Pt reduction and re-deposition of Pt atoms onto an atomically rough surface is faster than the diffusion of Pt species on the surface of the particles [19]. On the other hand, far from the cathode-membrane interface, but still in the membrane, faceted type Pt shapes are dominant because diffusion of Pt ions in the ionomer to the faceted Pt nanoparticles is fast, relative to interfacial kinetics of Pt addition on the growing faceted surfaces. Additional EDS analysis of both types of particles show that they are pure Pt and do not contain Co (Figure 8a and b). Co remains in cationic form after Pt_3Co dissolution, while Pt^{2+} is reduced to metallic Pt by crossover H_2 within the membrane ionomer. Dissolved Co ions cannot be reduced by crossover hydrogen because the reduction

Figure 8: Particles precipitated in the membrane: TEM images, diffraction pattern (insets) and EDS analysis a) close to the interface and b) far from the interface after 10K cycles under high potential operating condition.

potential of Co/Co^{++} is less than that of H_2/H^+ and the enthalpy of mixing of Pt and Co is too small, therefore Co ions remain in the ionic form in the membrane.

5. Conclusions

In this work, we studied the degradation of the cathode side of four different MEAs after 10K potential cycles, by changing humidity, upper limit potential and temperature. The experiments show that in the MEA operated under high potential we observe the most severe particle growth, the largest particle loss from the cathode, and the highest particle precipitation in the membrane. This, in turn, results in the loss of the active surface area of the catalyst nanoparticles. On the other hand, no significant particle growth and particle loss happens in the low humidity sample. It is well known that high potential accelerates particle dissolution while low humidity restricts the ion transport in the ionomer. Thus,

we can conclude that to restrict the nanocatalysts degradation on the cathode of the MEAs, it is critical to control the Pt dissolution and diffusion in the cathode as a main mechanism of surface area loss.

Moreover, we demonstrate that two different particle morphologies can be found inside the cathode, spherical particles arising from Ostwald ripening and non-spherical particles resulting from aggregation and coalescence of two or more particles. The highest and the lowest amount of non-spherical aggregated particles in the high potential and low humidity MEAs, respectively, in addition to the increasing amount of coalescence inside the cathode in regions closer to the cathode/membrane interface show a significant role of particle dissolution and ion migration on the coalescence of particles. This is in contrast to the belief that particle movement on the cathode causes coalescence. Given the data, we propose two mechanisms responsible for particle aggregation and coalescence, deposition of dissoluble Pt between two particles with consequent bridging, and modified electrochemical Ostwald ripening until adjacent particles make a contact to each other and finally coalesce. Evidence of these mechanisms for coalescence is provided by EDS analysis of the particles.

We also observe that the amount of Co in the spherical particles increases with the particle size. This can be explained by the formation of Pt-rich surfaces on the larger particles through the deposition of dissoluble Pt on the surfaces via Ostwald ripening which restrict Co leaching from the larger particles. Note, that the deposition of dissoluble Co does not happen because of the low enthalpy of the mixing. In addition, we observe that the atomic fraction of Co in the non-spherical aggregated particles is independent of size. An EDS analysis of the particles aggregated through the bridging mechanism shows very low amounts of Co (less than 3 at%) while the amount of Co in particles resulting from necking of spherical particles depends on the size of those individual particles.

Further EDS analysis across the cathode shows an increase in Co atomic fraction by decreasing the distance to the membrane from region C to region B for the high potential and high temperature samples. However, inside region A in the cathode Co at% drops significantly due to the higher amount

of coalescence via Pt preferential deposition between particles with consequent bridging.

Finally we identify two types of particle morphologies precipitated in the membrane, dendritic polycrystalline particles in regions nearby the cathode/membrane interface, and faceted single crystalline particles in regions far from the interface. Both types contain only Pt, as Co cannot precipitate because of the small enthalpy of mixing and low reduction potential of Co ions.

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- [1] V. Jalan, E. J. Taylor, Importance of interatomic spacing in catalytic reduction of oxygen in phosphoric acid, *Journal of the Electrochemical Society* 130 (11) (1983) 2299–12302.
- [2] F. L. D.A. Landsman (Ed.), *Handbook of Fuel Cells: Fundamentals, Technology and Applications*, John Wiley & Sons, Chichester, 2003, p. 811.
- [3] H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, Activity benchmarks and requirements for pt, pt-alloy, and non-pt oxygen reduction catalysts for pemfcs, *Appl. Catal.* 56 (1-2) (2005) 9–35.

- [4] V. R. Stamenkovic, B. S. Mun, M. Arenz, K. J. Mayrhofer, C. A. Lucas, G. Wang, P. N. Ross, N. M. Markovic, Trends in electrocatalysis on extended and nanoscale pt-bimetallic alloy surfaces, *Nat. Mater.* 6 (3) (2007) 241–247.
- [5] S. Mukerjee, S. Srinivasan, Enhanced electrocatalysis of oxygen reduction on platinum alloys in proton exchange membrane fuel cells, *Journal of Electroanalytical Chemistry* 357 (1993) 201–224.
- [6] H. Colon-Mercado, B. Popov, Stability of platinum based alloy cathode catalysts in pem fuel cells, *J. Power Sources* 155 (2006) 253–263.
- [7] C. Wang, D. van der Vliet, K.-C. Chang, H. You, D. Strmcnik, J. A. Schlueter, N. M. Markovic, V. R. Stamenkovic, Monodisperse Pt_3Co nanoparticles as a catalyst for the oxygen reduction, *J. Phys. Chem.* 113 (2009) 19365–19368.
- [8] Huang, Y. Zhang, J. Kongkanand, A. Wagner, F. J. Li, J. Jorne, Transient platinum oxide formation and oxygen reduction on carbon-supported platinum and platinum-cobalt alloy electrocatalysts, *J. Electrochem. Soc.* 161 (1) (2014) F10–F15.
- [9] B. Hammer, J. K. Nørskov, Theoretical surface science and catalysis—calculations and concepts, *Adv. Catal.* 45 (2000) 71–129.
- [10] R. R. Adzic, J. Zhang, K. Sasaki, M. B. Vukmirovic, M. Shao, J. X. Wang, A. U. Nilekar, M. Mavrikakis, J. A. Valerio, , F. Uribe, Platinum monolayer fuel cell electrocatalysts, *Top. Catal.* 46 (2007) 249–262.
- [11] E. Christoffersen, P. Liu, A. Ruban, H. L. Skriver, , J. K. Nørskov., Anode materials for low-temperature fuel cells: A density functional theory study, *Journal of Catalysis* 199 (2001) 123–131.
- [12] J. R. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jonsson, Origin of the overpotential for oxygen reduction

- at a fuel-cell cathode, *Journal of Physical Chemistry B* 108 (2004) 17886–17892.
- [13] D. P. Wilkinson, J. Zhang, R. Hui, J. Fergus, X. Li (Eds.), *Proton Exchange Membrane Fuel Cells : Materials Properties and Performance*, CRC Press, 2010.
 - [14] U. Paulus, A. Wokaun, G. Scherer, T. Schmidt, V. Stamenkovic, N. Markovic, P. Ross, Oxygen reduction on high surface area pt-based alloy catalysts in comparison to well defined smooth bulk alloy electrodes, *Electrochem. Acta* 47 (2002) 3787–3798.
 - [15] V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas, N. M. Markovic, Improved oxygen reduction activity on Pt₃Ni (111) via increased surface site availability, *Science* 315 (2007) 493–497.
 - [16] B. Patrick, H. C. Ham, Y. Shao-Horn, L. F. Allard, G. S. Hwang, P. J. Ferreira, Atomic structure and composition of Pt₃Co nanocatalysts in fuel cells: An aberration-corrected stem haadf study, *Chem. Mater.* 25 (4) (2013) 530–535.
 - [17] L. Dubau, F. Maillard, M. Chatenet, L. Guetaz, J. Andre, E. Rossinot, Durability of Pt₃Co/c cathodes in a 16 cell pemfc stack: Macro/microstructural changes and degradation mechanisms, *J. Electrochem. Soc.* 157 (12) (2010) B1887–B1895.
 - [18] P. J. Ferreira, G. J. la O, Y. Shao-Horn, D. Morgan, R. Makharia, S. Kocha, H. A. Gasteiger, Instability of pt/c electrocatalysts in proton exchange membrane fuel cells a mechanistic investigation, *J Electrochem Soc* 152 (2005) A2256–A2271.
 - [19] P. J. Ferreira, Y. Shao-Horn, Formation mechanism of pt single-crystal nanoparticles in proton exchange membrane fuel cells, *Electrochemical and Solid State Letters* 10 (3) (2007) B60–B63.

- [20] Y. Shao-Horn, W. C. Sheng, S. Chen, P. J. Ferreira, E. F. Holby, D. Morgan, Instability of supported platinum nanoparticles in low-temperature fuel cells, *Top Catal.* 46 (2007) 285–305.
- [21] R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishik, Scientific aspects of polymer electrolyte fuel cell durability and degradation, *Chem. Rev.* 107 (2007) 3904–3951.
- [22] R. M. Darling, J. P. Meyers, Kicells model of platinum dissolution in pem-fcs, *Journal of the electrochemical Society* 150 (2003) A1523–A1527.
- [23] R. M. Darling, J. P. Meyers, Mathematical modal of platinum movement in pem fuel cells, *J Electrochem Soc* 152 (11) (2005) A242–A247.
- [24] W. Bi, Q. Suna, Y. Denga, T. F. Fuller, The effect of humidity and oxygen partial pressure on degradation of pt/c catalyst in pem fuel cell, *Electrochimica Acta* 54 (2009) 1826–1833.
- [25] M. Gummalla, S. C. Ball, D. A. Condit, S. Rasouli, K. yu, P. J. Ferreira, D. J. Myers, Z. Yang, Effect of particle size and operating conditions on Pt₃Co pemfc cathode catalyst durability, *Catalysts* 5 (2015) 926–948.
- [26] S. Chen, W. Sheng, N. Yabuuchi, P. J. Ferreira, L. F. Allard, , Y. Shao-Horn, Origin of oxygen reduction reaction activity on Pt₃Co nanoparticles: atomically resolved chemical compositions and structures, *J. Phys. Chem. C.* 113 (2008) 1109–1125.
- [27] M. Watanabe, K. Tsurumi, T. Mizukami, T. Nakamura, , P. Stonehart, Activity and stability of ordered and disordered co/pt alloys for phosphoric acid fuel cells, *J. Electrochem. Soc.* 141 (1994) 2659.
- [28] S. Chen, H. A. Gasteiger, K. Hayakawa, T. Tada, Y. Shao-Horn, Platinum-alloy cathode catalyst degradation in proton exchange membrane fuel cells:

Nanometer-scale compositional and morphological changes, *Journal of The Electrochemical Society* 157 (2010) A82–A97.

- [29] C. E. Carlton, S. Chen, P. J. Ferreira, L. F. Allard, , Y. Shao-Horn, Sub-nanometer-resolution elemental mapping of Pt₃Co nanoparticle catalyst degradation in proton-exchange membrane fuel cells, *J. Phys. Chem. Lett* 3 (2012) 161–166.
- [30] M. Asoro, Coalescence and sintering in metallic nanoparticles: in-situ transmission electron microscopy (tem) study, ph.d. dissertation, Tech. rep., University of Texas at Austin, Austin, TX, (2012).
- [31] M. Asoro, P. Ferreira, D. Kovar, In situ transmission electron microscopy and scanning transmission electron microscopy studies of sintering of ag and pt nanoparticles, *Acta M* 81 (2014) 173–183.
- [32] A. K. Niessen, A. R. Miedema, F. R. Deboer, , R. Boom, Enthalpies of formation of liquid and solid binary alloys based on 3d metals: Iv. alloys of cobalt, *Physica B & C* 151 (1988) 401–432.