Activity, Stability, and Degradation Mechanisms of Dealloyed PtCu$_3$ and PtCo$_3$ Nanoparticle Fuel Cell Catalysts

Frédéric Hasché,* Mehtap Oezaslan, and Peter Strasser$^{[a]}$ 

A key challenge in today’s fuel cell research is the understanding and maintaining the durability of the structure and performance of initially highly active Pt fuel cell electrocatalysts, such as dealloyed Pt or Pt monolayer catalysts. Here, we present a comparative long-term stability and activity study of supported dealloyed PtCu$_3$ and PtCo$_3$ nanoparticle fuel cell catalysts for the oxygen reduction reaction (ORR) and benchmark them to a commercial Pt catalyst. PtCu$_3$ and PtCo$_3$ were subjected to two distinctly different voltage cycling tests: the “lifetime” regime [10000 cycles, 0.5–1.0 V vs. RHE (reversible hydrogen electrode), 50 mV s$^{-1}$] and the corrosive “start-up” regime (2000 cycles, 0.5–1.5 V vs. RHE, 50 mV s$^{-1}$). Our results highlight significant activity and stability benefits of dealloyed PtCu$_3$ and PtCo$_3$ for the ORR compared with those of pure Pt. In particular, after testing in the “lifetime” regime, the Pt-surface-area-based activity of the Pt alloy catalysts is still two times higher than that of pure Pt. From our electrochemical, morphological, and compositional results, we provide a general picture of the temporal sequence of dominant degradation mechanisms of a Pt alloy catalyst during its life cycle.

Introduction

The proton-exchange membrane fuel cell converts chemical energy directly into electrical energy with the single product of water. It is one of the promising technologies for low emission and noise energy production in different fields, for example, in automotive or portable applications. The overall reaction and noise energy production in different fields, for example, in automotive or portable applications. The overall reaction of a hydrogen/oxygen fuel cell is [Eq. (1)]:

$$2H_2 + O_2 \rightarrow 2H_2O$$ (1)

With the rate-limiting oxygen reduction reaction (ORR) on the cathodic side [Eq. (2)]:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E_0 = +1.23 \text{ V vs. RHE}$$ (2)

Currently, platinum nanoparticles supported on carbon, such as Vulcan XC 72R, are the most widely used electrocatalysts for fuel cell application. However, the slow catalytic kinetics of the ORR [Equation (2)], the high material cost for the noble metal platinum, and the gradual platinum degradation are the major barriers for cost-efficient and durable fuel cell cathode catalysts. To overcome the activity limitation, a number of different Pt-based catalyst concepts, such as platinum monolayer catalysts,[1,2] Pt skin catalysts,[3,4] and dealloyed Pt core–shell bimetallic nanoparticles,[5–7] have been developed in the last decade. These catalysts have shown high platinum mass-based activity (current/mass of platinum, A mg$^{-1}$Pt) and high platinum surface-area-specific-based activity (current/real Pt surface area, A$^{-2}$Pt) and are promising candidates for supporting the U.S. Department of Energy (DOE) activity goal of 0.44 A mg$^{-1}$Pt at 900 mV cell voltage in a real membrane electrode assembly.[8] All these concepts are associated with a decrease in the noble metal quantity, and they reduce the cost gap for a commercial application. However, the long-term durability requirement of fuel cell electrocatalysts has not been met to date, with performance losses of less than 40% (electrochemical area) of beginning-of-life activities for over 5000 h.[9] The recent data show that multimetallic nanoparticle electrocatalysts are suitable systems to meet this goal in half-cell experiments.[10-12]

The common operating voltage range for cathode electrocatalysts can be split into two regimes: a “lifetime” regime, which represents a normal, general operation range for a fuel cell with a voltage potential at and below 1.0 V vs. RHE (reversible hydrogen electrode); and a “start-up” regime, which represents voltage potentials rising up to 1.5 V vs. RHE during start-up and shutdown or partial fuel starvation.[10] These long-term stability tests are accelerated degradation tests to simulate long-term behavior of fuel cell electrocatalysts. The gradual loss of platinum can be traced back by decreasing the platinum electrochemically active surface area (ECSA). Platinum ECSA loss mechanisms are addressed: 1) metal coarsening,[11,12] that is, particle growth based on a free-energy-driven dissolution/precipitation process (Ostwald ripening), 2) metal cluster migration and coalescence (Smoluchowski ripening),[13] 3) metal loss by dissolution into the electrolyte,[14] and 4) support corrosion associated with a loss of electrical contact of metal nanoparticles.[12,15,16] In particular, the voltage potentials up to 1.5 V vs. RHE dramatically decrease the efficiency of the electrocatalyst because of carbon support corrosion and particle dissolution.[14,17–22]

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In this study, we correlate key macroscopic and microscopic descriptors of electrocatalyst stability, such as ECSA, ORR performance, chemical composition, and nanoparticle size, for dealloyed PtCu$_3$, PtCo$_3$, and Pt nanoparticle fuel cell electrocatalysts. We compare and determine changes before, during, and after voltage cycling tests in the two distinct regimes (lifetime and start-up) to obtain more insight into the dominant catalyst degradation mechanisms. We conclude that particle growth and coarsening is the dominant short-term degradation mechanism of Pt and Pt alloys until a critical (quasi-stable) particle size, $D_{crit}$, is achieved. At later stages, carbon corrosion associated with particle detachment becomes dominant. Predominantly, under corrosive start-up voltage cycling conditions, the Pt and base metal dissolution as well as the net loss into the electrolyte play a parallel dominant role as carbon corrosion.

Results and Discussion

Structural characterization of PtCu$_3$, PtCo$_3$, and Pt nanoparticles

The X-ray diffraction (XRD) profiles of the synthesized high-surface-area carbon (HSAC)-supported Pt–Cu and Pt–Co alloy nanoparticles in an atomic ratio of 1:3 and the commercial untreated pure Pt/HSAC are shown in Figure 1. The vertical dotted lines in Figure 1 indicate the reference powder diffraction patterns of Pt, whereas the additional dotted lines in a) and b) are the reference powder diffraction patterns of Co and Cu, respectively, as tabulated in the powder diffraction file (PDF) database of the international center for diffraction data (ICDD), in particular PDF(Pt)#00-004-0802, PDF(Cu)#00-004-0836, PDF(Co)#00-015-0806.[22]

For PtCo$_3$/HSAC (Figure 1 a) and PtCu$_3$/HSAC (Figure 1 b), the Pt alloys exhibit multiple crystal phases. The (111), (200), and (220) reflections for the alloys were shifted to higher 2$q$ angles with respect to pure platinum, which indicated the contraction of the lattice by inserting cobalt or copper in the fcc platinum lattice. No reflections of the residual pure fcc platinum phase were found for the Pt–Cu alloy sample shows a pure fcc copper phase with sharp reflections at 2$q$= 43.3, 50.4, and 74.1°, which indicates a large crystallite size, whereas no pure cobalt was detected for the Pt–Co alloy. As shown in Figure 1 c, the broad reflections of a pure fcc Pt/HSAC catalyst at 2$q$= 39.8, 46.2, and 67.5° show a small crystallite size. The quantification by the Rietveld refinement of the Pt alloy crystal phase structures is published in Ref. [24].

To investigate the mean particle size and chemical composition of the Pt alloy nanoparticle catalysts before and after electrochemical testing, we used transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The results are summarized in Table 1, in which the notation “initial” denotes active dealloyed Pt alloy catalysts with a core–shell nanostructure after the electrochemical treatment, as described in the Experimental Section under “Cyclic voltammetry.”

The mean particle size for the synthesized PtCu$_3$/HSAC and PtCo$_3$/HSAC nanoparticle catalysts is 4.3±1.6 and 4.0±1.0 nm, respectively, obtained from the evolution of TEM images by counting of more than 400 particles. Both Pt alloy catalysts ex-

Table 1. Mean particle size and chemical composition for Pt/HSAC, PtCu$_3$/HSAC, and PtCo$_3$/HSAC catalysts before and after electrochemical stability testing.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mean particle size by TEM [nm]</th>
<th>Chemical composition by EDS [at%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As synthesized</td>
<td>10000 cycles</td>
</tr>
<tr>
<td>Pt/HSAC</td>
<td>2.3 ± 0.7</td>
<td>3.1 ± 0.7</td>
</tr>
<tr>
<td>PtCu$_3$/HSAC</td>
<td>4.3 ± 1.6</td>
<td>4.4 ± 1.6</td>
</tr>
<tr>
<td>PtCo$_3$/HSAC</td>
<td>4.0 ± 1.0</td>
<td>4.6 ± 1.8</td>
</tr>
</tbody>
</table>
hbit a similar mean particle size after the thermal treatment, which rules out the stability benefit through the initial particle size. For the commercial untreated pure Pt/HSAC nanoparticle catalysts, the mean particle size is 2.3 ± 0.7 nm. The difference in the mean particle sizes of the pure Pt/HSAC and Pt bimetallic alloy catalysts is caused by annealing for 7 h at 800 °C for alloy formation.24,25

We established the chemical composition of the Pt–Cu and Pt–Co alloy nanoparticles by using EDS. Table 1 shows the as-synthesized compositions with an almost desired atomic ratio of platinum to metal of 1:3, PtCu2:3:Cu37:2 and PtCo2:0:Co20:2. After an identical electrochemical dealloying protocol, the initial chemical composition of the dealloyed Pt–Cu and Pt–Co alloy nanoparticles changed drastically because of the dissolution of the non-noble metal (copper or cobalt) from the particle surface. On the basis of earlier studies, we assume the formation of highly active core–shell nanoparticles with a platinum-enriched shell and a copper/cobalt-enriched alloy core.24,25,26–27 Finally, the initial chemical composition of the (dealloyed) core–shell bimetallic nanoparticles was Pt53:2:Cu37:2 and Pt63:2:Co20:2. The fraction of removed cobalt in the Pt alloy nanoparticles was significantly higher than that for copper, which is in line with the relative dissolution potentials.

### Activity and stability of Pt and Pt alloy nanoparticle catalysts in the lifetime and start-up voltage cycling regimes

The mass-transport-corrected activities of Pt/HSAC, PtCu3/HSAC, and PtCo3/HSAC nanoparticle catalysts for the ORR before and after the electrochemical stability testing are summarized in Table 2. From the linear sweep voltammetry curves, the intrinsic kinetic current for each initial catalyst was estimated at 0.9 V vs. RHE at room temperature. Here, \( i_{\text{max}} \) is the platinum mass-based activity and \( j_{\text{specific}} \) is the platinum surface-area-specific-based activity for the ORR. Both dealloyed PtCu3/HSAC and PtCo3/HSAC nanoparticle catalysts show two to three times higher initial platinum mass-based activity, \( i_{\text{max}} \), and three to four times higher initial platinum surface area specific based activity, \( j_{\text{specific}} \), than the commercial pure platinum nanoparticle catalyst. All measured initial activities are in full agreement with values published in literature.24,25,26–28–30

### Lifetime voltage cycling regime: Figure 2 shows the changes in the platinum surface-area-specific-based activities before (solid symbols) and after (hollow symbols) 10 000 voltage cycles from 0.5 to 1.0 V vs. RHE at 50 mV s\(^{-1}\) in 0.1 m HClO\(_4\).

![Figure 2. Platinum surface-area-specific-based activity Tafel plot for PtCo/HSAC (squares), PtCu3/HSAC (circles), and Pt/HSAC (triangles) catalysts before (solid symbols) and after (hollow symbols) 10 000 voltage cycles from 0.5 to 1.0 V vs. RHE at 50 mV s\(^{-1}\) in 0.1 m HClO\(_4\).](image)

### Table 2. ORR activities for Pt/HSAC, PtCu3/HSAC, and PtCo3/HSAC catalysts before and after electrochemical stability testing.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( i_{\text{max}} ) (0.9 V vs. RHE) [A mgPt(^{-1})]</th>
<th>( j_{\text{specific}} ) (0.9 V vs. RHE) [µA cm(^{-2})]</th>
<th>( \Delta ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/HSAC</td>
<td>Initial(^a) 0.14 ± 0.01</td>
<td>Initial(^b) 0.00 ± 0.00</td>
<td>191 ± 20</td>
</tr>
<tr>
<td>PtCu3/HSAC</td>
<td>0.44 ± 0.08</td>
<td>743 ± 104</td>
<td>566 ± 5</td>
</tr>
<tr>
<td>PtCo3/HSAC</td>
<td>0.34 ± 0.15</td>
<td>661 ± 266</td>
<td>380 ± 106</td>
</tr>
</tbody>
</table>

\( \Delta \) Mean value was determined from six (three start-up + three lifetime) independent measurements. \( \Delta \) Mean value was determined from three independent measurements.

The mean particle size of the Pt alloys remains almost unchanged after 10 000 voltage cycles, as shown in Figure 2 (see columns 3–5). However, the mean particle size of the Pt alloys decreases by 24 and 42%, respectively, whereas \( j_{\text{specific}} \) for the Pt/HSAC nanoparticle catalyst increased by 30%. The increase in \( j_{\text{specific}} \) for the Pt/HSAC nanoparticle catalyst after 10 000 voltage cycles can be explained by the growth of the particle size from 2.3 ± 0.7 to 3.1 ± 0.7 nm (35%; see Table 1). The \( j_{\text{specific}} \) decreased dramatically for both Pt alloys after 10 000 voltage cycles, as shown in Table 2 (see columns 3–5). However, the overall chemical base metal content for both Pt alloys after the lifetime stability test protocol (see Table 1). Therefore, the decrease in \( j_{\text{specific}} \) is probably caused by the rearrangement of Pt atoms on the particle surface, which results in changes in defect densities (increased surface roughness), surface morphology, and Pt shell thickness. In parallel, the observed slight base metal losses from the near-surface region would lead to an increase in the platinum shell thickness of the core–shell nanoparticles. These processes reduce the lattice strain in the Pt-enriched shell of the particles and hence the intrinsic specific ORR activity of the Pt alloy catalysts.24

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Nevertheless, the resulting platinum surface-area-specific-based activity, \( j_{\text{specific}} \), of Pt alloy nanoparticle catalysts is still two times higher than that of a commercial pure platinum nanoparticle catalyst after "lifetime" testing.

**Start-up voltage cycling regime:** Figure 3 shows the changes in platinum surface-area-specific-based activities before (solid symbols) and after (hollow symbols) 2000 start-up voltage cycles from 0.5 to 1.5 V vs. RHE at 50 mV s\(^{-1}\) for PtCo\(_3\)/HSAC (squares), PtCu\(_3\)/HSAC (circles), and Pt/HSAC (triangles) nanoparticle catalysts.

![Figure 3. Platinum surface-area-specific-based activity Tafel plot for PtCo\(_3\)/HSAC (squares), PtCu\(_3\)/HSAC (circles), and Pt/HSAC (triangles) catalysts before (solid symbols) and after (hollow symbols) 2000 voltage cycles from 0.5 to 1.5 V vs. RHE at 50 mV s\(^{-1}\) in 0.1 M HClO\(_4\).](image)

In combination with Table 2 (see columns 3, 6, and 7), \( j_{\text{specific}} \) for the Pt/HSAC nanoparticle catalyst increased by 43 % whereas \( j_{\text{specific}} \) decreased by 62 and 57 % for the PtCu\(_3\)/HSAC and PtCo\(_3\)/HSAC nanoparticle catalysts, respectively. Under this strong corrosion and dissolution condition, the mean particle size grows very fast from 2.3 ± 0.7 to 5.6 ± 1.5 nm (144 %) for Pt/HSAC, from 4.3 ± 1.6 to 6.8 ± 2.2 nm (58 %) for PtCu\(_3\)/HSAC, and from 4.0 ± 1.0 to 7.0 ± 2.8 nm (75 %) for PtCo\(_3\)/HSAC (see Table 1). The platinum surface-area-specific-based activity, \( j_{\text{specific}} \), increased only for the Pt/HSAC catalyst. For Pt alloys, \( j_{\text{specific}} \) decreased dramatically. Table 1 reveals a significant increase in the chemical composition, from initially Pt\(_{53.2}\)Cu\(_{37.2}\) to a final composition Pt\(_{33.2}\)Cu\(_{57.2}\) and from an initial composition of Pt\(_{100}\)Co\(_{20}\) to a final one of Pt\(_{50}\)Co\(_{50}\) after 2000 start-up voltage cycles up to 1.5 V vs. RHE; this change is caused by the strong corrosion conditions. The strong dissolution of copper or cobalt from the Pt alloy core–shell nanoparticles induced a decrease in the geometric strain of the platinum shell, which initially led to the improved performance of the ORR. The decrease in \( j_{\text{specific}} \) clearly related to the change in the morphology and the chemical composition of the Pt alloys. The final values of \( j_{\text{specific}} \) of the alloy catalysts are similar to those of pure platinum particles due to the same particle size.

In summary, PtCu\(_3\) and PtCo\(_3\) alloy nanoparticle catalysts exhibit higher initial platinum mass and platinum surface-area-specific-based ORR activities as compared with the commercial pure platinum nanoparticle catalyst. After 10,000 lifetime voltage cycles up to 1.0 V vs. RHE, the Pt alloys still exhibit two times higher \( j_{\text{specific}} \) than that of the commercial pure platinum. The Pt alloys retain their chemical composition after 10,000 lifetime voltage cycles. Furthermore, after 2000 start-up voltage cycles up to 1.5 V vs. RHE, the \( j_{\text{specific}} \) values for Pt alloys approximate rapidly to those for pure platinum at around 7 nm due to the change in the morphology and the composition of the almost completely dealloyed particles. The activity loss is related to the morphological surface change as well the decrease in the compressive lattice strain of Pt alloy particles.

**Particle growth and platinum ECSA loss mechanisms**

*Evolution in particle size distribution:* Figures 4–6 show the particle size distributions with the corresponding TEM images for Pt/HSAC, PtCu\(_3\)/HSAC, and PtCo\(_3\)/HSAC nanoparticle catalysts;

![Figure 4. Evolution of the particle size distributions and the corresponding TEM images (scale bar of 10 nm) for the Pt/HSAC nanoparticle catalyst: a) as synthesized, b) after 2000 voltage cycles from 0.5 to 1.5 V vs. RHE, and c) after 10,000 voltage cycles from 0.5 to 1.0 V vs. RHE at 50 mV s\(^{-1}\) in 0.1 M HClO\(_4\).](image)
During lifetime voltage cycling, the particle size grew by 35, 2, and 15 % (see Table 1, column 4) for the Pt/HSAC, PtCu3/HSAC, and PtCo3/HSAC catalysts, respectively. The TEM images after lifetime testing (see parts c of Figures 4–6) show a nearly unchanged nanoparticle bulk density behavior compared with the as-synthesized catalysts (see parts a of Figures 4–6). Here, we assume that the Pt alloys and pure platinum particles had achieved a stable D_initial whereas the influence of the carbon corrosion, particle detachment, and dissolution/Pt loss into the electrolyte is negligible for this voltage regime. The critical particle size is dependent on the upper turning potential of the applied voltage cycles.

Initial ECSA of dealloyed PtCu3, PtCo3, and Pt: Table 3 summarizes the absolute and normalized platinum ECSA for all catalysts before and after the electrochemical stability testing for both protocols.

The initial Pt alloys show a lower ECSA compared with the commercial pure platinum. The reduced ECSA is caused by the difference in the mean particle size of the as-synthesized Pt alloys (see Table 1, column 2). Generally, small particles show higher values of the ECSA than do large particles. In Table 3, the PtCu3/HSAC and PtCo3/HSAC catalysts exhibit almost the same values of the ECSA due to the similar mean particle sizes (see Table 1, column 2). The results for ECSA of the Pt alloys and pure platinum are in good agreement with the values published in the literature.

Evolution of the normalized platinum electrochemical active surface area (N-ECSA): We now turn to the platinum ECSA trends combined with the mean particle size changes to clarify the main loss mechanisms of Pt alloys and pure platinum. Figure 7 shows the experimentally determined and normalized ECSA (N-ECSA) for Pt/HSAC (triangles), PtCu3/HSAC (circles), and PtCo3/HSAC (squares) nanoparticle catalysts under lifetime (solid symbols) and start-up (hollow symbols) conditions. The N-ECSA was calculated as follows [Eq. (3)]:

\[
N\text{-ECSA}(\text{cycle##}) = \frac{\text{ECSA}(\text{cycle##})}{\text{ECSA}(\text{initial})} \times 100\% 
\]

\[
(3)
\]

N-ECSA trends in the lifetime stability regime: We now discuss the curves of the N-ECSA for all catalysts in the lifetime regime. The N-ECSA decreased by 27 and 6 % for Pt and PtCu3, respectively, whereas it increased by 7 % for PtCo3 (see Table 3, column 5). Generally, the increase in the particle size leads to a

![Figure 5. Evolution of the particle size distributions and the corresponding TEM images (scale bar of 10 nm) for the PtCu3/HSAC nanoparticle catalyst: a) as synthesized, b) after 2000 voltage cycles from 0.5 to 1.5 V vs. RHE, and c) after 10 000 voltage cycles from 0.5 to 1.0 V vs. RHE at 50 mV s\(^{-1}\) in 0.1 m HClO\(_4\).](image)

![Figure 6. Evolution of the particle size distributions and the corresponding TEM images (scale bar of 10 nm) for the PtCo3/HSAC nanoparticle catalyst: a) as synthesized, b) after 2000 voltage cycles from 0.5 to 1.5 V vs. RHE, and c) after 10 000 voltage cycles from 0.5 to 1.0 V vs. RHE at 50 mV s\(^{-1}\) in 0.1 m HClO\(_4\).](image)
A careful observation of Figure 7, however, reveals that for platinum there is a steady decrease in the initial ECSA correlated with the increase in the mean particle size, which slows down after around 4000 voltage cycles. We assume that this is the point at which a quasi-stable stationary critical particle size, $D_{\text{critical}}$, has been reached. Beyond that point, the N-ECSA loss for platinum is no longer controlled by particle coarsening, but rather by carbon corrosion, particle detachment, and dissolution/Pt loss into the electrolyte.

For PtCu$_3$ and PtCo$_3$ nanoparticle catalysts, the overall nominal change in the values of N-ECSA is nearly negligible. This observation is in agreement with TEM results from Figures 5 and 6, which shows a comparable mean particle size before and after voltage cycling. But the evolution of the N-ECSA curves of the Pt alloys shows important differences to that of pure platinum. Both Pt alloys show an increase in N-ECSA during the first 1000 cycles (up to 4000 voltage cycles) and afterward a steady decrease. During the first 1000 voltage cycles, we observed a slight increase in the N-ECSA, which could be related to 1) a slight initial dissolution of copper and cobalt atoms (see Table 1, columns 8–9) from the particle surface associated with an increase in the surface roughness of the particles and 2) particle surface carbon poison removal due to the synthesis. These processes would be in line with the mechanisms for the lower $I_{\text{sp hace}}$ discussed above. On the basis of these experimental observations, we conclude that a quasi-stable, critical particle size ($D_{\text{critical}}$) must have already existed at the beginning of the lifetime test or has been quickly attained during the initial phase of the voltage cycling test. It is worth noting that again beyond around 4000 voltage cycles in Figure 7, the rate for the ECSA loss of the Pt alloys approaches that of pure Pt. This may suggest a physically similar ECSA loss mechanism, for instance, based on support corrosion. According to this scenario, an Ostwald-type ECSA loss mechanism would now no longer be dominant, whereas the N-ECSA loss is now largely controlled by carbon corrosion, particle detachment, and dissolution/Pt loss into the electrolyte.

We summarize our results in the lifetime regime by highlighting that Pt and Pt alloy nanoparticle catalysts appear to arrive at a voltage-dependent critical quasi-stable diameter, $D_{\text{critical}}$, of 3–4 nm after around 4000 voltage cycles. Beyond that, ECSA losses are largely induced by carbon corrosion, particle detachment, and dissolution/Pt loss into the electrolyte.

**N-ECSA trends in the start-up stability regime:** During cycling in the start-up regime, the carbon corrosion and metal dissolution are the dominant mechanisms.$^{14,18}$ A much more drastic decrease in the N-ECSA was observed for all catalysts compared with that in the lifetime regime. The N-ECSA reduced by 69, 52, and 38% for Pt, PtCu$_3$, and PtCo$_3$, respectively (see Table 3, column 7), correlate well with the changes in the mean particle size (see Table 1, column 5). But again, looking at the actual run of the N-ECSA loss in Figure 7, significant differences between Pt and Pt alloys are obvious. At the beginning, a steady decrease is observed for Pt, and after around 1000 voltage cycles, the loss curve slows down. The two ranges—the initial steady decrease and the following slow down—are very similar to the N-ECSA run for the lifetime stability test. However, $D_{\text{critical}}$ is reached earlier and is larger due to the higher upper turning potential of 1.5 V vs. RHE. When $D_{\text{critical}}$ has been reached in the first 1000 voltage cycles, the N-ECSA loss is no longer controlled by the particle growth, but rather by the carbon corrosion, particle detachment, and dissolution/Pt loss into the electrolyte, in which the slope of the N-ECSA loss curve is steeper than that in the lifetime regime.

This characteristic N-ECSA loss behavior of Pt is principally observed for PtCu$_3$ and PtCo$_3$. More rapid dissolution of Cu or Co and the removal of carbon poison from the particle surface during cycling up to 1.5 V vs. RHE that results in a rapid increase in surface roughness which leads to the initially fast N-ECSA increase during the first 250 voltage cycles. A rapid base metal loss is evidenced by the Cu/Co content of less than 10 at.% for the Pt alloys (see Table 1). After quick Cu/Co leaching, the runs of the N-ECSA loss curves of the Pt alloys are similar to that of pure Pt. This suggests that the nearly completely dealloyed Pt alloys now approach the Pt characteristic for ECSA and final ORR activities, as shown in column 6 of Table 2.

In summary, the early stage of the voltage cycling test of the Pt alloys in the start-up regime is dominated by two competing processes, namely, rapid metal dealloying/dissolution and particle growth, which give rise to the complex N-ECSA curves. Particle growth leads to a decrease in the N-ECSA; in contrast, strong dealloying causes an increase in the N-ECSA, owing to the enhanced surface roughness. The Pt alloy particles eventually reach a quasi-stable mean particle diameter, $D_{\text{critical}}$, and a stable Pt-rich chemical composition. At this point, the rate of N-ECSA loss slows down and approaches the behavior of pure Pt. The later stages of the degradation process in the start-up regime are dominated by carbon corrosion associated with
Conclusions

In this study, we examined the activity, stability, and degradation mechanisms of dealloyed PtCu$_3$/HSAC (high-surface area carbon) and PtCo$_3$/HSAC nanoparticle catalysts under two distinct voltage cycling protocols—highly relevant to fuel cell operation—a “lifetime” regime (10,000 voltage cycles from 0.5 to 1.0 V vs. RHE with 50 mV s$^{-1}$) and a “start-up” regime (2000 voltage cycles from 0.5 to 1.5 V vs. RHE with 50 mV s$^{-1}$). From our experimental data and correlation of the platinum electrochemically active surface area (ESCA), particle size distribution, particle bulk density, chemical composition, and oxygen reduction activity, we conclude the following:

- The PtCo$_3$ and PtCu$_3$ nanoparticle catalysts clearly demonstrate enhanced cycling durability compared to the pure Pt nanoparticle catalyst in both voltage cycling regimes.
- The dealloyed Pt alloy nanoparticle catalysts show a two to three times higher initial platinum mass-based activity, $i_{mass}$, and a three to four times higher initial platinum surface-area-specific-based activity, $i_{specific}$, than the commercial pure platinum nanoparticle catalyst.
- The dealloyed Pt alloy nanoparticle catalysts still show two times higher $i_{specific}$ at the end of the typical lifetime operating condition than pure Pt.
- All catalysts reach a voltage-dependent critical mean particle size, $D_{critical}$, at which the particle size growth rate decreases to low values. This particle coarsening is the dominant ECSA loss mechanism at the early stages of the catalyst life cycle, in particular for pure Pt. Once $D_{critical}$ is reached, the ECSA loss is mainly controlled by carbon corrosion associated with particle detachment. In the case of corrosive voltage cycling in the start-up regime, strong oxidation of carbon and dissolution of Pt become dominant mechanisms for a rapid ECSA loss and accelerate the net loss of Pt into the electrolyte.
- The ECSA loss for Pt alloys during the initial stage is a complex behavior of particle growth and base metal dissolution associated with the rearrangement of Pt surface atoms. It is manifested by an initial increase in the ECSA followed by a decrease in the ECSA at a rate very similar to that of pure Pt. The concurrent decrease in the specific activity is probably related to an increase in the Pt shell thickness by redeposition and base metal loss.
- The critical particle size ($D_{critical}$) for electrocatalysts under the present conditions was reached at around 4000 voltage cycles in the lifetime regime whereas it was reached already at around 1000 voltage cycles for the start-up regime.
- The critical particle size is strongly dependent on the maximum voltage range. In the lifetime regime, $D_{critical}$ at 3–
4 nm is smaller than $D_{\text{initial}}$ at 5–7 nm in the start-up regime.

- The chemical composition stability of the dealloyed PtCu$_3$ and PtCo$_3$ nanoparticle catalysts is voltage dependent. Under “lifetime” testing, the composition changes only slightly. In contrast, under “start-up” testing, the Pt alloys show significant compositional base metal losses. The final copper/cobalt concentration is lower than 10 at.%.

Thus, we provide an evolutionary life-cycle model of the dealloyed PtCu$_3$ and PtCo$_3$ nanoparticle fuel cell catalysts that addresses the temporal sequence of dominant degradation processes.

## Experimental Section

### Synthesis of PtCu$_3$/HSAC and PtCo$_3$/HSAC alloy nanoparticle precursor electrocatalysts

PtCu$_3$/HSAC [21.9 wt % Pt, Brunauer–Emmett–Teller (BET) surface area ≈330 m$^2$ g$^{-1}$] and PtCo$_3$/HSAC [22.1 wt % Pt, BET surface area ≈246 m$^2$ g$^{-1}$] alloy nanoparticle precursor electrocatalysts supported on HSAC were synthesized through the wet impregnation and freeze-drying route, followed by annealing in a tube furnace under reductive atmosphere.[25,26] A commercial 28.2 wt % Pt/HSAC nanoparticle electrocatalyst (TEC10E30E, Lot#108-0331, TTK, BET surface area ≈400 m$^2$ g$^{-1}$) was impregnated by using an aqueous precursor solution of Cu(NO$_3$)$_2$·2.5H$_2$O (Sigma-Aldrich, #467855) or Co(NO$_3$)$_2$·6H$_2$O (Alfa Aesar, #010694). After sonification, the well-dispersed suspension was frozen in liquid N$_2$ and subsequently freeze-dried under vacuum. The resulting dried powder was annealed at 800 °C for 7 h in a tube furnace under reductive atmosphere (4 vol % H$_2$, 96 vol % Ar, quality 5.0; Air Liquide). Before the maximum temperature had been reached, the sample was thermally pretreated at 250 °C for 2 h to decompose the precursor anion. All chemicals were used as received from the delivery companies.

### Electrochemical stability testing

The electrochemical stability testing was performed by using a rotating disk electrode (RDE) technique. A custom-made, three-compartment electrochemical glass cell was used as a three-electrode setup, with a Pt mesh as the counter electrode and a mercury–mercury sulfate electrode as the reference electrode. The working electrode was a commercial glassy carbon electrode (GC electrode) with a fixed diameter of 5 mm (PINe Instruments). The RDE experiments were conducted in a HClO$_4$ electrolyte solution (0.1 m) deaerated through bubbling with nitrogen under room temperature. To estimate the platinum electrochemically active surface area (ECSA), CV profiles were recorded between 0.06 and 1.00 V vs. RHE at a scan rate of 100 mV s$^{-1}$. The lifetime stability testing was performed with 10 000 voltage cycles from 0.5 to 1.0 V vs. RHE at a scan rate of 50 mV s$^{-1}$. During the run-time, after 500, 1000, 1500, 2000, 4000, 6000, 8000, and 10 000 voltage cycles, three complete CV profiles were measured to determine the platinum ECSA. The platinum ECSA was calculated by using the mean integral charge of the hydrogen adsorption/desorption area with a double-layer current corrected at 0.4 V vs. RHE and with 210 μC cm$^{-2}$, which assumed one hydrogen atom per one platinum atom. The start-up stability testing was realized with 2000 voltage cycles from 0.5 to 1.5 V vs. RHE at a scan rate of 50 mV s$^{-1}$. During the run-time, after 250, 500, 750, 1000, 1250, 1500, 1750, and 2000 voltage cycles, three full CV profiles were recorded to evaluate the values of the platinum ECSA. Before the measurement of the initial activity and stability testing, all catalysts were pretreated by voltammetric cycling—the so-called electrochemical dealloying. The dealloying procedure consisted of three full CV profiles (0.06–1.00 V vs. RHE at a scan rate of 100 mV s$^{-1}$), followed by 200 fast CV profiles from 0.06 to 1.00 V vs. RHE at a scan rate of 500 mV s$^{-1}$, and finally three full CV profiles (0.06–1.00 V vs. RHE at a scan rate of 100 mV s$^{-1}$) to leach off the less non-noble metal from the particle surface of the Pt alloys. This voltammetric pretreatment of the PtCu$_3$/HSAC and PtCo$_3$/HSAC alloy nanoparticle precursor electrocatalysts offered the formation of highly active bimetallic core–shell nanoparticles.[6,25,26] For comparison, a commercial untreated pure Pt/HSAC nanoparticle electrocatalyst was pretreated voltammetrically by using the same dealloying process. The resulting dealloyed catalysts after the voltammetric activation are denoted as “initial” catalysts in our paper. All electrode potentials were converted into and reported in the RHE scale.

### Experimental error

For all the reported values of each catalyst, we used data points from three independent measurements. The origin of the error is based on the limited reproducibility of the preparation of the thin catalyst film on the GC electrode. This is an intrinsic error of the RDE technique, but up to now it is the best and accepted method for the ORR activity testing in the electrochemical community.

### Linear sweep voltammetry

For the determination of the activity for the ORR, linear sweep voltammetry (LSV) measurements were conducted before and after the electrochemical stability testing procedure by using the RDE technique. The intrinsic kinetic current at 0.9 V vs. RHE was corrected with the mass transport diffusion limiting current between 0.2 and 0.5 V vs. RHE. All LSV experiments were performed by using a rotating speed of 1600 rpm and a scan rate of 5 mV s$^{-1}$ in the oxygenated HClO$_4$ electrolyte (0.1 m) and under oxygen atmosphere at room temperature by sweeping the potential from 0.06 V vs. RHE anodically to the open circuit potential (around 1.1 V vs. RHE). All reported activities were established at 0.9 V vs. RHE and compared with each other.
XRD measurements

The structural characterization of PtCu$_3$/HSAC, PtCo$_3$/HSAC, and Pt/HSAC nanoparticle precursor electrocatalysts was performed by using a D8 ADVANCE X-ray Diffractometer from Bruker AXS equipped with a position-sensitive LynxEye detector (PSD) and a CuK$_\alpha$ source by setting the voltage to 40 kV and the current to 40 mA. The XRD profiles for each catalyst were recorded by using the following scan parameters: $2\theta$ range from 15 to 80°, with a step size of 0.01°; holding time of 7 s step$^{-1}$; variable divergence slit of 4 mm; PSD iris anticattering slit setting of 13; sample rotation of 15 rpm.

TEM measurements

The morphology and the particle size distribution of the Pt alloys and pure platinum nanoparticle catalysts before and after electrochemical testing was investigated by using an FEI Tecnai G$^2$ 20 S-TWIN transmission electron microscope equipped with a GATAN MS794 P charge-coupled device camera. The microscope was operated by using an accelerating voltage of 200 kV. For the sample preparation, the catalyst powder was suspended in a solution of 2-propanol and water. The suspension was pipetted onto a Cu or Au grid with the holey carbon film and subsequently dried in air. The analysis of the TEM images was performed by using the analySIS FIVE software (SIS, Soft Imaging Systems, Olym- pus) to determine the particle size distribution (by counting more than 400 particles) for PtCu$_3$/HSAC, PtCo$_3$/HSAC, and Pt/HSAC nanoparticle precursor electrocatalysts before and after electrochemical stability testing.

Energy dispersive X-ray spectroscopy measurements

The chemical composition of Pt alloy nanoparticle precursor cata-
ysts before and after electrochemical testing was determined by using a high-resolution Hitachi S-4000 scanning electron microscope equipped with a cold field emitter and an energy dispersive X-ray spectroscopy (EDS). The EDS was operated at an accelerating voltage of 20 kV, a beam current of 0.4 nA, and a working distance of 2 mm. The sample was prepared on a carbon tab (PLANCO). The EDS scans for each sample were analyzed and averaged on a large range of different sample positions.

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