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COMMUNICATIONS

Degradation of Carbon-Supported Pt Bimetallic Nanoparticles by Surface Segregation

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In addition to their activity, the long-term stability of nanoparticle (NP) catalysts is of major importance for their large-scale implementation. Accordingly, the persistence of electrocatalysts in low-temperature fuel cells plays a decisive role in their success as future energy conversion systems. However, the highly positive cathodic potentials, the acidic environment of the membrane electrolyte, and extensive load-cycle changes during mobile applications are challenging even for Pt, the catalyst material of choice in polymer electrolyte membrane (PEM) fuel cells.[1]

Alloying Pt with other transition metals has already been proven to be beneficial for the activity of the oxygen reduction reaction (ORR).[2−5] Furthermore, the stability of Pt bimetallic or multimetallic NPs is often suggested to be superior to that of plain Pt NPs.[6] While it has been shown that the amount of dissolution of the non-noble component is enhanced under potential cycling relative to potential hold conditions,[7] it is generally assumed that after the non-noble component has been leached from the surface, the remaining core−shell structure is stabilized against further degradation processes.[8] Moreover, it has even been suggested that alloying can prevent particle agglomeration under certain conditions.[9,10] However, the segregation of atoms to the surface of particles under reactive conditions, which is crucial for other catalytic systems,[11−14] has not been studied to date. In this communication, we present data on the degradation of a Pt bimetallic NP catalyst indicating that continuous surface segregation even at room temperature is detrimental to the stability of the composition of these types of catalysts in fuel cell applications.

The degradation of a bimetallic Pt NP catalyst was studied in alkaline solution utilizing an unleached carbon-supported PtCo catalyst. The nominal atomic ratio was 3:1 Pt/Co, and the average particle size was ~5 nm. In contrast to the case of an acid electrolyte, transition metals such as Fe, Ni, and Co are not leached from the electrode but remain stable in alkaline solution.[7] The oxidation state of the atoms on the surface thereby depends on the applied potential and can easily be determined by cyclic voltammetry as a surface-sensitive technique. Thus, cyclic voltammograms (CVs) recorded in alkaline solution can provide semiquantitative information on the composition of the outermost atomic layer of the electrode material (Figure 1) and can be applied to detect changes due to surface segregation induced by an electrochemical treatment (Figure 2).

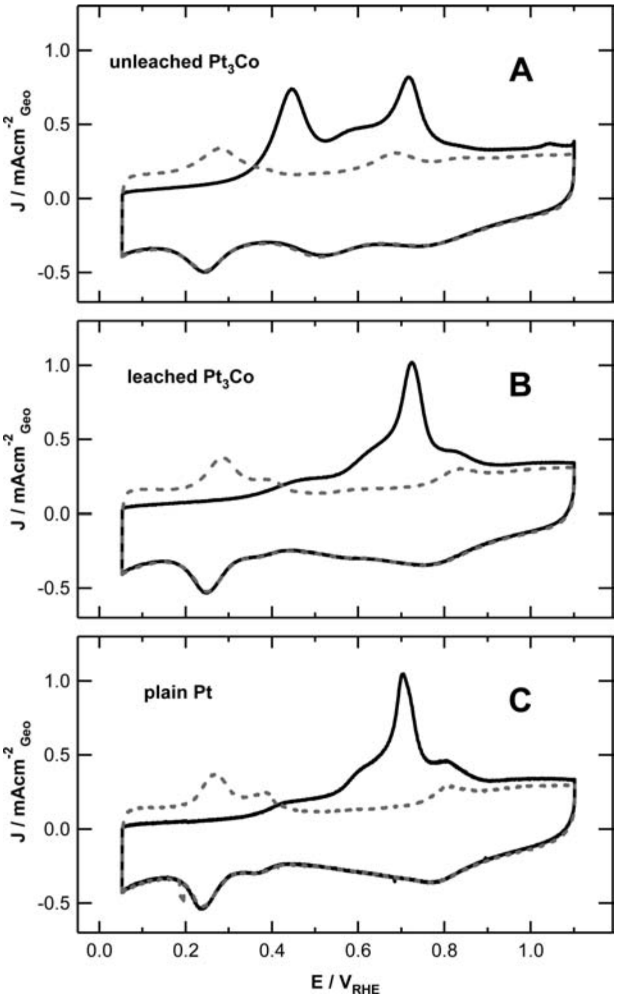

Figure 1. CVs in Ar-purged 0.1 M KOH electrolyte recorded at a scan rate of 50 mV s^{-1} at room temperature (gray dashed curves) for (A) an unleached Pt_3Co catalyst, (B) a leached Pt_3Co catalyst, and (C) a plain Pt catalyst for comparison. Black solid lines are CO-stripping curves for the same catalysts.

As demonstrated in Figure 1, the CVs of (A) unleached Pt_3Co and (B) acid-leached Pt_3Co samples provide the first evidence of their different surface composition. Typical features for Pt electrodes, underpotentionally deposited hydrogen (H_{upd}) in the potential region of 0.05 V_{RHE} and 0.4 V_{RHE}, and adsorption/desorption of oxygenated species above 0.7 V_{RHE} are slightly reduced for the unleached Pt_3Co. Instead, a well-defined current peak couple emerges at ~0.7 and 0.5 V_{RHE} in the positive- and negative-going scans, respectively. On the basis of the Pourbaix diagram of Co, this peak couple can be attributed to the change in the oxidation state of Co surface atoms from 2+ to 3+.[15] In contrast, the Co features do not appear in the CV of the leached Pt_3Co, which is virtually identical to that of plain Pt (Figure 1C). Further confirmation of the different surface composition can be obtained from the oxidation behavior of a preadsorbed CO monolayer in Figure 1 [so-called CO stripping (solid black lines)]. Again the leached Pt_3Co and plain Pt catalysts behave very similarly, with CO oxidation starting at ~0.3 V_{RHE} and a broad shoulder that evolves into a peak at ~0.7 V_{RHE}. In the CO stripping curve of the unleached Pt_3Co, however, a second peak at 0.45 V_{RHE} occurs, while the intensity of the peak at 0.7 V_{RHE} diminishes. This can be attributed to the

10.1021/ja9074216 CCC: $40.75

oxidation of adsorbed CO on Pt in the vicinity of oxidized Co surface atoms, which occurs at lower potentials than on a plain Pt surface as a result of a bimetallic promotion effect.

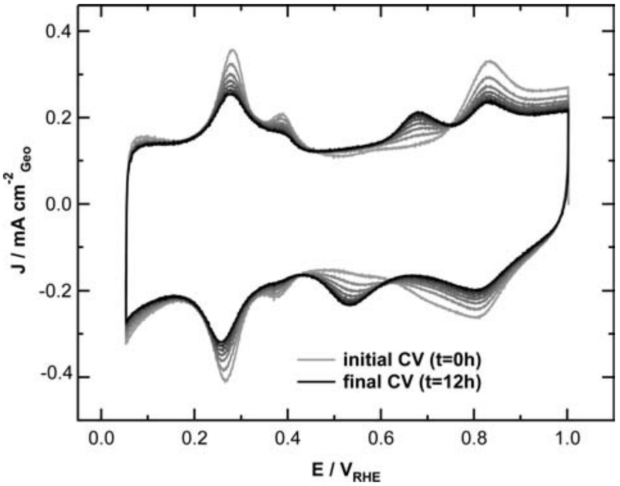

Figure 2. CV series (50 mV s^{-1} scan rate at room temperature) testing the stability of a leached Pt_3Co catalyst in Ar-purged 0.1 M KOH electrolyte. The gradual segregation of Co atoms to the surface due to potential cycling is demonstrated by displaying one CV recorded every 2 h between the initial CV (brightest gray solid curve) and the final CV after 12 h (dark solid curve).

Since different surface compositions of the nanoparticle catalysts can be distinguished unambiguously by cyclic voltammetry in alkaline electrolyte, changes upon electrochemical treatment also can now be probed in situ. In previous work, the long-term deterioration of the performance has been claimed to be negligible after an initial leaching of the surface alloying material.[6] A different picture evolves, however, from studying a leached Pt_3Co catalyst by overnight potential cycling (50 mV s^{-1} scan rate between 0.05 and 1.0 V$_{RHE}$), as shown in Figure 2. The initial CV resembles that of a plain Pt surface, as described in Figure 1. The increasing Co features in the CVs recorded every 2 h thereafter clearly indicate the gradual accumulation of Co surface atoms on the NPs. Additionally, the CO stripping curves before and after the experiment (not shown) also change in a manner consistent with Figure 1. Because of alternating formation and reduction of an oxide layer during the potential treatment, the surface composition and the chemical state of the NPs change with time. In contrast to our recent study, where Pt segregated to the surface under the influence of a reducing CO atmosphere,[16] the dynamic oxidizing conditions in this case induce quite the opposite effect of Co segregating toward the surface. It is interesting to note that milder treatments such as a constant-potential hold do not lead to such a severe effect; on the other hand, for instance, increasing the positive potential limit can dramatically accelerate the surface segregation. Moreover, repeating the experiment after subsequent leaching of the segregated Co from the surface causes segregation of additional internal Co atoms. Our investigations suggest that the surface segregation is initiated by the oxophilic character of Co, but roughening of the NP surface by subsurface oxygen might also be conducive.[14,17]

In view of these results, it is expected that surface segregation also occurs in the acidic environment of PEM fuel cells, leading to continuous dealloying of PtCo catalysts due to Co dissolution. Indeed, initial investigations of the surface segregation process induced by potential cycling in acid electrolyte suggest such a behavior. As demonstrated by means of ICP−OES, the ratio of Co to Pt atoms in the catalyst decreases with the number of potential cycles (see the Supporting Information). Additional investigations utilizing the recently developed IL-TEM methodology[18] in combination with EDX are on the way.

In summary, we have qualitatively demonstrated by electrochemical investigations in alkaline electrolyte that even at room temperature, continuous surface segregation can occur for Pt bimetallic catalysts under certain conditions. Particularly when the potential is cycled in typical fuel cell cathode application ranges, Co atoms segregate to the surface of Pt_3Co NPs. Since in the acidic environment of PEM fuel cells any non-noble alloying material at the surface immediately dissolves into the electrolyte, such catalysts are expected to degrade steadily during operation until only Pt NPs remain. As a consequence, in order to fulfill key durability requirements for PEM fuel cells, specific attention to strategies for stabilization of the catalyst structure is required.[19,20]

Acknowledgment. This work was supported by the DFG through the Emmy-Noether Project ARE852/1-1. K.J.J.M. expresses his gratitude to the Austrian FWF for an Erwin-Schrödinger Scholarship. K.H. thanks the German FCI for a Chemistry Funds Scholarship. The authors acknowledge G. K. H. Wiberg, S. J. Ashton, and T. Soini for their support and Dr. T. Tada of Tanaka Kikinzoku Kogyo for supplying the catalysts.

Supporting Information Available: Complete ref 1 and experimental details on the catalyst sample, electrochemical measurements, and catalyst treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA9074216