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PEMFC Cathode Catalyst Degradation: Model Study on the Stability and ORR Performance of Pt/C and PtCo/C Electrocatalysts

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M. Lennartz, Umicore – Heterogeneous Catalysts

Alloying of platinum with other transition metals such as Co can improve the oxygen reduction reaction (ORR) activity compared to pure Pt [1-6]. However, the alloyed Pt-based bimetallic catalysts suffer from leaching of non-noble component resulting in changes in the surface composition and a corresponding variation of the ORR performance [7-10]. Therefore, the long-term stability of carbon supported Pt-based cathode catalysts used in polymer electrolyte membrane fuel cells (PEMFCs) for automotive applications is one of most important subjects to be overcome for the commercialization of PEMFCs. Although a fuel cell performance loss is unavoidable, the degradation rate could be minimized based on a better understanding of the underlying mechanisms under relevant operating conditions. The cathode catalyst is exposed to strongly corrosive conditions, which include acidic environment, high O₂ concentration, elevated temperatures and high potentials [11,12]. Under these conditions, the catalyst may loose activity due to a decay of the electrochemical active surface area. This may be caused by a number of different processes such as sintering or migration of the nanoparticles on the carbon support, dissolution of Pt, and corrosion of the carbon support, besides the leaching of the non-noble metal [12]. Depending on the application, the requirements for the fuel cell lifetime vary significantly, ranging from 5000 h for cars to 20000 h for buses and 40000 h of continuous operation in stationary applications [12]. Although the lifetime targets for automobiles are much lower, the cathode catalyst should operate under extremely harsh conditions, such as dynamic cycling under multiple start-up/shut-down cycles [12-15].

Pt-based catalyst – Dissolution of the non-noble metal at cathode operation conditions

The stability of bimetallic Pt electrocatalysts, alloyed with non-noble metal such as Co, is an important issue, which affects the long-term performance of the catalyst. In particular, cathode catalysts which are operating at high potentials where Co leaching could appear. Therefore, the stability of the carbon-supported Pt₃Co (from TKK) catalyst at potentials relevant to cathode operation ($E > 0.5 V_{RHE}$) was studied and compared with that of a Pt/C catalyst (20 wt. % from E-Tek) as reference. For the evaluation of the potential dependence of the Co dissolution, the potential was cycled (10 cycles at 10 mV s⁻¹) in the supporting electrolyte (0.5 M H₂SO₄) from 0.06 up to 0.5, 0.85 and 1.16 V_{RHE}, respectively.

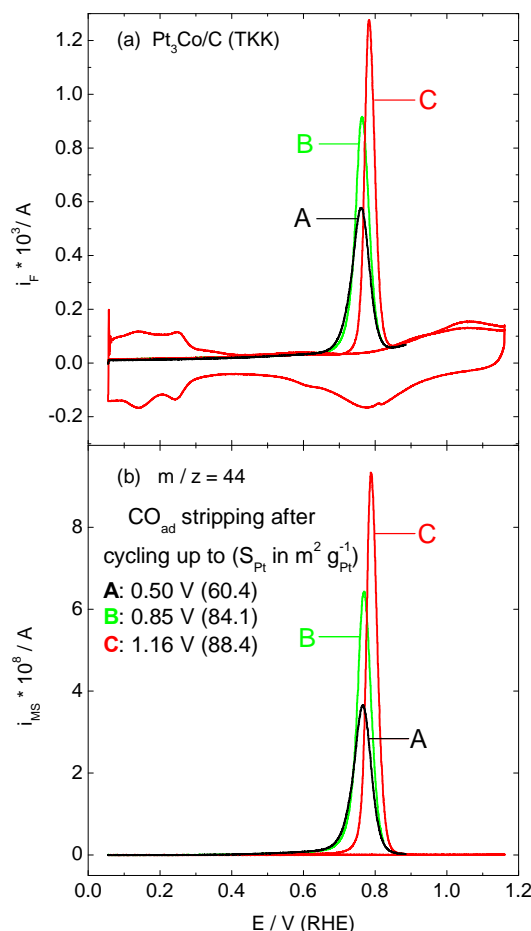


Figure 1: Faradaic (a) and mass spectrometric (b) currents during pre-adsorbed CO_{ad} monolayer strippings on $\text{Pt}_3\text{Co/C}$ catalyst in 0.5 M H_2SO_4 electrolyte after potential cycling with increasing the upper limit. RT; Pt loading: $70 \mu\text{g cm}^{-2}$, Potential scan rate 10 mV s^{-1} , electrolyte flow rate $20 \mu\text{l s}^{-1}$.

After each upper potential increment, the active Pt surface area was characterized by pre-adsorbed CO_{ad} monolayer oxidation (CO_{ad} stripping), using a Differential Electrochemical Mass Spectrometry (DEMS) set-up, following simultaneously both the Faradaic current and the mass spectrometric current of CO_2 formation ($m/z = 44$) [16,17]. Subsequently, a potential cycle was recorded on the CO -free electrode for comparison. The results clearly showed that the active Pt surface area on the $\text{Pt}_3\text{Co/C}$ catalyst increases when the upper potential is increased to $E > 0.5 \text{ V}_{\text{RHE}}$ (Fig. 1), which can be attributed to the partial dissolution of the non-noble metal from the catalyst surface at high potentials (relevant to cathode operation), resulting in a Pt enrichment with time. In contrast, the active Pt surface on the Pt/C catalyst remained constant after two consecutive CO_{ad} strippings.

Cathode catalyst stability – Accelerated Degradation Test

The resulting change in surface composition, which is especially important for bimetallic catalysts containing a non-noble component, was probed in the ORR activity/selectivity after potential cycling at high scan rate (accelerated degradation test, ADT).

Accelerated degradation testing, as a catalyst aging method for model studies in an electrochemical half-cell, is an attractive alternative for reducing time and costs of the experiment due to the increase in sample throughput, and provides a basis for understanding the origin and mechanism of the fuel cell performance losses. In contrast to real PEMFCs degradation tests, which require prolonged testing periods, ADT tests are relatively fast. In addition, PEMFCs degradation tests are often affected by experimental problems related to catalyst utilization, water management and undefined mass transport conditions.

Catalyst stability and ORR performance as a function of catalyst loading and degradation

In the present study, we have tested the influence of the Pt-loading (70 and 10 μg_{Pt} per geometric surface area) on the relative loss of the active Pt surface area (S_{Pt}) and the ORR activity/selectivity. These issues were investigated on Pt (50 wt. %), heat-treated Pt (50 wt. %) and Pt_3Co carbon supported catalysts. All catalysts were supplied by Umicore AG (Germany). Simulating a dynamic cycling process, the loss of the S_{Pt} (determined by integration of the H-adsorption current after double-layer correction) and the ORR characteristics were investigated by Rotating Ring Disk Electrode (RRDE) measurements.

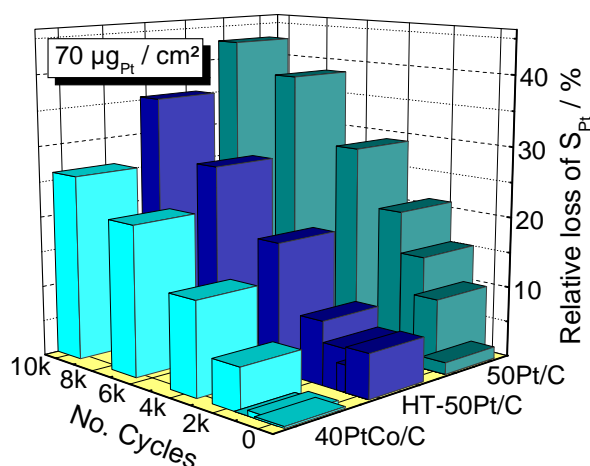


Figure 2: Relative loss of the active Pt surface area as a function of (i) catalyst and (ii) the number of cycles at high potentials ($0.5 \leftrightarrow 1.1 \text{ V}_{\text{RHE}}$). Pt loading: $70 \mu\text{g cm}^{-2}$.

ADT treatment consisted of cycling the electrode potential between 0.5 and 1.1 V_{RHE} at 55 °C. After a certain number of cycles, S_{Pt} and the corresponding ORR performance were determined. The mean particle size and particle size distribution for each catalyst were determined before and after the ADT measurements of each specific number of cycles by Transmission Electron Microscopy (TEM) measurements performed at the Institute of Material Science, Technische Universität Darmstadt.

The loss of electrochemical surface area is proportional to the amount of catalyst deposited (or catalyst film thickness), thus the lower the Pt content the higher is the relative loss and vice versa (data not shown). For different catalyst film thicknesses (i.e., Pt loading), the $\text{Pt}_3\text{Co}/\text{C}$ sample always showed less surface area loss than the Pt/C samples. Figure 2

shows the relative S_{Pt} loss for the three catalysts investigated with a Pt loading of $70 \mu\text{g}_{Pt} \text{ cm}^{-2}$.

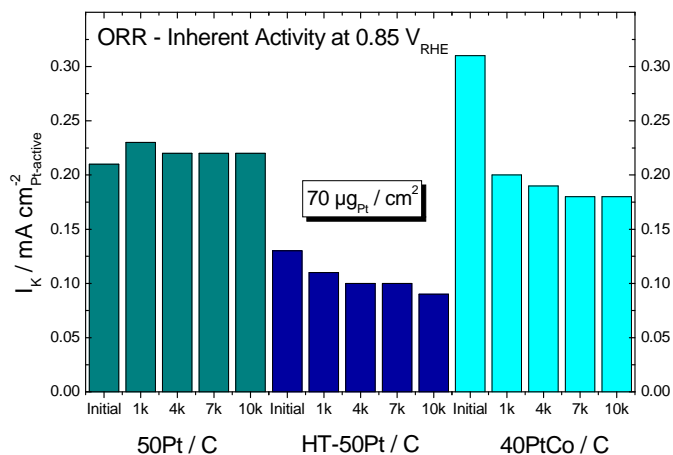


Figure 3: Active Pt surface area normalized ORR kinetic currents at $0.85 V_{RHE}$ as a function of the catalyst after accelerated degradation test (E cycling: $0.5 \leftrightarrow 1.1 V_{RHE}$). Potential scan rate: 5 mV s^{-1} . Pt loading: $70 \mu\text{g}_{Pt} \text{ cm}^{-2}$. Temperature: 55°C . Rotation rate: 1600 rpm.

At high Pt loading, the active Pt surface area normalized ORR kinetic currents showed that the decrease of the S_{Pt} causes negligible changes in the inherent ORR activity (Fig. 3) and selectivity for all tested catalysts. For the low loading Pt catalyst, the Pt particle growth (migration / coalescence; dissolution / agglomeration) results in a significant loss of the electrochemical surface area, accompanied by a reduction of the inherent ORR activity (data not shown) and a significant increases of the hydrogen peroxide production (Fig. 4).

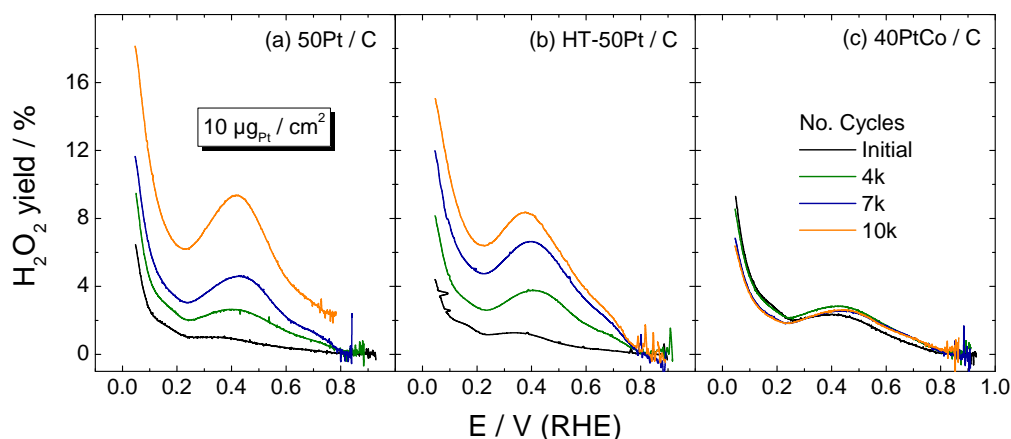


Figure 4: Hydrogen peroxide yields as a function of the applied potential on 50 wt. % Pt/C (a); heat-treated 50 wt. % Pt/C (b) and 40 wt. % Pt in PtCo/C (c) catalysts, after accelerated degradation test. Pt loading: $10 \mu\text{g}$ per cm^2 . Temperature: 55°C . Rotation rate: 1600 rpm. Potential scan rate: 5 mV s^{-1} .

Here, the long-term degradation of the catalysts layer induces an inhomogeneous Pt distribution. We suggest that this agglomeration increases the H₂O₂ production due to a lower probability of its further reduction to water over Pt-free areas even at potentials relevant for fuel cell cathode operation. The Pt₃Co/C catalyst did not show any significant changes in the H₂O₂ yield at these potentials, although the active surface area decreases considerably as well. Overall, the bimetallic Pt₃Co/C catalyst showed a better long-term stability and less change in the ORR performance than the Pt/C catalysts.

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