Activity–stability relationships of ordered and disordered alloy phases of Pt$_3$Co electrocatalysts for the oxygen reduction reaction (ORR)

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Abstract

We report on synthesis–structure–activity–stability relationships of Pt$_3$Co nanoparticle electrocatalysts for the oxygen reduction reaction (ORR). We have synthesized Pt$_3$Co alloy electrocatalysts using liquid impregnation techniques followed by reductive annealing at high and low temperatures. We have performed detailed structural X-ray diffraction (XRD)-based structural characterization (symmetry, lattice parameters and composition) of individual Pt–Co alloy phases before and, importantly, after electrochemical rotating disk electrode (RDE) measurements. This enables us to directly evaluate the corrosion stability of various Pt–Co alloy phases under typical fuel cell cathode conditions.

Pt$_3$Co prepared at low annealing temperatures (600 °C) resulted in multiple phases including (i) a disordered face-centered cubic (fcc) Pt$_{95}$Co$_5$ phase and (ii) an ordered face-centered tetragonal (L10) Pt$_{50}$Co$_{50}$ phase; high temperature annealing (950 °C) resulted in a single ordered primitive cubic (L12) Pt$_3$Co phase. The ordered alloy phases in both catalysts were not stable under electrochemical treatment: The ordered face-centered tetragonal (fct) phase showed corrosion and dissolution, while the ordered primitive cubic (L12) Pt$_3$Co phase transformed into a disordered structure. The ordered primitive cubic structure exhibited higher resistance to sintering.

Low annealing temperatures resulted in higher Pt surface-area specific activities for ORR. Kinetic Tafel analysis confirmed a general shift in the formation potential of oxygenated surface species, such as Pt–OH, for both alloy catalysts. Reduced OH coverage alone proved insufficient to account for the observed activity trends of the two alloy catalysts.

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1. Introduction

Pt–Co binary alloys for use as fuel cell cathode electrocatalysts have been studied from the mid/end 1980s [1–6] and are currently one of the most widely studied candidates to replace pure Pt cathode fuel cell electrocatalysts [7–20]. Unlike earlier studies, recent studies are entirely focused on Pt–Co materials for use in Polymer Electrolyte Membrane fuel cells (PEM-FCs). Some studies correlated orbital vacancies and electronic structure [13,17] of Pt–Co alloys with their electrochemical activity; other recent studies focused on relations between synthesis parameters [19,21], segregation phenomena [15,22,23], and electrochemical activity.

When it comes to the structural analysis of Pt–Co alloys, most studies considered X-ray diffraction profiles after synthesis, that is, before the electrocatalytic testing. For the Pt$_{50}$Co$_{50}$ (= PtCo) stoichiometry, ordered face-centered tetragonal (fct) single alloy phases were mainly observed [13,16,19,20], while for Pt$_3$Co$_{25}$ (henceforth referred to as Pt$_3$Co) stoichiometries, disordered face-centered cubic (fcc) single phases were typically reported [12,14,15,17]. Super lattice reflections [12] or peak shoulders [21] – indications of multiple phases – remained largely unaddressed. In virtually all studies, no structural characterization of the electrocatalyst was provided after the electrochemical activity testing, which hampered stability evaluations of individual phases.

In this paper, we address the issue of phase uniformity of a Pt$_3$Co bimetallic alloy and investigate the occurrence of multiple alloy phases as a function of synthesis conditions. We also report structural characterization of the Pt$_3$Co electrocatalyst after electrochemical testing and correlate activity...
characteristics of individual phases with their stability under electrochemical conditions. In particular, we were able to compare the corrosion stability and their resistance to sintering of a L12 primitive cubic Pt3Cu structure [24], an ordered fct PtCo, as well as of Pt1–xCo, disordered fcc phases.

2. Experimental

2.1. Catalyst synthesis

Platinum–Cobalt binary electrocatalysts (overall molar stoichiometry Pt:Co 75:25) were synthesized by adding appropriate amounts of solid Co precursor (Co(NO3)2·6H2O, Sigma–Aldrich #239267) to weighted amounts of powder electrocatalysts consisting of about 30 wt.% platinum nanoparticles supported on a high surface area carbon. Water was added to the supported catalyst powder and the mixture was ultrasonicated to form a thick slurry (Branson Sonifier 150). The mixture was subsequently frozen in liquid nitrogen, and then freeze-dried in vacuum (50 mTorr) overnight at room temperature. The resulting fine black powders were annealed to a maximum temperature of 600°C (low temperature, “low-T”) and 950°C (high temperature, “high-T”) for 7 h under 4% hydrogen atmosphere (Ar balance) and slowly cooled down at about 3 K/min to room temperature (non quenching conditions [21]). The final Pt weight loading of the 75:25 alloys was about 27 wt.%.

2.2. Electrode preparation

The preparation of rotating disk powder catalyst electrodes followed procedures published earlier [25–27]. Prior to electrode preparation, a 5 mm diameter glassy carbon rotating disk electrode (RDE) was polished to a mirror finish using 5.0 µm and 0.05 µm alumina suspension (Buehler Inc.). A catalyst ink was prepared by mixing the catalyst powder in 20 ml of an aqueous solution (18.2 MΩ Millipore) containing 5 wt.% Nafion® solution (Sigma, #274704). A 10 µl aliquot was dispensed onto the rotating disk electrode resulting in a Pt loading of about 14 µg Pt/cm² geometric surface area. The ink was then dried for 10 min in air.

2.3. Electrochemical measurement

The electrochemical cell was a custom-made, three-compartment cell. The working electrode was a commercial glassy carbon rotating disk electrode of 5 mm fixed diameter (Pine Instruments, AFE2M050GC). The reference electrode was a Luggin–Haber capillary to minimize uncompensated resistance (the distance to the working electrode was about 5 mm). All electrode potentials were subsequently converted into the reversible hydrogen electrode (RHE) scale. For this purpose, the zero point of the RHE scale under the chosen conditions was determined via H2 oxidation/reduction measurements at a hydrogen partial pressure of 1 atm. All potentials reported here refer to the RHE scale. The counter electrode was a piece of platinum gauze to ensure large surface area. A commercial rotator from pine instrument was used to conduct the rotating disk experiment. The electrolyte was 0.1 M HClO4, prepared by diluting 70% redistilled HClO4 (Sigma #311421) with de-ionized water (18.2 MΩ, Millipore Gradient system). The disk potential was controlled with a potentiostat, BiStat (Princeton Applied Research, Ametek). All measurements were conducted at room temperature. At the beginning of electrochemical measurements, electrocatalysts were immersed into the electrolyte under potential control and held at 0.06 V/RHE until the measurements commenced.

Cyclic voltammetric (CV) measurements were conducted in deaerated electrolyte, under N2 atmosphere. The electrocatalyst were first pretreated using 200 CV scans between 0.06 V and 1.2 V at a scan rate of 1000 mV/s. Thereafter, the potential was scanned at 100 mV/s from 0.06 V to 1.2 V and back to 0.06 V. The electrochemical platinum surface area (Pt-ESA) of the catalyst was determined from the mean integral charge of the hydrogen adsorption and desorption areas after double-layer correction, using 196 µC cm²Pt as the conversion factor.

Linear sweep voltammetry (LSV) measurements were conducted by sweeping the potential from 0.06 V anodically to the open circuit potential (around 1.0 V) at the scan rate of 5 mV/s. The currents measured were corrected for mass-transport interference. Mass and specific activities were established at 900 mV/RHE, at room temperature.

The electrochemical behavior (CV and LSV) of the Pt–Co catalysts was compared to a 28.2 wt.% platinum electrocatalyst supported on a high surface area support that was obtained from Tanaka Kikinzoku Corporation.

2.4. Laboratory-source X-ray diffraction (XRD)

The electrocatalysts were structurally characterized before electrochemical testing using a laboratory X-ray source. Laboratory-source XRD was conducted using a Siemens D5000 (θ/2θ) Diffractometer (Bragg Brentano configuration) equipped with a Braun (Garching Germany) Position Sensitive Detector (PSD) with an angular range of 8°. The Cu Kα source was operating at a potential of 35 kV and a current of 30 mA. 2θ diffraction angles ranged from 20° to 70°, using step scans of 0.02°/step and a holding time of 10–30 s per step. Advanced X-ray Solution (X-ray commander, Bruker AXS) software was used to control the diffractometer from a desktop computer.

The XRD sample holder was a custom made 3 cm × 3 cm plexi-glass with a 1 cm width × 2 cm length × 1 mm depth well in the center of the sample holder to hold the powder sample. The catalyst powder was poured into the well and carefully flattened to a smooth surface with a piece of glass slide so that the surface is flushed with the surface of the plexi-glass.

Composition estimation of disordered (substitutional solid solution) Pt–Co alloy phases with face-centered cubic symmetry was based on the linear relationship between molar Co content and size of resulting lattice parameters (Vegard’s Law) [28]. The lattice parameters for pure Pt and pure Co used were 3.923 Å and 3.419 Å, respectively. All X-ray diffraction patterns were analyzed using Jade 7.5 (MDI): peak profiles of individual
reflections were obtained by a non-linear least-square fit of the $K_{\alpha_2}$ and background corrected data. Instrumental broadening was determined using an alumina standard under identical measurement conditions. Particle sizes were estimated using observed line broadening in combination with the Scherrer equation at the most intense fundamental reflections [29,30].

2.5. Synchrotron-based X-ray diffraction

Tested Pt–Co/Nafion® catalyst films were structurally characterized using Synchrotron-based X-ray diffraction. RDE films were transferred onto circular double-sided adhesive carbon paper tape (Ted Pella Inc., CA) using a pressure decal transfer. The RDE film was first pressed onto the adhesive tape and then the shaft was gently removed leaving the catalyst film on the pad. Some catalyst films were directly casted on graphitic carbon paper tape, electrochemically tested for oxygen reduction reaction (ORR), and subsequently characterized. Diffraction measurements were conducted at the Stanford Synchrotron Radiation Laboratory (SSRL), Menlo Park, CA at beamline 2–1. Dry sample films were mounted vertically onto the goniometer head and measured in transmission ($\theta–2\theta$ configuration). Detector collimation was 2 mrad Soller slits. A scintillation detector collected data between $2\theta$ of 20° and 100° using radiation of

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![Graph](https://example.com/graph.png)

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**Fig. 1.** (a) X-ray diffraction profile of the Pt$_3$Co electrocatalyst annealed at 600 °C (low-T catalyst). Dark peaks indicate the face-centered cubic (fcc) Pt$_{95}$Co$_5$ phase, lighter peaks stem from the fundamental reflections of a face-centered tetragonal (fct) phase. Stick pattern indicate peak positions of fcc pure Pt and fct Pt$_{50}$Co$_{50}$ (=PtCo). (b) X-ray diffraction profile of the Pt$_3$Co electrocatalyst annealed at 950 °C (high-T catalyst). A single primitive cubic Pt$_3$Co face formed under these conditions. Stick pattern indicate peak positions of the primitive cubic Pt$_3$Co phase.
λ = 1.5505 Å. The raw data was converted into Cu Kα wavelength of λ = 1.5418 Å to enable comparison with lab data.

3. Results and discussion

3.1. Phase structure of the Pt3Co catalyst prior to electrochemical testing

Pt3Co catalysts were synthesized at a higher (referred to as the ‘high-T’ alloy) and a lower temperature (referred to as the ‘low-T’ alloy) to study the effect of synthesis conditions on alloy phase uniformity, structure, activity, and stability.

Fig. 1a shows the X-ray diffraction pattern of the Pt–Co material annealed at 600°C and 7 h (low-T conditions) before electrochemical testing. Two distinct alloy phases – one ordered and one disordered – formed under these conditions: one phase was identified as a disordered face-centered cubic phase with an estimated molar composition of Pt95Co5. Its mean crystallite size was estimated at 3.5 nm. The second alloy phase that formed under the low-T conditions was consistent with a tabulated[31] ordered face-centered tetragonal Pt50Co50 alloy phase. The (0 0 1) (partially overlapping with a broad carbon peak) and the (1 0 0) superlattice reflections at 25° and 34° respectively, confirm the formation of this ordered phase. The crystallite size was estimated at 6 nm. Structural details of the observed alloy phases are tabulated in Table 1. The ordered tetragonal phase follows the generic L10 (CuAu) structure [24] consisting of alternating (0 0 1) planes of only Co or Pt atoms; depending on the choice of the unit cell, it is often described as a primitive tetragonal lattice with P4/mmm symmetry [31].

The occurrence of an ordered fct phase is consistent with previous reports on Pt–Co alloy synthesis at comparable conditions [19,21]; however, many recent studies focused on an overall molar Pt:Co ratio of 1:1. Our findings suggest that both Co and Pt atoms gradually alloy with their complementary pure metal, forming particles of Pt-rich and Co-rich phases. The absence of un-annealed pure Co crystallites suggests that the ordered fct Pt50Co50 phase is kinetically favored over other disordered Co-rich phases; according to the Pt–Co phase diagram [32], the ordered fct phase is also the thermodynamically favored structure at 600°C. Pt is initially present as small particles of about 2–3 nm. Co appears either to be initially present in large conglomerates or to sintering very rapidly during the reductive annealing process explaining the large Pt50Co50 particles and small Pt95Co5 particles. Given the overall molar Pt:Co ratio of 3:1, we expect the Pt95Co5 fcc and the Pt50Co50 fct phases to be present in a ratio of about 2:1, which is consistent with the peak areas in Fig. 1a.

In contrast to Fig. 1a, high temperature (950°C/7 h) annealing resulted in a single primitive cubic Pt3Co alloy phase (Fig. 1b) with a crystallite size of about 5 nm. The formation of a single phase material at high annealing temperatures is generally expected, yet the observed primitive cubic L12 (Cu3Au type) structure has rarely been reported before [33].

Our structural data is consistent with earlier work yet is more detailed in the analysis of the alloy phases present: ordering of
Fig. 2. First three cyclic voltammetric profiles of the low-T Pt3Co catalyst before electrochemical conditioning compared to the (pretreated) Pt standard cyclic voltammogram. Conditions: 0.1 M HClO4, 100 mV/s, room temperature, deaerated conditions.

Pt–Co lattices was generally observed at annealing temperatures of about 600 °C [18] and above [18,19]. Sustained high temperature annealing (>800 °C) resulted in a single ordered phase, while lower annealing temperatures produced multiple alloy phases [18,20]. Because multiple phases are generally undesired, they were typically not analyzed, nor discussed.

3.2. Cyclic voltammetry, linear sweep voltammetry, and tafel behavior

Electrocatalysts pretreatment included a cycling protocol of 200 fast voltammetric cycles, which constitutes a much more severe conditioning procedure than used in earlier reports [13–16,23,27,34,35]. The procedure was chosen to ensure a time-stable and reproducible CV response of the catalyst surface.

Fig. 2 illustrates the very first 3 slow (100 mV/s) potential cycles of the low-T Pt3Co in N2 saturated solution, prior to the fast conditioning cycles, in comparison to CV profile by the Pt/C standard material. The catalyst was immersed in the electrolyte at 0.06 V/RHE and the potential was held at that potential for about one minute. A small amount of adsorbed hydrogen is oxidized on the first anodic scan (CV1). No significant formation of surface Pt–OH could be observed on these initial scans. On the second and third potential cycle, a hydrogen adsorption region starts to emerge, yet remains small compared to the Pt/C catalysts or compared to the hydrogen adsorption region after the 200 fast conditioning cycles (see Fig. 3). From Fig. 2, we infer that a significant amount of Co atoms are initially present in the top catalyst layer and causes a reduction of the observed hydrogen adsorption charge. The initial 3 CVs of the high-T Pt3Co look qualitative very similar to Fig. 2, yet the hydrogen adsorption charge is smaller than that for the low-T material.

As seen in Fig. 3, the hydrogen adsorption charge and the electrochemical Pt surface-area increase for both catalysts after fast potential cycling. The high-T material, however, exhibits a smaller Pt surface-area compared to the low-T catalyst. Assuming spherical particles, the reduced Pt surface-area of the high-T material is consistent with its increased particle size caused by the high temperature treatment (see Table 1). This finding suggests that the amount of Co atoms in the top layer after pretreatment is negligible, in particular in combination with the severe CV pretreatment.

The water activation and Pt–OH formation peaks are now clearly discernible in Fig. 3 for the two Pt–Co catalysts. For both catalysts the onset of the water activation and Pt–OH formation on alloy surfaces is shifted to higher potentials [15,17], with the peak potential, $E_{Pt-OH}$, following the order $E_{Pt-OH} (high-T Pt3Co) > E_{Pt-OH} (low-T Pt3Co) > E_{Pt-OH} (Pt)$ (see inset of Fig. 3). A previously suggested kinetic model for the ORR [15,36] links the delayed formation of Pt–OH surface layers to a larger number of available surface sites for adsorption of molecular oxygen considering a $(1 - \theta_{OH})^x$ term in the rate equation. A shift in $E_{Pt-OH}$ has therefore been suspected to correlate with increases in the ORR activity.

Fig. 4a reports the linear sweep voltammetry of the low-T Pt3Co catalyst in comparison to the Pt/C standard catalyst. The shift in potential in the $I$–$E$ graph of the bimetallic suggests a significant improvement in the oxygen reduction activity. The Pt–Co catalyst reaches its diffusion limited regime already at at 0.75 V/RHE. The LSV of the high-T Pt3Co catalyst looks very similar with slightly reduced diffusion limited current. Fig. 4b shows the corresponding Tafel plot using the Pt surface area specific current densities (units $\mu$A/cm² Pt). This metric represents the intrinsic electrochemical activity of an electrocatalyst comparable to a turn-over-number. At high potentials (>0.9 V/RHE) in Fig. 4b, the Tafel slopes of the two Pt–Co bimetaals as well as pure Pt are about ~60 mV/decade. This unusual Tafel slope has been explained by a kinetic model that assumed Temkin adsorption conditions of oxygen on a Pt–OH covered catalyst surface [15,36–38]. The model also predicted that catalysts with a delayed Pt–OH coverage should show deviations from the
−60 mV/decade at higher potentials. In Figs. 3 and 4b, the Pt3Co alloy catalysts confirm this model prediction accurately: The high-T material with the largest delay in Pt–OH formation shows deviation from the initial slope already at about 0.9 V/RHE, followed by the low-T alloy and pure Pt.

An absolute activity comparison of the Pt–Co catalyst with pure Pt is shown in Fig. 4c. The absolute specific activity of Pt (about 190 μA/cm² Pt) reported here coincides very well with earlier RDE studies [26] (190–200 μA/cm² Pt). The low-T Pt3Co catalyst offers a 2.5-fold activity enhancement (Fig. 4c), while the high-T material shows a 1.5x enhancement compared to pure Pt. This activity gains are in line with previously reported specific activity enhancements of Pt–Co catalysts [8,10,14,15,19,26]: Xiong and Manthiram [19] reported a 2.5-fold enhancement at 0.85 V/RHE for a PtCo catalyst prepared at 650 C, and attributed the enhancement to an ordered fct PtCo phase. It is conceivable that the observed activity enhancement of our low-T catalyst is similarly caused by the ordered fct phase identified in Fig. 1a. Obradovic et al. [17,39] reported a three-fold enhancement in specific activity at 0.9 V/RHE, and Paulus et al. showed that a Pt3Co catalyst annealed at high temperatures was about twice as active as pure Pt [14,15]. Teliska et al. [17] report a somewhat higher pure Pt activity of about 400 μA/cm² Pt (Fig. 10 in [17]), and report 800 μA/cm² Pt for a Pt3Co catalyst annealed at high temperatures, again about a factor of two.

As discussed earlier, trends in the peak potential of Pt–OH formation, E_{Pt–OH}, correlate quite well with observed Tafel slopes. Fig. 4 shows, however, that these trends alone are insufficient predictors for trends in the actual ORR activity of Pt alloys. Instead, for the present Pt3Co catalysts, activation barriers of the adsorption/reduction of O2 appear to dominate the trends in the overall activities.

3.3. Catalyst phase structure and stability after electrochemical testing

We have developed a method to transfer our RDE-tested electrocatalysts into a synchrotron-based X-ray diffractometer. The high photon flux and brightness of a synchrotron source, enabled
Fig. 5. (a) XRD background profile of a graphitic carbon paper/tape used to support the tested alloy catalyst during characterization (profile a); XRD pattern of the low-T Pt₃Co alloy catalyst after electrochemical conditioning and testing for ORR (profile b). (b) Blow-up of profile b of (a) near the region of the most intense fundamental reflections. Stick pattern indicate peak positions of a fcc Pt phase and the ordered fct Pt₅₀Co₅₀ phase. Light grey peaks indicate a disordered Pt₉₅Co₅ phase, dark grey peaks show presence of a fct Pt₅₀Co₅₀ phase.

us to probe the alloy phase structure after electrochemical testing with an acceptable signal/noise ratio.

Fig. 5a (profile b) gives an overview of the diffraction profile of the low-T electrocatalysts after RDE testing. Prior to XRD measurement, tested catalyst films were transferred onto flat supporting carbon paper. Diffraction profile ‘a’ in Fig. 5a corresponds to the catalyst-free support for comparison. The carbon paper causes sharp asymmetric graphite reflections that partially overlap with the alloy peaks. Fig. 5b is a blow up of the alloy relevant diffraction angles. Peak profile analysis revealed reflections predominantly from a Pt₉₅Co₅ alloy phase (particle size about 4 nm, see Table 1) with a minor contribution from reflections of the ordered fct phase (particle size about 8 nm). These results evidence the stability of the Pt₉₅Co₅ phase, but suggest dissolution, corrosion and/or perhaps preferred Co leaching of the ordered fct Pt₅₀Co₅₀ phase. Particle size analysis suggests that both phases have sintered under electrochemical conditions. We can now refine our picture about the relation between activity, structure and stability: The favorable ORR activity for the low-T material appears to arise in part from the Pt₉₅Co₅ alloy phase, but is more likely also a result of the residual amounts of the corroded Pt₅₀Co₅₀ alloy phase. Preferred base metal leaching
and associated surface roughening have in fact been described as a mechanism toward enhanced alloy activity in the literature [40]. If this conjecture is correct, it would raise questions about the long-term durability of the partially corroded Pt₅₀Co₅₀ phase and of the low-T catalyst as a whole.

Fig. 6a (profile 'b') and 6b depict the diffraction profile of the high-T Pt₃Co alloy. The initial single ordered primitive cubic Pt₃Co phase has transformed into a single disordered fcc Pt–Co alloy phase of approximate composition Pt:Co 75:25 and particle size of about 5 nm. This suggest that the ordered primitive cubic phase of the high temperature catalyst is not a stable atomic arrangement under electrochemical conditions, yet loses only negligible amounts of Co and appears more resistant to particle sintering compared to the low temperature alloy phases. Diffusion of Co and Pt within the lattice under electrochemical control may cause the transition from an ordered to a disordered material.

4. Conclusions

We have presented a detailed analysis of the alloy phase structure, the electrochemical ORR activity, and the alloy phase
stability of Pt₃Co nanoparticle electrocatalysts. The alloy phases of the catalyst materials have been characterized before and after electrochemical testing, which enabled us to directly assess the stability of individual alloy phases under electrochemical conditions.

Low temperature annealing resulted in multiple ordered (fct, L1₂) and disordered (fcc) Pt–Co phases, while high temperature annealing formed a single ordered primitive cubic (L1₂) Pt–Co phase. Pt-rich alloy phases generally showed a smaller mean particle size compared to Co-rich phases, and we associated this with the chosen synthesis method where small Pt particle gradually alloy with adjacent larger Co domains. Severe conditioning likely removed most, if not all, Co from the top layers of both catalysts.

It was concluded from a detailed XRD analysis performed after testing that the ordered alloy phases in both the high-T and low-T catalyst are not stable under electrochemical treatment. The ordered fct phase showed corrosion and dissolution, while the ordered primitive cubic phase transformed into a disordered structure. In addition, the ordered primitive cubic L₁₂ phase showed better resistance to electrochemical sintering compared to both phases of the low-T catalyst.

The low-T Pt₃Co catalyst exhibited clear advantages in its intrinsic Pt surface-area activity compared to the high-T catalyst, counter to the observed relative shifts in Pt–OH formation. Observed shifts in the Pt–OH formation, however, correlated well with changes in the Tafel slopes. Previous studies have shown that a reduced OH surface coverage may cause general activity enhancements over pure Pt; in the present study, however, trends in the OH coverage alone proved insufficient to accurately predict activity trends among Pt₃Co catalysts. Activity advantages associated with the Pt₃₀Co₅₀ phase compared to the Pt₃Co phase may account for the observed activity trends.

Our study underscores the complexity and trade-offs in regards of synthesis, catalyst activity, and catalyst degradation. More research is needed to better pinpoint prevailing degradation mechanism of individual alloy phases.

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