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Activity–stability relationships of ordered and disordered alloy phases of Pt_3Co electrocatalysts for the oxygen reduction reaction (ORR)

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Abstract

We report on synthesis–structure–activity–stability relationships of Pt_3Co nanoparticle electrocatalysts for the oxygen reduction reaction (ORR). We have synthesized Pt_3Co 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_3Co 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 ($L1_0$) $Pt_{50}Co_{50}$ phase; high temperature annealing (950 C) resulted in a single ordered primitive cubic ($L1_2$) Pt_3Co 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 ($L1_2$) Pt_3Co 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.

Keywords: Metal alloys; Fuel cell catalysis; Oxygen reduction reaction; Synthesis–property relationship; Kinetic measurements

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 (PEMFCs). 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 $Pt_{75}Co_{25}$ (henceforth referred to as Pt_3Co) 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_3Co bimetallic alloy and investigate the occurrence of multiple alloy phases as a function of synthesis conditions. We also report structural characterization of the Pt_3Co electrocatalyst after electrochemical testing and correlate activity

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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 L1$_2$ primitive cubic Pt_3Cu structure [24], an ordered fct PtCo, as well as of $Pt_{1-x}Co_x$ 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 ($Co(NO_3)_2{\cdot}6H_2O$, 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/cm^2 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 mercury–mercury sulphate electrode (EG&G, G0093) held by 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 H_2 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 $HClO_4$, prepared by diluting 70% redistilled $HClO_4$ (Sigma #311421) with deionized 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 N_2 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 $\mu C\ cm^2_{Pt}$ 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 ($\theta/2\theta$) 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