# Electroactivity of high performance unsupported Pt–Ru nanoparticles in the presence of hydrogen and carbon monoxide[☆]

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## ABSTRACT

The electrochemical activity of high performance unsupported (1:1) Pt–Ru electrocatalyst in the presence of hydrogen and carbon monoxide has been studied using the thin-film rotating disk electrode (RDE) technique. The kinetic parameters of these reactions were determined in $H_2$- and CO-saturated 0.5 M $H_2SO_4$ solutions by means of cyclic voltammetry, including CO stripping, and RDE voltammetry. Pt–Ru/Nafion inks were prepared in one step with different Nafion mass fractions, allowing determining the ionomer influence in electrocatalytic response and obtaining the kinetic current density in absence of mass-transfer effects, being 41 and 12 mA cm$^2$ (geometrical area), for $H_2$ and CO oxidation, respectively. These values correspond to mass activities of 1.37 and 0.40 A $mg_{Pt}^1$ and to specific activities of 1.52 and 0.44 mA $cm_{Pt}^2$. The Tafel analysis confirmed that hydrogen oxidation was a two-electron reversible reaction, while CO oxidation exhibited an irreversible behavior with a charge-transfer coefficient of 0.42. The kinetic results for CO oxidation are in agreement with the bifunctional theory, in which the reaction between Pt–CO and Ru–OH is the rate-determining step. The exchange current density for hydrogen reaction was 0.28 mA cm$^2$ (active surface area), thus showing similar kinetics to those found for carbon-supported Pt and Pt–Ru electrocatalyst nanoparticles.

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## 1. Introduction

Hydrogen is the most interesting fuel for polymer electrolyte fuels cells (PEFCs). It reacts in the anode to produce two electrons:

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

Platinum is the most active electrocatalyst for the hydrogen oxidation reaction (HOR). The main problem is the Pt poisoning by CO when $H_2$ is obtained from reforming [1].

The most extended solution to facilitate the CO removal from the Pt active sites consists in the use of Pt alloys such as Pt–Ru [2–4]. The increased CO-tolerance with respect to pure Pt has been explained by the bifunctional mechanism [2], according to which the RuOH species formed by water discharging, participate in the reaction. The CO molecules chemisorbed on the Pt sites are easier oxidized by the vicinal Ru–OH species, as expressed by reaction (2):

$$Pt–CO + Ru–OH \rightarrow Pt + Ru + CO_2 + H^+ + e^- \tag{2}$$

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However, the overall CO oxidation process involves two electrons:

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \qquad (3)$$

The difference between pure Pt and Pt–Ru electrocatalysts is that electronic dissociation of water on Pt–Ru occurs at a lower potential than that of platinum. A second contribution has been also pointed out, concerning an electronic effect produced by alloyed Ru on CO-poisoned Pt atoms, resulting in the weakening of the Pt–CO bond which facilitates its oxidation to $CO_2$ [3,4].

There are a large number of publications dedicated to the structural and electrochemical analyses of nanoparticulated Pt and Pt–Ru electrocatalysts [5–29]. The study of kinetic parameters of the HOR is generally conducted through the preparation of two-step catalyst ink deposition [14], which involves the direct deposition of aqueous electrocatalyst slurry on the electrode surface and subsequent coating of the dry layer with appropriate amount of ionomer solution, generally Nafion. The prepared electrode is then used as working electrode in the electrochemical cell where rotating disk electrode (RDE) voltammetry is conducted. This methodology allows obtaining the kinetic current density of HOR [6,7,10,19], the permeability of hydrogen molecule in the ionomer structure, and the critical thickness of the ionomer film below which mass transport through Nafion is not rate controlling, this limit being of 0.2–0.5 μm [7,10,14]. However, recent publications focused on the analysis of supported Pt and Pt–Ru electrocatalysts [27,29] have shown that the use of inks prepared in one step is a valid method, which approaches the membrane-electrode assembly (MEA) preparation for technical electrodes [30–37], to obtain kinetic data of the HOR. We assume that the one-step deposition ink technique coupled to RDE voltammetry can also be used to determine the kinetic parameters of CO oxidation on the Pt–Ru electrocatalysts. CO stripping voltammetry is a well-known technique to study the CO-tolerance [2,17], but it is based in the oxidation of a CO monolayer on the catalyst surface. However, in the RDE configuration, CO is continuously supplied from bulk solution to the electrode surface, as in the case of CO-contaminated hydrogen oxidation on a fuel cell anode catalyst, resulting in a more realistic approach. Besides, kinetic data of CO oxidation, such as the corresponding kinetic current density and the effect of Nafion content of the thin-film on the mass-transport properties, can be determined. On the other hand, the effect of ionomer mass fraction in the performance of PEFC has been widely discussed [38,39]. In our recent works dedicated to carbon-supported Pt and Pt–Ru electrocatalyst, optimal Nafion mass fractions in the catalyst inks which led to maximum electrochemically active surface area (ECSA) values were in the range 30–40% [27,29], in agreement with performance measurements using MEAs [31–34] and similar to the 25–33% found for the MEA composition of direct methanol fuel cells (DMFCs) using carbon-supported Pt–Ru as anodic electrocatalyst [36,37]. However, for our nanoparticulated Pt–Ru electrocatalyst it is expected a shift of this ionomer compositional range due to the different morphology between the supported and the unsupported electrocatalyst. In fact, the absence of ionomer

has led in at least one case, to the best performance of unsupported Pt–Ru in DMFCs, due probably to the proton conducting hydrous RuOx species in the catalyst [40].

In the present work, the electrochemical performance of a novel high performance (HP) commercial unsupported Pt–Ru electrocatalyst has been analyzed using the thin-film RDE technique with electrodes prepared by one-step deposition of electrocatalyst-Nafion inks on inert glassy carbon electrodes (GCs), evaluating the influence of the ionomer content in the film. The ECSA values of the different prepared inks and the CO oxidation potential of the electrocatalyst have been measured by CO stripping voltammetry in 0.5 M $H_2SO_4$. The $H_2$ and CO oxidation reactions were analyzed in order to determine their kinetic parameters working in the $H_2$-saturated and in the CO-saturated solutions, respectively.

## 2. Experimental

### 2.1. Materials and reagents

High performance (HP) unsupported HP 1:1 Pt–Ru alloy was purchased from E-Tek. The ionomer was a 5% solution of Nafion perfluorinated ion-exchange resin in a mixture of aliphatic low molecular weight alcohols (isopropanol:n-propanol in weight ratio 55:45) and water (15–25 wt.% in the mixture), supplied by Aldrich. Glassy carbon disk electrodes 3 mm in diameter were provided by Metrohm. Analytical grade 96% $H_2SO_4$ from Merck was used to prepare 0.5 M $H_2SO_4$ as the electrolyte for the electrochemical experiments. All solutions were prepared with high-purity water obtained with a Millipore Milli-Q system (resistivity > 18 MΩ cm). $H_2$ and Ar gases were Linde 5.0 (purity ≥ 99.999%), while CO gas was Linde 3.0 (purity ≥ 99.9%).

### 2.2. Electrochemical experiments

Aqueous inks of electrocatalyst concentration in the range 2.5–10 mg ml$^{-1}$ were prepared by sonicating for 45 min different amounts of Pt–Ru electrocatalyst, Millipore Milli-Q water, and the ionomer solution. The Nafion composition in the inks varied between 10 and 80%. Stirred volumes of each ink in the range 1.5–2.5 μl were deposited by means of a digital micropipette, Labopette Variabel from Hirschmann or Witopet from Witeg, on the surface of the GC disk electrode, carefully weighting such volumes with an AG 245 Mettler-Toledo analytical balance (accuracy of ±0.01 mg). The recently prepared electrodes were dried for 24 h in a clean desiccator at room temperature. Afterwards, the working electrode was ready to use in the Ecochemie Autolab RDE. The final Pt loads on the GC surface were in the range 25–30 μg cm$^{-2}$. Prior to the ink deposition, the GC tip was consecutively polished with aluminum oxide pastes of 0.3 and 0.05 μm (Buehler Micropolish II deagglomerated α-alumina and γ-alumina, respectively) on a Buehler PSA-backed White Felt polishing cloth until achieving a mirror finish, being rinsed with Millipore Milli-Q water in ultrasonic bath between the polishing steps.