



# Kinetic study of CO desorption from PtRu/C PEM fuel cell anodes: Temperature dependence and associated microstructural transformations

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## ARTICLE INFO

### Article history:

Received 28 January 2009

Revised 1 May 2009

Accepted 1 May 2009

Available online 29 May 2009

### Keywords:

CO tolerance

Catalysis

Platinum

Ruthenium

Desorption

Isotope exchange

Temperature dependence

PEM fuel cell

## ABSTRACT

The temperature dependence of the CO desorption process on a carbon-supported platinum–ruthenium alloy catalyst has been investigated using isotopic exchange experiments. The kinetics of CO desorption on PtRu/C catalyst have been studied as a function of temperature and flow rate. Desorption rate constants have been determined for a temperature range between 25 °C and 150 °C. All PtRu/C results have been compared with those obtained for the Pt/C catalyst under similar experimental conditions. Quite different desorption rate constants have been observed. The variation in apparent Arrhenius parameters (frequency factor  $A$  and activation energy  $E_a$ ) for PtRu/C and Pt/C could possibly explain their different degrees of poisoning by CO in proton exchange membrane fuel cells (PEMFCs) and the underlying adsorption/desorption processes. The effect of temperature treatment on the PtRu/C catalyst properties has also been investigated with respect to CO desorption kinetics and to the associated microstructural transformations.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are expected to achieve commercial application in a wide variety of areas including the automotive industry, because of having the inherent properties of high current density, being lightweight, operating at low temperatures, and containing no corrosive materials [1]. Platinum is currently the catalyst of choice for both the anode and cathode processes due to the high current densities obtained [2]. A possible source of hydrogen for the anode reaction is the reformation of hydrocarbons, by partial oxidation or steam reforming. This results in hydrogen containing, amongst other impurities, significant levels of CO. CO levels can be reduced down to ppm levels (by pressure swing adsorption or via the water gas shift reaction) but as little as 20 ppm CO is known to poison the platinum catalyst by blocking sites for hydrogen adsorption [3]. Platinum–ruthenium catalysts have attracted considerable interest in recent years as highly active and more CO tolerant anode catalysts in PEMFCs, both for the electrooxidation of CO-contaminated H<sub>2</sub>-rich fuel gas and for the electrooxidation of methanol in direct methanol fuel cells [4,5]. Three possible effects have been identified to ex-

plain increased CO tolerance of platinum–ruthenium catalyst compared to pure platinum: the bifunctional mechanism, the ligand effect mechanism and the “detoxification” mechanism. The bifunctional mechanism suggests that the overpotential for CO oxidation to CO<sub>2</sub> is reduced by the presence of ruthenium through water dissociation at ruthenium, which is more facile than on Pt. This mechanism has been demonstrated extensively in the literature both theoretically [6–9] and experimentally [10–18]. Alternatively, the ligand effect mechanism suggests that combining platinum with ruthenium leads to a reduction in the Pt–CO bond strength, leading to a higher rate of CO oxidation at the surface. This mechanism has also been demonstrated both theoretically [6–9,19–22] and experimentally [15,22] but has been shown to have a less significant effect on the rate of CO oxidation than the bifunctional mechanism [24,25]. Similarly to the ligand effect mechanism, the “detoxification” mechanism involves a weakening of the Pt–CO bond strength due to the presence of ruthenium. However, in this case, this bond strength weakening is proposed to lead to a lower equilibrium CO coverage leaving more free sites for hydrogen oxidation [26,27].

Therefore, the issue of CO tolerance should be considered from the point of view of both the electrochemical CO oxidation and the equilibrium attained through the adsorption/desorption process, since the kinetically predominant of these two processes will govern the surface coverage of the CO species at steady-state. While the CO oxidation mechanisms, both bifunctional and ligand effect mechanisms, have been extensively investigated in the literature

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[6–23], only a few studies have been performed on the CO adsorption/desorption process [26,27]. The fundamental study of the CO adsorption/desorption process is, however, essential to better understand the CO poisoning behaviour on PEM fuel cell anodes.

In this study, CO isotope exchange experiments have been carried out to follow the CO desorption kinetics from supported PtRu to help understand the role of Ru in providing increased tolerance to CO in PEM fuel cells. CO isotope exchange experiments taking place at either the liquid–solid interface, in the electrochemical environment, or the gas–solid interface, were used in previous studies to help elucidate the mechanisms involved in CO tolerance at PEM fuel cell anodes. However, the actual environment within the fuel cell lies somewhere between these two conditions, as the supported catalyst is exposed to a humidified gas stream. CO exchange at the liquid–solid interface under the electrochemical environment was mainly studied using *in situ* infrared detection in an external reflection configuration [28–30]. Weaver et al. reported the infrared spectra for CO adsorbed at ordered Pt(111) aqueous interfaces for various  $^{12}\text{CO}/^{13}\text{CO}$  mixtures [28,29]. Korzeniowski et al. probed qualitative structural features of the adlayers formed by CO at step sites and on terrace planes of Pt(335) and Pt(111) in the aqueous electrochemical environment [30]. They observed a site-dependent vibrational coupling of CO on the well-defined step and terrace sites on monocrystalline Pt. Lately, they studied the isothermal desorption of CO from a polycrystalline Pt electrode using an infrared spectroelectrochemical cell capable of operating at temperatures between ambient and 70 °C and found solvent influences upon CO adlayer stability [31,32]. CO exchange at the gas–solid interface was studied by monitoring the changes in the adlayers on Pt(111) by infrared spectroscopy and by following the desorption of  $^{13}\text{CO}$  from carbon-supported Pt and PtRu catalysts by mass spectrometry [33–35]. Andersen et al. used infrared spectroscopy to investigate the CO desorption rate dependence on CO partial pressure over a Pt(111) single crystal [33]. Davies et al. performed similar experiments over supported commercial Pt and PtRu fuel cell catalyst [34,35]. They found that the rates of desorption for equivalent partial pressures are many orders of magnitude higher for the single crystal surface than for the nanoparticulate catalysts. This was attributed to the facets of the nanoparticles being considerably smaller than the unit cell obtained on Pt(111), hereby quantising the coverages obtained on these facets at coverages at which the CO is more strongly bound. The CO exchange rates measured at room temperature and under dry conditions for a CO concentration of 100 ppm in argon or hydrogen on both Pt/C and PtRu/C are, however, considered as high compared to the equivalent electrochemical CO oxidation rate measured under the operating conditions of the fuel cell, suggesting that the adsorption/desorption process may have a significant influence with regard to the poisoning effect of CO on the PEM fuel cell anode [34,35]. It has, however, to be noted that these investigations were not performed under electrochemical conditions. Recently Behm et al. investigated on a Pt electrode the room temperature desorption and exchange of CO in a saturated CO adlayer at potentials far below the onset of oxidation by isotope CO exchange experiments using a novel set-up for the simultaneous *in situ* IR spectroscopic and online mass spectrometric detection of adsorbed species under controlled mass transport conditions [36]. They reported that adsorbed CO exchanges rapidly under these experimental conditions. This fast exchange was attributed to a decrease in the desorption barrier, caused by a combination of two effects: a slight increase in adsorbed CO coverage upon increasing the CO pressure and a pronounced decay of the CO adsorption energy with coverage, due to lateral repulsive  $\text{CO}_{\text{adsorbed}}-\text{CO}_{\text{adsorbed}}$  interactions.

The aim of the present work is to investigate for a real industrial catalyst the effect of increasing temperature on the CO exchange

rate over a range that is of relevance to the operating PEM fuel cell. Currently, the research community is engaged in the development of new membranes for the PEM fuel cell capable of operating at higher temperatures than the current industry standard, the Nafion membrane, which is limited by its need for humidification by water to less than 100 °C. Therefore, a temperature range between 25 °C and 150 °C has been used for the measurements. The temperature-dependent kinetics of CO desorption from Pt/C catalyst have been recently investigated by Davies et al. [27] and the measured rates of desorption are high compared with the rates of oxidation measured from polarisation curves obtained with high concentrations of CO in argon [13]. However, the CO exchange rate on the PtRu/C catalyst at temperatures above room temperature has not previously been investigated. So there is a need to determine whether the CO oxidation mechanism or the CO adsorption/desorption process has a greater influence on the steady-state CO coverage and consequently the CO tolerance of the PtRu catalyst.

In this study, data have been obtained for a temperature range of 25 to 150 °C for a current industrial PtRu/C system. The kinetics of CO desorption on PtRu/C catalyst were investigated as a function of the temperature and the flow rate. Desorption rate constants were deduced from the CO desorption kinetics data and the results were compared with those previously published for Pt/C under similar conditions [27]. The apparent Arrhenius parameters, both the frequency factor  $A$  and the activation energy  $E_a$ , were also deduced from the temperature-dependent kinetic study of CO desorption for both PtRu/C and Pt/C and results were compared. Finally, the effect of temperature treatment on the properties of the PtRu/C catalyst was investigated studying the kinetics of CO desorption on an “already tested” sample, and associated microstructural transformations were characterised by X-ray diffraction and microscopy techniques such as Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

## 2. Material and methods

### 2.1. Material

Commercial PtRu catalysts from Electrochem Inc. supported on Vulcan carbon XC72 and bound to Toray carbon paper diffusion layers with a Teflon binder were used for the CO desorption kinetics experiments. The catalyst loading was 1 mg/cm<sup>2</sup> Pt (20 wt%) and 0.5 mg/cm<sup>2</sup> Ru (10 wt%). Contrary to the Nafion binder, which enables experiments only below 100 °C for water management reasons, a Teflon binder ensures the ability to perform experiments at higher temperatures (up to 150 °C in this study). All gases used (argon, hydrogen, 1000 ppm  $^{12}\text{CO}$  in argon mixture and 1%  $^{13}\text{CO}$  in argon mixture) were obtained from Linde and were of the highest commercially available purity. For the 1%  $^{13}\text{CO}$  in argon gas mixture, the CO has been enriched to the ratio 99%  $^{13}\text{CO}/1\% ^{12}\text{CO}$ .

### 2.2. Methods

#### 2.2.1. CO desorption kinetics

CO desorption kinetics experiments have been performed using a flow cell based on a conflate design in a flow mode. Circular catalyst samples of diameter 3.6 cm were used in the flow cell. A gas dosing system allowed a fast interchange between various gases. The intrinsic delay of the system when switching gases has been demonstrated as having negligible effects on the experiments for the conditions used and there is no significant increase in the cell pressure due to the resistance of the cell/sample, when the flow rate is varied [27]. The gas was extracted from the cell via a quartz tube sniffer and both its content and composition were measured in “real time” using a quadrupole mass spectrometer. The flow cell

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