



# CO desorption kinetics at concentrations and temperatures relevant to PEM fuel cells operating with reformat gas and PtRu/C anodes

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## ABSTRACT

The kinetics of the CO desorption process have been determined using isotopic exchange experiments at concentrations and temperatures relevant to PEM fuel cells operating with reformat gas and commercial carbon supported platinum–ruthenium alloy anodes. The CO desorption kinetics have been studied as a function of CO concentration, temperature and flow rate. Desorption rate constants have been determined experimentally for a wide range of concentrations (100–500 ppm) and temperatures (25–150 °C) and have been extrapolated to one order of magnitude lower CO concentration range between 10 and 100 ppm, which is directly relevant to PEM fuel cells operating with reformat gas. The desorption rates measured for the 100–500 ppm CO concentration range appear to be significantly larger than previously published CO oxidation data, suggesting that the CO desorption process plays a more significant role in determining the equilibrium CO coverage at the fuel cell anode than the electrochemical CO oxidation process. The proposed desorption rate values at the lower 10–100 ppm CO concentration range and at relevant temperatures are believed to be of added value for the modelling of PEM fuel cells operating with reformat gas and PtRu/C anodes, since significantly different empirical values have been used up to now for the modelling of the CO desorption process. The variation of the apparent Arrhenius parameters as a function of CO concentration provides also some insight into the CO poisoning effect and the underlying adsorption/desorption processes.

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## 1. Introduction

Amongst the different types of fuel cells, proton exchange membrane fuel cells (PEMFCs) are being developed for transportation, portable and small stationary applications [1]. Platinum is currently a catalyst component or catalyst of choice for the anode and cathode processes, respectively, due to the high current densities obtained [2]. A possible source of hydrogen for the anode reaction is the reformation of hydrocarbons using partial oxidation, steam reforming or autothermal reforming. These processes produce a reformat rich in hydrogen, but containing, amongst other impurities, 1–2% of CO. Since a PEMFC cannot tolerate such high CO levels, a variety of further stages such as a combined water gas shift reaction and preferential oxidation or a pressure swing absorption can be performed to reduce the CO content to less than 100 ppm, but as little as 20 ppm CO is known to poison the platinum catalyst by blocking sites for hydrogen adsorption [3–6]. Platinum–ruthenium catalysts have attracted considerable interest in recent years as the most effective catalysts for H<sub>2</sub> oxidation in the presence of CO for low

temperature fuel cell applications [4,5,7–9]. Extensive research has focused on gaining a better understanding of the catalytic activity enhancement, in the presence of CO, of PtRu catalysts compared to Pt catalysts through electrochemical, spectroscopic and theoretical studies [3,9,10]. Three possible effects have been identified to explain increased CO tolerance of PtRu catalyst compared to pure Pt, namely, the bifunctional mechanism [11–23], the ligand effect mechanism [11–14,24–29] and the “detoxification” mechanism [30–32]. Whereas the bifunctional and ligand effect mechanisms explain the improved CO tolerance by a favored electrochemical oxidation of CO at the PtRu surface, the “detoxification” mechanism proposes, as an explanation, a lower equilibrium CO surface coverage at the PtRu surface, simply via the CO adsorption/desorption process. 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. The fundamental study of the CO adsorption/desorption process is thus essential to a better understanding of the poisoning effect of CO at the PEMFC anode.

The CO isotope exchange technique, used in this study, has already been extensively carried out to help elucidate the

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mechanisms involved in CO tolerance at PEMFC anodes. Numerous CO isotope exchange studies performed at either the liquid–solid interface, in the electrochemical environment, or the gas–solid interface, are reported in the literature [33–44]. It has however to be pointed out that the actual environment within a PEM fuel cell lies somewhere between these two conditions as the supported catalyst is exposed to a humidified gas stream. At the liquid–solid interface, the CO exchange was studied in the electrochemical environment using mass spectrometry during CO<sub>adsorbed</sub> stripping [33], in situ monitoring of the adsorption process using radioactive tracer techniques [34,35], and in situ infrared detection in an external reflection configuration [36–40]. At the gas–solid interface, the CO exchange was mainly studied in the absence of an electrochemical environment using infrared spectroscopy [41] and mass spectrometry [42,43]. The CO desorption rate dependence on CO partial pressure was investigated on a Pt(1 1 1) single crystal [41] and on supported commercial Pt and PtRu fuel cell catalysts [42,43]. A linear dependence of the CO exchange rate with the CO partial pressure was observed in the logarithmic scale ( $\ln k$  vs.  $\ln p$ ) [42,43]. This pressure dependence of the exchange rate was explained by considering a change in CO surface coverage with different CO pressures and a subsequent reduction in the CO binding energy. High pressure scanning tunnelling microscopy studies on a Pt(1 1 1) surface also displayed a pressure dependence of the coverage in good agreement with the results from the CO isotope exchange experiments. The rates of desorption were however found to be many orders of magnitude higher for the single crystal surface compared to the nanoparticulate catalyst at similar partial pressures.

The CO exchange rates on supported commercial Pt and PtRu fuel cell catalysts, measured at room temperature, under dry conditions, in the absence of a potential and for a 100 ppm CO concentration in the gas stream, are significant compared to the equivalent electrochemical CO oxidation rates measured under the operating conditions of the fuel cell [42,43]. Recently, the CO exchange rates were measured at room temperature, under dry conditions and, for the first time, in the presence of a potential, on a Pt electrode for CO concentrations ranging from 1% CO in argon to 100% CO [44]. A fast exchange of adsorbed CO compared to the extremely low adsorbed CO oxidation rate was reported at potentials far below the onset of oxidation. A decrease in the desorption barrier due to a combined 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 CO<sub>adsorbed</sub>–CO<sub>adsorbed</sub> interactions were suggested to explain this fast exchange. These various investigations suggest that the adsorption/desorption process may have a significant influence with regard to the CO poisoning effect at PEMFC anodes.

An operating temperature below 100 °C due to the water assisted conduction mechanism of the industrial Nafion membrane and hydrogen containing less than 100 ppm CO are currently used at the industrial scale for PEM fuel cells operating with reformat gas [45]. An increase of the operation temperature is however highly desired for the development of PEMFC technologies, since it would enable enhanced CO tolerance, faster reaction kinetics, easier water management, and reduced heat exchanger requirement [46]. The temperature-dependent kinetics of CO desorption from Pt/C and PtRu/C catalysts at a fixed CO concentration of 1000 ppm have been recently studied for the 25–150 °C temperature range [31,32] and the measured rates of desorption are large compared with the rates of oxidation measured from polarisation curves obtained with high concentrations of CO in argon [18]. This CO concentration is however far higher than the CO concentrations present in PEM fuel cells operating with reformat gas. There has been no previous study of

the CO exchange rate at CO concentrations relevant to PEMFCs operating with reformat gas and at temperatures higher than room temperature on PtRu/C catalyst.

The aim of the present work is to determine CO desorption rate constants over concentration and temperature ranges that are of relevance to PEM fuel cells operating with reformat gas and commercial PtRu/C anodes. The kinetics of CO desorption are investigated as a function of CO concentration, temperature and flow rate. Desorption rate constants are measured for CO concentrations ranging from 100 to 500 ppm and for a temperature range of 25–150 °C. The apparent Arrhenius parameters are determined as a function of the CO concentration and results are discussed in relation to the CO poisoning effect and the underlying adsorption/desorption processes. Finally, the desorption rate constants are extrapolated to one order of magnitude lower concentration range between 10 and 100 ppm, which is directly relevant to the proton exchange membrane fuel cells operating with reformat gas.

## 2. Material and methods

### 2.1. Material

Commercial PtRu catalysts from Electrochem Inc. supported on Vulcan carbon XC72 and bound to Toray carbon paper gas 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%). An average catalyst particle size of 4.4 nm was determined using the Debye–Scherrer broadening of X-ray diffraction data and transmission electron microscopy images [32]. 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 a temperature of 150 °C in this study). All gases used (argon, hydrogen, 1000 ppm <sup>12</sup>CO in argon mixture and 1% <sup>13</sup>CO in argon mixture) were obtained from Linde and were of the highest commercially available purity. The required 100–500 ppm CO concentration range was obtained by additional dilution of the 1000 ppm <sup>12</sup>CO in argon gas mixture. For the 1% <sup>13</sup>CO in argon gas mixture, the CO was enriched to the ratio 99% <sup>13</sup>CO/1% <sup>12</sup>CO.

### 2.2. Methods

CO desorption kinetics experiments were performed in a flow cell using circular catalyst samples of diameter 3.6 cm. A gas dosing system allowed a fast interchange between various gases. The intrinsic delay of the system when switching gases was demonstrated of having negligible effects on the experiments for the conditions used and there was no significant increase in the cell pressure due to the resistance of the cell/sample, when varying the flow rate [31]. 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 temperature was set using an oven. The experimental setup is given in Fig. 1.

The procedure for the determination of the CO desorption kinetics was described in detail in Refs. [31,32,43]. In summary, the catalyst surface was initially saturated by isotopically labelled <sup>13</sup>CO at a given temperature using a 1% <sup>13</sup>CO in argon gas mixture. The residual <sup>13</sup>CO was then removed from the flow cell using argon. Unlabelled <sup>12</sup>CO at concentrations ranging from 100 to 500 ppm in argon was allowed to flow through the cell at a given temperature and mass 29 corresponding to <sup>13</sup>CO was measured by a mass spectrometer in order to obtain the <sup>13</sup>CO desorption profile. This procedure was performed at flow rates of 90 and 120 ml/min,

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