



Temperature dependence of CO desorption kinetics at a novel Pt-on-Au/C PEM fuel cell anode

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ABSTRACT

A Pt-on-Au/C fuel cell anode catalyst has been obtained by electrochemical deposition of platinum on carbon-supported gold nanoparticles. Its composition, structure and nanoparticle size distribution have been characterised before and after the desorption experiments using microstructural techniques. The temperature dependence of the CO desorption process on this system has been investigated using isotopic exchange experiments. The CO desorption kinetics have been studied as a function of temperature and flow rate. Desorption rate constants have been measured for a temperature range between 25 and 150 °C. These desorption rate constants have been compared with the benchmarking desorption rate data obtained for the commercial Pt/C catalyst under similar experimental conditions. A comparable desorption rate constant for the Pt-on-Au/C and Pt/C systems has been obtained at 25 °C. The dependence in temperature of the desorption rate constants for the novel Pt-on-Au/C system is however much lower than that observed for the Pt/C system. This suggests that the nature of the substrate has a significant influence on the catalyst surface properties. It shows that, in surface-modified catalysts, the interactions between underlayer and overlayer materials are worthy of consideration, since they can significantly modify the intrinsic properties of the active sites. The kinetics of the CO desorption process have been discussed with regard to the CO tolerance issue at the PEM fuel cell anode.

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1. Introduction

Among 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]. The platinum catalyst is however subject to poisoning by CO for PEMFC systems operating with reformat gas [3]. Platinum–ruthenium catalysts have attracted considerable interest in recent years as highly active and more CO tolerant anode catalysts [4,5]. A mechanistic understanding at the atomic level of the fundamental physicochemical processes involved in improving CO tolerance is however still required if we are to develop a novel low cost and CO tolerant competitor to the current state-of-the-art Pt and PtRu anode catalysts. Three mechanisms have been suggested to explain improved CO tolerance of PtRu catalyst compared to pure Pt: the bifunctional mechanism [6–12], the ligand effect mechanism [11–15] and the “detoxification” mechanism [16–18]. Electronic ligand and strain effects were also proposed

in CO and CO/H₂ temperature-programmed desorption studies on bimetallic Pt/Ru(0001) surfaces [19]. Whereas the bifunctional and ligand effect mechanisms explain the improved CO tolerance by a favoured electrochemical oxidation of CO at the PtRu surface, the “detoxification” mechanism proposes a lower equilibrium CO surface coverage at the PtRu surface, simply via the CO adsorption/desorption process. Therefore, both the electrochemical CO oxidation and the equilibrium attained through the adsorption/desorption process should be considered as physicochemical processes affecting the CO tolerance, since the kinetically predominant of these two processes will govern the CO surface coverage at steady-state.

In the search for a cheaper and more CO tolerant, yet highly active, competitor to the current state-of-the-art Pt and PtRu catalysts for the hydrogen oxidation reaction, core–shell and alloy nanoparticle catalysts have been considered as promising candidates, since the physicochemical properties of core–shell and alloy systems can potentially be superior compared to their individual components. A combined Pt–M (where M is another metal) core–shell or alloy system could potentially minimise the amount of expensive Pt (while maintaining high activity) and increase the CO tolerance by stabilising Pt against CO poisoning [20–22]. Recently, density functional theory calculations have identified the Pt–Au-based systems as potential candidates for the hydrogen evo-

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lution reaction [23,24]. A high catalytic activity of the Pt–Au-based systems, even higher than that of pure Pt, has been reported for some specific catalytic reactions such as hexane conversion [25], ethylene glycol oxidation [26], methanol oxidation [27–32] and formic acid oxidation [32–35]. The increase in catalytic activity of the Pt-modified Au nanoparticles has been explained by the utilisation enhancement of Pt in these electrocatalysts and a possible enhancement effect of Au atoms [27,22,35]. The structure of the Pt–Au-based system, core–shell or alloy, as well as the relative ratios of each component have been demonstrated to affect, in most cases, the performance of the system. Thus, the deposition of Pt particles of various sizes on Au substrate has been shown to affect the level of CO oxidation [36,37]. This has been explained by the variation in Pt particle size and possibly also Pt nanoparticles–Au substrate interactions. A clear interaction between Au and Pt and its effect on catalytic reactivity has been demonstrated, since a stronger CO binding has been observed when Pt was deposited as an overlayer on a Au(111) substrate [38]. This increase in reactivity for CO on Pt has been attributed to the correlation between adsorbate binding energy changes with a shift in the position of the Pt overlayer d-band centre. Extensive studies have been also performed on the interactions of CO with other bimetallic surfaces such as PdAu [39–42].

The aim of the present work is to investigate for a novel potential PEM fuel cell anode catalyst the CO desorption process over a temperature range that is of relevance to the operating PEM fuel cell. The fundamental understanding of the CO desorption process involved in improving CO tolerance is expected to help developing novel low cost and CO tolerant PEM fuel cell anode catalysts. A temperature range between 25 and 150 °C has been used for the measurements, since the research community is currently engaged in the development of new PEMFC membranes capable of operating at higher temperatures than the current industry standard, the Nafion membrane, limited by its need for humidification by water to less than 100 °C. The kinetics of CO desorption from the benchmarking commercial Pt/C and PtRu/C catalysts have been investigated at room temperature and as a function of the temperature under dry conditions and in the absence of a potential [17–19,43,44]. 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. 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 [45]. 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. Comparing the results for CO isotope exchange experiments under the electrochemical environment with the results from the gas phase isotope exchange experiments on supported Pt catalyst [20], it was found that the presence of electrolyte and the applied potential do not cause a significant stabilisation of the adlayer against exchange. Therefore, it was suggested that, at a typical PEMFC operation temperature of 80 °C, CO_{adsorbed} desorption will be sufficiently fast in an electrochemical environment that it can contribute significantly to keep the steady-state CO_{adsorbed} coverage at tolerable levels even in contact with CO-contaminated feed gas, if the CO concentration is not too high.

All these investigations suggest that the adsorption/desorption process may have a significant influence with regard to the CO poisoning effect at PEMFC anodes. No exchange rate on PEMFC anode catalysts other than the benchmarking commercial Pt/C and PtRu/C catalysts has however been investigated. There is nevertheless a need to determine the CO desorption rate constants on novel PEMFC anode catalysts for a better understanding of the CO tolerance issue and if we are to develop novel low cost and CO tolerant

catalysts based on the fundamental understanding of the processes involved.

In this study, a Pt-on-Au/C fuel cell anode catalyst has been obtained by electrochemical deposition of platinum on carbon-supported gold nanoparticles. Its composition, structure and nanoparticle size distribution have been characterised, before and after the desorption experiments, using microstructural techniques such as X-ray diffraction, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The CO desorption kinetics have been investigated as a function of temperature and flow rate. Desorption rate constants have been deduced from the CO desorption kinetics data and have been compared with the benchmarking desorption rate data obtained for the commercial Pt/C and PtRu/C catalysts under similar experimental conditions.

2. Materials and methods

2.1. Material synthesis

Pt-on-Au catalyst nanoparticles supported on Vulcan carbon XC72 and bound to Toray carbon paper gas diffusion layers with a Teflon binder were used for the CO desorption kinetic experiments. A Teflon binder was used instead of a Nafion binder to ensure the ability to perform the experiments up to a temperature of 150 °C, the Nafion binder being limited to temperatures below 100 °C for water management reasons. The Au nanoparticles supported on Vulcan carbon XC72 powder were purchased with a loading of 20% from E-TEK. The Au nanoparticles were mixed into a 2.5:1 ethanol (96%):Teflon slurry and drop-cast onto Toray carbon paper gas diffusion layers. Pt was deposited onto the Au/C-paper system electrochemically from a Pt mesh counter electrode (99.99%) using anodic dissolution of Pt and Pt ion transfer from the Pt mesh counter electrode to the surface of the Au working electrode. Using the Au sample as the working electrode, a Pt mesh as the counter electrode, and a saturated calomel electrode as the reference electrode, the potential of the working electrode was swept at 50 mV/s during cyclic voltammetry to potentials greater than the corrosion potential for Pt (~+1.18 V vs. NHE) [46]. The potential applied to the working electrode was between –0.35 and +1.0 V vs. SCE, which, using an electrolyte with a pH ~ 0.3–0.4, ranged from ~–0.1 to +1.27 V vs. NHE. During deposition of the Pt from the counter electrode, the hydrogen evolution reaction was monitored for an increase in activity. The cycling for Pt deposition was performed during a 24 h period, leading to a maximum current, which coincides with a minimisation of the Au reduction peak. At this point, a grey discoloration of the Au surface was visible to the eye and Pt HUPD (hydrogen under potential deposition) features were apparent. Based on the Pt HUPD features, the Pt amount deposited on the Au/C nanoparticles can be estimated to a few monolayers. The electrochemical characterisation of the Pt-on-Au system using cyclic voltammetry was given in [47].

All gases used (argon, hydrogen, 1000 ppm ¹²CO in argon mixture and 1% ¹³CO in argon mixture) were obtained from Linde and were of the highest commercially available purity. For the 1% ¹³CO in argon gas mixture, the CO was enriched to the ratio 99% ¹³CO/1% ¹²CO.

2.2. Methods

2.2.1. Microstructural characterisation of the Pt-on-Au/C system Scanning electron microscopy

The morphology of the Pt-on-Au/C surface, both before and after the desorption experiments up to 150 °C, was investigated using a Zeiss Supra 50 field-emission gun scanning electron microscope.

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