

Steady State Isotopic Transient Kinetic Analysis Study of PEM Fuel Cell Anodes (SPA)

Exploratory Research Project Final Report

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Acronyms

IE	Institute for Energy
IRMM	Institute for Reference Materials and Measurements
PEMFC	Proton Exchange Membrane Fuel Cell
PSA	Pressure Swing Absorption
SeIOx	Selective Oxidation
SSITKA	Steady State Isotopic Transient Kinetic Analysis
TOF	Turnover frequency

Abstract

The hydrogen oxidation reaction at Proton Exchange Membrane Fuel Cell anodes is poisoned by part per million levels of carbon monoxide, present even after purification steps following the production of hydrogen by the reformation of hydrocarbons. Whilst platinum is the catalyst of choice for the oxidation of pure hydrogen, platinum/ruthenium alloys are shown to be more tolerant when ppm levels of CO are present. It has recently been demonstrated that there is a dynamic equilibrium between CO adsorbed on platinum or platinum/ruthenium nanoparticles and CO in the gas phase, and that this equilibrium is affected by the competitive adsorption between CO and hydrogen.

The purpose of this research to perform Steady State Isotopic Transient Kinetic Analysis (SSITKA) experiments using the isotopic exchange between ^{13}CO and ^{12}CO to investigate the competitive adsorption of hydrogen and CO on commercial Pt and PtRu catalysts.

For 1400ppm CO in hydrogen little difference was observed in the measured exchange rates for Pt and PtRu at room temperature, however there is a more significant effect observed at 100ppm CO in hydrogen, where the rates on PtRu are considerably slower than on Pt. This can be attributed to increased competition on PtRu for CO and H adsorption, leading to lower equilibrium coverage of CO on the PtRu surface.

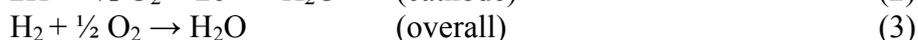
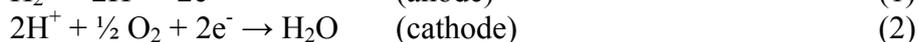
Preliminary measurements were also made regarding the temperature dependence of this process in the range relevant to the fuel cell (25-90°C).

This work was performed as a joint venture between the Institute for Energy (IE) and the Institute for Reference Materials and Measurements (IRMM), as IE have the experience in the area of PEM fuel cell catalysis whilst IRMM have the pre-existing Isotope Ratio Mass Spectrometry instrumental capabilities with the required resolution to perform measurements at these concentration levels, along with fast switching capabilities for applying the traditional SSITKA technique to this system.

1. Introduction

The Proton Exchange Membrane Fuel Cell (PEMFC) is a prospective technology for a variety of applications. PEM Fuel Cells are the most likely fuel cells to achieve use in automotive applications due to their low operating temperatures and their inherent properties of being lightweight, producing high current densities and containing no corrosive materials [1].

At the anode of the PEMFC hydrogen dissociation and subsequent oxidation to protons occurs. This electrode is generally platinum-based due to the high hydrogen oxidation currents obtained and the stability of platinum under the operating conditions of the fuel cells [2]. These protons then pass through a proton-conducting, but electrically insulating, polymer membrane to the cathode, where they react with oxygen to form water. The reactions occurring are therefore:



This process is spontaneous producing electrical energy and some heat.

If the hydrogen used within the fuel cell is obtained from clean sustainable resources (such as that produced by electrolysis using electrical energy obtained from wind or solar power) then the only product of the fuel cell is water. However, if the hydrogen feed to the anode of the PEMFC is produced from reformation of hydrocarbons by partial oxidation or steam reforming (for example in an onboard reformer for automotive applications) this will produce hydrogen containing significant levels of both carbon monoxide and carbon dioxide. A variety of further stages of purification can be performed to remove the CO (for example, Pressure Swing Absorption (PSA) or Water Gas Shift reaction followed by selective oxidation (SeOx)) but it is known that as little as ppm levels of CO in the anode feed gas can poison the hydrogen oxidation reaction on platinum by binding strongly to the platinum surface and blocking sites for hydrogen dissociation [3].

It has been demonstrated that alloying platinum with a second metal, usually ruthenium, can increase the tolerance of the anode to CO adsorption [4]. There are currently two main proposed mechanisms for this promotion:

- (i) The bi-functional effect [5]: alloying platinum with ruthenium, at an optimal ratio of 50:50 reduces the over-potential required for the oxidation of adsorbed CO to CO₂ [6-10]. This reduction in over-potential is associated with the dissociation of water being more facile on ruthenium than on platinum.
- (ii) The detoxification mechanism [11-13]: alloying platinum with ruthenium alters the chemical properties of the surface platinum due to electronic effects. This has been demonstrated to weaken the CO bond strength, and subsequent equilibrium surface coverage. (Note: It has also been suggested that this weakening of the CO bond could affect the CO oxidation rate in mechanism (i) (often described as the ligand effect), but it has previously been demonstrated that the oxygen dissociation is the predominant effect with regard to that mechanism [14,15])

It has recently been shown that there is a dynamic equilibrium between CO adsorbed on platinum or platinum/ruthenium catalysts, and CO in the gas phase, on a time-scale relevant to the behaviour of fuel cell anodes [16, 17]. Hence, in this exploratory research project we have performed Steady State Isotopic Transient Kinetic Analysis (SSITKA) experiments using the isotopic exchange between ¹³CO and ¹²CO to investigate the competitive adsorption of hydrogen and CO at concentrations relevant to PEM fuel cells.

2. Theory

2.1 SSITKA methodology (*Steady-State Isotopic Transient Kinetic Analysis*)

Steady state isotopic transient kinetic analysis (SSITKA) was mainly developed as a technique for studying surface reactions. SSITKA makes it possible to deconvolute the contributions to the turnover frequency (TOF), which at steady state for first order reactions is the product of the intrinsic rate constant (K) and surface coverage (θ)

$$\text{TOF} = K \times \theta \quad (4)$$

The turnover frequency represents the number of molecules reacting per chemisorption site per second and has the unit of s^{-1} . This measure has become a reference in fundamental studies of catalytic reactions, especially for metal catalysts.

SSITKA involves the use of isotopically labelled species to obtain information regarding surface coverage, surface residence times, site heterogeneity, activity distributions, and concentration of adsorbed reaction intermediates and identification of possible mechanisms. The technique is based upon the detection of isotopic labels in the reactor effluent species versus time following a switch (step change) in the isotopic labelling of one of the reactant species in the reactor feed. In addition to maintaining isothermal and isobaric reaction conditions, the reactant and product concentrations and flow rates remain undisturbed during the step change. Thus, in the absence of isotopic mass effects, steady-state reaction conditions are maintained under isotopic-transient operation.

Although often referred to in the literature as SSITKA, the use of isotopic tracing only requires for interpretation purposes that reactions do not change significantly during the isotopic transient period.

It must be emphasized that it is common in SSITKA theory to consider the catalyst surface to be composed of a system of interconnected pools, also termed compartments, where each pool represents a homogeneous or well-mixed sub-system within the reaction pathway. A separate pool is assumed to exist for each unique adsorbed reaction-intermediate species or type of catalytically active site.

Therefore, the simplest process is for one with only one compartment – one catalytically active site, as could be considered the adsorption-desorption process for a species A (fig.2.1).

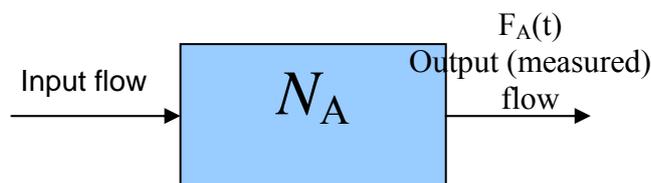


Fig.2.1. Schematic representation of an one-pool SSTKIA system

Basically, this process could be expressed as



or



where the first part shows the adsorption process and the second, desorption. τ is the average residence time for the adsorption process on N active surface species X - in this case CO molecules adsorbed on Pt or Ru surface atoms and X is the intermediate phase which for the investigated case is the CO adsorbed molecule. The reciprocal, $1/\tau$, has unit of s^{-1} and, consequently, expresses a form of turnover frequency.

For the mass balance for the intermediate product A_{ad} under stationary conditions we will have:

$$\frac{dN_X}{dt} = (\text{production rate of X} - \text{consumption rate of X}) \quad (7)$$

The SSITKA experiment consists of the measurement of the increase in the concentration and/or the waste of an isotope species by a mass spectrometer after fast switching between two reactant isotopes. *The flow rate and the partial pressure of the individual components must remain unchanged.* In this way, by switching from isotope A to its isotope A' at the time $t=0$, the concentration decrease of the output A and the concentration rise of the output A' is measured. Equation (7) can then be rewritten in the following form:

$$\frac{dN_A}{dt} = \text{consumption rate } X = -k \cdot N_A = -\frac{N_A}{\tau} \quad (8)$$

After integration of this equation, it will be obtained:

$$N_A = N_A^0 \cdot e^{-\left(\frac{t}{\tau}\right)} \quad (9)$$

where N_A^0 represents the concentration of adsorbed molecules under stationary conditions. Practically, it is the sum of the concentrations of both adsorbed isotopic phases A and A':

$$N_A^0 = N_A + N_{A'} \quad (10)$$

Dividing (9) by the total concentration of the adsorbed phase X, the standardized function for the concentration decrease of isotope A during the change of reactant A to its isotope A' is obtained:

$$F_A(t) = \frac{N_A}{N_A^0} = e^{-\left(\frac{t}{\tau}\right)} \quad (11)$$

By the same reasoning, the increase of the concentration of isotope A' can be formulated accordingly

$$F_{A'}(t) = \frac{N_{A'}}{N_A^0} = 1 - e^{-\left(\frac{t}{\tau}\right)} \quad (12)$$

These standardized functions are the transient curves of the two products for the simplest case of the adsorption-desorption process. The sum of the two functions $F_A(t)$ and $F_{A'}(t)$ is at any moment always equal to unity (normalized functions). Typical transient curves for the decrease of the concentration of desorbed phase A and the rise of the concentration of desorbed phase A' are shown below.

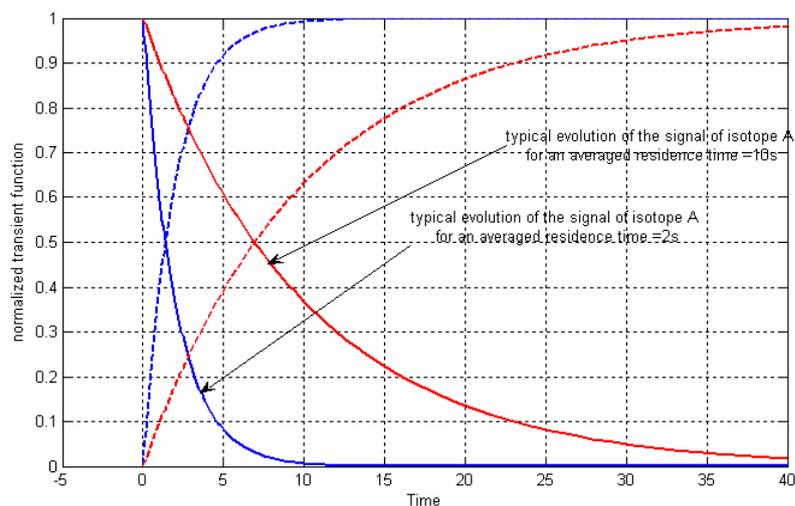


Fig. 2.2 Typical response for the evolution of the signal for the two isotopes for two different residence times

It can easily be shown that the averaged residence time on the catalyst surface for the adsorption-desorption process is simply determined by the area under the normalized (standardized) transient curve (see the figure). Indeed, integrating equation (11) results in the following expression:

$$\int_0^{\infty} F_A(t) dt = \int_0^{\infty} e^{-\left(\frac{t}{\tau}\right)} dt = \tau \cdot e^{-\left(\frac{t}{\tau}\right)} \Big|_0^{\infty} = \tau \quad (13)$$

As mentioned already, this time is identical to the reciprocal value of the rate constant of a first order irreversible reaction. The measured averaged surface residence times are corrected for the inherent delay of the system, with the use of the inert gas switching (Ar to Kr for example (Fig.2.2)).

Therefore, in order to calculate the averaged residence time on the catalyst surface for the adsorption-desorption reaction, the area between the Ar transient and the A' transient measured functions is computed (see Fig.2.3).

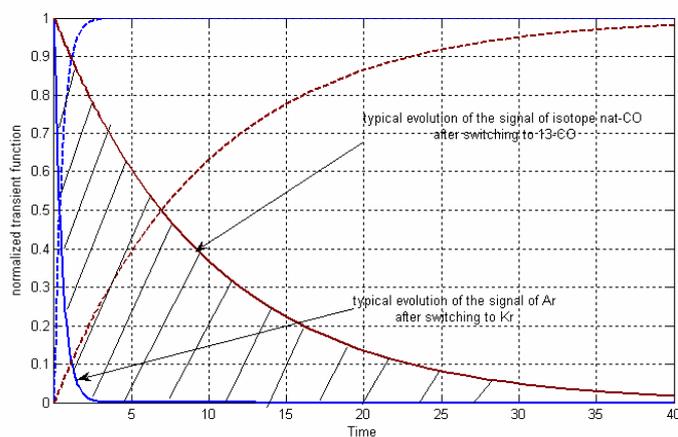
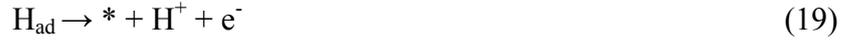
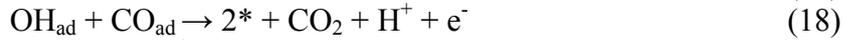


Fig. 2.3: Typical data analysis for a set of data including subtraction of the inert gas transient

2.2 CO and H competitive adsorption on Pt and PtRu

The reactions occurring at the fuel cell anode can be described as follows:



where * is the adsorption site on the catalyst surface.

In our simplified environment, without humidification or an induced potential, only the first two reactions can occur, the adsorption/desorption of CO and hydrogen for which the equilibrium rate constants, K_{CO} and K_{H_2} , can be defined.

For CO diluted with an inert gas, the Langmuir adsorption isotherm for associative adsorption can be defined as:

$$\theta_{\text{CO}} = \frac{K_{\text{CO}} p_{\text{CO}}}{1 + K_{\text{CO}} p_{\text{CO}}} \quad (20)$$

where θ is the coverage and p is the partial pressure.

However, when we perform the SSITKA experiment we have both isotopically labelled and unlabelled CO present in our system.

Therefore:



The following three expressions have previously been derived for isotopic exchange experiments involving CO adsorption/desorption in an inert diluent (i.e. where the diluent does not compete for adsorption sites with CO) [16]:

$$\frac{d\theta_{^{12}\text{CO}}}{dt} = k^+ p_{^{12}\text{CO}} \theta_* - k^- \theta_{^{12}\text{CO}} \quad (23)$$

$$\frac{d\theta_{^{13}\text{CO}}}{dt} = k^+ p_{^{13}\text{CO}} \theta_* - k^- \theta_{^{13}\text{CO}} \quad (24)$$

$$\theta_* = 1 - \theta_{^{13}\text{CO}} - \theta_{^{12}\text{CO}} \quad (25)$$

where k^+ is the rate constant for the adsorption process and k^- is the rate constant for the desorption process.

It should now be considered what will happen in the presence of hydrogen. There are three possible scenarios to consider for interpretation of the data which will be discussed in terms of the ^{12}CO species. As previously discussed in section 2.1 the sum of the ^{12}CO and ^{13}CO responses will always be unity (for the normalised functions).

(I) CO adsorption/desorption strongly predominates (effect of hydrogen diluent insignificant); no CO re-adsorption

After the isotopic switch occurs, in a situation where there is no significant re-adsorption of the desorbing gas, equation (23) reduces to:

$$\frac{d\theta_{^{12}\text{CO}}}{dt} = -k^- \theta_{^{12}\text{CO}} \quad (26)$$

and therefore,

$$\theta_{^{12}\text{CO}} = \theta_{^{12}\text{CO}}^0 e^{-k^- t} \quad (27)$$

This is the direct equivalent of the generic equation (9) for our specific system. A plot of $\ln(\theta)$ vs. t provides a direct measure of the rate of desorption.

These assumptions have been previously shown to be valid at low concentrations of CO in an inert diluent at room temperature (where insignificant re-adsorption rates were observed) [16]. Under these conditions, no dependence on flow-rate was observed above 20ml/min.

(II) CO adsorption/desorption strongly predominates (effect of hydrogen diluent insignificant); CO re-adsorption

In this scenario the adsorption term for the desorbing species must be considered and equation (23) must be considered in its entirety.

This scenario can be distinguished from (I) by a strong dependence on flow-rate. It has been previously proposed [18, 19], that the concentration of ^{12}CO in the gas phase will decrease as:

$$C = \frac{\theta_{^{12}\text{CO}} k^-}{q + \frac{\theta_{^{12}\text{CO}} k^-}{C_0}} \exp \left[- \frac{k^-}{1 + \frac{\theta_{^{12}\text{CO}} k^-}{q C_0}} t \right] \quad (28)$$

Where q represents the flow rate and C_0 denotes the concentration of ^{12}CO at $t = 0$ (i.e. at the point of isotopic switch). Therefore the initial gradient of a semi-logarithmic plot can now be defined as an apparent desorption rate constant k^{app} where:

$$k^{app} = \frac{k^-}{1 + \frac{\theta_{^{12}\text{CO}} k^-}{q C_0}} \quad (29)$$

Rearranging gives:

$$\frac{1}{k^{app}} = \frac{1}{k^-} + \frac{\theta_{CO}}{C_0} \frac{1}{q} \quad (30)$$

meaning that a plot of $1/k^{app}$ versus $1/q$ should provide a linear response, with an intercept of $1/k^-$, the unidirectional desorption rate constant.

The above model has previously been used when there was significant re-adsorption (at temperatures of 50°C and higher) at concentrations of 1000ppm in argon [19]. It has also been demonstrated that no significant difference in the rate of exchange of CO at any given pressure is observed on going from Pt to PtRu catalysts when the diluted gases used is argon since the CO states will be filled to the same desorption energy for the two catalysts [17].

(III) Competition with H₂

When hydrogen is used as the diluent gas, as has been performed in this project, we would expect to see a deviation from the behaviour proposed by the two models given above. Experiments performed at a single flow rate at room temperature presented in [17] by a pseudo-SSITKA approach have indeed observed a disparity between the data observed with Ar and H₂ as carrier gas.

In the instance where competitive adsorption occurs, the isotherms governing CO and hydrogen coverage are, by analogy to equation (20):

$$\theta_{CO} = \frac{K_{CO} p_{CO}}{1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}}} \quad (31)$$

$$\theta_H = \frac{\sqrt{K_{H_2} p_{H_2}}}{1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}}} \quad (32)$$

In real terms for these experiments, this will lead to a deviation from the expected behaviour according to scenario II.

3. Experimental

A gas inlet system has been set-up for the SSITKA analysis system as shown in figure 3.1.

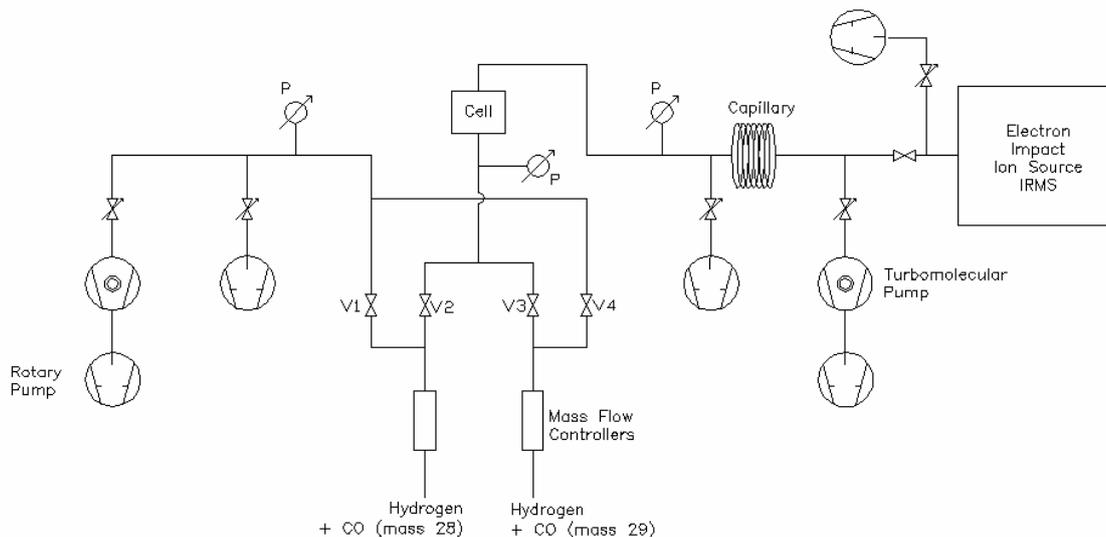


Fig. 3.1 Schematic of the gas inlet system used in the experiments

Gases mixtures were prepared from CO 4.7, hydrogen 6.0 and ^{13}C isotopically enriched CO. Flow rates used for the experiments ranged from 10-100ml/min.

The samples used were commercial Pt/C and PtRu/C from Electrochem Inc with metal loadings of 1 mg/cm^2 . These consist of the nanoparticulate metal supported on Vulcan carbon powder and subsequently bound to a Toray carbon sheet gas diffusion layer using a Teflon binder (this is more resistant to temperature than the Nafion binder which is necessary in the full Membrane Electrode Assembly (MEA)).

Initially, using the set-up presented in Figure 3.1 a flow of a neutral gas (N_2) was set-up in order to determine the response time of the system for subtraction from the obtained data.

A series of experiments were then performed according to the following procedure:

Initially a flow of unlabelled CO in hydrogen was passed through the cell (valve V2 open, valve V1 closed) $P_{\text{cell}} = 1 \text{ bar}$. A mixture of isotopically enriched CO in hydrogen, with the same total CO concentration, was flowed through a "dummy" line simultaneously (valve V4 open, valve V3 closed) under the same conditions of pressure and flow. After a time (usually in excess of one hour, in order to obtain an initial state of the surface covered with ^{12}CO), the valves were switched so the isotopically labelled mixture flowed through the cell, and the unlabelled mixture to the dummy line (valves V1 & V3 open, valves V2 & V4 closed). The mass 28 and 29 response was then measured using the electron impact ion source IRMS.

This procedure was followed for different flow rates, concentrations and temperatures for both Pt/C and $\text{Pt}_{0.5}\text{Ru}_{0.5}/\text{C}$ as described in the following section.

4. Results

Initially the exchange was performed with the Pt samples for a concentration of 1400ppm CO in hydrogen at 25°C as shown in figure 4.1. Data was obtained for a range of flow-rates and a flow-rate dependence was observed. This experiment was repeated for the PtRu catalyst (as shown in figure 4.2).

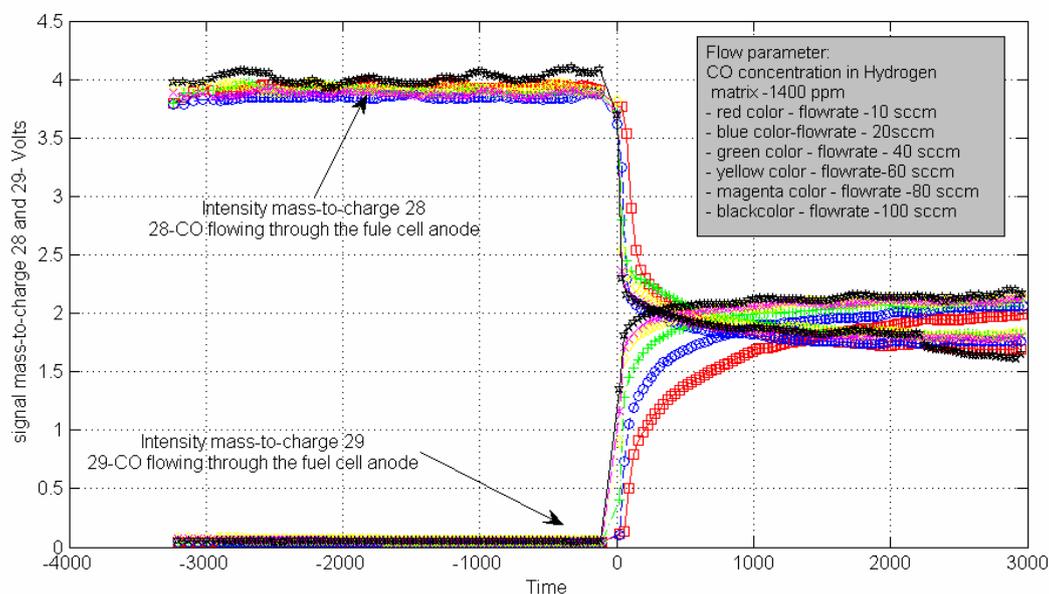


Fig. 4.1: Flow dependent CO exchange on Pt catalysts at 25°C and 1400ppm CO in H₂

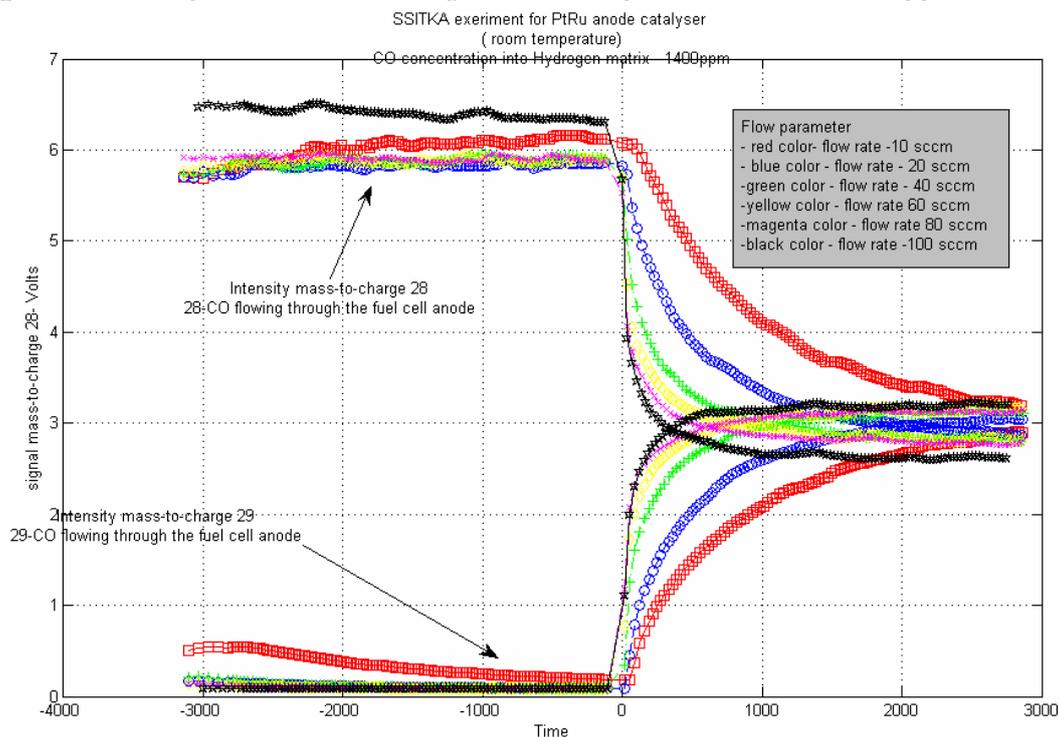


Fig. 4.2: Flow dependent CO exchange on PtRu catalysts at 25°C and 1400ppm CO in H₂

Data was then obtained for 100ppm CO in hydrogen at 25°C for both the Pt (Fig. 4.3) and the PtRu (figure 4.4) catalysts. This is the typical order of magnitude of CO concentration at which low temperature PEM fuel cells are able to operate with the use of more CO-tolerant PtRu catalysts. However, at these concentrations, the pure Pt catalysts are known to poison very quickly.

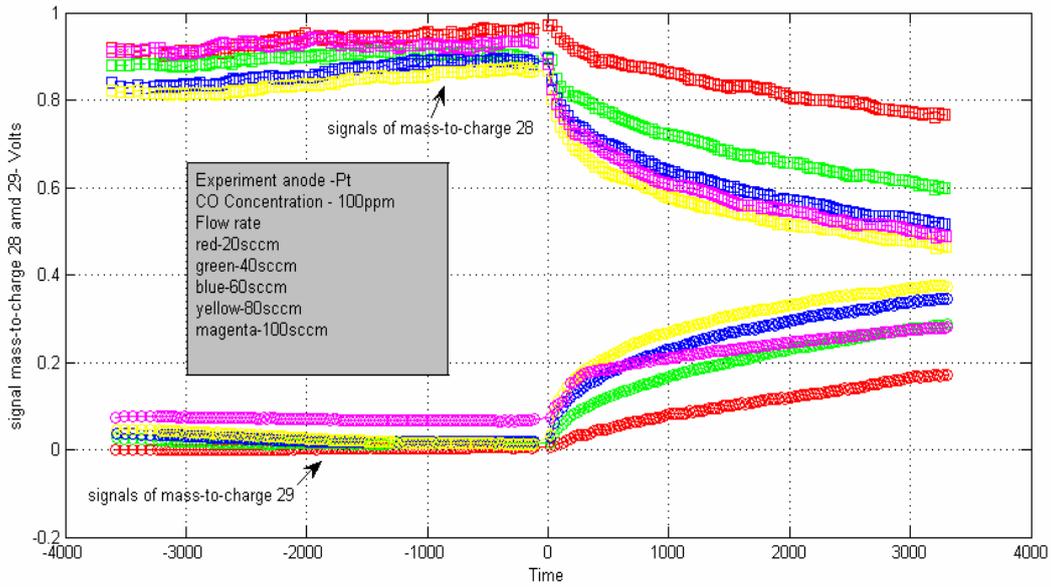


Fig. 4.3: Flow dependent CO exchange on Pt catalysts at 25°C and 100ppm CO in H₂

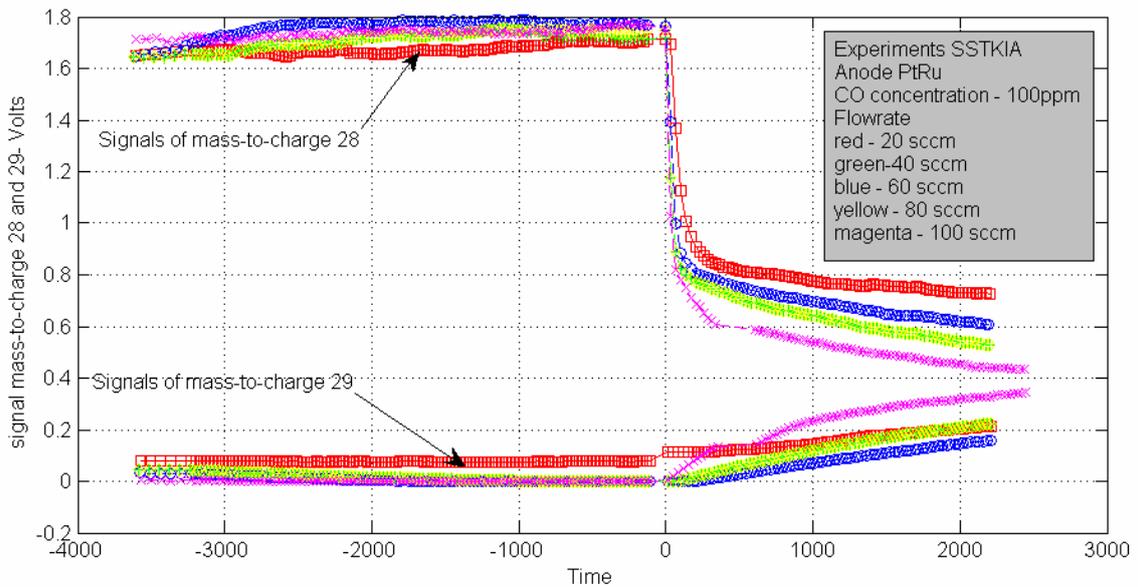


Fig. 4.4: Flow dependent CO exchange on PtRu catalysts at 25°C and 100ppm CO in H₂

To determine the kinetic parameters the change in the mass 29 signal was used. This is more accurate than using the mass 28 signal as the 29 signal starts from the background zero value. If there is a slight difference in the two concentrations of the initial gases then this error will be incorporated into the mass 28 signal.

A switch was also performed with an inert gas (nitrogen) to determine the lag time for the experiment when there is no adsorption-desorption event. By analogy to equation (12) the regression function for this normalised nitrogen result is:

$$y_{nitro} = 1 - a_{nitro} \cdot e^{-\left(\frac{t}{b_{nitro}}\right)} \quad (33)$$

These values were determined for each flow-rate used and subtracted from the mass 29 experimental data prior to the fitting of that data. They are given in Table 1 below.

The exponential regression which was then applied to the mass 29 experimental data for the two different concentrations and catalyst materials was therefore:

$$y_{29} = 1 - a_{29} \cdot e^{-\left(\frac{t}{b_{29}}\right)} \quad (34)$$

where a_{29} and b_{29} are the values listed in Table 1.

Flow rate (sccm)	CO concentration	Catalyst	Nitrogen		Hydrogen+CO	
			a	b	a-29	b-29
10	1400	Pt	9.9144	359.0264	0.2845	1358.02
20	1400	Pt	23.4874	251.5877	0.2267	1177.85
40	1400	Pt	56.8516	189.3382	0.1963	1104.52
60	1400	Pt	85.3862	166.8216	0.1744	1065.81
80	1400	Pt	95.2661	157.0364	0.1582	1020.37
100	1400	Pt	95.6176	152.213	0.1644	1069.65
10	1400	PtRu	9.9144	359.0264	0.3357	1520.39
20	1400	PtRu	23.4874	251.5877	0.2537	1150.02
40	1400	PtRu	56.8516	189.3382	0.192	1024.12
60	1400	PtRu	85.3862	166.8216	0.1717	982.8224
80	1400	PtRu	95.2661	157.0364	0.1595	972.5363
100	1400	PtRu	95.6176	152.213	1.1567	934.8023
20	100	Pt	23.4874	251.5877	0.534	3036.02
40	100	Pt	56.8516	189.3382	0.4429	2511.03
60	100	Pt	85.3862	166.8216	0.3969	2238.94
80	100	Pt	95.2661	157.0364	0.3743	2127.3
100	100	Pt	95.6176	152.213	0.3104	2026.1
20	100	PtRu	23.4874	251.5877	0.3518	4776.7
40	100	PtRu	56.8516	189.3382	0.5933	3879.03
60	100	PtRu	85.3862	166.8216	0.5331	3314.92
80	100	PtRu	95.2661	157.036	0.5329	3334.43
100	100	PtRu	95.6176	152.213	0.5252	3167.04

Table 1: Coefficients for the data obtained at room temperature.

By comparison of the exponential term in equation 34 with equations 28-30 it can be seen that $1/b = k_{app}$, therefore a plot of b versus $1/q$ should provide us with an intercept of $1/k$ and therefore we can obtain a value for the unidirectional rate constant for the desorption rate for these conditions. The plot of b_{29} versus $1/q$ is given in figure 4.5.

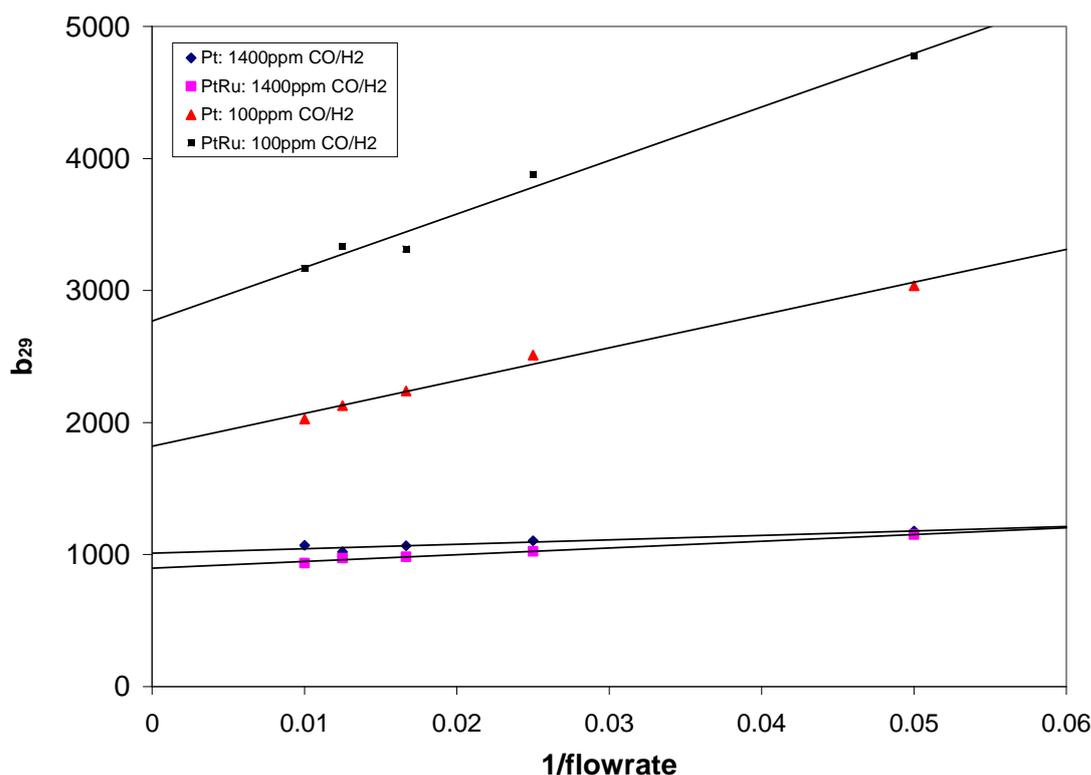


Fig.4.5: Plot of b_{29} versus $1/q$ for Pt and PtRu catalysts under different concentrations of CO in hydrogen.

From this chart the y-intercepts for the individual sets of conditions can be determined, and the unidirectional rate constants can be derived as given in Table 2.

Catalyst	Concentration (CO in H ₂)	Intercept	k^- (s ⁻¹)
Pt	1400	1009	9.91×10^{-4}
PtRu	1400	872	1.15×10^{-3}
Pt	100	1821	5.49×10^{-4}
PtRu	100	2769	3.61×10^{-4}

Table 2: Derived rates for the four sets of data

It can be observed that at 1400ppm there is little difference between the observed rates on Pt and PtRu, however at the lower concentration of 100ppm it is clear that the rate of exchange of CO is considerably slower on PtRu than on Pt alone. Similar behaviour was also observed in [17] for 100 and 1000ppm CO in hydrogen using a pre-dosing technique (rather than traditional SSITKA) however, in this previous paper data was only obtained for a single flow-rate (20mL/min) under the assumption that the exchange rate was independent of flow-rate at these concentrations. Whilst it can be seen from our data that this will give a relatively accurate value at 1000ppm (the gradient of the plot is very “flat”, it is clearly not the case in our experiments at 100ppm where the rate becomes more strongly dependent on mass transfer.

Finally, the effect of temperature was investigated for a concentration of 100ppm CO in H₂ at a flow-rate of 60mL/min for both Pt (Figure 4.6) and PtRu (Figure 4.7).

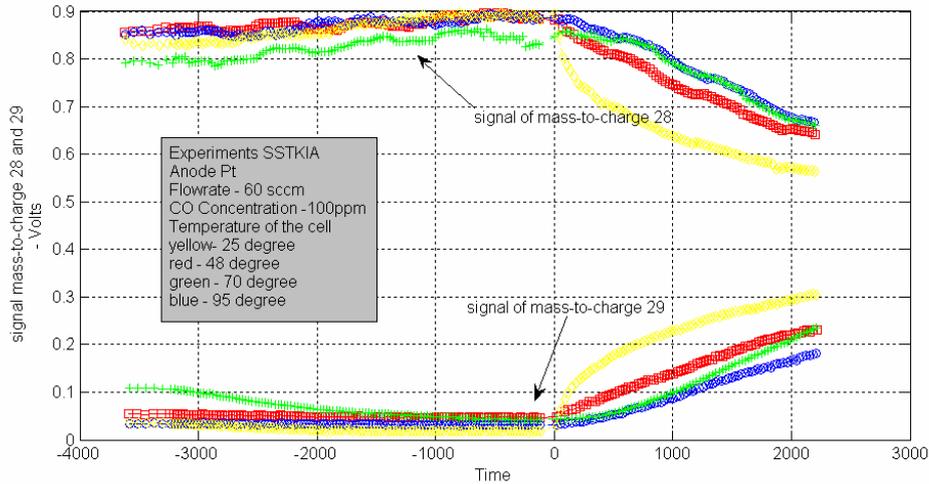


Fig. 4.6: Temperature dependent CO exchange on Pt catalysts at 60ml/min and 100ppm CO in H₂

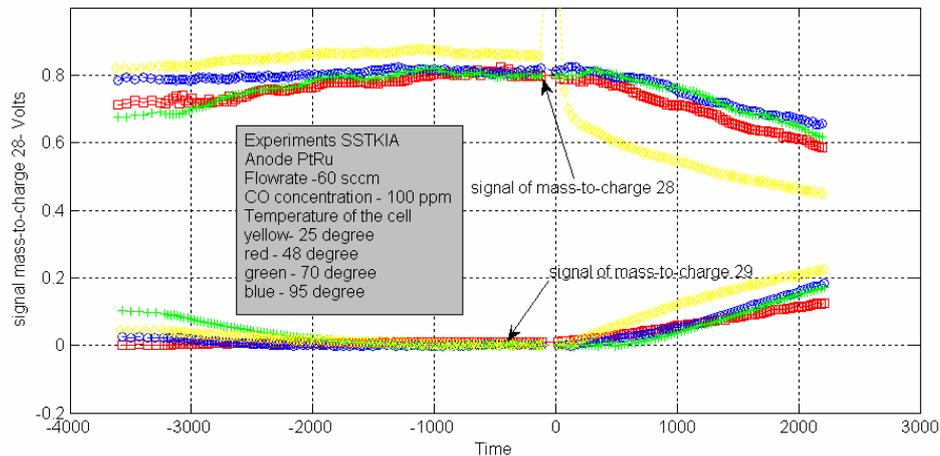


Fig. 4.7: Temperature dependent CO exchange on PtRu catalysts at 60ml/min and 100ppm CO in H₂

In these cases it is much more difficult to derive any quantitative information from this data as there is only a clear exponential decay observed at room temperature. The most likely explanation for this is that initially all the arriving isotopically labelled species is exchanging, and the process is experiencing some mass transport limitations. It is apparent that a far more comprehensive model with additional flow dependent data for each temperature measured (for which there was not time available within this exploratory project) would be required for a conclusive interpretation to be possible.

5. Discussion

When fuel cells operate on hydrogen produced through reforming of hydrocarbons, it is necessary to use CO-tolerant catalysts as even ppm levels are known to poison the traditional platinum catalysts. Industrial manufacturers of fuel cell catalysts limit this problem through the use of a 50:50 alloy of platinum and ruthenium, which provides increased tolerance to CO poisoning. Of the two proposed mechanisms for this enhanced promotion, only one, the enhanced oxidation of CO to CO₂ has been investigated at any length within the literature.

In this study we have demonstrated that fast-switching SSITKA measurements can be performed to provide information on the adsorption/desorption rates of CO from Pt and PtRu catalysts at relevant concentrations of CO in hydrogen, therefore providing information regarding the competitive adsorption of these two species on Pt and PtRu. It is proposed that the adsorption/desorption rate of CO is important in controlling the equilibrium coverage of CO under the operating conditions of the fuel cell and therefore the subsequent rate of hydrogen oxidation.

Experiments have been performed at two concentrations; 1400ppm and 100ppm CO in hydrogen on both platinum and platinum/ruthenium catalysts. From fitting to the experimental data of the exponential increase in the desorbing CO-29 signal it can be seen that there is very little difference in the rate of exchange on Pt and PtRu at the higher CO concentration. In [17] it was also observed that at higher concentrations of CO there is little difference in behaviour between CO in hydrogen and in an inert diluent, implying that CO adsorption pre-dominates. This would imply that scenario II, outlined in section 2.2, is a good approximation at a concentration of 1400ppm in hydrogen.

However, when the concentration is lowered to 100ppm, there is increased competition between the hydrogen and CO and the subsequent rate of exchange on the PtRu surface is significantly lowered compared to the rate on pure Pt.

It is most likely that this originates from a lower equilibrium coverage for CO on the PtRu catalyst, which will naturally be beneficial for the hydrogen oxidation reaction under these conditions. It has previously been shown that the partial pressure of CO, the equilibrium coverage and the desorption rate are all strongly linked parameters for these systems [16]. It is clear that towards lower concentrations of CO in hydrogen, the increased competition for sites is leading to a lower exchange rate for CO. At concentrations from 100vppm CO upwards it has been shown that the rates of exchange under dry conditions are higher than the measured rates of oxidation of CO performed in electrochemical half-cells [16]. It is the balance between these two kinetic processes as lower concentrations of CO are reached, that will be the important factor in determining the subsequent mechanism of promotion of CO tolerance under a given set of conditions.

A previous isotopic exchange study has investigated the temperature and flow dependence of CO desorption for 1000ppm CO in Ar [19] which was the first time such a study has been performed on real commercial catalysts. We have attempted some preliminary temperature dependent exchange experiments for the lower concentration (100vppm) of CO in hydrogen at a single flow rate and, whilst it is apparent (and unsurprising) that there is an increase in the exchange rate with temperature, a more comprehensive study with flow-rate dependence would be required in order to draw any quantitative conclusions.

6. Conclusions

Steady State Isotopic Transient Kinetic Analysis experiments were performed for the CO exchange process in hydrogen carrier gas at 1400vppm and 100vppm concentrations at a range of flow rates and (for the lower concentration) at a range of temperatures relevant to fuel cell operation.

A dependence on flow rate was observed under all conditions. Rate constants for the desorption process were obtained by extrapolation of the data assuming a Langmuirian model.

For 1400vppm CO in hydrogen little difference was observed in the measured exchange rates for Pt and PtRu at room temperature, however there is a more significant effect observed at 100vppm CO in hydrogen, where the rates on PtRu are considerably slower than on Pt. This can be attributed to increased competition on PtRu for CO and H adsorption, leading to a lower equilibrium coverage of CO on the PtRu surface.

Preliminary data has also been obtained for the exchange at 100ppm CO in hydrogen at different temperatures in the range relevant to fuel cell operation (<100°C), however, considerably more data would be required to obtain quantitative information in these instances.

7. Further Work

The system created was able to obtain data at a sufficiently good resolution to obtain kinetic parameters at low concentrations of CO (100 vppm) in H₂. As discussed in earlier sections, however, the temperature dependent data obtained is only preliminary and could be expanded as a more detailed study with varying flow rates.

In addition, it would also be interesting to look at the effect of humidification on the gas stream (the inclusion of a third adsorption species), and eventually to aim to perform such exchange experiments in a single cell arrangement.

Finally, if novel catalyst materials could be made available, the comparison of the fundamental kinetic parameters of such novel materials with those obtained from the industrial standard catalysts could provide additional information regarding the potential of the novel materials as CO tolerant PEM fuel cell catalysts.

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Title: Steady State Isotopic Transient Kinetic Analysis Study of Proton Exchange Membrane Fuel Cell Anodes

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Abstract

The hydrogen oxidation reaction at Proton Exchange Membrane Fuel Cell anodes is poisoned by part per million levels of carbon monoxide, present even after purification steps following the production of hydrogen by the reformation of hydrocarbons. Whilst platinum is the catalyst of choice for the oxidation of pure hydrogen, platinum/ruthenium alloys are shown to be more tolerant when ppm levels of CO are present. It has recently been demonstrated that there is a dynamic equilibrium between CO adsorbed on platinum or platinum/ruthenium nanoparticles and CO in the gas phase, and that this equilibrium is affected by the competitive adsorption between CO and hydrogen.

The purpose of this research to perform Steady State Isotopic Transient Kinetic Analysis (SSITKA) experiments using the isotopic exchange between ^{13}CO and ^{12}CO to investigate the competitive adsorption of hydrogen and CO on commercial Pt and PtRu catalysts.

For 1400ppm CO in hydrogen little difference was observed in the measured exchange rates for Pt and PtRu at room temperature, however there is a more significant effect observed at 100ppm CO in hydrogen, where the rates on PtRu are considerably slower than on Pt. This can be attributed to increased competition on PtRu for CO and H adsorption, leading to lower equilibrium coverage of CO on the PtRu surface.

Preliminary measurements were also made regarding the temperature dependence of this process in the range relevant to the fuel cell (25-90°C).

This work was performed as a joint venture between the Institute for Energy (IE) and the Institute for Reference Materials and Measurements (IRMM), as IE have the experience in the area of PEM fuel cell catalysis whilst IRMM have the pre-existing Isotope Ratio Mass Spectrometry instrumental capabilities with the required resolution to perform measurements at these concentration levels, along with fast switching capabilities for applying the traditional SSITKA technique to this system.

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