Investigation of PtRu catalysts produced by a novel flame deposition method for high temperature PEMFC applications*: Time-resolved In situ* QEXAFS studies

Abstract

Time resolved XANES experiments have been performed to investigate the behaviour of both commercial and novel Proton Exchange Membrane fuel cell anode catalysts in specific dry gas environments relevant to the operational fuel cell. Redox cycles were performed using hydrogen followed by oxygen, or carbon monoxide followed by oxygen over a temperature range of 25-200°C.

Introduction

The hydrogen oxidation reaction at the anode of Proton Exchange Membrane fuel cells (PEMFC) is poisoned by low levels of CO. If the hydrogen to be used is not produced from sustainable sources but instead from the reformation of hydrocarbons, it becomes difficult to remove trace levels of CO. Platinum provides the best current densities for hydrogen oxidation if pure hydrogen is used [1], however CO is known to strongly poison the platinum catalyst even at ppm levels[2]. It has been found that by alloying the platinum with ruthenium more CO-tolerant catalysts can be produced.

It has been demonstrated that alloying platinum with a second metal, usually ruthenium, can increase the tolerance of the anode to CO adsorption [3]. There are currently two proposed mechanisms for this promotion:

(i) The bifunctional effect [4]: It can be demonstrated that the alloying of platinum with ruthenium, at an optimal ratio of 50:50 reduces the overpotential required for the oxidation of adsorbed CO to CO_2 [5-9]. This reduction in overpotential is associated with the dissociation of water being more facile on ruthenium than on platinum.
(ii) The ligand effect [10-12]: Here, alloying of platinum with ruthenium alters the chemical properties of the surface platinum due to electronic effects. This has been demonstrated to have a strong effect on the CO bond strength, and subsequent equilibrium surface coverage.

Currently, there is debate as to which is the predominant factor. It is clear that PtRu catalysts offer a significant tolerance to CO in the potential range (below 0.25V) where no CO electro-oxidation occurs on this surface, hence implying that in this regime the second mechanism is the most appropriate.

Current developments in membrane technology are attempting to increase the temperature at which the PEM fuel cells can operate (this is currently limited to 100°C by the use of Nafion membranes which require the solvation of water molecules in order to be proton conducting). Hence it is of interest to investigate the behaviour of the carbon-supported dispersed anode catalysts in the range of 20-200°C as it is known that the effect of CO will decrease with temperature.

We have previously performed isotopic exchange experiments (Steady State Isotopic Transient Kinetic Analysis – SSITKA) to investigate the dynamic behaviour of the adsorbed CO overlayers and a distinct dependence of the desorption rate on the partial pressure was observed even at room temperature. This implies that the system is much more dynamic than previously thought.

Previous in-situ EXAFS studies have been performed on the behaviour of PEM fuel cell anode catalysts in the operational conditions of a fuel cell (a comprehensive review is given in [13]). However, there are many competing processes occurring at the PEM fuel cell anode and it is apparent that the balance of these processes will be altered significantly by changes in conditions. In the operating cell it is necessary to consider the competitive adsorption of CO, hydrogen and water, the effect of this balance on the oxidation state of the platinum/ruthenium particles, the degree of segregation of platinum and ruthenium within these particles and any subsequent morphological changes, and finally the influence of the electrochemical potential induced by the oxidation reaction and the overall cell temperature.

Within this work we hope to begin to isolate the effects of these individual parameters on the catalyst particles by undertaking a series of experiments which will look at the effect of a stepwise addition of these parameters.

Initially, within the period of beamtime undertaken at ID26 we have examined in detail the time-resolved behaviour of exposing commercial catalysts and those prepared by a novel flame deposition method, on exposure to dry oxidative and reductive environments over a temperature range from 20-200°C. The gases used were pure hydrogen, 1% CO in argon and 20% oxygen in argon. The intention is to obtain relevant fundamental information on the kinetics of the processes occurring at a fuel cell anode. It will also provide relevant information regarding the induction time of fuel cell anodes and the effect of air bleeds used to remove CO from the anode surface.

By utilising QEXAFS we can determine the dynamic behaviour of the particles and demonstrate the correlation between the segregation of Pt/Ru (and any morphological changes) and its dependency on the gaseous environment and temperature. In addition it will demonstrate whether the catalyst displays a tendency to sinter in this increased temperature range.

Our request to utilise QEXAFS on ID26, rather than on BM 29 (or indeed dispersive EXAFS on ID24) was made for the following reasons. Firstly, though total metal loadings cannot be considered dilute (a maximum loading of 20wt% can be used as at higher loadings agglomeration is observed), these systems are supported upon thin small carbon supports. As such at normal or even 45 degree incidence the beam only samples a very small amount of metal (a metal loading of $1 mgcm^{-2}$ is typical which corresponds to 3-6 x 10^{18} $atoms/cm^2$**)**.

Experimental method

In our experiments we have utilised commercial catalysts (Electrochem inc.) but utilising a Teflon binder instead of the normal Nafion binder. This allows exploration of the effect of temperature up to 200°C without any risk of decomposition of the Nafion. The catalysts consist of PtRu nanoparticles supported on a Vulcan carbon powder and then bound to Toray carbon paper.

In addition we have also investigated Pt and PtRu catalysts made in-house at the Danish Technical University by a novel flame deposition method which are deposited directly on the Toray carbon paper without the need for a binder

For these experiments initially on Pt and $Pt_{0.5}Ru_{0.5}$ were used (the industrially relevant stoichiometries). An existing cell was utilised in transmission and/or fluorescence measurements at Pt L_{III} and Ru K edges and interfaced to the mass spectrometer facility available from ID24 to permit concurrent analysis of changes in feedstock composition during experimentation.

Preliminary Results

Experiments were performed usually by an initial reduction of the “as delivered” catalyst followed by an oxidation cycle and a further reduction cycle. The reduction cycles were performed using 1% CO in argon or pure hydrogen. The oxidation cycles were performed using 20% oxygen in argon.

These redox cycles were performed over a range of temperatures between 20 and 200°C and for both the commercial and in-house prepared samples.

Initially an EXAFS spectrum was obtained, followed by fast XANES spectra obtained on exposure to the change in gas environment and/or temperature. A further EXAFS spectrum was obtained after the event. For each condition the experiments were repeated at both the Pt L_{III} and Ru K edges. A new sample was used for each measurement so that each measurement was obtained on a sample with the same “history”.

This has led to significant amounts of data that needs to be processed, however a sample of the obtained data can be seen in figures 1 and 2.

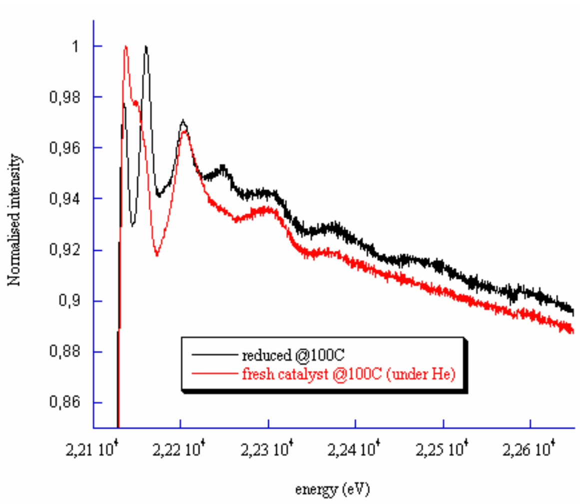

Figure 1: QEXAFS spectrum of the Ru K edge for a commercial PtRu sample prior and after reduction under 1 bar hydrogen at 100°C

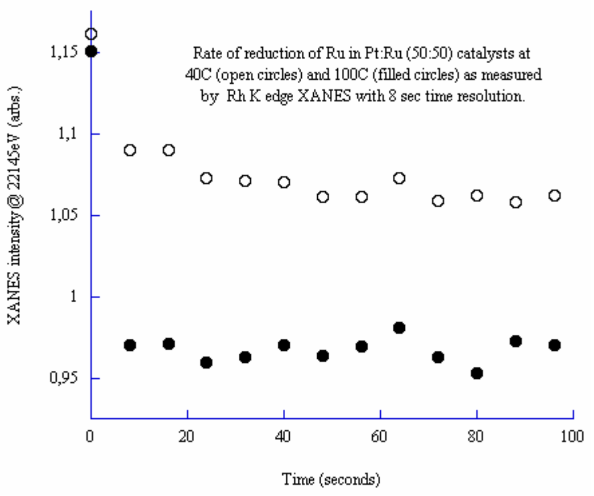

Figure 2: Plot of the Ru K edge XANES intensity at 22145eV for the reduction of the PtRu sample at 40 and 100°C in hydrogen.

From figure 1 the difference between the EXAFS spectra for the reduced and oxidised species can be clearly seen. The change in the Ru K edge XANES intensity at 22145eV with time for samples reduced at

40 and 100°C is evident. It should also be noted, whilst it needs further investigation, that there were differences observed between the behaviour of the commercial catalysts and the catalysts produced by the novel flame deposition where the reduction rate was observed to be significantly slower.

What has become clear is that, for the most part, the kinetics of the reduction and oxidation processes observable are too fast to be quantified from a kinetic stand point using Quick XANES with a time resolution of ca. 8 secs on ID26. Over the most part of the temperature range of interest (T>50°C) structural change occurs within the time it takes to make the first measurement. At 40°C, the kinetics can be observed, however, it seems evident from the full set of data that at different temperatures a different final state is reached. Significant further data processing is naturally still required at this stage, however it is intended that a publication on this issue will be prepared before the end of 2005.

Conclusions

We have made considerable measurements on the reduction/oxidation of PtRu fuel cell anode catalysts over a temperature range of 20-200°C using hydrogen or 1%CO in argon as the reductive gas and 20% oxygen in argon as the oxidative gas.

What has become initially clear from our measurements, is that whilst certain new information can be obtained from this data, the kinetics of the reduction and oxidation processes observable are too fast to be quantified from a kinetic stand point using Quick XANES with a time resolution of ca. 8 secs on ID26 in the dry environment at the operational temperature of the fuel cell (approx. 100°C – it is necessary to decrease the temperature in order to obtain kinetic information). The next phase of our research should therefore include the use of dispersive XANES/EXAFS on ID24 combined with introducing the effect of humidity on the system. It is apparent that the presence of water will compete with the reduction processes that we observe as being kinetically fast under these dry conditions.

References

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