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Performance of methanol oxidation catalysts with varying Pt:Ru ratio as a function of temperature

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Abstract

This paper describes the effects of varying the Pt to Ru ratio in carbon-supported catalysts for methanol oxidation as a function of temperature. Previously these effects were studied in isolation, but now it is shown that the composition of a given catalyst as a function of temperature is extremely important for its activity towards methanol oxidation. Platinum rich 3:2 atomic ratio catalysts perform better than a 1:1 catalyst at 25 °C, where only Pt is believed to be active towards methanol dehydrogenation, since this process is a highly thermally activated process on Ru sites. This result is reversed at 65 °C, where the 1:1 catalyst displays much higher currents across the entire range of polarization. This may result from methanol dehydrogenation occurring on both Ru and Pt sites at higher temperatures. At an intermediate temperature, 45 °C, the 3:2 catalyst is seen to perform better at lower current values, while the 1:1 catalyst is superior at higher current densities, with the crossover occurring at 62 A g^{-1}. As a consequence, when designing fuel cell catalysts, the composition of the catalyst employed should be tailored with respect to the exact operating conditions, in order to promote optimum fuel cell performance.

1. Introduction

Fuel cells offer the possibility of revolutionizing power generation in all aspects of life. This is especially true of direct methanol fuel cells (DMFCs) due to the convenience of utilizing a liquid fuel that possesses a high energy density. Methanol can also be easily and inexpensively transported and stored. It is handled much like gasoline, so the existing fuel infrastructure could still be used to a great extent after initial conversion and adaptation to the chemical properties of methanol. Also, methanol is not dependent on crude oil, a vital factor with the demand for mobility constantly increasing, and is easily obtainable from natural gas or renewable biomass resources. Extensive reviews and articles on the principles of operation of DMFCs, as well as progress to date in their development and application, have been published [1–7].

There are many factors hampering the widespread introduction of DMFCs as viable power sources for various applications. Especially in the field of mobile applications, most material components in fuel cell systems are still far too expensive, the systems are much more complex than was expected, and there remain such issues as catalyst deactivation due to CO poisoning and water-flooding of active sites. The requirements placed on the various systems differ significantly, and thus the operating conditions required will also vary. One of the most important factors is the temperature at which the cell is operated, as this has a major effect on the performance of Pt based methanol oxidation catalysts [8]. However, the majority of the results published utilize a Pt–Ru catalyst, either supported or unsupported, at elevated temperature (>90 °C) [5, 8–14]. This is because the chemisorption and subsequent dehydrogenation of methanol on Ru sites is significantly less favored than on Pt sites, but is strongly activated by temperature [8]. Thus, as part of the well-known 'bi-functional' mechanism for methanol oxidation [1–7], a Ru rich sample might be expected to perform better at higher cell operating temperatures. However, in many cases while the use of higher temperatures leads to improved performance from cells, it also increases the rate of methanol crossover and decreases membrane stability [12]. The number of authors who report data for the operation of DMFCs at lower temperatures (typically 25 °C to 65 °C) is limited [15–17]. It has been found by many groups that Ru has the most pronounced effect on the methanol oxidation rate when mixed with Pt in a 1:1 ratio [5, 6, 8, 9, 17, 18–22]. This is still an uncertain argument, but generally these authors have found the 1:1 atomic ratio Pt–Ru catalysts to be the best performing at high temperatures (90 °C to 130 °C). Furthermore, a Ru-rich catalyst shows inferior performances under high temperature operating conditions [6]. Some results indicate that a 3:2 ratio is also promising [8, 23, 24]. Gasteiger et al. have observed methanol oxidation occurring more readily at room temperature on Pt–Ru alloys having low Ru contents [8]. Jusys et al. have found that in the technologically interesting regime of 0.4–0.5 V vs RHE, Pt–Ru catalysts containing small to medium amounts of Ru (3:2 atomic ratio) are most active at room temperature [25].

Although much work has been performed on catalysts for methanol oxidation, very few have investigated the performance of the catalysts over a range of temperatures, and to the best of our knowledge, none have studied the effect of varying the atomic ratio of Pt and Ru in the catalyst as a function of temperature. This work investigates the relative performance of two Pt–Ru catalysts, 3:2 and 1:1 atomic ratio, supported on carbon black over a temperature range from 25 °C to 65 °C. The catalysts are prepared from sulphito complex precursors, since by using this method, no chlorides are present when depositing the metal onto the carbon support, and it is known to produce fine particles with uniform dispersion [12].

2. Experimental details

2.1. *Preparation of carbon-supported Pt–Ru anode catalysts*

Both of the catalysts investigated were produced in the following manner. First, the catalyst precursors, $Na_6Pt(SO_3)_4$ and $Na_6Ru(SO_3)_4$, were prepared from H_2PtCl_6 and $RuCl_3$, respectively [12]. $Na_6Pt(SO_3)_4$ was dissolved in 0.5 M H_2SO_4 which was further diluted down using Millipore® water (18 MΩ); the pH was adjusted to 5.0 by the addition of 10% NaOH solution. 30% H_2O_2 was added dropwise with constant stirring causing a small amount of gas evolution. The pH was readjusted to 5.0. The required amount of $Na_6Ru(SO_3)_4$ was dissolved in 0.5 M H_2SO_4 and added dropwise to the Pt solution with constant stirring, causing more gas evolution. The amount of the precursor used was varied to give either a Pt:Ru, atomic ratio of 1:1 or 3:2 in the final catalysts. After gas evolution had ceased, the pH of the solution was again raised to 5.0. A carbon slurry consisting of Vulcan XC-72R carbon black dispersed in Millipore® water was agitated in an ultrasonic water bath and then added slowly to the solution. This mixture was stirred for 30 min to allow thorough mixing. $H_2(g)$ was bubbled through the solution for 1 h. The suspension was then allowed to settle overnight, filtered and washed with copious amounts of hot Millipore® water. Following this, the catalyst was dried overnight at 80 °C.

Once dried, 100 mg of the catalyst powder was mixed with 353 mg Nafion® solution (5% in aliphatic alcohols, Du Pont) and then diluted with a 1:1 mixture of Millipore™ water and 2-propanol (Merck). The resulting ink was then placed in an ultrasonic bath until the catalyst powder had fully dispersed, (about 15 min). This ink was then sprayed onto a piece of TGPH-060 Toray carbon paper which was kept at 130 °C throughout the process. A more detailed description of this procedure to prepare gas diffusion electrodes by the hot spraying method can be found elsewhere [26].

2.2. *Electrochemical half-cell measurements*

To test the anode catalysts in a half cell arrangement, a 12 mm diameter disc was mechanically punched out of the electrode sheet and placed in a Kel-F® electrode holder. Electrical contact was established to the rear of the electrode by means of a gold wire. A silicon rubber washer was used to seal the electrode into the holder, and this also maintained the geometrical area of the electrode exposed to the electrolyte at 0.5 cm^2. The design of the electrode holder allowed for a stream of Ar gas to pass around the back of the electrode. In turn, the holder was placed in a water-jacketed three-electrode glass cell fitted with a Luggin capillary contacting the reference electrode (Hg/Hg_2SO_4 (MMS), Sentek-UK Ltd), which was positioned outside the thermal jacket of the cell in order to maintain isothermal operation at room temperature. The counter electrode consisted of a Pt gauze positioned at the opposite side of the cell to the working electrode. The cell design also facilitated the purging of the electrolyte with Argon during operation.

The electrodes were tested for methanol oxidation in an Argon saturated electrolyte consisting of 1.5 M CH_3OH (methanol) and 1 M H_2SO_4 at 25, 45 and 65 °C. Cyclic voltammetry and polarization data were collected using a HEKA PG310 potentiostat/galvanostat system. At each temperature 10 cyclic voltamograms (CV) were collected, followed by two steady state polarization curves. The CVs were run between −650 and 850 mV vs MMS, at a scan rate of 20 mV s^{-1}. Polarization data was collected with the cell under galvanostatic control. Each value was collected after allowing the electrode to reach a steady-state equilibrium, usually after 3–5 min. The data collection was halted when the cell was no longer giving a steady potential for a given current.

3. Results and discussion

Figure 1 shows typical examples of the first 10 CVs in 1 M H_2SO_4 and 1.5 M MeOH, for the 1:1 atomic Pt–Ru catalyst, at 25 °C. These show methanol oxidation commencing on the positive sweep at about −0.25 V vs MMS, and ceasing when monolayer oxide passivates the surface after ca. 0.55 V vs MMS. On the reverse sweep, oxidation of methanol recommences at about 0.15 V vs MMS, with the increased availability of catalytically active surface sites following the reduction of the oxide layer. An electrode conditioning process can clearly be seen as the methanol oxidation current increases with the number of cycles and the forward scan peak position shifts to higher potentials. This process appears to be constant after nine cycles since the 9th and 10th (and subsequent) cycles overlap each other. It is widely accepted that the state of an electrode surface is a reflection of its past history, and that its electrochemical response is a function of the pretreatment of the electrode. Thus, because of this conditioning effect, the electrodes for each catalyst were subjected to identical testing regimes to prevent any differences observed arising from the electrode history. The actual cause and effect of this conditioning is unknown, but is being investigated more thoroughly and will be reported shortly [27]. Important effects of cycling may include (a) possible catalyst rearrangement, and (b) Nafion® swelling and movement within the catalyst layer. It is reasonable to suppose that such a conditioning process could be utilized to increase the performance of any Pt–Ru/C catalysts towards methanol oxidation. The CV responses of the 3:2 atomic Pt–Ru catalyst are very similar in nature to those shown in Figure 1. This catalyst also showed a similar conditioning effect, but slightly larger currents are passed.

To investigate the effect of temperature on the activity of the two carbon supported Pt:Ru catalysts towards methanol oxidation, polarization experiments were carried out at 25, 45 and 65 °C. Figure 2 shows the mass activity plots for the two catalysts obtained at 25 °C.

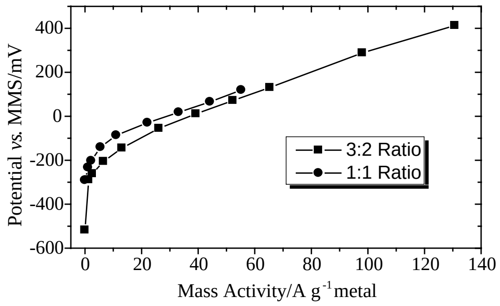

Fig. 2. Mass activity curves for 3:2 and 1:1 atomic ratio, 30% w/o Pt–Ru/C catalysts, at 25 °C in 1 M H_2SO_4 and 1.5 M MeOH.

Such mass activity plots take into account normalization for the loadings used. It is clearly seen that the 3:2 catalysts demonstrate superior performance at all of the currents investigated, over the entire range of polarization. This result is therefore consistant with the CV data presented in Figure 1. It is also interesting to note that the 3:2 catalyst is able to maintain a much higher value for the maximum current drawn from the cell than the 1:1 catalyst, at this operating temperature: 130 A g^{-1} compared to 55 A g^{-1}.

Upon raising the temperature to 45 °C both the catalysts show increased currents in the CV responses due to methanol oxidation, with the increase most noticeable for the 1:1 Pt–Ru catalyst. An example of the effect for this catalyst is presented in Figure 3, where the 10th CV is recorded at each temperature. This result is to be expected from the increase of methanol oxidation kinetics with temperature. However, as shown in Figure 4, the I/V plots for the two catalysts differ significantly from those obtained at 25 °C. Most notably the two curves now cross over with the 1:1 catalyst displaying a superior performance at currents above 62 A g^{-1}, while at currents below this level, the 3:2 catalyst offers a superior performance. It is also noticeable that the maximum currents that can be sustained by each catalyst at 45 °C are now very similar with the 1:1 catalyst having a slightly higher value at 220 A g^{-1} compared to 196 A g^{-1} for the 3:2 catalyst. While this

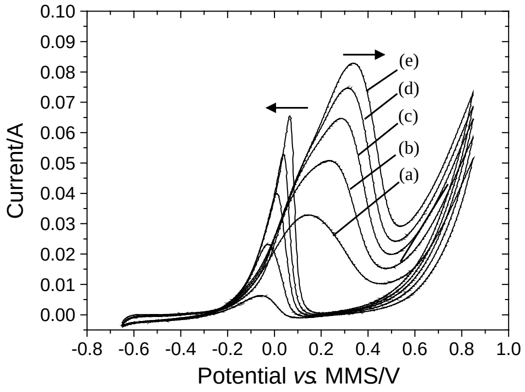

Fig. 1. (a) 1st, (b) 3rd, (c) 5th, (d) 7th and (e) 10th cyclic voltamogram (−0.65 to 0.85 V vs MMS) of 30% w/o 1:1 Pt:Ru/C catalyst at 25 °C in 1 M H_2SO_4 and 1.5 M MeOH, at 20 mV s^{-1}.

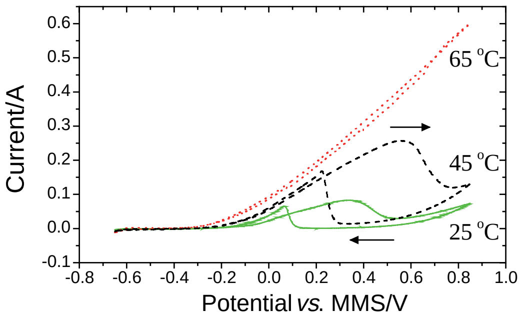

Fig. 3. 10th cyclic voltamogram (−0.65 to 0.85 V vs MMS) of the 30% w/o 1:1 Pt–Ru/C catalyst at 25, 45 and 65 °C in 1 M H_2SO_4 and 1.5 M MeOH at 20 mV s^{-1}.

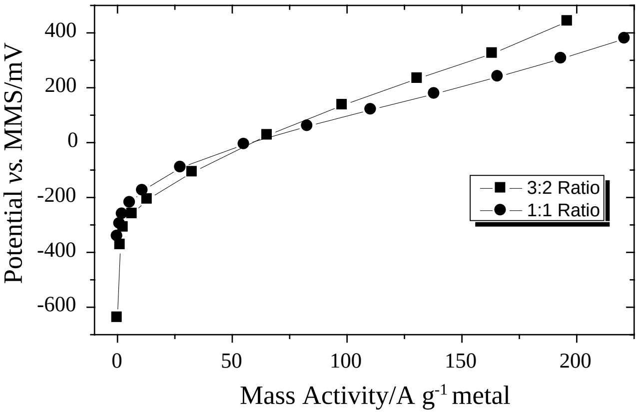

Fig. 4. Mass activity curves for 3:2 and 1:1 atomic ratio, 30% w/o Pt–Ru/C catalysts, at 45 °C in 1 M H_2SO_4 and 1.5 M MeOH.

represents a significant increase for the 3:2 catalyst over its value at 25 °C, the value for the 1:1 catalyst at 45 °C is a dramatic improvement on the 55 A g^{-1}, seen at the lower temperature.

Figure 3 also shows an example of a CV recorded at 65 °C for the 1:1 catalyst. This CV has a completely different shape to the proceeding CVs, recorded at 25 and 45 °C, indicating that there are significant temperature effects on the activity of the 1:1 catalyst. The CV for the 3:2 catalyst at 65 °C did not change in the same way and there is only a small increase in the current passed, with the 'classical' methanol oxidation shape in the CVs being retained at each temperature.

The effect on the mass activity plots of raising the temperature to 65 °C for both supported catalysts is demonstrated in Figure 5. The change in methanol oxidation behaviour is remarkable, with the 1:1 catalyst now displaying a superior performance compared to the 3:2 catalyst at all current values, although the 3:2 catalyst is still close in performance to the 1:1 catalyst at current densities lower than 30 A g^{-1}. The maximum sustainable current is again increased for both catalysts, with the 1:1 catalyst highest at 386 A g^{-1} compared to 260 A g^{-1}, for the 3:2 catalyst. The change in relative performance of the two catalysts clearly indicates that the 1:1 catalyst has a greater temperature dependence than the 3:2 catalyst. It is possible even that both catalysts operate a different mechanism towards methanol oxidation. It is known that the ratio of Pt to Ru has a dramatic effect on the performance of the catalyst obtained towards methanol oxidation. Methanol oxidation is most often explained in terms of the bifunctional mechanism [1, 3, 4, 6, 9]. According to this view, Pt is the species responsible for dissociative dehydrogenation of methanol, while the Ru sites provide a source of oxygenated species for removal of carbon containing fragments. It is known from the literature that as temperature increases, methanol dehydrogenation also occurs on Ru sites [3, 4, 6, 28]. Hence, a ratio of 1:1 should be a more favourable composition for operation at higher temperatures, since more active sites for the dehydrogenation step are provided. But at lower temperatures, only Pt is found to be active towards methanol dehydrogenation, since this process is a highly thermally activated process on Ru sites, that is, Ru sites play no part in the dehydrogenation process and instead only serve for removal of carbon containing species at low temperature [8]. Hence, at low temperatures, a Pt rich 3:2 catalyst is required to promote faster methanol oxidation kinetics relative to a 1:1 catalyst.

Platinum is also known to be reasonably active towards CO oxidation at higher temperatures, although still not as active as ruthenium, and thus the oxidation mechanism may be different to that at lower temperatures, where a higher platinum content in the form of a 3:2 catalyst is needed to show higher performance towards methanol oxidation. These factors obviously suggest that temperature has a dramatic effect on the composition and surface morphology of the 1:1 Pt–Ru catalyst, since its methanol oxidation behaviour is so radically different at the higher temperature. Arico et al. believe that catalysts characterized by a higher degree of alloying and metallic behaviour on the surface appear to be more active towards methanol oxidation at higher temperatures [29]. Since CO poisoning is less prevalent at these temperatures, they believe that the physico-chemico properties of the catalysts have less influence on

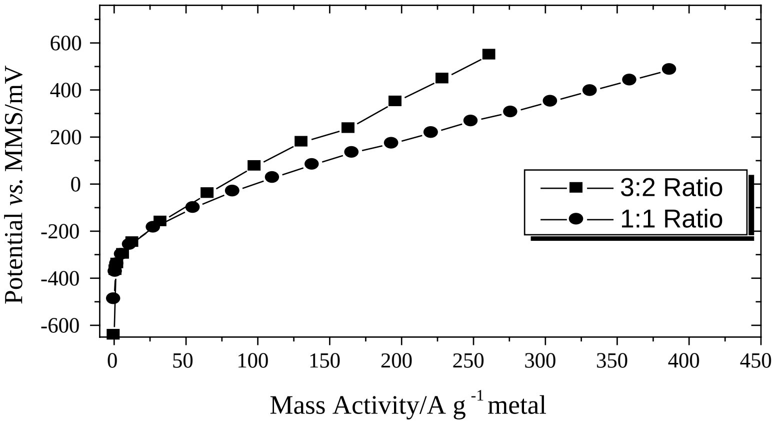

Fig. 5. Mass activity curves for 3:2 and 1:1 atomic ratio, 30% w/o Pt–Ru/C catalysts, at 65 °C in 1 M H_2SO_4 and 1.5 M MeOH.

the anode electrochemical behaviour in an operating fuel cell at higher temperatures.

There is still an ongoing dispute over which catalyst is better under a given set of conditions, and the need for significant further investigation of both the electrochemical behaviour and the morphology and composition of each of the different catalysts, in an effort to correlate structure and reactivity is evident. It would be appropriate to examine the powder X-ray diffraction patterns of both the 1:1 and 3:2 Pt–Ru/C catalysts, in an attempt to determine structural differences between the two catalysts [30]. The use of a technique such as X-ray photoelectron spectroscopy (XPS), might help determine whether there are changes in the electronic environments around the various metallic sites due to charge transfer, or if activation occurs directly as a result of the formation of weakly bonded oxygen providing species on Ru-sites, in the neighbourhood of methanolic residues adsorbed on platinum sites [30]. Temperature-dependent methanol stripping voltammetry may also provide further electrochemical evidence of differences in performance for the two catalyst systems [29]. Initial experiments involving variations in the catalyst weight loading and associated changes in morphology by use of transmission electron microscopy (TEM) have been reported recently [26, 28]. TEM analysis can show variations in average particle size and whether or not particles tend to aggregate as the ratio of Pt to Ru is varied. Such features would have a dramatic effect on the electrocatalytic behaviour of the catalysts concerned. A further systematic TEM and EXAFS study of the catalysts, will be reported shortly [31]. It is hoped that this will help determine particle structure and composition and attempt to relate this to reactivity. Therefore, the significant conclusion from the present results is that when designing fuel cell catalysts, the composition of the catalyst used should be tailored with respect to the exact operating conditions in order for the fuel cells to perform at optimum levels.

4. Conclusions

The operating temperature has a marked effect on the performance of a catalyst for methanol oxidation and it can even change the relative performance of catalysts of varying composition. Therefore, it is obvious that the operational temperature of a DMFC fuel cell has a direct effect on the choice of optimum catalyst for the system. A Pt–Ru catalyst with an atomic ratio of 3:2 would be more suitable for low temperature fuel cells, but due to the reversal of behaviour observed at higher temperatures, a catalyst with a 1:1 atomic ratio would demonstrate higher activity and make a more suitable choice for DMFCs operating at elevated temperature. The results also show that in order to be able to properly assess the performance of a catalyst it is necessary to mimic the actual operating conditions as carefully as possible.

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