

# A comparative study of PtRu and PtRuSn thermally formed on titanium mesh for methanol electro-oxidation

L.X. Yang<sup>1</sup>, R.G. Allen, K. Scott\*, P. Christenson, S. Roy

*School of Chemical Engineering and Advanced Materials, University of Newcastle, Merz Court, Newcastle upon Tyne, NE17RU, UK*

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## Abstract

PtRu and PtRuSn catalysts have been made by thermal decomposition of chloride precursors on different types of and combinations of titanium mesh for the electro-oxidation of methanol. The catalytic activity of the electrodes is determined by galvanostatic polarization measurement and SEM is employed to study their morphology and structure. The electrochemical performance of the catalysts thermally deposited on a double layer titanium mesh shows a large increase in catalytic activity for methanol electro-oxidation, compared to other electrodes. Such an electrode, with a different anode structure to that of carbon supported catalyst, possesses good electrochemical performance and may be a promising alternative anode for direct methanol fuel cells (DMFCs).

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## 1. Introduction

Direct methanol fuel cells (DMFCs) have received great attention due to their potential use as low temperature power sources [1]. A major challenge for the successful application of the DMFCs is the enhancement in catalytic activity of platinum-based anode catalysts towards the electro-oxidation of methanol. It is well known that the addition of Ru- to Pt-based catalysts significantly lowers the overpotential for the methanol oxidation reactions through a so-called bifunctional mechanism [2,3], in which the atoms of different metals act independently and perform different functions. Methanol adsorption and decomposition takes place on platinum, while the alternative metal (Ru) atoms provide preferred sites to bind OH species. Attempts have been made to develop catalysts that either enhance the oxidation of CO and/or that are

simply more CO tolerant, by alloying platinum with other metals. Among the binary systems, the Pt-Ru combination has proved to be the most successful at enhancing electrocatalytic activity. Other platinum combinations, such as tin [4], molybdenum [5] and tungsten [6,7] have been tried successfully. Ternary systems, such as Pt-Ru-W and Pt-Ru-Sn have also been studied and it is claimed that the addition of W and Mo to the binary Pt-Ru catalyst improves electrocatalytic activity towards ethanol oxidation [8]. While the main approach discussed above is to change the catalyst composition and, hence change the mixed electrical configuration, attempts have been made to increase the catalytic activity by preventing the main catalyst particles from growing. The methods included, using different methods to prepare the carbon supported Pt-based catalysts in the presence of higher metal loadings [8] or to directly use finer carbon powders to increase the dispersion of the catalysts particles on the carbon supports.

In the present work, instead of carbon powder, a titanium mesh was employed as the catalyst support, to prepare PtRu and PtRuSn catalyzed electrodes by thermal decomposition of chloride precursors. Our preliminary results have shown

\* Corresponding author. Tel.: +44 191 2228 700; fax: +44 191 2225 292.

E-mail addresses: [lianxi.yang@nrc.gc.ca](mailto:lianxi.yang@nrc.gc.ca) (L.X. Yang), [k.scott@ncl.ac.uk](mailto:k.scott@ncl.ac.uk) (K. Scott).

<sup>1</sup> Present address: Shape Transfer Processes, Integrated Manufacturing Technologies Institute, Room 240-1, 800 Collip Circle, Ontario N6G 4X8, London. Tel.: +519 430 7133; fax: +519 430 7064.

that the characteristics of electrochemical methanol oxidation on catalysed titanium mesh are comparable to those achieved with carbon-supported PtRu catalysts [9,10]. With the aim of further improving the electrochemical performance, combinations of different types of titanium mesh are also employed as supports. It is shown that the catalytic activity of the catalysts supported on such a combination is further improved and may be a promising alternative anode for DMFCs.

## 2. Experimental

A thermal decomposition method was used to prepare electrocatalyst on a titanium mesh support. The method mainly consists of etching titanium mesh in 10% oxalic acid at 80 °C for 1 h; rinsing with distilled water under agitation in an ultrasonic water bath; applying the catalyst layer to the etched substrate by dipping in a precursor (e.g. 0.2 M metal chloride in isopropanol) and finally firing the sample in an atmosphere at 400 °C for 1 h. The electrodes fabricated in this way were designated PtRu/Ti and PtRuSn/Ti (Pt:Ru = 0.5:0.5 in atomic ratio; Pt:Ru:Sn = 0.5:0.4:0.1). The catalyst loading was measured by weighing the sample before and after catalyst application, using a digital balance accurate to within 0.01 mg.

Different types of Ti mesh supplied Dexmet were used in this study (Fig. 1) and their measured geometric parameters are listed as in Table 1.

Table 1  
Measured geometric parameters of the titanium mesh (Dexmet Corporation)

Parameters	Type 1	Type 2	Type 4
		<i>Opening size (mm)</i>	
LWD	1.28	1	0.52
SWD	0.72	0.64	0.36
		<i>Strand width (mm)</i>	
SW	0.14	0.18	0.08
Measured mesh thickness (mm)	0.2	0.35	0.1

Images of the mesh and catalysts were taken with a JEOL 6300 SEM, equipped with a computer with digital image software. Electrochemical measurements were performed, using a Gill AC potentiostat (ACM Instruments), controlled by a Windows Personal Computer loaded with ACM Sequencing Software. All experiments were conducted in an N<sub>2</sub>-de-aired three-electrode cell. The working electrodes were lacquered (Microshield, Hi-Tek Products Ltd.), leaving a window of 1 cm<sup>2</sup> exposed; the counter electrode was a platinum mesh measuring 25 mm × 25 mm and the reference electrode was a mercury sulfate (MMS) (Hg/Hg<sub>2</sub>SO<sub>4</sub>/0.5 M (0.617 V, RHE). In this paper all electrode potentials are reported versus the reversible hydrogen electrode (RHE). Electrolytes of 0.5 mol dm<sup>-3</sup> (M) H<sub>2</sub>SO<sub>4</sub> + *x* M CH<sub>3</sub>OH were prepared with reagent grade chemicals and deionised water.

The data from galvanostatic electrochemical measurements was collected after 3-min polarisations. These

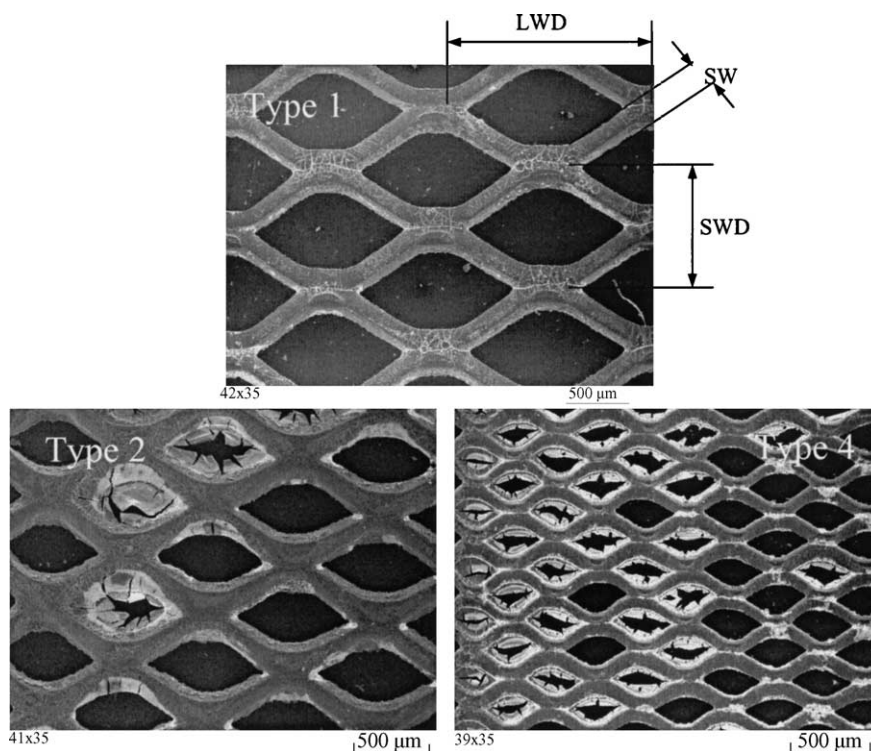


Fig. 1. SEM Image of PtRu catalysts thermally deposited on Ti mesh, showing the morphologies of the different mesh types.

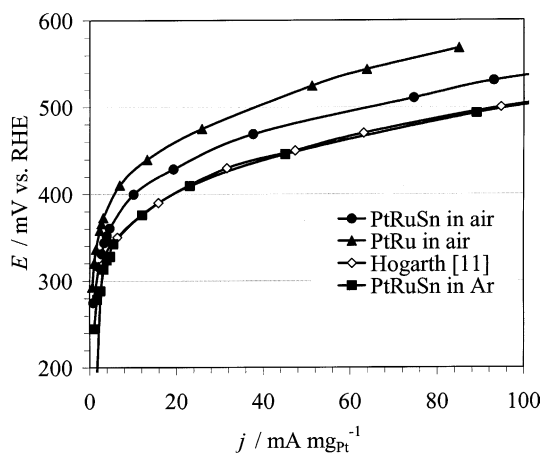


Fig. 2. Galvanostatic polarisation plots in 2 M  $\text{CH}_3\text{OH}$  + 0.5 M  $\text{H}_2\text{SO}_4$  ( $60^\circ\text{C}$ ) on PtRu/Ti and PtRuSn/Ti catalysts thermally formed at  $400^\circ\text{C}$  in air and argon respectively (Ti mesh is Type 1).

measurements were obtained after the anodes were conditioned by immersing and cycling, between 0.0 and 900 mV in 0.5 M  $\text{H}_2\text{SO}_4$  until a stable electrode state was reached.

### 3. Results

The methanol oxidation activities on the Pt-based mixed oxide catalysts, thermally formed on the titanium mesh supports, were mainly determined from potential-time transients recorded at different constant current densities. The data obtained is presented as potential-current plots. To investigate the effect of Ru and Sn additives on the Pt catalytic activity for methanol electro-oxidation, the monitored currents were normalized for the Pt mass and are, hence referred to  $j$  ( $\text{mA mg Pt}^{-1}$ ) in the associated figures. This allows for more direct comparison of the anode catalytic activity between the different electrodes.

#### 3.1. Effect of Sn addition

Fig. 2 shows the catalytic activity obtained from galvanostatic polarisation measurements in 2 M  $\text{CH}_3\text{OH}$  + 0.5 M  $\text{H}_2\text{SO}_4$  ( $60^\circ\text{C}$ ) on thermally formed PtRu/Ti and PtRuSn/Ti electrodes. The polarised potentials at a current of  $80 \text{ mA mgPt}^{-1}$  on PtRu/Ti and PtRuSn/Ti thermally formed in air are 550 and 510 mV, respectively. This shows that the addition of Sn increased the catalytic activity of the PtRu mixed oxide. The value on the PtRuSn/Ti electrodes thermally formed in argon is about 480 mV, showing a further improvement of the catalytic activity. Fig. 2 also gives the catalytic activity of a carbon-supported PtRu catalysts (1.5 mg loading with a 1:0.5 atomic ratio of Pt:Ru) [11] for a comparison. It shows that the activity of the PtRuSn catalysts thermally formed on the titanium mesh in argon is comparable to one of the most active carbon supported catalysts.

#### 3.2. Effect of titanium mesh type

To increase the catalytic activity, different types of titanium mesh are used as supports to thermally deposit the PtRu catalysts. Fig. 5 shows the galvanostatic performance on the different electrodes in 2 M  $\text{CH}_3\text{OH}$  + 0.5 M  $\text{H}_2\text{SO}_4$  ( $60^\circ\text{C}$ ). The PtRu catalyst, thermally formed on Type 2 mesh possesses the highest catalytic activity with a polarisation potential 460 mV at a current density of  $80 \text{ mA mgPt}^{-1}$ . This value is 550 and 490 mV, for the Type 1 and Type 4, respectively. The above results can be attributed to the different opening areas of the mesh supports, as shown in Table 1. This data indicates that an increase in the catalytic activity can be achieved by employing different catalyst supports due to the variation in available mesh (and thus catalyst) surface area.

#### 3.3. Effect of different combinations of the titanium mesh as supports

To further improve the catalytic activity, different combinations of titanium mesh and carbon paper have been used as the catalyst support. Fig. 6 shows the electrochemical performance on the PtRu catalysts thermally deposited on a double layer structure of titanium–titanium (Ti–Ti structure) as well as on a triple layer support of titanium–carbon paper–titanium (Ti–C–Ti). Prior to applying the catalysts the two mesh layers were connected by spot welding.

A significant increase in catalytic activity has been achieved with the catalysts deposited on the double layer mesh. The measured potential of the catalyst deposited on single mesh (Type 4) is about 490 mV at a current density of  $80 \text{ mA mgPt}^{-1}$  (Fig. 5, Type 4). This value on the double layer mesh is approximately 350 mV, some 140 mV lower than on the single mesh. The onset potential for the two electrodes is also significantly different: a value of about 200 mV on the double layer (Fig. 6) and approximately 270 mV on the single layer (Fig. 5). Thus, such an electrode, with a different anode structure to that of carbon supported catalysts, possesses an exceptional good catalytic activity for methanol oxidation and may be a promising alternative electrode for fuel cells.

The catalytic activity on the triple layer structure (Ti–C–Ti) is lower than that of double layer. The measured potential on the electrode at  $100 \text{ mA cm}^{-2}$  is only 380 mV (Fig. 6). It is evident that different combinations of the optimized catalysts (e.g. PtRuSn) and different support structure are very important to increase the catalytic activity and need to be further investigated.

### 4. Discussion

Generally, two models are described to explain the mechanism affecting the catalytic activity by additives: either to provide sites for water adsorption in a bi-functional model

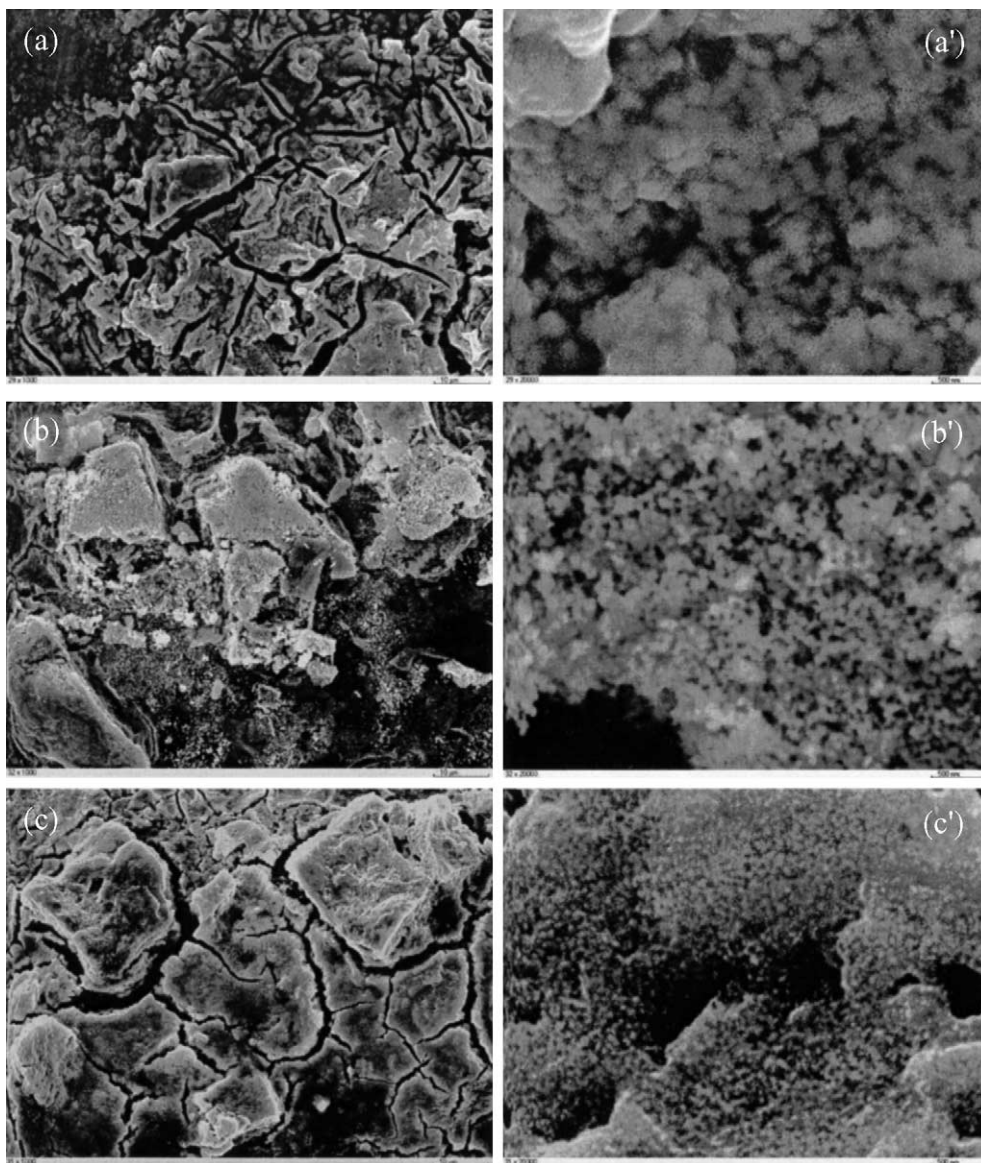


Fig. 3. SEM images on the different electrodes as thermally formed in argon at different temperature (a–a': PtRu/Ti at 500 °C; b–b': PtRuSn/Ti at 500 °C and c–c': PtRuSn/Ti at 400 °C). The magnification of images a, b and c is 10 μm and of a', b' and c' is 500 nm.

or to modify the electronic properties of Pt by contributing d-electron density in an electronic model [12]. It is likely that the addition of Sn and Ru to the Pt increases the activity of oxidation of methanol in both ways by forming the mixed oxide catalysts.

SEM was employed to look at morphology and structure of the catalysts. The SEM images of the thermally formed catalysts on titanium mesh at different temperatures and in different atmospheres are shown in Fig. 3. At low magnification the morphologies appear similar with a uniform distribution of small cracks (Fig. 3a–c). However, close inspection of the electrodes at high magnification reveals that the catalysts consist of ultra-fine particles both in the flat planes and in the microscopically visible cracks (Fig. 3a'–c'). In particular, the particle size depends on the firing condition, such as heat treatment temperature and firing atmosphere. For example,

while the particle size for the PtRuSn electrode thermally formed at 400 °C (Fig. 3c') was of 50 nm, a much bigger size (ca. 120 nm) was obtained with the electrode formed at 500 °C (Fig. 3b'), indicating a significant firing temperature effect. The addition of Sn also significantly reduces the particle size of Pt-based oxide catalyst; a particle size of approximately 200 nm for the PtRu electrodes was observed (Fig. 3a'), compared to 120 nm for the PtRuSn electrodes (Fig. 3b').

The surface areas of the catalysts can be roughly estimated according to the following equation, assuming homogeneously distributed and spherical particles [6]:

$$S = \frac{3}{r\rho} \quad (1)$$

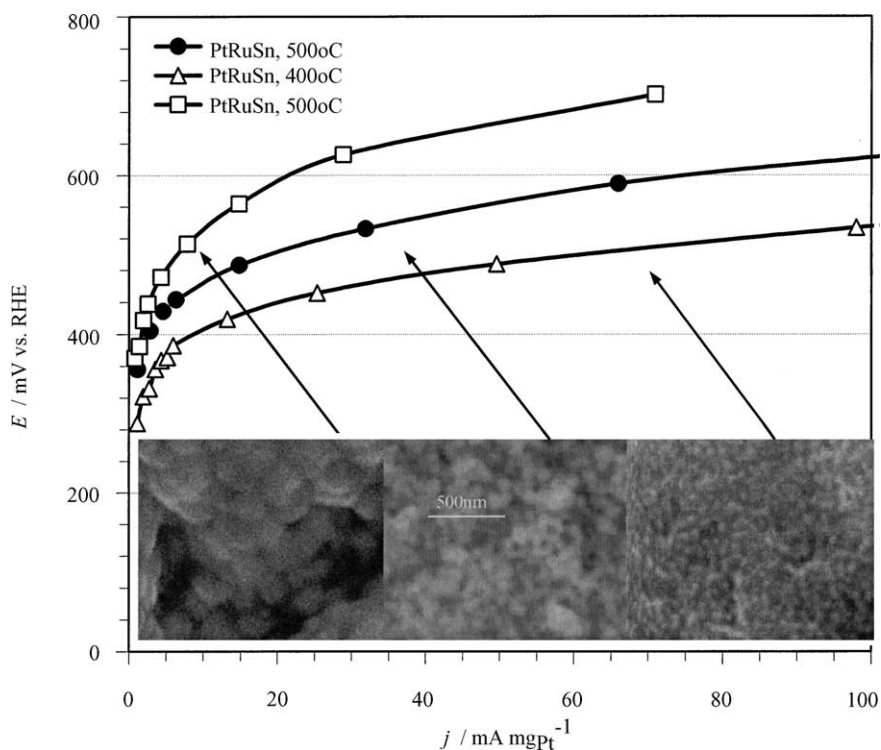


Fig. 4. Galvanostatic polarisation plots in 2 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> (60 °C) on PtRu/Ti and PtRuSn/Ti catalysts thermally formed in argon at different temperatures, showing the correlation of the particle size (from SEM images, insertion) and catalytic activity (Ti mesh is Type 1).

where  $r$  is the particle radius and  $\rho$  the density of either the PtRu or PtRuSn alloy. While the particle radius is assumed to be equivalent to one half of the average PtRu and PtRuSn diameter estimated from SEM images, the  $\rho$ -values are calculated, using the atomic percentages of Pt (at.%<sub>Pt</sub>), Ru (at.%<sub>Ru</sub>) and Sn (at.%<sub>Sn</sub>) as well as the Pt ( $\rho_{Pt}$ ), Ru ( $\rho_{Ru}$ ) and Sn ( $\rho_{Sn}$ ) densities of 21.45, 12.41 and 7.31 g cm<sup>-3</sup> [13], respectively, using the following equation:

$$\rho = \sum \rho_i \times (\text{at}\%_i) \tag{2}$$

where  $i$  represents Pt, Ru or Sn.

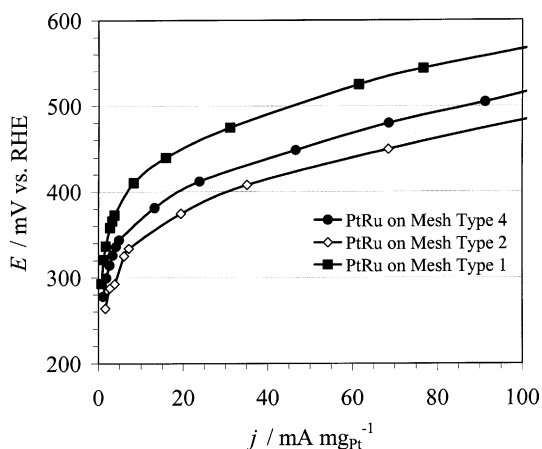


Fig. 5. Galvanostatic polarisation plots in 2 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> (60 °C) of the PtRu catalysts thermally deposited on the different mesh types at 400 °C in air for 1 h.

The surface areas, thus calculated are: 1.7, 3.0 and 7.3 m<sup>2</sup> g<sup>-1</sup>, for PtRu thermally formed at 500 °C and PtRuSn formed at 500 and 400 °C, respectively. Therefore, a significant increase of the surface area by the addition of Sn to PtRu is observed. This is evidently one reason why the electrochemical activity of the mixed oxide PtRuSn, with a nominal tin content about 10 mol%, can be increased. Fig. 4 shows that there is some correlation between the catalyst morphology and microstructure and the electrode electrochemical activity, if it is assumed that the mechanism of methanol oxidation

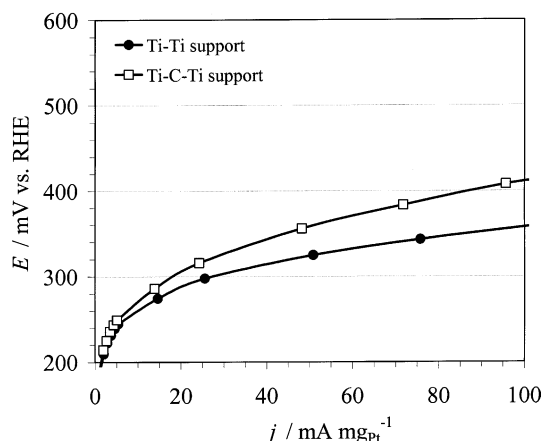


Fig. 6. Galvanostatic polarisation plots in 2 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> (60 °C) of the PtRu catalysts thermally formed at 400 °C in air on different structure support (Ti-Ti is titanium Type 4). (Ti-C-Ti: Ti is titanium Type 4 and C is carbon paper).

is the same on both types of electrodes. The decrease in particle size by the addition of Sn to the catalysts was also reported in other systems [14,15].

It should again be noted that the calculation of these surface area is only approximate and the values obtained need to be used with caution. It has been frequently reported that the incorporation of ruthenium or tin into the platinum crystal lattice can be evidenced from XRD. A lower lattice constant of fee Pt lattice due to ruthenium incorporation was observed [6,8] and a higher lattice constant in the case of tin [8]. The lattice changes are usually indications of an alloy formation. However, evidence from XPS has also showed that not all of the Ru phase or tin phase is incorporated into the Pt lattice [6]. Therefore, the assumption of the formation of an alloy, using Eq. (1) to calculate catalyst surface areas unavoidably causes errors.

It is also noted that the calculated surface areas of the PtRu catalysts prepared in this study is only approximately one 10th of that of the PtRu catalyst supported on carbon powders prepared, using a chemical reduction route, commonly used for the preparation of fuel cell catalysts [6]. It is therefore, obvious that the area factor is not the only reason for such low catalyst surface area of the PtRu catalysts thermally prepared on titanium mesh having a comparable catalytic activity to that of the carbon-supported catalysts (Fig. 2). While the catalytic surface area plays an important role for the catalysts thermally prepared on titanium mesh, their electronic properties may make significant contributions to their electrochemical performance.

The catalysts prepared thermally at the temperature range employed in this work are actually composed of metal oxides, such as RuO<sub>2</sub> and SnO<sub>2</sub> [14–16]. It is known that RuO<sub>2</sub> and SnO<sub>2</sub> both have a tetragonal rutile structure and the ionic radius of the two metals differs only by 5%. They have the same valence and satisfy the Hume-Rothery conditions for the formation of a substitutional solid solution [14]. In turn, at the temperature employed for the thermal preparation, the Ru or Sn is more likely incorporated into the Pt lattice to partly form the PtRuSn ternary alloy, as opposed to the carbon supported catalyst prepared at the lower temperature used in the chemical routine. Thus, the bifunctional mechanism may play a more important role in promoting the Pt catalytic activity with the addition of Ru and Sn. Additionally, it is reported that catalysts for ethanol oxidation have found increased performance with the addition of Sn to the PtRu, which can be possibly explained by the complementary interaction of SnO<sub>2</sub> and RuO<sub>2</sub> [17]. The ratio of the two metals within the catalyst layer is important, as reflected by the data shown in Fig. 2. Electrodes formed in an Argon atmosphere were found by EDX to be rich in Sn, while those prepared in Air, were found to be rich in Ru. This was independent of the Pt loading, which was not seen to change with a change in thermal atmosphere. This topic is still in its early stages of research in many institutes, including our own. Indeed, our current results demonstrate the need for further exploration of the mechanisms involved.

In addition, ruthenium dioxide essentially exhibits metallic behaviour with a resistivity of about  $5 \times 10^{-5}$  ohm cm [18]. This high conductivity explains its use as an electrode. Most importantly, a metastable solid solution of RuO<sub>2</sub>/TiO<sub>2</sub>, or even an extremely fine mixture of the two components, can be formed at temperatures between 300 and 500 °C [19], which is the temperature range employed in this study. The electronic interaction between Ru and Ti by forming a mixed RuO<sub>2</sub>/TiO<sub>2</sub> layer between the catalyst layer and titanium substrate could significantly decrease the ohmic effect due to formation of TiO<sub>2</sub> oxide on the titanium substrate.

## 5. Summary

PtRu and PtRuSn catalysts have been thermally deposited on various types of titanium mesh structures. The resultant catalytic performance of such electrodes for the electro-oxidation of methanol shows a significant improvement over previous electrodes [9,10]. The addition of Sn decreases the particle size of the mixed catalysts and, hence increases the catalytic activity for electro-oxidation of methanol. The most significant improvement has been obtained on the catalysts thermally deposited onto double layer Ti mesh.

The electrochemical data so far collected for the catalysts coated on Ti mesh are interesting, but not fully representative of the electrodes employed in real DMFC. The catalytic performance of the catalysts in the DMFC will be significantly affected by the potential absence of electrolyte in the methanol solution (for polymer electrolyte cells), diffusion process in the membrane, cathode performance and methanol cross-over, etc. The studies on the cell performance of the catalysts prepared by different methods are under progress.

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