# A NEW DIRECT METHANOL FUEL CELL

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Direct methanol fuel cells (DMFCs) operated at relatively low temperatures have received much attention; they are promising candidates for portable and stationary power source and electric vehicle applications. Compared to fuel cell systems using reformed $H_2$ from methanol, direct methanol fuel cells have the advantage of simple system design and cell operation. In spite of the improved performance of DMFCs using polymer electrolyte membranes (PEMs), obstacles such as low activity of reported methanol electro-oxidation catalysts still prevent their widespread commercial applications [1].

The syntheses of the catalysts can be achieved using different methods. The common preparation techniques range from impregnation, colloids, electrodeposition, sol-gel and thermal decomposition methods, etc [2]. Electrocatalytic anodes for industrial use should possess properties such as a high conductivity, thin layer of catalyst (low loading) on a cheap support to minimise electrode cost, and high physical stability. Takasu et al. have compared different methods, including thermal decomposition and sol-gel methods, to design Ru-based oxide-coated electrodes and recommended that the thermal decomposition method was an effective way for preparing highly active catalysts [3].

The present work was directed to the preparation of electrocatalyst by thermal decomposition of chlorine precursors, for electrooxidation of methanol. The electrodes were successfully operated in acidic methanol electrolytes. The catalysts have been characterized using cyclic voltammetry, AC impedance and steady state polarizations.

## ELECTROCHEMICAL ACTIVITY

It was reported [4] that for a thermally prepared $RuO_2$ catalyst on a Ti support, whilst their bulk characteristics were unchanged for the duration of the electrochemical experiments, the electrochemical behavior did change, especially in the early life of electrodes. Their electrochemical changes were attributed to so-called “hydration effects” or maturation process [5]. This process was evidenced from progressive changes in the voltammetric charges and capacitances [4], and from the electrochemical behavior which was strongly affected by the electrochemical history of the electrode. Therefore, in this work great care was taken to ensure that a stable state of the electrode was reached prior to recording voltammograms. The electrodes were cycled between 0.0 and 900 mV in 0.5 M $H_2SO_4$ until negligible variation of the current was observed. At this point the stable state of the electrode has been reached and the electrode was described as a mature. All results presented here were obtained on matured electrodes.

Fig 1 shows a typical voltammogram in acidic methanol for a Pt electrode by thermal decomposition at 400$^{o}$C. The voltammogram has a number of characteristic features. On the forward sweep a polarisable region (double layer region) is observed at the potential below 0.5 V. Generally, anodic current in this region is very low and is attributed to a progressive charge/discharge distribution due to heterogeneity of the catalyst surface. With an increase in potential, an anodic peak is observed (Peak I in Fig 1) at the potential range of 500-700mV. This peak may be attributed to dehydrogenation of methanol. This process is slow on the surface of catalysts at lower potentials, and shows an activation energy of 35 kJ mol$^{-1}$. The co-adsorbed water and methanol molecules on the platinum can also take place and has been evidenced by kinetics isotope studies on methanol oxidation [6].

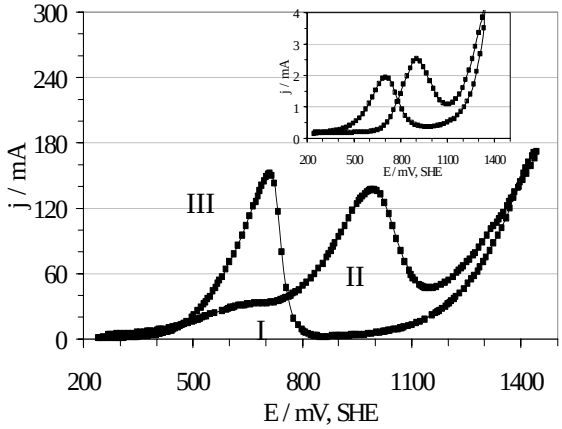


Fig 1 Voltammograms in 2M MeOH+0.5M$H_2SO_4$ (20$^o$C) on Pt thermally formed 400$^o$C (sweep rate 100mV $s^{-1}$). The insertion is on Pt metal (sweep rate 20mV $s^{-1}$).

The process related to peak I seems to be less obvious on the platinum metal electrode (Fig 1, insertion), indicating that the methanol dehydrogenation may occur more readily on the hydrated platinum oxide surface. The hydroxide bonding is presented on the oxide surface due to thermal treatment and subsequent hydration and maturation of the catalysts in electrolytes.

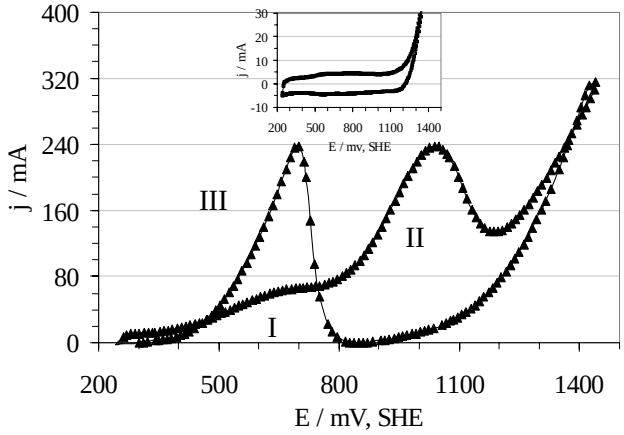


Fig 2 Voltammograms in 2M MeOH+0.5M$H_2SO_4$ (20$^o$C) on PtRu thermally formed at 400$^o$C (sweep rate 100mV $s^{-1}$). The insertion is on Ru (sweep rate 20mV $s^{-1}$).

The behavior of the PtRu electrode (Fig 2) is similar to that of the Pt electrode although peak currents are significantly higher (by an approximate factor of 2). Furthermore, the ruthenium alone possesses little activity for electro-oxidation of methanol (Fig 2, insertion) although the catalytic activity promotion of Ru with Pt catalyst is significant as indicated by comparing Fig 1 to Fig 2.

Bulk methanol oxidation begins at about 800mV and soon reaches its maximum peak at about 900mV (Peak II) and then the current begins to decline as the surface is poisoned by the formation of carbon oxides. At a potential greater than 1100 mV, methanol oxidation is driven to the catalyst surface resulting in further methanol oxidation. On the reverse sweep, re-oxidation of methanol begins at about 800 mV and reaches its peak at around 600 mV (Peak III), after which strongly bonded surface intermediates begin to block the catalyst surface.

The DMFC is usually operated with a solid polymer proton conducting membrane and with Nafion$^R$ ionomer coated onto the carbon supported electrocatalysts. To see the effect of the Nafion coating on the electrochemical performance, voltammograms were obtained on Pt with and without Nafion coating. Before performing the test, the Nafion coated electrodes were dried at 80$^o$C for half an hour and then immersed in distilled water for 24 hours. Results show that Nafion coating has only a minor effect on the performance of the electrodes even though a negative effect is anticipated due to the Nafion coating layer presenting a possible mass transfer barrier for methanol.

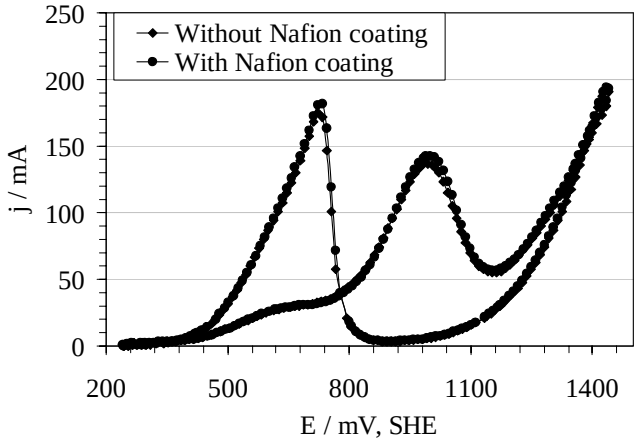


Fig 3 Voltammograms in 2M MeOH + 0.5M $H_2SO_4$ (20°C) on Pt electrode formed at 400°C (sweep rate 100mV $s^{-1}$), showing effect of the Nafion coating on the voltammetric behaviour.

Fig. 4 shows steady state anode polarisation characteristics of electrocatalysts incorporating tin with Pt/Ru. The incorporation of Sn has clearly a beneficial effect on catalyst activity with significant reduced polarisation achieved. The areas of the electrocatalysts have been estimated as 40, 100 and 190 $cm^2_{true}$ (in 1 $cm^2$ and 1mg catalysts loading) for the electrodes PtRu thermally formed at 500°C and, PtRuSn formed at 400 and 500°C respectively; Therefore, significant increase of the true area by addition of Sn to PtRu is obtained. This is evidently a reason why the electrochemical activity is increased on the mixed oxide with a nominal compositional tin content about 10 mol%. Fig 4 also shows that the catalyst morphology, microstructure and electrochemical activity. The decrease of particle size by addition of Sn to the catalysts was also reported on other systems [7,8].

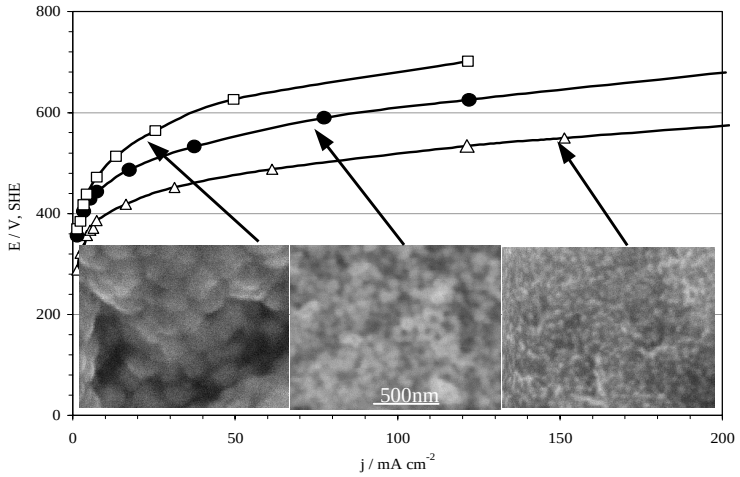


Fig 4 Galvanostatic polarisation plots in 2M MeOH+0.5M$H_2SO_4$ (60°C) on PtRu and PtRuSn catalysts thermally formed in argon, showing the correlation of the particle size (from SEM images, insertion) and catalytic activity. Δ PtRuSn, 400°C
● PtRuSn, 500°C, ❑ PtRu, 500°C

## CONCLUSIONS

PtRu and PtRuSn catalysts have been prepared by thermal decomposition of respective chloride precursors. The resulted catalytic performance of such electrodes for electrooxidation of methanol shows significant improvements over past electrodes. The addition of Sn decreases the particle size of the mixed catalysts and hence increases the catalytic activity for electro-oxiation of methanol.

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