



## Short communication

## A liquid–gas phase mixed-reactant fuel cell with a RuSeW cathode electrocatalyst

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## ABSTRACT

Some data in mixed-reactant fuel cells (MRFC) at Newcastle using formic acid, methanol and ethanol are reported. The importance of using a fuel-tolerant selective cathode catalyst has been identified. The influence of fuel and oxidant conditions and feeding patterns has been evaluated. The cell performance using air, oxygen and hydrogen peroxide is reported. The highest peak power density of  $16 \text{ mW cm}^{-2}$  was obtained with formic acid. The MRFC gave power densities approximately half those of a conventional, un-mixed-reactant fuel cell.

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## 1. Introduction

Fuel cells operated with mixed reactants have attracted academic and industrial interest for a long time [1,2] and there were some renewed research activities in recent years [3–7]. The main driving force to develop a mixed-reactant fuel cell (MRFC) was to speed up commercialisation of the fuel cell technology via reducing capital and material costs. There are several challenging issues for further development of the MRFC technology, such as electrode selectivity, performance potentials and lifetime. Measures have been introduced to solve some of these problems, such as the use of fuel-tolerant cathode catalysts [6] and changing reaction selectivity by adjusting electrode hydrophobicity [7]. However, research and development in MRFCs has been relatively slow, compared to other fuel cells, and more studies are required to address the challenging issues. This paper reports some recent research at Newcastle in MRFCs using a ruthenium–selenium–tungsten cathode catalyst and fuels of methanol, ethanol and formic acid.

## 2. Experimental

A conventional fuel cell configuration was used in this research. Gas diffusion layers for membrane electrode assemblies were made using Ketjen-300J carbon black ( $1 \text{ mg cm}^{-2}$ , Akzo Nobel),

Teflon (20 mass% Teflon of the overall catalyst and carbon weights) and carbon paper (Toray, TGP120, E-TEK). Electrocatalyst layers were made from carbon-supported catalysts, Nafion® ionomer (15 mass% of the overall catalyst and carbon) and isopropanol. Catalyst loadings were  $1.52 \text{ mg PtRu cm}^{-2}$  for anodes (using 60 wt.% PtRu on Vulcan XC-72R with the atomic ratio of Pt to Ru 1:1, E-TEK) and  $2 \text{ mg Pt, Ru or RuSe cm}^{-2}$  for Pt, Ru, RuSe and RuSeW cathodes.

Procedures for fabrication of cathode catalysts were reported elsewhere [8–11] and are briefly described below. The solution was bubbled with nitrogen under mechanical stirring, selenium (0.04 g, 99%, Riedel-deHaen) was dissolved in 500 ml of boiling xylene (anhydrous, 97%) for 2 h. Carbonyls (0.5 g  $\text{Ru}_3(\text{CO})_{12}$ , 99% and 0.24 g  $\text{W}(\text{CO})_6$ , 97%) were then added to the solution and refluxed for 12 h. Finally, carbon powder (0.3 g, Vulcan XC-72R, Cabot) was added to the solution and refluxed for another 20 h. After filtered, washed with dry ether and dried overnight, the products were annealed at  $360^\circ\text{C}$  for 1 h under a hydrogen atmosphere before being cooled to room temperature at a nitrogen atmosphere. The catalyst formula is  $\text{RuSe}_{0.20}\text{W}_{0.28}$  determined by the EDX measurement.

Methanol (ACS reagent, 99.8%), ethanol (ACS reagent, 95.0%) and formic acid (ACS reagent,  $\geq 96.0\%$ ) were used as fuels and  $\text{O}_2$  (BOC), air (BOC) and  $\text{H}_2\text{O}_2$  (50 wt.% in  $\text{H}_2\text{O}$ ) as oxidants. All reagents were from Sigma–Aldrich unless otherwise stated.

The cell was operated in three modes:

- (i) Series mixed mode, i.e., a fuel and oxidant mixture was formed in a vaporiser at a desired temperature. The mixture was fed to the cathode chamber first and then passed through the anode chamber before being recycled to a reservoir.

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- (ii) Mixed-anolyte mode, i.e., a fuel and oxidant mixture was fed only to the anode chamber and an oxidant passed through the cathode chamber.
- (iii) A conventional “un-mixed” fuel cell.

The cell potential was measured under constant current conditions and anode polarisation curves were measured in fuel cells, referring to a pseudo-dynamic hydrogen electrode (designated as DHE). The reference has proved to be reproducible, simple and convenient to use [12,13]. The DHE was formed by passing hydrogen gas through the cathode (the hydrogen cathode) and an anode polarisation curve (without IR-corrected) was recorded. The cathode polarisation data were calculated from the cell voltage, anode potential and ohmic voltage drop (measured using electrochemical impedance spectroscopy).

Other experimental details can be found in [8–11].

### 3. Results and discussion

#### 3.1. Influence of cathode catalyst

Fig. 1 shows polarisation curves for MRFCs with Pt, Ru, RuSe and RuSeW cathodes using a mixture feed of methanol and oxygen. The MRFC with the Ru cathode gave higher cell voltage at a fixed current density than that with Pt. The open circuit potential was some 200 mV higher with the Ru cathode than with the Pt cathode, i.e., 0.595 V vs. 0.405 V. The use of RuSe further improved performance and the best performance was achieved using the RuSeW cathode. The open circuit potential was 0.598 and 0.586 V for the cell with the RuSe and RuSeW cathode, respectively. Peak power densities for MRFCs with Ru-based cathodes were between 11 and 13.5  $\text{mW cm}^{-2}$ . The results were due to the differences in activity and selectivity for oxygen reduction of the catalysts. All Ru-based catalysts have previously shown to give better methanol tolerance than Pt and the addition of Se and W enhanced the catalyst activity for oxygen reduction [8–10]. The data confirm the crucial role of the catalyst selectivity for operation of MRFCs.

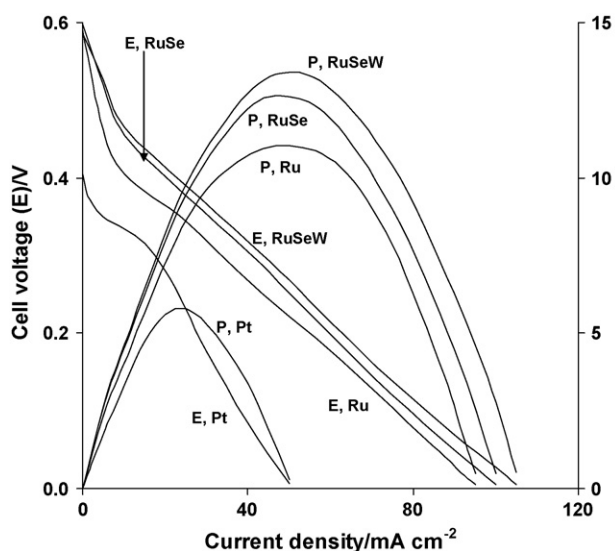


Fig. 1. Cell characteristics of mixed-reactant fuel cells with different cathodes. Active area:  $4 \text{ cm}^2$ . Cathode: carbon-supported Pt, Ru,  $\text{RuSe}_{0.19}$  or  $\text{RuSe}_{0.20}\text{W}_{0.28}$  ( $2 \text{ mg Pt, Ru or RuSe cm}^{-2}$ ). Anode: carbon-supported PtRu ( $1.52 \text{ mg PtRu cm}^{-2}$ ). Membrane: Nafion® 117. Feed: 1 M methanol ( $10 \text{ cm}^3 \text{ min}^{-1}$ ) +  $\text{O}_2$  ( $200 \text{ cm}^3 \text{ min}^{-1}$ , ambient pressure). Operation mode: series mixed. Temperature:  $90^\circ\text{C}$ . Data were collected from the first run.

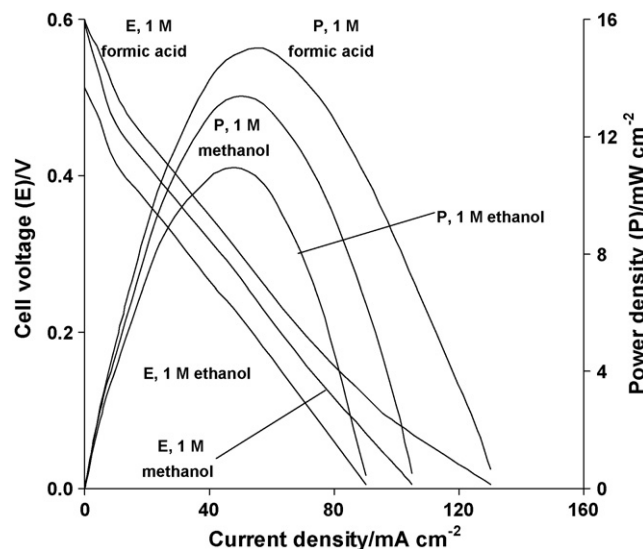


Fig. 2. Effect of fuel type on the performance of mixed-reactant fuel cells. Feed: 1 M methanol, ethanol or formic acid ( $10 \text{ cm}^3 \text{ min}^{-1}$ ) +  $\text{O}_2$  ( $200 \text{ cm}^3 \text{ min}^{-1}$ , ambient pressure). Other conditions as in Fig. 1.

#### 3.2. Influence of fuel

Fig. 2 shows the MRFC performance with different fuels. Formic acid gave superior performance (peak power density of  $15 \text{ mW cm}^{-2}$ ) to both methanol and ethanol. Power densities followed the order of formic acid > methanol > ethanol, reflecting the activity and selectivity for fuel oxidation on the PtRu anode.

The effect of the fuel concentration on cell performance was also investigated. In the case of the MRFC with formic acid, the best performance (peak power density of  $16 \text{ mW cm}^{-2}$ ) was observed at 2 M and the worst performance was at 10 M (peak power density of  $6.5 \text{ mW cm}^{-2}$ ).

In order to identify the reasons for different performance, electrode polarisation measurements were made. Fig. 3 shows cell and electrode polarisation curves, obtained in situ of the MRFC

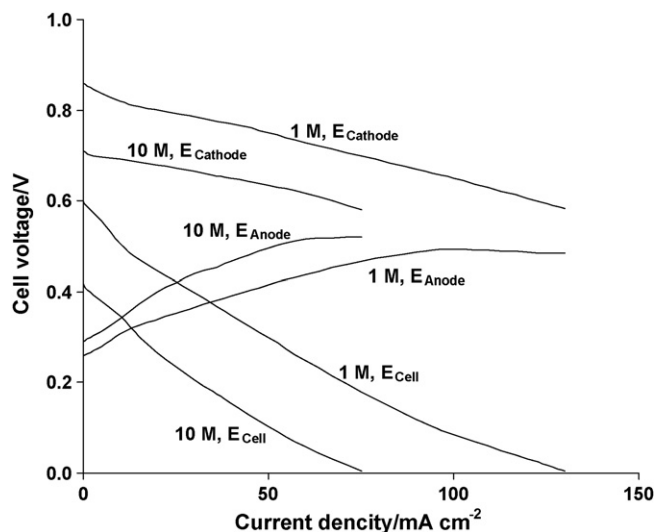


Fig. 3. Effect of fuel concentration on the polarisation feature of mixed-reactant fuel cells. Feed: 1 or 10 M formic acid ( $10 \text{ cm}^3 \text{ min}^{-1}$ ) +  $\text{O}_2$  ( $200 \text{ cm}^3 \text{ min}^{-1}$ , ambient pressure). The anode polarisation curve was IR-corrected. Other conditions as in Fig. 1.

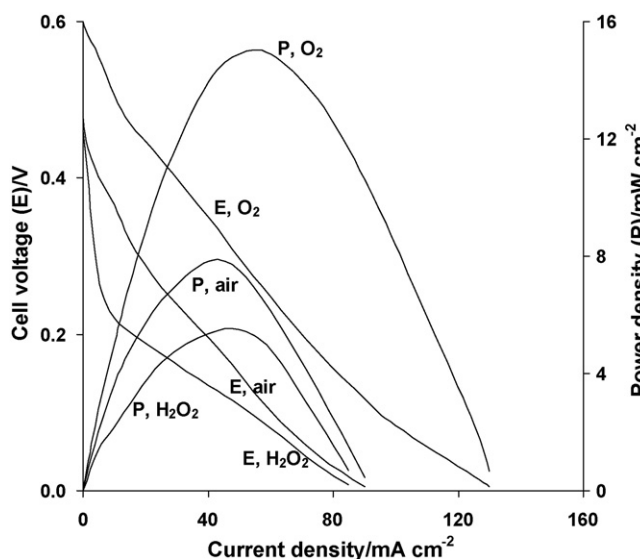


Fig. 4. Effect of oxidants on the performance of mixed-reactant fuel cells. Feed: 1 M formic acid ( $10 \text{ cm}^3 \text{ min}^{-1}$ ) +  $\text{O}_2$  or air ( $200 \text{ cm}^3 \text{ min}^{-1}$ , ambient pressure) or 1 M  $\text{H}_2\text{O}_2$  ( $10 \text{ cm}^3 \text{ min}^{-1}$ ). Other conditions as in Fig. 1.

with 1 and 10 M formic acid. The anode polarisation curve was IR-corrected. It was found that, at a fixed current density, the cathode potential fell significantly using the higher formic acid concentrations, although the anode potential decreased when the formic acid concentration was increased from 1 to 10 M, indicating an improved anode performance. For example, at a current density of  $50 \text{ mA cm}^{-2}$ , although the anode potential decreased 20 mV, the cell voltage fell by 200 mV, due to the lower cathode potential. The increased cathode polarisation may be attributable to two factors: (i) greater blocking effect on cathode active sites with increasing fuel concentration; (ii) limited fuel tolerance of the cathode. In practice, fuel concentration needs to be optimised for operation of MRFCs.

In addition to the reported performance with Ru-based cathode catalysts, it is worthwhile to note that the MRFC with the Pt cathode did not generate power when a 4 M formic acid fuel was used, further demonstrating that catalyst selectivity plays a decisive role for operation of MRFCs.

### 3.3. Influence of oxidant

Fig. 4 shows the performance of the MRFC with liquid formic acid as fuel and air, oxygen and hydrogen peroxide as oxidants. The use of hydrogen peroxide was considered to enable a MRFC to be operated with a single liquid phase and potentially improve performance over a two-phase system. As shown, the use of a liquid oxidant, i.e.,  $\text{H}_2\text{O}_2$ , produced a lower performance than with gas oxidants. The peak power density was  $6 \text{ mW cm}^{-2}$  compared with  $8 \text{ mW cm}^{-2}$  with air. As the cell performance was more dependent on the cathode than on the anode, the supply of oxidant to the cathode surface played a major role for successful operation of MRFCs. The observation was hardly explained based on redox potentials because the  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  couple has higher standard potential ( $E^0 = +1.77 \text{ V}$  vs. NHE) than the  $\text{O}_2/\text{H}_2\text{O}$  couple ( $E^0 = +1.23 \text{ V}$  vs. NHE). The inferior performance of  $\text{H}_2\text{O}_2$  compared with  $\text{O}_2$  may be attributed to slow reduction rates, as at most other electrode surfaces [14]. This topic should be addressed in future study. The above data have also been demonstrated the use of hydrogen peroxide as oxidant may require using a different pH to optimise performance.

### 3.4. Influence of temperature

The cell temperature affected the MRFC performance, for instance, with liquid formic acid as fuel and oxygen as oxidant, the MRFC worked better at  $60^\circ\text{C}$  than at  $25^\circ\text{C}$  and the performance was a maximum at  $90^\circ\text{C}$ . It seems that, in spite of the fact that the oxygen solubility decreased in the two-phase system as temperature increased, the kinetics of oxygen reduction was improved significantly by the higher temperature.

### 3.5. Lifetime

Fig. 5 presents an example regarding lifetime of mixed-reactant fuel cells. As can be seen, the MRFC potentials fell with increased use. Considering that the OCV is continuously coming down, deterioration of performance with time could not be due to mass transfer limitations. Cathode blocking as well as fuel tolerance could be the reasons. Another possible reason may be lower durability of the RuSeW catalyst under MRFC operating conditions, which is worthwhile to investigate in a further work. This is a major concern for operation of MRFCs, which should be a main issue to be addressed in future. Different approaches should be taken to solve the problem, particularly through modifications of component structures and cell configuration.

### 3.6. Comparison of fuel cell operation

Fig. 6 compares the performance of the formic acid MRFC with that of the conventional cell counterpart; the latter showed higher performance than the former, e.g.,  $33.6 \text{ mW cm}^{-2}$  vs.  $14.9 \text{ mW cm}^{-2}$  in peak power density. To help determine the difference in mixed and un-mixed-reactant performance, data were collected in the mixed-anolyte mode. The cell operated using the mixed-anolyte gave only small decrease in performance compared with the conventional cell and was much better than the MRFC. Therefore, it is reasonable to assume that the main reason for the lower performance of the MRFC, compared to the conventional one, was due to a significant reduction in the cathode performance. Another reason was the dilution of fuel and oxidant in the MRFC, which reduced reactant concentrations for both anode and cathode. It was clear

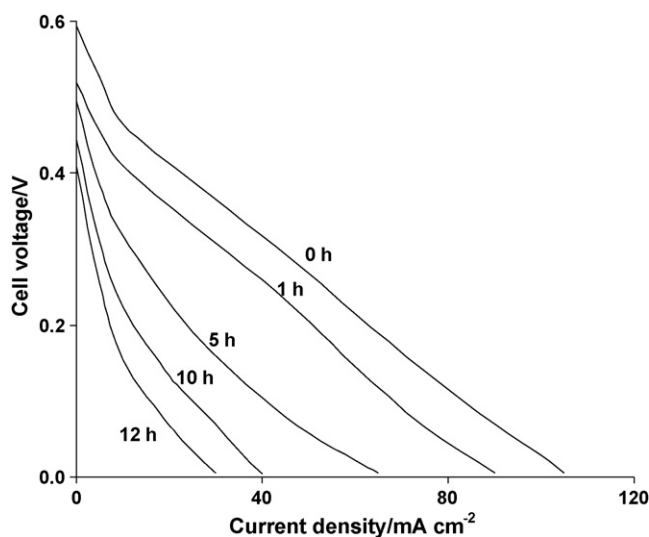
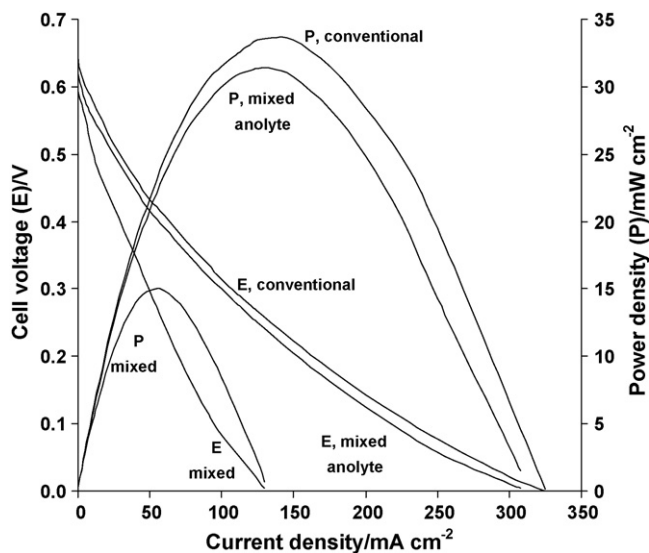


Fig. 5. Changes of the cell polarisation curves with time. Feeding: 1 M methanol ( $10 \text{ cm}^3 \text{ min}^{-1}$ ) +  $\text{O}_2$  ( $200 \text{ cm}^3 \text{ min}^{-1}$ , ambient pressure). Other conditions as in Fig. 1.



**Fig. 6.** Comparison of conventional and mixed-reactant fuel cells. Feed: 1 M formic acid ( $10 \text{ cm}^3 \text{ min}^{-1}$ ) +  $\text{O}_2$  ( $200 \text{ cm}^3 \text{ min}^{-1}$ , ambient pressure). Feeds: (i) series mixed mode: 1 M formic acid ( $10 \text{ cm}^3 \text{ min}^{-1}$ ) +  $\text{O}_2$  ( $200 \text{ cm}^3 \text{ min}^{-1}$ , ambient pressure). (ii) Conventional mode: 1 M formic acid ( $10 \text{ cm}^3 \text{ min}^{-1}$ ) for the anode chamber and  $\text{O}_2$  ( $200 \text{ cm}^3 \text{ min}^{-1}$ , ambient pressure) for the cathode chamber. (iii) Mixed-anolyte mode: 1 M formic acid +  $\text{O}_2$  ( $200 \text{ cm}^3 \text{ min}^{-1}$ , ambient pressure) for the anode chamber and  $\text{O}_2$  ( $200 \text{ cm}^3 \text{ min}^{-1}$ , ambient pressure) for the cathode chamber. Other conditions as in Fig. 1.

that the cathode was affected more detrimentally than the anode, which indicates the direction for future research.

Similar results were observed for the alcohol fuel cells. The conventional cells had better performance than the MRFCs. For instance, as reflected in peak power density,  $23.8 \text{ mW cm}^{-2}$  vs.  $13.4 \text{ mW cm}^{-2}$  for 1 M methanol and  $20.5 \text{ mW cm}^{-2}$  vs.  $10.9 \text{ mW cm}^{-2}$  for 1 M ethanol.

These power generation and polarisation characteristics at different conditions are very important to understand the mechanism of the power generation at the MRFC.

Overall, the mixed-reactant fuel cell was a feasible power source, although there were challenging issues, such as lower performance and shorter lifetime, compared to the conventional one.

#### 4. Conclusion

The present work demonstrated that the pre-condition for operation of mixed-reactant fuel cells is to use selective cathode catalysts. Only those that exhibit high tolerance to a mixture of fuel and oxidant could generate power. The data showed the significant effect of fuel and oxidant conditions on the cathode performance, which played a decisive role in the cell performance.

This work illustrated that the most challenging issue is to increase lifetime of MRFCs, which will require an approach using modifications of the cell structure and operation mode. The performance of a mixed-reactant fuel cell was not unexpectedly inferior to that of a conventional fuel cell. The attraction of the mixed-reactant fuel cell is its much simpler practical operation which can potentially lead to a more compact and lower weight power source, based on pure per unit mass and volume.

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