

# A mixed-reactants solid-polymer-electrolyte direct methanol fuel cell

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## Abstract

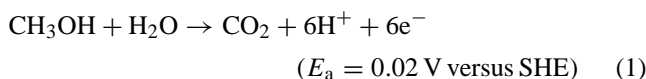
Mixed-reactants solid-polymer-electrolyte direct methanol fuel cells (SPE-DMFCs) with a PtRu/C anode and a methanol-tolerant oxygen-reduction cathode catalyst have been assembled and have been subjected to galvanostatic polarisation studies. The oxygen-reduction cathode was either of the FeTMPP/C, CoTMPP/C, FeCoTMPP/C and RuSe/C. It was found that the SPE-DMFC with the RuSe/C cathode yielded the best performance. It has been possible to achieve power densities of approximately 50 and 20 mW/cm<sup>2</sup> while operating a mixed-reactants SPE-DMFC at 90 °C with oxygen and air fed cathodes, respectively. Interestingly, these SPE-DMFCs exhibit no parasitic oxidation of methanol with oxygen.

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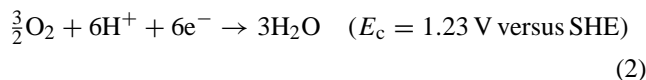
*Keywords:* SPE-DMFC; PtRu/C anode; Oxygen-reduction cathode; Mixed-reactants fuel cells

## 1. Introduction

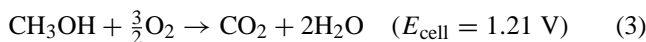
Solid-polymer-electrolyte direct methanol fuel cells (SPE-DMFCs) are presently under active development particularly for applications in transport and various portable electronic devices [1]. In a SPE-DMFC, methanol is oxidised at the anode according to the reaction



Protons generated at the anode pass through the solid-polymer-electrolyte membrane, usually Nafion<sup>®</sup>-117, to combine with electrons and the oxidant air or oxygen simultaneously reducing to water as,



Accordingly, the net cell reaction in a SPE-DMFC is the production of CO<sub>2</sub> and H<sub>2</sub>O as,



During the last decade, significant advances have been made in the development of the DMFC. Peak power densities of 450 and 300 mW/cm<sup>2</sup> under oxygen and air-feed operation, respectively, and a power density of 200 mW/cm<sup>2</sup> at a cell potential of 0.5 V have been reported for cells operating at temperatures around 100 °C under pressurised condition with platinum loadings of 1–2 mg/cm<sup>2</sup> [2]. Besides, the development of DMFC stacks for both transportation and portable applications has gained momentum in the last 2–3 years, and stack power densities of 1 kW/dm<sup>3</sup> and an overall efficiency of 37% at a design point of 0.5 V per cell have been accomplished [3]. The performance of DMFCs is thus competitive with respect to the reformer-based hydrogen/air PEFCs, especially if one considers the complexity of the latter as a whole system [4]. However, further innovations in the DMFCs would be mandatory for their commercial realisation [5]. A step in this direction appears to be the development of mixed-reactants direct methanol fuel cells (MRDMFCs) which rely upon the selectivity of anode and cathode electrocatalysts to separate the electrochemical oxidation and reduction of the oxidant without the need for physical separation of fuel and oxidant [6,7]. Accordingly, in a MRDMFC, the methanol fuel and oxidant oxygen (or air) are mixed together before feeding to the fuel cell. It is noteworthy that the selective-electrode fuel cells with mixed-reactants feed has been considered both for solid-oxide fuel cells [8] as well as polymer-electrolyte fuel cells [9,10]. In the MRDMFCs, there would be no need for gas-tight structures within the stack providing

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relaxation for sealing and reactants/products delivery structures [7].

In a MRDMFC, cathode selectivity is paramount and is accomplished by using an oxygen-reduction catalyst which besides being tolerant to methanol does not oxidise it. Such catalysts of current interest are: (a) macrocyclic complexes, namely transition-metal tetra-methyl phenylporphyrins (TMPPs) such as FeTMPP, CoTMPP, FeCoTMPP [11–13] and transition-metal tetra-azaanulenes such as CoTAA [14], (b) transition-metal chalcogenides based on Chevrel phases such as Mo<sub>4</sub>Ru<sub>2</sub>Se<sub>8</sub> [15–21], and (c) transitional-metal clusters with sulphur or selenium such as RuS and RuSe [22]. Among these, the latter class of catalyst materials and, in particular, ruthenium-based cluster catalyst with selenium (RuSe) has been reported to be attractive for its selective catalytic activity towards oxygen-reduction reaction in the presence of methanol [22]. Anodic selectivity is typically achieved with the PtRu bimetal catalyst [6].

During the present study, we have assembled and tested MRDMFCs with membrane-electrode assemblies (MEAs) comprising a carbon-supported PtRu anode, a cathode containing either of the above mentioned carbon-supported transition-metal TMPPs or a carbon-supported selenium containing ruthenium-based cluster catalyst (RuSe/C), and Nafion<sup>®</sup>-117 or Nafion<sup>®</sup>-112 membrane as the electrolyte. The findings of the present study could also be significant to the development of conventional SPE-DMFCs where methanol crossover through the Nafion<sup>®</sup> membrane electrolyte from anode to the cathode results in a poor catalytic activity at the cathode [3,23,24].

## 2. Experimental

SPE-DMFCs were assembled with Nafion<sup>®</sup>-117 based membrane electrode assemblies (MEAs), which employed carbon-supported 60 wt.% PtRu in (1:1) atomic ratio as the anode catalyst and carbon-supported 60 wt.% Pt as the cathode catalyst. The ink for the catalytic layers of the anode was prepared from PtRu/C powder, Nafion<sup>®</sup> ionomer (10 wt.%) and *n*-butyl acetate followed by its mixing [25,26]. The ink for the catalytic layers of the cathode was prepared from Pt/C powder, Nafion<sup>®</sup> ionomer (10 wt.%) and iso-propyl alcohol followed by its mixing [25,26]. The PtRu catalyst loading on the anode was kept as 1.46 mg/cm<sup>2</sup> (1 mg/cm<sup>2</sup> of Pt and 0.46 mg/cm<sup>2</sup> of Ru) and the Pt/C catalyst loading at the cathode was kept as 4.6 mg/cm<sup>2</sup> of Pt. The catalyst loading on the cathode was intentionally kept high to minimise methanol crossover effect during the prolonged operation of the cell [27].

In an experimental SPE-DMFC, the anode and cathode of the MEA were in contact with high-density graphite blocks, impregnated with phenolic resin, into which were cut the gas/liquid flow channels. The ridges between the channels provided the electrical contact to the carbon electrodes and the total machined geometrical area of 25 cm<sup>2</sup> was taken as

the active area of the cell. Electrical heaters were mounted at the rear of the graphite blocks to maintain the desired cell temperature which was controlled through a temperature controller and monitored by thermocouples buried in the graphite blocks. Gold-plated metallic bolts were screwed into the blocks to allow electrical contact.

For selective-reactants anode tests, where the methanol fuel is not mixed with the oxidant oxygen (or air), a solution of 1 M aqueous methanol was fed to the anode at a feed rate of ca. 15 cm<sup>3</sup>/min and the un-reacted fuel returned to the storage reservoir where the CO<sub>2</sub> gas product was condensed to trap any methanol vapour prior to its release to the atmosphere. For the mixed-reactants anode tests, air or oxygen was fed to the anode of the SPE-DMFC at a feed rate of ~1 dm<sup>3</sup>/min along with 1 M aqueous methanol. On polarising the anode galvanostatically, hydrogen was evolved at the cathode in accordance to the reaction



which also served as a reference electrode [6,28]. Similar polarisation data were obtained by replacing air with nitrogen to examine any parasitic oxidation of methanol with oxygen.

The cathode employed in the MRDMFCs were (i) FeTMPP, CoTMPP and FeCoTMPP obtained from Scientific Generics (UK) which were supported onto Vulcan XC-72R carbon in-house, and (ii) carbon-supported RuSe catalyst (RuSe/C) synthesised in-house by reacting a mixture of Ru<sub>3</sub>(CO)<sub>12</sub>, Se and Vulcan XC-72R carbon at 140 °C with xylene in nitrogen under refluxing conditions for about 40 h. The resultant mass was filtered, washed with diethyl ether, dried in air and subjected to reduction in a stream of hydrogen at 300 °C for about 5 h. Inks for all these catalysts were prepared by mixing the catalyst material with Nafion<sup>®</sup> ionomer and iso-propyl alcohol.

Subsequently, SPE-DMFCs were assembled with MEAs comprising a cathode containing a methanol-tolerant selective catalyst, PtRu/C catalyst at the anode (total metals loading of 1.46 mg/cm<sup>2</sup>), and Nafion<sup>®</sup>-117 or Nafion<sup>®</sup>-112 membrane as the electrolyte. These SPE-DMFCs were operated with both selective-reactants, employing separate feeds for methanol fuel and the oxidant oxygen (or air), and mixed-reactants configurations as described in Table 1.

The experimental set-up for operating the SPE-DMFCs in the separated-reactants and mixed-reactants configurations is shown schematically in Fig. 1. In the separated-reactants SPE-DMFC, methanol fuel is fed to the anode from the storage tank through a peristaltic pump with valves V1 and V3 closed, and V2 open. Following the anode reaction, un-reacted methanol and product CO<sub>2</sub> leave from the anode outlet, and a valve V4 is closed and valve V5 is open, these collect into the storage tank where the methanol vapour is entrained through a condenser and gaseous CO<sub>2</sub> is vented to the atmosphere. The flow rate of the oxidant oxygen or air is controlled and monitored prior to being heated and valve V1 is closed. Accordingly, the oxygen (or air) passes

Table 1  
Types of SPE-DMFCs and their operational details

Cell type	Nafion <sup>®</sup> membrane type	Cell configuration	Anode reactants	Cathode reactants	Anode catalysts with loadings (mg/cm <sup>2</sup> PtRu/C)	Cathode catalysts with loadings (mg/cm <sup>2</sup> )	Maximum power density (mW/cm <sup>2</sup> )
SPE-DMFC 1	Nafion <sup>®</sup> -117	SR	Methanol	Oxygen	1.46	1 FeTMPP/C	7
SPE-DMFC 2	Nafion <sup>®</sup> -117	SR	Methanol	Oxygen	1.46	1 CoTMPP/C	2
SPE-DMFC 3	Nafion <sup>®</sup> -117	SR	Methanol	Oxygen	1.46	1 FeCoTMPP/C	7
SPE-DMFC 4	Nafion <sup>®</sup> -117	SR	Methanol	Oxygen	1.46	1 RuSe/C	13
SPE-DMFC 5	Nafion <sup>®</sup> -117	MR	Methanol + oxygen	Methanol + oxygen	1.46	1 FeTMPP/C	9
SPE-DMFC 6	Nafion <sup>®</sup> -117	MR	Methanol + oxygen	Methanol + oxygen	1.46	1 CoTMPP/C	4
SPE-DMFC 7	Nafion <sup>®</sup> -117	MR	Methanol + oxygen	Methanol + oxygen	1.46	1 FeCoTMPP/C	8
SPE-DMFC 8	Nafion <sup>®</sup> -117	MR	Methanol + oxygen	Methanol + oxygen	1.46	1 RuSe/C	32
SPE-DMFC 9	Nafion <sup>®</sup> -117	SR	Methanol	Oxygen	1.46	2 RuSe/C	36
SPE-DMFC 10	Nafion <sup>®</sup> -117	SR	Methanol	Oxygen	1.46	2.5 RuSe/C	46
SPE-DMFC 11	Nafion <sup>®</sup> -117	SR	Methanol	Oxygen	1.46	3 RuSe/C	35
SPE-DMFC 12	Nafion <sup>®</sup> -117	MR	Methanol + oxygen	Methanol + oxygen	1.46	2 RuSe/C	46
SPE-DMFC 13	Nafion <sup>®</sup> -117	MR	Methanol + oxygen	Methanol + oxygen	1.46	2.5 RuSe/C	48
SPE-DMFC 14	Nafion <sup>®</sup> -117	MR	Methanol + oxygen	Methanol + oxygen	1.46	3 RuSe/C	35
SPE-DMFC 15	Nafion <sup>®</sup> -112	SR	Methanol	Oxygen	1.46	2.5 RuSe/C	45
SPE-DMFC 16	Nafion <sup>®</sup> -112	MR	Methanol + oxygen	Methanol + oxygen	1.46	2.5 RuSe/C	44
SPE-DMFC 17	Nafion <sup>®</sup> -112	SR	Methanol	Air	1.46	2.5 RuSe/C	21
SPE-DMFC 18	Nafion <sup>®</sup> -112	MR	Methanol + air	Methanol + air	1.46	2.5 RuSe/C	20

SR and MR stand for selective reactants and mixed reactants, respectively.

directly to the cathode, and subsequent to the cathode reaction, the un-reacted oxygen (or air) and product water emerge from the cathode exhaust. As valve V4 is closed and valve V6 is open, the un-reacted oxygen (or air) and product water pass through a condenser where any excess methanol which would have crossed over the membrane electrolyte and remained un-reacted in the cell is collected while the un-reacted oxygen (or air) is vented to the atmosphere.

In the mixed-reactants SPE-DMFC, a mixture of methanol and oxygen (or air) is fed to the cathode of the cell by keeping the valve V1 open and valve V2 closed. Following the cathode reaction, the un-reacted oxygen (or air) and methanol along with product water from the cathode exhaust are directed to the anode through valve V4 with both

valves V5 and V6 closed. Subsequent to the anode reaction, un-reacted oxygen (or air) and methanol along with product water and CO<sub>2</sub> are directed to the storage tank through valve V3 while keeping the valve V2 closed. On reaching the storage tank, the methanol vapour is condensed and returned to the tank while un-reacted oxygen (or air) along with CO<sub>2</sub> is vented to the atmosphere. The anode and cathode flow-fields depicting the reactants/products delivery structures in the SPE-DMFCs are shown in Fig. 2(a) and (b), respectively.

Both, FeTMPP and CoTMPP were characterised by nuclear magnetic resonance (NMR) and ultra violet (UV) spectroscopy. X-ray powder diffraction (XRD) pattern for RuSe/C catalyst was obtained on a Siemens D-5005 X-ray Diffractometer using Cu K $\alpha$  radiation at a scan rate of

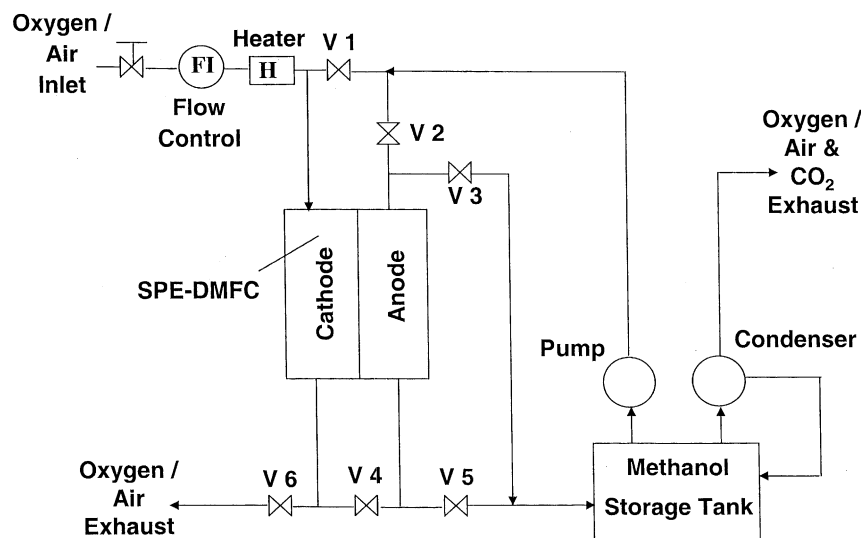


Fig. 1. Schematic diagram of the experimental set-up for testing the selective-reactants and the mixed-reactants SPE-DMFCs.

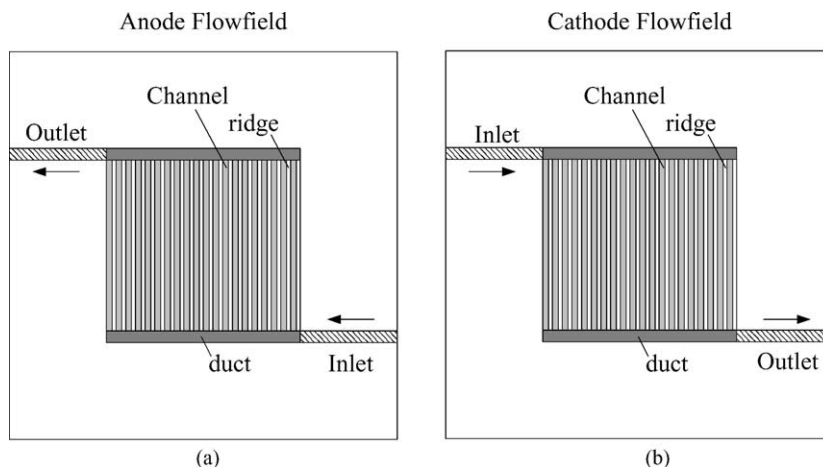


Fig. 2. (a) Anode and (b) cathode flow-fields depicting the reactants and products delivery structures in the SPE-DMFCs.

2°/min. A rotating (100)-oriented silicon disc was used as the sample holder. The XRD pattern was analysed following the Joint Committee of Powder Diffraction Standards (JCPDS) files. The catalyst was also subjected to energy dispersive analysis by X-rays (EDAX) employing a Jeol JSM-840A scanning electron microscope to determine the composition of its constituent elements.

### 3. Results and discussion

The galvanostatic polarisation data for the selective-reactants and mixed-reactants anode tests are given in Fig. 3(a) and (b), respectively. There was no significant

difference between the polarisation data of the mixed-feed anode with methanol plus air and mixed-feed anode with methanol plus nitrogen which is akin to the findings of Barton et al. [6]. This suggests that there was no parasitic oxidation of methanol with oxygen in the air during the mixed-reactants operation of the SPE-DMFC. The small difference in the anode polarisation data during the selective-reactants and mixed-reactants anode tests seen in the mass-polarisation region was possibly because the mixed feed helped scavenging carbon dioxide from the catalytic sites ameliorating oxidation of methanol at the anode. It is noteworthy that a SPE-DMFC operating at 1 A load would require  $7.06 \times 10^{-8} \text{ dm}^3/\text{s}$  of liquid methanol at the anode, and will result in a  $\text{CO}_2$  exhaust of  $3.87 \times 10^{-5} \text{ dm}^3/\text{s}$  (if

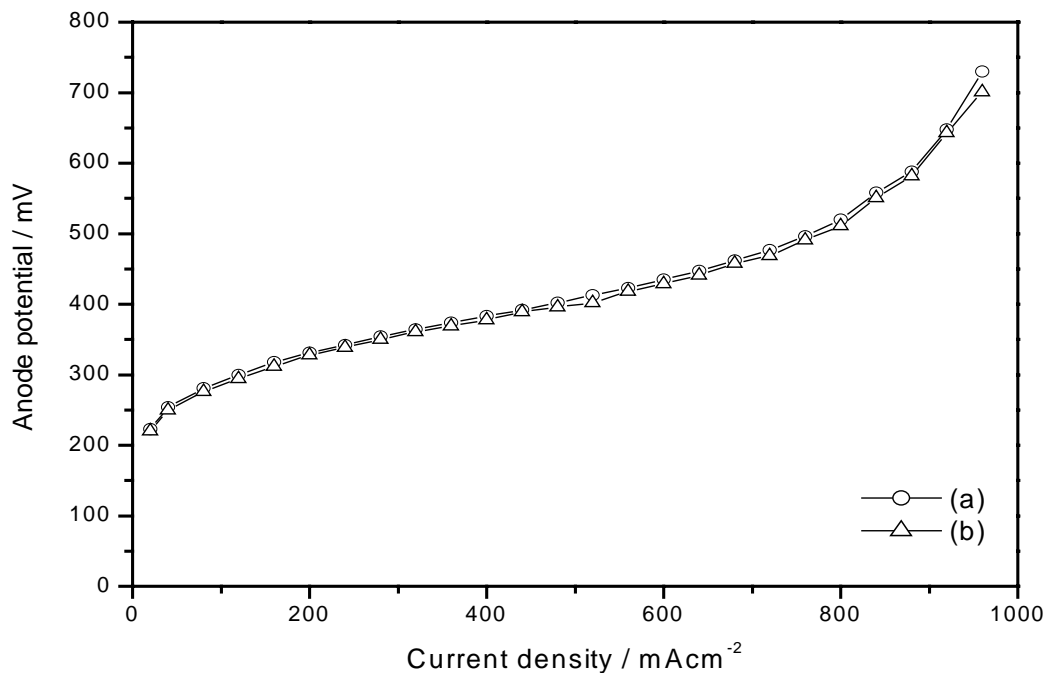


Fig. 3. Polarisation data obtained at 90°C for (a) selective-reactants anode, and (b) mixed-reactants anode.

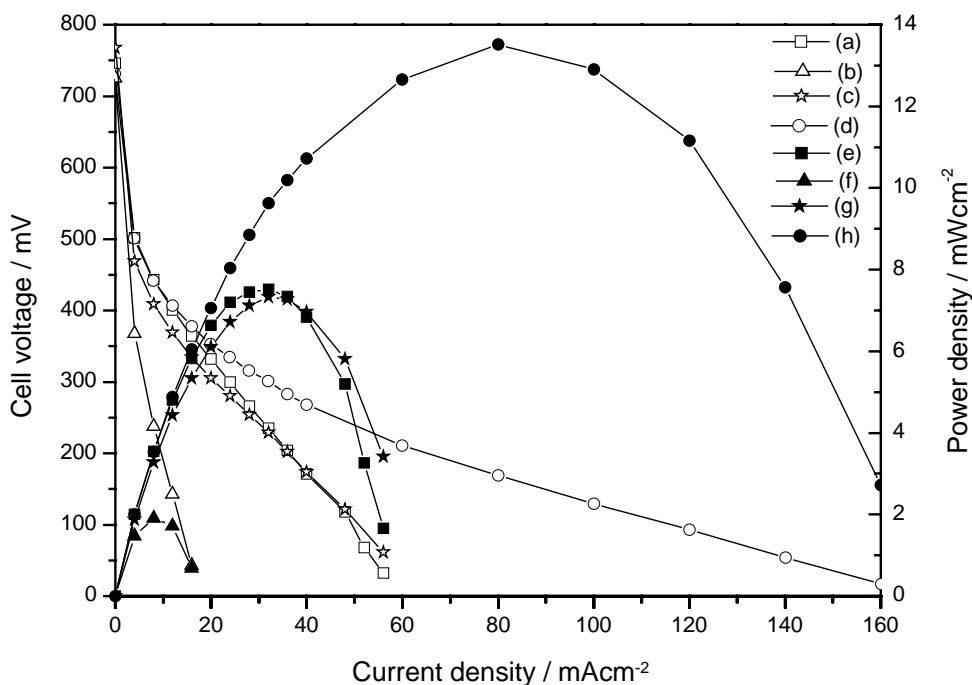


Fig. 4. Polarisation data obtained at 90 °C for (a) SPE-DMFC 1, (b) SPE-DMFC 2, (c) SPE-DMFC 3, and (d) SPE-DMFC 4. The corresponding power density data for the SPE-DMFCs are shown in (e), (f), (g), and (h), respectively.

present as gas) at its anode. This represents about 550-fold volume increase in the anode compartment of the cell during its operation and suggests that CO<sub>2</sub> removal from the anode should improve the cell performance.

Galvanostatic polarisation data for the selective-reactants SPE-DMFCs 1–4 with PtRu(1:1)/C anode (loading of

1 mg/cm<sup>2</sup> of Pt and 0.46 mg/cm<sup>2</sup> of Ru) and various selective cathodes (loading of 1 mg/cm<sup>2</sup>) catalysts while operating the cells at 90 °C with 1 M methanol feed on the anode and oxygen at a feed rate of 1 dm<sup>3</sup>/min on the cathode are given in Fig. 4. The corresponding polarisation data for the mixed-reactants SPE-DMFCs 5–8 at 90 °C

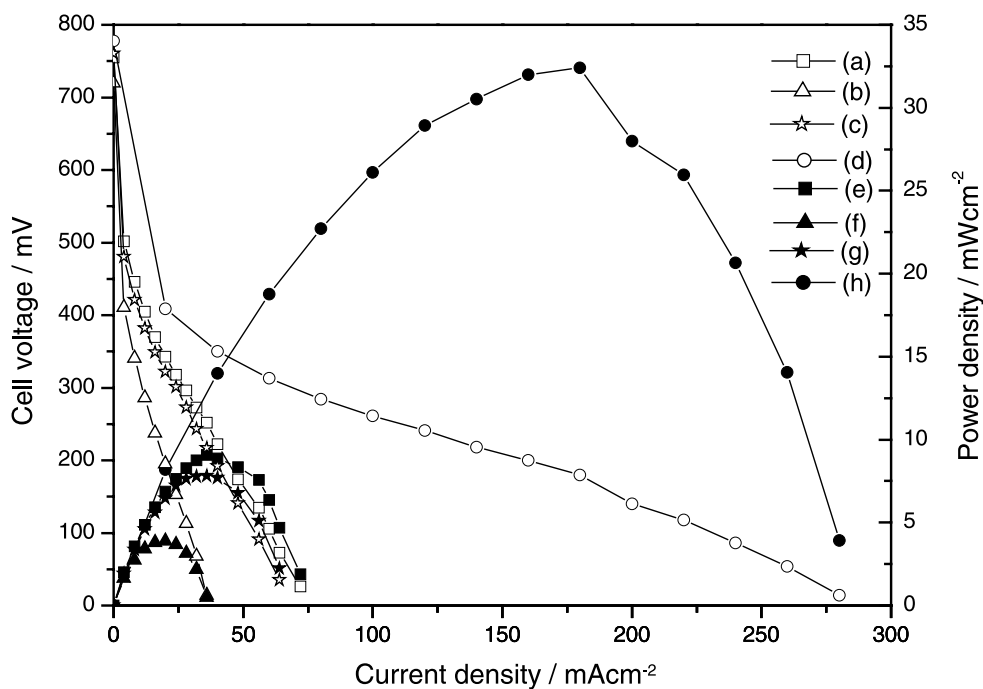


Fig. 5. Polarisation data obtained at 90 °C for (a) SPE-DMFC 5, (b) SPE-DMFC 6, (c) SPE-DMFC 7, and (d) SPE-DMFC 8. The corresponding power density data for the SPE-DMFCs are shown in (e), (f), (g), and (h), respectively.

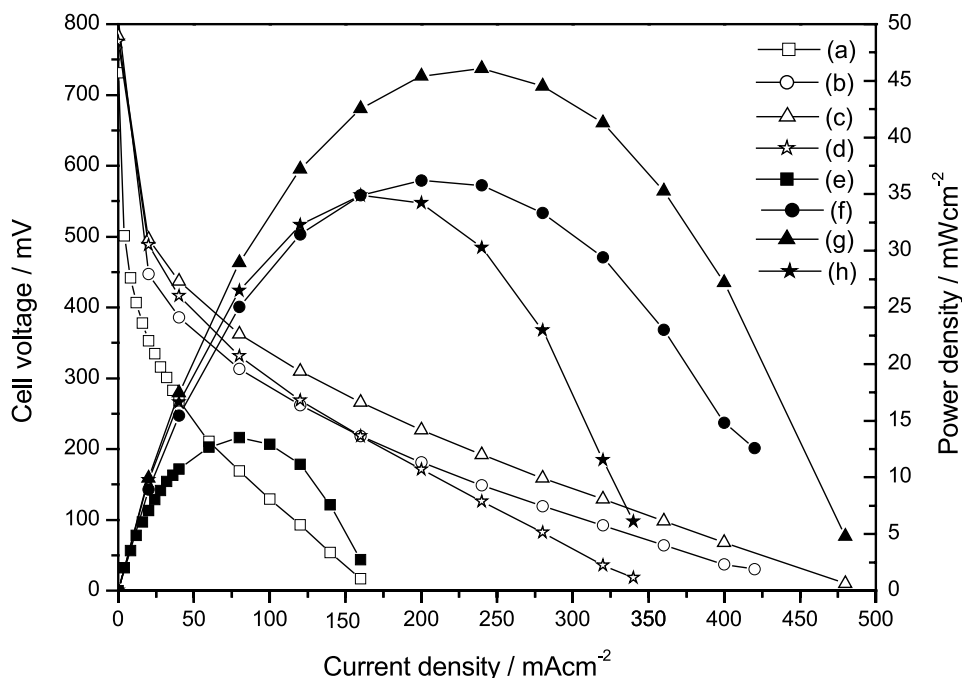


Fig. 6. Polarisation data obtained at 90 °C for (a) SPE-DMFC 4, (b) SPE-DMFC 9, (c) SPE-DMFC 10, and (d) SPE-DMFC 11. The corresponding power density data for the SPE-DMFCs are shown in (e), (f), (g), and (h), respectively.

with 1 M methanol plus 1 dm<sup>3</sup>/min oxygen feed on both the anode and the cathode are shown in Fig. 5. Among the selective-reactants SPE-DMFCs 1–4, the performance of SPE-DMFC 4 with a maximum attainable power density of 13 mW/cm<sup>2</sup> is superior. The performance of the SPE-DMFC 8 with a maximum attainable power density of 32 mW/cm<sup>2</sup> is superior among the mixed-reactants SPE-DMFCs 5–8. Overall it appears that the RuSe-based catalysts give better performance to any of the TMPP catalysts. Accordingly, we have investigated the performance of the SPE-DMFCs 4 by systematically varying the RuSe/C catalyst loading at the cathode while keeping the PtRu/C catalyst loading at the anode constant as earlier. The performance data obtained at 90 °C for these SPE-DMFCs 9–11 are shown in Fig. 6. Among these SPE-DMFCs, the best performance with a maximum power density of 46 mW/cm<sup>2</sup> is seen for the SPE-DMFC 10. In a similar fashion, the performance of the SPE-DMFC 8 was compared with that for SPE-DMFCs 12–14 (Fig. 7). From the data in Fig. 7, we find that the best performance is exhibited by the SPE-DMFC 13 with a maximum attainable power density of 48 mW/cm<sup>2</sup>. Under the condition of this work a loading of 2.5 mg/cm<sup>2</sup> of RuSe gave the superior performance.

The X-ray powder diffraction pattern for the RuSe/C catalyst presented in Fig. 8 shows all the characteristic peaks due to the ruthenium metal. The broad feature at a diffraction angle of  $2\theta \sim 25^\circ$  can be attributed to (002) plane of the hexagonal structure for Vulcan XC-72R carbon [29], whereas the diffraction peak observed at  $2\theta = 32.58^\circ$

is due to the (100)-oriented silicon wafer, which was used as the substrate for catalyst powder. Born et al. [22] have reported that a selenium-free catalyst even after refluxing in selenium-containing solution shows its XRD pattern similar to the selenium-free catalyst, but exhibits higher catalytic activity. According to them, the activity enhancement due to Se is related to an interfacial effect due to the binary structure of the catalyst [30]. An EDAX examination of the RuSe/C catalyst suggested the amount of selenium in the catalyst to be as low as 5% while the ruthenium metal content in the catalyst was estimated to be about 40%.

We have also assembled and tested a selective-reactants SPE-DMFC 15 which is similar to the SPE-DMFC 10 but employs Nafion<sup>®</sup>-112 membrane electrolyte in place of Nafion<sup>®</sup>-117 membrane electrolyte. The performance data obtained at 90 °C for such a selective-reactants SPE-DMFC 15 are shown in Fig. 9(b). The SPE-DMFC 15 was also operated in the mixed-reactants configuration, and the performance data obtained at 90 °C for such a mixed-reactants SPE-DMFC 16 are shown in Fig. 10(b). The maximum attainable power densities for SPE-DMFCs 15 and 16 are 45 and 44 mW/cm<sup>2</sup>, respectively. We have also operated the SPE-DMFC 15 both in selective-reactants and mixed-reactants configurations with air in place of oxygen, and the performance data at 90 °C for the SPE-DMFCs 17 and 18 are shown in Figs. 9(c) and 10(c), respectively. The data show that while it is possible to achieve a maximum power density of 45 mW/cm<sup>2</sup> while operating the SPE-DMFCs with oxygen, a maximum power density of

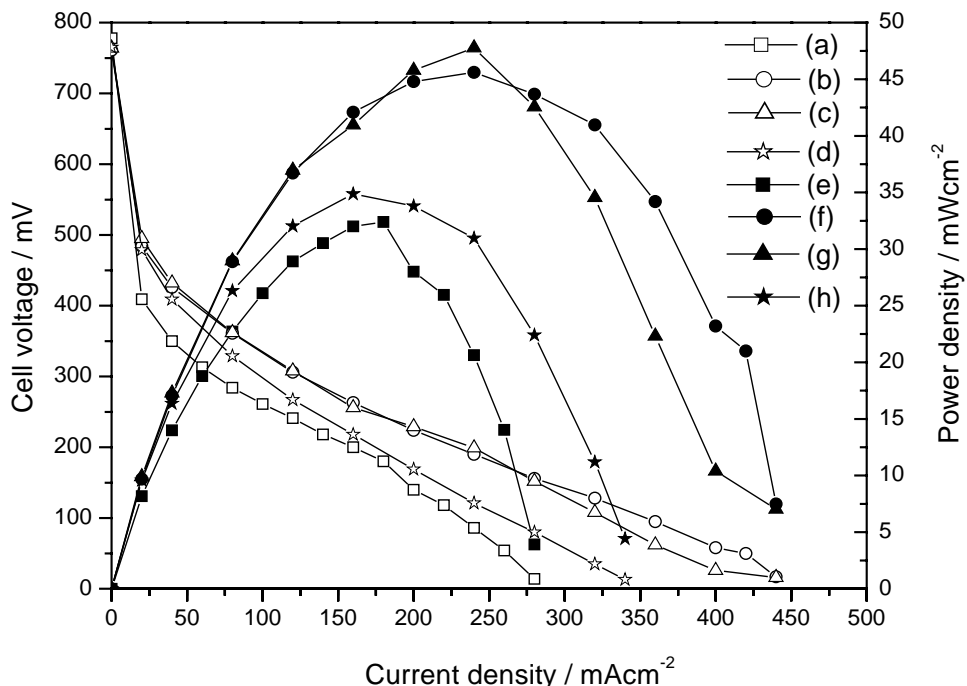


Fig. 7. Polarisation data obtained at 90°C for (a) SPE-DMFC 8, (b) SPE-DMFC 12, (c) SPE-DMFC 13, and (d) SPE-DMFC 14. The corresponding power density data for the SPE-DMFCs are shown in (e), (f), (g), and (h), respectively.

only about 20 mW/cm<sup>2</sup> could be achieved while operating these with air.

In relation to SPE-DMFCs 10 and 13 which employ Nafion<sup>®</sup>-117 membrane electrolyte, we expected a superior performance for SPE-DMFCs 15 and 16, both of which employ Nafion<sup>®</sup>-112 membrane electrolyte, which is much

thinner (51 μm) than Nafion<sup>®</sup>-117 (183 μm). Estimates of the ohmic polarisation for the SPE-DMFCs arising due to Nafion<sup>®</sup>-117 and Nafion<sup>®</sup>-112 membrane electrolytes over the entire polarisation range are approximately 48 and 15 mV, respectively [31]. However, we observed a similar performance for both types of MEAs. It should be noted that

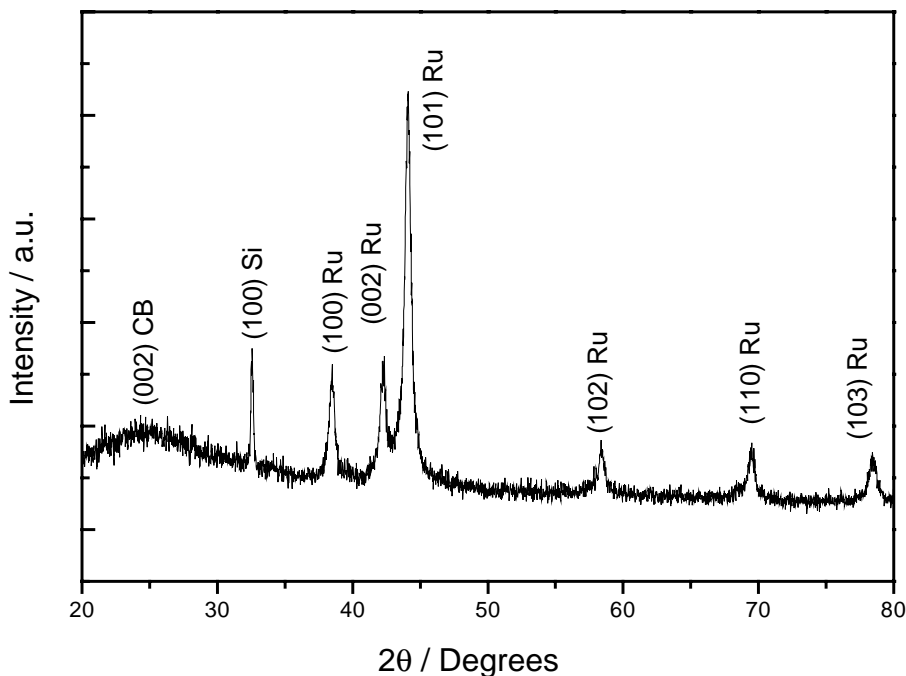


Fig. 8. Powder X-ray diffraction pattern for RuSe/C catalyst.

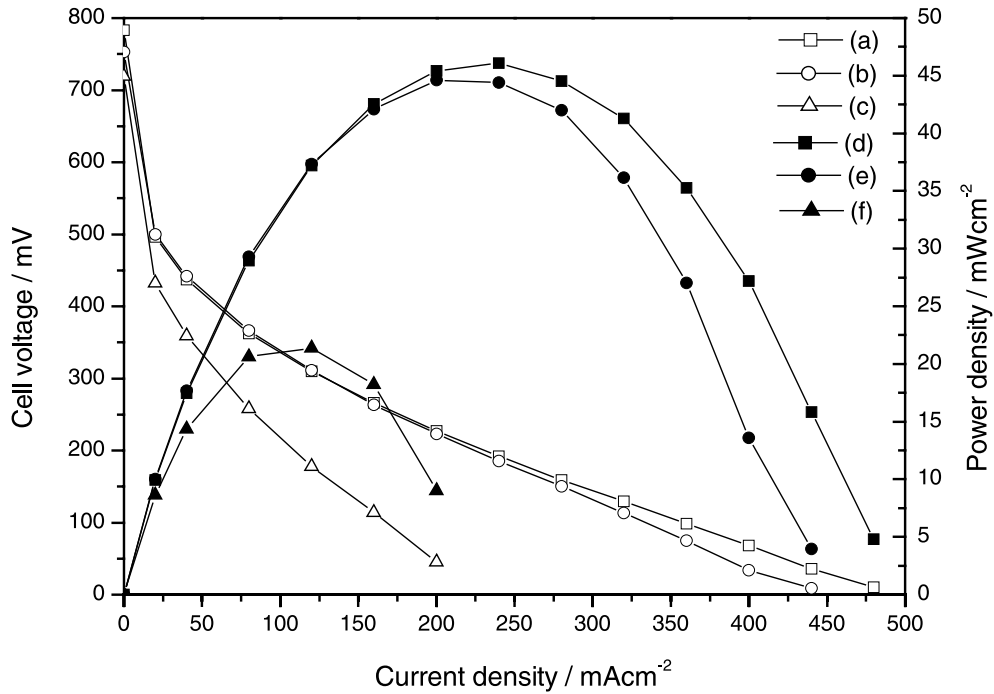


Fig. 9. Polarisation data obtained at 90 °C for (a) SPE-DMFC 10, (b) SPE-DMFC 15, and (c) SPE-DMFC 17. The corresponding power density data for the SPE-DMFCs are shown in (d), (e), and (f), respectively.

all the SPE-DMFCs (10, 13, 15 and 16) exhibited potential drops of ~800 mV in their entire polarisation range due to various polarisation components, i.e. the ohmic voltage contribution is only a small portion of the overall voltage.

A factor which may explain the similarity in behaviour may be in the fabrication of the MEA with a thinner membrane electrolyte and the water retention characteristics. Such issues will be examined in more detail in subsequent studies.

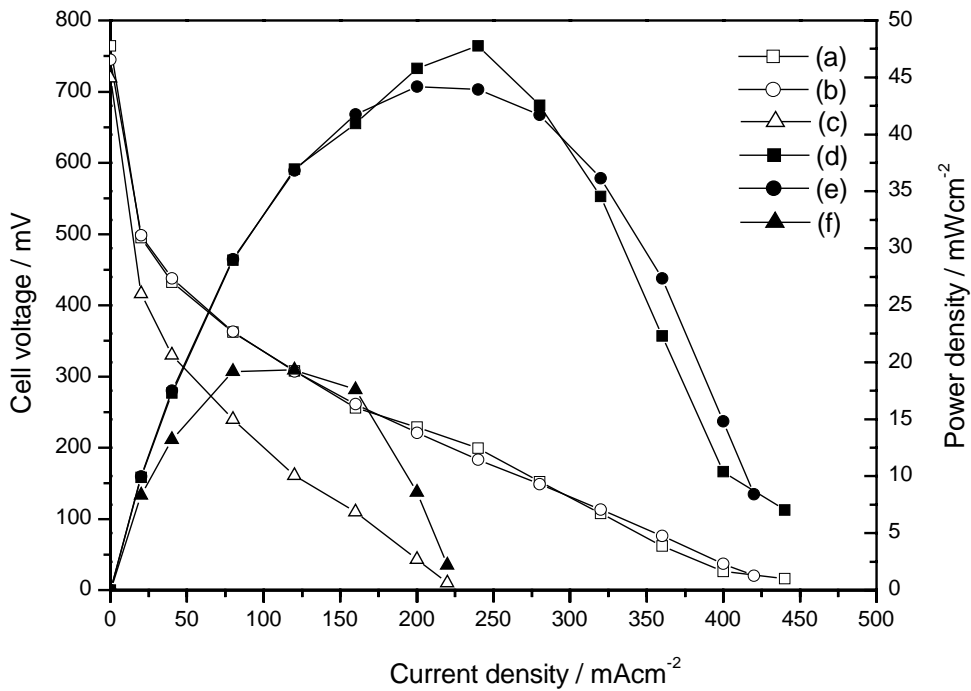


Fig. 10. Polarisation data obtained at 90 °C for (a) SPE-DMFC 13, (b) SPE-DMFC 16, and (c) SPE-DMFC 18. The corresponding power density data for the SPE-DMFCs are shown in (d), (e), and (f), respectively.



#### 4. Conclusions

In this study, we have shown that it is feasible to assemble and operate a mixed-reactants SPE-DMFC with its performance similar to the selective-reactants SPE-DMFC. It has been possible to attain maximum power densities of about 50 and 20 mW/cm<sup>2</sup> while operating the mixed-reactants SPE-DMFC at 90 °C with methanol plus oxygen and methanol plus air, respectively. It is, however, noteworthy that the operating conditions for our MRDMFC are not yet fully optimised, and further improvements in the cell performance are highly likely.

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