The direct methanol fuel cell (DMFC) is a low temperature fuel cell operating at temperatures of 30 to 130°C. The DMFC is powered by a liquid fuel (usually considered essential for transport uses) and is therefore regarded by some as the ideal fuel cell system. In this paper, the DMFC is compared to the hydrogen-fuelled proton exchange membrane fuel cell (PEMFC) which was discussed in detail in the January and July issues. While a typical DMFC is less efficient than a PEMFC, work to improve its performance with new electrocatalyst materials for utilisation in the membrane electrode assemblies has proved successful. This work is described here and some possible commercial uses for the DMFC are also considered.

Two of the most advanced low temperature fuel cells are the proton exchange membrane fuel cell (PEMFC) and the direct methanol fuel cell (DMFC). The DMFC directly consumes liquid fuel (methanol), while the PEMFC is fuelled by hydrogen. Operating a fuel cell with liquid fuel is considered by some to be essential for transport applications – for compatibility with the existing petroleum distribution network. The DMFC also has some system-related advantages over the PEMFC, making it of interest to fuel cell developers. For instance, the DMFC has no need for a fuel processor (or reformer) to convert a liquid hydrocarbon fuel (gasoline) into a consumable source of hydrogen. This considerably reduces the complexity and cost of the system. The DMFC system does not require the complex humidification and heat management hardware modules used in the PEMFC system: the dilute methanol-water mixtures circulating around the DMFC provide the necessary humidification and heat management.

If it can meet the performance required of a commercially viable device, the DMFC system will be potentially more cost effective than the PEMFC. Performance has been a major problem for the DMFC: it typically produces only one third of the PEMFC's power density. Hence, the DMFC community has made great efforts to bring the performance closer to that of the PEMFC, and particularly to extend the maximum operating temperature. The majority of the work has involved developing materials, such as new anode and cathode electrocatalysts and new proton conducting polymers, to promote the efficiency of the membrane electrode assemblies (MEAs) used in the DMFC stack. Advanced MEA designs have also been developed. Since most effort has been directed towards increasing the efficiency of the MEA components, the DMFC system itself has remained relatively undeveloped compared to the PEMFC – particularly for transport use.

However, interest in producing low temperature (< 60°C) ambient-pressure portable DMFC systems has increased recently. This is because the power densities now accessible by state-of-the-art MEAs may be enough for these systems to become competitive with leading secondary battery technologies. This area could thus become a near-term market opportunity for the DMFC, with transport uses being a longer-term goal, if further performance gains can be achieved.

**Comparison of PEMFCs and DMFCs**

The PEMFC and DMFC have much in common, in particular their MEAs. The MEA and its components were described in detail in Part I (1). The MEA of a DMFC usually consists of five layers which include gas and liquid diffusion layers, and electrocatalyst layers with a polymeric proton conducting acidic membrane in between (2). The proton conducting membrane acts as an electronic insulator between the electrodes, but allows protons
Fig. 1. The performance losses seen in a typical DMFC MEA operating with dilute MeOH and air at 80°C, compared to those in a PEMFC. The PEMFC is operating with pure hydrogen. A list of factors affecting the efficiencies of both fuel cells is on the right in the Figure.

to migrate efficiently from the anode to the cathode. The membrane also functions as a physical barrier to prevent mixing of the reactants. In addition, a soluble form of the membrane material is used to impregnate the electrocatalyst layers to extend the membrane interface. This provides a proton conducting pathway.

While the structures of the MEAs used in the PEMFC and DMFC are similar, the performance of each is very different. A comparison of the performance of the two fuel cells and the factors which limit their efficiencies is shown in Figure 1.

The DMFC has a maximum thermodynamic voltage of 1.18 V at 25°C, defined by its anode and cathode half-cell reactions:

Anode reaction: \( \text{CH}_3\text{OH} + \text{H}_2\text{O} = \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \)  
\( E^\circ_a = 0.046 \text{ V} \) (i)

Cathode reaction: \( \frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- = 3\text{H}_2\text{O} \)  
\( E^\circ_c = 1.23 \text{ V} \) (ii)

Cell reaction: \( \text{CH}_3\text{OH} + \text{H}_2\text{O} + \frac{3}{2}\text{O}_2 = \text{CO}_2 + 3\text{H}_2\text{O} \)  
\( E^\circ_{\text{cell}} = 1.18 \text{ V} \) (iii)

In comparison, the PEMFC has a maximum thermodynamic voltage of 1.23 V at 25°C. In practice, the cell voltage in both fuel cells is much less than this, see Figure 1. For example, at a current density of 500 mA cm\(^{-2}\), the cell voltage is typically around 0.75 V for the PEMFC (1) and 0.4 V for the DMFC (3). Therefore, the power density and efficiency are considerably higher in the PEMFC (61 per cent) than in the DMFC (34 per cent).

The Effect of Poor Kinetics

Both types of fuel cell are limited by the poor electrochemical activity of their cathodes, for reasons described in Part I (1). This reduces the cell voltage of both by up to 0.4 V at 500 mA cm\(^{-2}\).

However, unlike the PEMFC (when operated with pure hydrogen), the DMFC anode is also limited by poor electrochemical activity (kinetic loss [8] in Figure 1). This can account for a further loss in cell voltage of more than 0.3 V at 500 mA cm\(^{-2}\) (at 90°C).

To increase both the anode and cathode activities in the DMFC, the electrocatalysts employed are usually unsupported (with high Pt loadings of typically 5 to 10 mg Pt cm\(^{-2}\) for each electrode) rather than the carbon-supported electrocatalysts used in the PEMFC. This Pt loading is too high.
for commercial exploitation of the DMFC (but it
does of course dramatically increase the power
densities attainable by the MEA). By contrast, typ-
ical PEMFC electrodes are carbon-supported
electrocatalysts, loaded at 0.2 to 0.5 mg Pt cm⁻².

Fuel Crossover

Another critical effect, which reduces the effi-
ciency of the DMFC, is fuel crossover (methanol
crossover [4] in Figure 1). Methanol and water readi-
ly diffuse through all the commercially available
polymeric membrane electrolytes (such as Nafion),
and significant quantities of methanol and particu-
larly water pass from the anode to the cathode.
This reduces the cathode efficiency in two ways.

First, any methanol that comes into contact with
the cathode electrocatalyst will reduce the efficien-
cy of the oxygen reduction reaction by a compet-
ing electrochemical process — known as the mixed
potential effect. Second, the cathode structure
becomes waterlogged or flooded, and is no longer
an efficient structure for gas diffusion (mass trans-
port loss, [3] in Figure 1). Both these effects can
reduce the cell voltage by a further 0.2 to 0.3 V,
particularly when practical air flows are used.

In practice, the effects of methanol crossover
can be reduced to a large extent by careful design
of the MEA structure or by the application of
novel membrane materials (4) or cathode electro-
catalyst materials (5, 6). The use of thick
membrane materials, such as Nafion 117 (∼ 180
µm), in preference to those used in the PEMFC,
such as Nafion 112 (50 µm), is often a sensible
choice. Using a thick membrane does increase the
cell resistance (electrolyte resistance [5] in Figure 1),
but it is usually easily outweighed by an improved
performance as a result of reduced crossover.

A further consequence of the high methanol
crossover rates in commercially available materials
is that to reduce it, the DMFC anode must be sup-
plied with dilute methanol fuel, typically 0.5 to 1.0
molar concentration. This presents problems for
system design because, in addition to the methanol
fuel, large quantities of water must be stored,
adding to the size and complexity of the system.
It is particularly awkward for applications where
space is limited, such as portable devices. As the
methanol concentrations used in the DMFC are
low, the anode structure has to be designed to allow
both efficient diffusion of the liquid fuel into the
electrocatalyst layer and effective removal of the
product carbon dioxide (CO₂). Correct design of
the anode electrode structure is very important for
limiting anode mass transport losses ([6] in Figure 1).

Anode Electrocatalyst Limitations

Although the electrooxidation of methanol is
thermodynamically driven (by the negative Gibbs
free energy change, ΔG, in the fuel cell), in prac-
tice, the rate of methanol electrooxidation is
severely limited by poor reaction kinetics. To
increase the efficiency of the anode reaction, it is
necessary to understand the reaction mechanism.
Indeed, there are now probably over 100 published
papers that deal with identifying the nature and
rate limiting steps of this reaction (7).

The most likely reaction scheme to describe the
methanol electrooxidation process is shown in
Figure 2 (Steps i to viii). Only Pt-based electrocat-
alysts display the necessary reactivity and stability
in the acidic environment of the DMFC.
Spectroscopic studies on polycrystalline Pt have
shown that methanol is electrosorbed in a complex
process analogous to dehydrogenation. Sequential
stripping of protons and electrons is believed to
take place (Steps i to iv), leading to the formation
of carbon-containing intermediates, such as linear-
ly bonded -CO_ads and -CHO_ads (8, 9).

Although the vast majority of these studies have
been carried out on bulk polycrystalline or single
crystal metallic Pt surfaces, it is possible to study
the methanol electrosorption process on finely
divided electrocatalysts in a single cell. Methanol
electrosorption appears to occur spontaneously
when the anode and cathode of an MEA are con-
ected externally by an electrical circuit. Hence,
when methanol comes into contact with the elec-
trocatalyst, an electric current flows between the
two electrodes. This occurs for only a brief period
of time until the electrocatalyst becomes poisoned
with surface-bound intermediates, such as -CO_ads.

The results of an experiment in which three dif-
ferent anode electrocatalysts were exposed to a
dilute methanol/water mixture are shown in
Fig. 2 A reaction scheme describing the probable methanol electrooxidation process (Steps i to viii) within a DMFC anode. Only Pt-based electrocatalysts show the necessary reactivity and stability in the acidic environment of the DMFC to be of practical use.

Figure 3. The electrocatalysts were 40 wt.% Pt/Vulcan XC72R carbon black, 20 wt.% Pt, 10 wt.% Ru/Vulcan XC72R and PtRu black alloy. The loadings on each electrode were: 1 mg Pt cm\(^{-2}\) and 0.5 mg Ru cm\(^{-2}\) (ruthenium). Experiments were carried out at 90°C in a 50 cm\(^2\) in-house designed single cell using Nafion 112 membrane-based MEAs with Pt black cathodes (4 mg cm\(^{-2}\)). The half-cell behaviour of the anode was studied by supplying pure hydrogen to the cathode, which then functioned as a reversible hydrogen electrode (RHE) and also as a counter electrode.

Electrosorption was carried out under potentiostatic control at 75 mV (vs. RHE) with a 2 M methanol solution for a period of 20 minutes. This potential was chosen because it is below the threshold potential at which the electrosorbed methanol would be electrooxidised to CO\(_2\). The cell was then flushed with pure water for a further 20 minutes to remove any unreacted methanol.

As Figure 3 shows, a charge was produced by each electrocatalyst when it came into contact with methanol (at ~ 400 s). The charge levelled out after a few minutes, suggesting that the electrocatalyst surface became poisoned and was unable to

Fig. 3 Three anode electrocatalysts (loadings: 1 mg Pt cm\(^{-2}\), 0.5 mg Ru cm\(^{-2}\)) in a single cell, with Nafion 112 membrane-based MEAs, exposed to dilute methanol/water at 90°C. The cathodes are Pt black (4 mg Pt cm\(^{-2}\)). At ~ 400 s after methanol contact, the electrocatalysts produce charge which levels out as the surface becomes poisoned and stops reacting. Cyclic voltammetry confirmed an intermediate species was present.
Table I

Surface Areas of Electrocatalyst Materials Pt and PtRu Determined with Gas-Phase CO and Electrochemically with CO and Methanol, and the Resulting Stripping Peak Potentials

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Electrocatalyst surface area, m² g⁻¹ Pt or m² g⁻¹ PtRu</th>
<th>Stripping peak potential, mV (vs. RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO, gas-phase</td>
<td>CO, electrochemical (EPSA_Co)</td>
</tr>
<tr>
<td>40 wt.% Pt/XC72R</td>
<td>67</td>
<td>40</td>
</tr>
<tr>
<td>20 wt.% Pt, 10 wt.% Ru/XC72R</td>
<td>139</td>
<td>80</td>
</tr>
<tr>
<td>PtRu alloy black</td>
<td>83</td>
<td>46</td>
</tr>
</tbody>
</table>

react further with methanol. It was not possible to quantify the rate of this reaction since a few seconds were required to pass the methanol solution through the flow field and across the entire area of the electrode. The presence of an intermediate species was confirmed by ramping the anode potential up to 0.9 V (vs. RHE) at a scan rate of 10 mV s⁻¹. This resulted in an electrooxidation peak (stripping peak) for each electrocatalyst, shown in Figure 4 (corresponding to Steps vi to viii in Figure 2). Water electrosorption is believed to occur leading to the formation of -OH_ads species which then react with the intermediate species to form CO₂ (10, 11). This process results in the stripping peaks. As the nature of the surface-bound intermediate was unknown but was believed to be -CO-like, the experiments were repeated but with CO gas passing through the fuel cell instead of methanol. A CO_ads-stripping peak was recorded for each electrocatalyst, see Figure 4. In addition to the elec-

![Figure 4](image_url)

**Fig. 4** Stripping peaks (electrosorbed methanol intermediates and electrosorbed carbon monoxide (CO_ads)) for three anode electrocatalysts. The peaks probably correspond to Steps vi to viii in the reaction scheme of Figure 2.
trochemical measurements, the gas-phase CO chemisorption areas of the electrocatalysts were determined. The data are summarised in Table I, and show the CO gas-phase and CO electrochemical surface areas for each electrocatalyst. The CO gas-phase surface areas correspond to the absolute maximum metal surface area. The electrochemically determined CO values, however, correspond to the electrode platinum surface area (EPSACO), which is the total metal area in contact with the proton conducting polymer in the electrode. For each electrocatalyst the EPS&O was less than the gas-phase value, indicating that not all the electrocatalyst in the electrodes was utilised.

Table I also summarises the EPSAMeOH values of each anode electrocatalyst, determined using the methanol electrosorption (or electrosorbate) stripping peak. (The dominant surface-bound intermediate was assumed to be CO_ads.) These were found to agree well with the CO-stripping values (EPSACO) for the 40 wt.% Pt/XC72R and 20 wt.% Pt, 10 wt.% Ru/XC72R electrocatalysts. However, the values for the PtRu alloy black were somewhat different. A further difference was observed in the stripping-peak positions of each electrocatalyst, see Figure 4 and Table I. The Ru-containing electrocatalysts produced stripping peaks at much lower potentials than the pure Pt electrocatalyst, showing that the removal of the surface-bound intermediates was promoted by Ru. This is believed to occur more readily for PtRu alloys since Ru is more easily electrooxidised than pure Pt, and forms Ru-OH_ads at lower potentials (12). The -OH_ads species are then believed to spill over onto neighbouring Pt sites where they react with -CO_ads. This occurs at lower potentials than with pure Pt.

Another interesting observation was made concerning the relative positions of the methanol and -CO_ads stripping peaks. For 40 wt.% Pt/XC72R the methanol stripping peak was observed at a lower potential (438 mV) than the CO stripping peak (538 mV). This could be an indication that the pure Pt electrocatalyst was not completely poisoned by the methanol, although the similar EPSA values from the methanol (EPSAMeOH) and CO (EPSACO) experiments make this debatable. Further, the presence of a shoulder on both the methanol and CO stripping peaks also suggests that the electrocatalyst contains either two types of reaction site or crystallites with differing activities that were resolvable by both techniques.

One final point to consider is the relevance of the EPSA values determined by each technique. Although the values in Table I are normalised for the Pt and Ru content of the electrocatalysts, it is not clear how the Ru components interact with CO in the gas-phase and in the electrochemical experiments. For example, the Ru (or Ru oxides) may not be covered with a complete monolayer of CO during the electrochemical measurements. This process is also probably strongly dependent on time, temperature and the particle size of the electrocatalyst. Similarly, the significance of the EPSA values determined with methanol are open to debate. Although methanol is believed to preferentially electrosorb on Pt sites, the process probably requires an ensemble of Pt atoms. Therefore, for complete poisoning, the methanol fragments must be mobile enough to release the Pt ensembles so further reaction with methanol can occur.

Nevertheless, the use of methanol stripping voltammetry appears to give an excellent indication of the available electrocatalyst surface area for methanol electrooxidation. This strongly complements the measurements that are routinely carried out with CO.

Better Anode Electrocatalyst Materials

The search undertaken for more active anode electrocatalyst materials for methanol electrooxidation in acid electrolyte is illustrated by studies similar to the one above. The electrocatalyst needs to provide both an efficient mechanism for methanol dehydrogenation and an efficient mechanism to electrooxidise -CO_ads to CO₂.

Of great importance are materials that might combine with Pt to promote Steps iv to viii in Figure 2, and Ru in particular significantly increases the activity of Pt for methanol electrooxidation. Other studies have looked at elements that form binary alloys with Pt (Ru, Sn, Re, Au, Mo, W, Pd, Rh (13–20)), and ternary (PtRuSn (21)) and
quaternary alloys (PtRuIrOs (22)).

At the Johnson Matthey Technology Centre, the focus of DMFC anode development has been on using carbon-supported high surface area electrocatalysts. Figure 5 presents anode half-cell polarisation data for a series of Vulcan XC72R-supported Pt materials. These include pure Pt, and alloys of Pt with iridium (PtIr), palladium (PtPd), osmium (PtOs), rhodium (PtRh), tungsten (PtW), gallium (PtGa), ruthenium (PtRu), ruthenium-rhodium (PtRuRh) and ruthenium-tin (PtRuSn).

Steady-state measurements were performed at 80°C in 1 M sulfuric acid electrolyte containing 2 M methanol. Prior to the methanol electrooxidation studies, the in situ electrochemical metal area (ECA, m² g⁻¹ Pt) of each electrode was determined using CO stripping voltammetry. Unlike the EPSA CO measurement, this value corresponds to the maximum available Pt surface area in the electrode. The sulfuric acid can make effective contact with the entire electrocatalyst surface because it floods the electrodes, as it also does in the gas-phase CO chemisorption experiment. Thus, the performance of each electrocatalyst is not limited by electrode structure or by the EPSA effects that are seen in the MEAs. Using the ECA value for each electrode, the half-cell polarisation data were corrected to give the intrinsic activity of the electrocatalysts (specific activity, mA cm⁻² Pt). Hence, the activity of each anode electrocatalyst could be compared, independent of its surface area.

The half-cell data in Figure 5 show that the activities of the materials fall into two distinct bands. The most active electrocatalyst materials — those having the lowest potentials — all contain Ru. The elements Rh, Os and Ga appear to show promotional effects, but much smaller than that of Ru. Tungsten did not promote methanol electrooxidation on Pt, and Pd and Ir appeared to inhibit it.

The methanol electrooxidation activity of the PtRu was found to be the highest of the binary Pt-based alloys. A number of groups have claimed to have developed ternary or even quaternary materials with activities higher than PtRu alloy (23, 24). The rationale behind some of these materials is sometimes unclear and quite often their new materials are compared with what could be considered a poor PtRu alloy baseline. Figure 5 also compares the methanol electrooxidation data of two ternary materials, PtRuRh and PtRuSn. Both Rh and Sn have been shown to promote the activity of Pt for methanol electrooxidation, but neither were found

Fig. 5 Half-cell specific activity plots for Pt alloy materials in 1 M sulfuric acid/2 M methanol at 80°C, showing that Ru-containing electrocatalysts are the most active. A lower anode potential corresponds to a more active electrocatalyst for methanol electrooxidation.
to co-promote PtRu. This observation led to the conclusion that only modest improvements in the PtRu activity can be attained by adding co-promoting elements. Indeed, quite often, adding ternary or even quaternary electrocatalyst components can reduce the production friendliness of the material and dramatically increase its cost. Hence, at Johnson Matthey, the electrocatalyst development work has focused on optimising the PtRu alloy.

An Optimum Platinum:Ruthenium Ratio

There are a number of published papers which describe work to determine the optimum PtRu alloy composition for the DMFC anode (25, 26). For this type of study to be carried out successfully, the composition of the electrocatalyst must be controlled so that the surface structure is representative of the bulk alloy composition. (This can be challenging for carbon-supported electrocatalysts.) The composition of the electrocatalyst surface is determined by the chemical deposition process used to deposit the particles and/or by any post-treatment it receives, such as thermal annealing. The wide range of methods reported in the literature for preparing PtRu electrocatalysts therefore probably results in a range of materials with different surface compositions. This makes it difficult to assess which composition is most active for methanol electrooxidation. There is also evidence that different alloy compositions are favoured at high and low temperatures (27). Hence, it is probably only possible to select the most active PtRu alloy phase from a range of compositions prepared using the same deposition process and post-treatment conditions.

In order to determine the most active alloy composition for methanol electrooxidation, a range of PtRu/Vulcan XC72R electrocatalysts was prepared by an aqueous-based slurry route. Each electrocatalyst contained a fixed Pt loading (20 wt.%); the Ru loading was varied to give a range of atomic compositions from Pt100 to Pt30Ru70. The preparation involved codeposition of highly-dispersed mixed oxide particles onto the carbon, followed by drying and heat treatment. Characterisation by X-ray diffraction (XRD) was used to estimate the bulk alloy composition (from the Pt lattice parameter) and the average crystallite size (using Scherrer's equation (28)).

From Figure 6 (which shows some early work that used an experimental deposition technique) the bulk alloy composition and average crystallite size (as a function of alloy composition) can be seen. The XRD-determined bulk alloy compositions shown here are a reasonable match to the theoretical compositions. Alloys Pt90Ru10 and Pt60Ru30 had bulk alloy compositions identical to the theoretical compositions, but alloys from Pt70Ru30 to Pt80Ru20 appeared to be Pt-rich. Thus, part of the Ru was not being incorporated into the predominant crystalline face centred cubic (f.c.c.) PtRu phase but was present either in an amorphous Ru oxide phase or in an amorphous Ru-rich PtRu phase – but neither of these phases could be detected with XRD. X-ray photoelectron spectroscopy (XPS) measurements suggested that the electrocatalyst surface was indeed Ru-rich.

The XRD crystallite size data showed an interesting effect: the crystallite size of Pt100 was very large (~12 nm) but fell dramatically as the Ru content was increased to 30 at.% and above. The crystallite size of alloys with theoretical compositions between Pt70Ru30 and Pt60Ru40 was found to be between 2 to 3 nm. This suggests that Ru promotes the dispersion of the electrocatalyst. The effect was most noticeable for materials having

![Fig. 6 XRD data for a range of PtRu/XC72R electrocatalysts, showing alloy composition and average crystallite size. The diagonal dashed line represents the theoretical composition. These materials were used to assess the suitability of a new laboratory-scale chemical deposition process](image)
compositions (Pt$_{70}$Ru$_{30}$ to Pt$_{50}$Ru$_{50}$) which deviated most from the theoretical composition. Therefore, the unalloyed amorphous material that may reside on or near the surface of the PtRu alloy particles may help prevent sintering during the deposition or thermal reduction processes. For alloys Pt$_{50}$Ru$_{50}$ and Pt$_{80}$Ru$_{20}$ this effect was less prominent because all the Ru was incorporated into the bulk alloy.

To investigate the surface electrochemical behaviour of the PtRu alloy electrocatalysts and their activities for methanol electrooxidation, all the electrocatalysts were used to prepare electrodes suitable for testing in sulfuric acid electrolyte. Aqueous-based Nafion ionomer inks were prepared and carbon-fibre paper electrodes were manufactured using a coating process.

Figure 7 shows the half-cell methanol electrooxidation activity and the ECA (m$^2$ g$^{-1}$ PtRu) determined with CO-stripping voltammetry for each PtRu material. The methanol electrooxidation activities were determined in 1 M sulfuric acid and 2 M methanol at 80°C. The electrodes contained 0.35 mg Pt cm$^{-2}$. The methanol electrooxidation activity is compared at a mass activity of 100 mA mg$^{-1}$ Pt; electrocatalysts with lower anode potentials were the most active. (The mass activity corresponds to the current density corrected for the electrode Pt loading.) As expected, pure Pt was the least active material, requiring an anode potential of ~ 0.500 V (vs. RHE). However, its activity increased dramatically as the Ru content was increased to Pt$_{50}$Ru$_{50}$, but at higher Ru contents the activity became constant at ~ 0.340 V (vs. RHE).

Figure 7 also shows the theoretical (calculated from XRD data assuming spherical particles) and electrochemical (from CO-stripping voltammetry) metal surface areas as a function of alloy composition. The two sets of values compare well; the ECA values of Pt$_{30}$Ru$_{70}$ to Pt$_{70}$Ru$_{30}$ are the highest.

An examination of the data suggests that two effects may control the activity of the electrocatalysts. First, as the level of Ru was increased in the alloy to 30 at.% and above, the ECA of the electrocatalyst increased. The XRD data also suggest that part of the Ru was not incorporated into the Pt lattice but may have remained segregated on the surface of the particles, perhaps as an oxide. Further addition of Ru beyond Pt$_{50}$Ru$_{50}$ did not lead to a relative increase in the amount incorporated into the Pt lattice. Instead, the amount of unalloyed Ru remained essentially the same (as shown by the constant deviation of the XRD alloy composition versus the theoretical composition in Figure 6). Thus, the methanol electrooxidation activity of all these materials is roughly similar. It appears that good alloying of Ru into the Pt lattice
Table II

<table>
<thead>
<tr>
<th>Composition</th>
<th>XRD crystallite size, nm</th>
<th>XRD lattice parameter, Å</th>
<th>Calculated surface area, m² g⁻¹ Pt(Ru)</th>
<th>CO chemisorption metal area, ECA, m² g⁻¹ Pt(Ru)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt.% Pt, 10 wt.% Ru</td>
<td>1.9</td>
<td>3.877</td>
<td>174</td>
<td>139</td>
</tr>
<tr>
<td>40 wt.% Pt, 20 wt.% Ru</td>
<td>2.5</td>
<td>3.883</td>
<td>132</td>
<td>104</td>
</tr>
<tr>
<td>PtRu black</td>
<td>2.9</td>
<td>3.882</td>
<td>114</td>
<td>83</td>
</tr>
<tr>
<td>Pt black</td>
<td>6.5</td>
<td>3.926</td>
<td>43</td>
<td>24</td>
</tr>
</tbody>
</table>

Ru electrocatalyst had a slightly larger crystallite size (2.5 nm), while the PtRu black had the largest (2.9 nm). These are excellent dispersions, especially for the latter two, and this is very apparent when their crystallite sizes are compared to that of unsupported Pt black (6.5 nm) (HiSPEC™ 1000).

The improved dispersions found for PtRu electrocatalysts compared with a pure Pt electrocatalyst at a similar loading on carbon was described in Part II (29). The presence of Ru again appears to promote the dispersion, most probably through small amounts of surface-segregated Ru oxides (or surface enrichment with Ru) which prevent sintering. The XRD lattice parameter values for each PtRu electrocatalyst also show a shift from the value for pure Pt black. This is not indicative of exactly Pt₅₀Ru₅₀ alloy but of slightly Pt-rich alloy (compared to the theoretical composition).

Anode Electrocatalyst Structure

Unsupported PtRu alloy blacks are the most widely used electrocatalysts employed at the DMFC anode, primarily because they provide very high Pt loadings (2–10 mg Pt cm⁻²) to maximise the EPSA in the electrode. Such electrodes are very active for methanol electrooxidation but are too expensive for most commercial applications.

To investigate whether the metal loading could be reduced to a more economical level and find the effects on performance, a series of PtRu alloy electrocatalysts of composition Pt₅₀Ru₅₀ was prepared. The materials were PtRu black (HiSPEC™ 6000), and two Vulcan XC72R-supported electrocatalysts of composition 20 wt.% Pt, 10 wt.% Ru (HiSPEC™ 5000) and 40 wt.% Pt, 20 wt.% Ru. The crystallite sizes and lattice parameters were determined by XRD, see Table II. The smallest crystallite size was 1.9 nm for the 20 wt.% Pt, 10 wt.% Ru electrocatalyst. The 40 wt.% Pt, 20 wt.% Ru electrocatalyst had a slightly larger crystallite size (2.5 nm), while the PtRu black had the largest (2.9 nm). These are excellent dispersions, especially for the latter two, and this is very apparent when their crystallite sizes are compared to that of unsupported Pt black (6.5 nm) (HiSPEC™ 1000).

Specific Activity for Methanol Electrooxidation

To find the methanol electrooxidation activity of the electrocatalysts, flooded steady-state half-cell experiments were performed in 1 M sulfuric acid and 2 M methanol at 80°C. Electrodes were
prepared using electrocatalyst-containing aqueous Nafion inks, with a loading of ~ 1 mg Pt cm⁻². Figure 8 shows the specific activities of the three PtRu electrocatalyst materials; under the reaction conditions, the methanol electrooxidation activities were comparable. That is, the intrinsic kinetic activity of the electrocatalysts was unaffected by the electrocatalyst structure and no significant electrode structure effects were observed. The lack of electrocatalyst structure effects is probably due to the sulfuric acid electrolyte penetrating the entire electrode structure, and utilising all the electrocatalyst.

**MEA Anode Performance**

To study the effect of the anode electrode structure on the MEA performance, a series of experiments was carried in a 3 cm² micro-fuel cell. The electrodes described above (with 1 mg Pt cm⁻²) were used to prepare MEAs using Nafion 112 membrane and Pt black cathodes (4 mg Pt cm⁻²).

Figure 9 shows the results of pseudo anode half-cell (or half MEA) experiments at 90°C. In these experiments, the anode of the MEA was supplied with 2 M methanol fuel and the counter electrode with pure hydrogen. The fuel cell was then driven by a potentiostat and the anode potential (vs. RHE) was measured as a function of the current density. The resistance of the MEA was determined using current-interrupt techniques.

Although the intrinsic activities of the electrocatalysts had been identical in sulfuric acid electrolyte (Figure 8) this was not the case when these electrocatalysts were employed in the anode of an MEA. Within the MEA, their anode performance appears to be linked to a number of factors.
including electrocatalyst utilisation (the extent of the electrocatalyst/ionomer interface), the thickness of the electrocatalyst layer and its porosity.

The anode containing the 20 wt.% Pt, 10 wt.% Ru electrocatalyst had the lowest performance of the three anode electrocatalysts, see Figure 9. This anode had the highest EPSA (EPSAMOH = 78 m² g⁻¹ PtRu) but corresponded to the thickest electrode layer (at 1 mg Pt cm⁻²). Its performance suggests it was suffering from mass transport limitations at current densities > 200 mA cm⁻². It seems that methanol could not enter the entire structure and CO₂ could not escape. At current densities > 1000 mA cm⁻² this was particularly severe.

This observation suggested that the PtRu black should have the best performance of the three materials as it produced the thinnest electrocatalyst layer, but this is not the case. The PtRu black anode has a significantly better performance only at high current densities (> 1000 mA cm⁻²). At low current densities, when kinetic control is attained, the performances of the PtRu black and 20 wt.% Pt, 10 wt.% Ru anodes were almost identical. (Kinetic control is attained when mass transport does not occur and only electrocatalyst kinetics limit performance.)

In fact, the 40 wt.% Pt, 20 wt.% Ru electrocatalyst had the highest performance of the three over the complete range of current densities. This electrocatalyst seems to produce the best compromise between available electrocatalyst surface area (when operating in the MEA) and electrocatalyst layer thickness (to minimise mass transport losses). At a current density of 500 mA cm⁻² (corresponding to an anode potential of 0.35 V (vs. RHE)) its potential was about 30 mV lower than that of the PtRu black electrocatalyst and more than 50 mV lower than that of the 20 wt.% Pt, 10 wt.% Ru electrocatalyst. This is an excellent performance with none of the mass transport limitations shown by the 20 wt.% Pt, 10 wt.% Ru electrocatalyst. The reason for its superior performance over PtRu black is not easy to explain.

One aspect is the EPSA; the 40 wt.% Pt, 20 wt.% Ru electrocatalyst has a higher available EPSA (EPSAMOH = 59 m² g⁻¹ PtRu) than the PtRu black (EPSAMOH = 39 m² g⁻¹ PtRu). However, EPSA values should only at best be considered as corresponding to the maximum accessible electrocatalyst surface area. In operation the actual active surface area of the anode may be lower than the EPSA value or may change dynamically with current. The real utilisation of the 40 wt.% Pt, 20 wt.% Ru electrocatalyst may therefore be significantly higher than that of the PtRu black.

Following the micro-fuel cell experiments, MEAs of area 50 cm² were prepared with the same anode and cathode electrodes as before but this time with Nafion 117 membrane (instead of Nafion 112), see Figure 10. The resulting MEAs were tested in a DMFC single cell at 90°C. Methanol fuel (0.75 M) was supplied to the anode of the MEA at ambient
pressure and at a flow 4.5 times in excess of stoichiometry \( \lambda_{\text{MeOH}} = 4.5 \) (a stoichiometry of 1 is the amount needed to sustain the current). The cathode was supplied with unhumidified air at a pressure of 30 psig at a flow 5 times stoichiometry \( \lambda_{\text{air}} = 5 \).

The data in Figure 10 show the same clear trend as the pseudo anode half-cell data in Figure 9. The MEA containing the 40 wt.% Pt, 20 wt.% Ru electrocatalyst gave the highest performance (0.5 V at 228 mA cm\(^{-2}\)) compared with 20 wt.% Pt, 10 wt.% Ru (0.5 V at 187 mA cm\(^{-2}\)) and PtRu black (0.5 V at 187 mA cm\(^{-2}\)); all had the same Pt loading of 1 mg Pt cm\(^{-2}\). Figure 10 also gives current-interrupt resistance data for the same series of MEAs, also showing that the structure of the anode did not influence the resistance of the MEA. That is, the performance difference was entirely due to the change in anode structure.

Therefore it appears that 40 wt.% Pt, 20 wt.% Ru gives an MEA performance superior to those of 20 wt.% Pt, 10 wt.% Ru and PtRu black. Excellent single cell performance have been attained with MEAs containing only 1 mg Pt cm\(^{-2}\) with power densities exceeding 100 mW cm\(^{-2}\). This shows that careful choice of the anode structure is important to maximise DMFC MEA performance and that the levels of PtRu electrocatalyst can be reduced significantly from the 2–10 mg Pt cm\(^{-2}\) levels that are traditionally employed.

The Effect of Membrane Thickness

Nafion 117 membrane is the preferred electrolyte for the DMFC. It is the thickest (~180 μm) available commercial fuel cell membrane. The rate of methanol crossover through Nafion 117 is low compared to, for instance, the thinner Nafion 112 membrane (50 μm). New membrane materials to help reduce the methanol crossover rate are being developed, but it is unlikely that any of the current candidates will completely eliminate it as all low-temperature proton conducting polymer materials only function efficiently in a fully hydrated state. Methanol, being completely miscible with water, is carried by the water as it diffuses through the membranes.

In the PEMFC, thinner membrane materials (such as 30 μm) are preferred as they offer reduced ionic resistance and thus increased MEA performance. They also help to reduce the MEA cost. For the DMFC, it would be advantageous to use thinner membrane materials to reduce the ionic resistance of the MEA. However, there is a sensible lower thickness limit beyond which the rate of methanol crossover becomes too high and/or the membrane is no longer strong enough to maintain the large pressure differentials often needed.

**Cathode Improvements**

With careful design of the cathode, it has been possible to use Nafion 112 membrane as an alternative to Nafion 117, without significant loss in performance. Data from a 50 cm\(^2\) single cell containing MEAs with Nafion 117 and Nafion 112 membranes is shown in Figure 11. Both MEAs contained a 40 wt.% Pt, 20 wt.% Ru (1 mg Pt cm\(^{-2}\)) anode and a Pt black (4 mg Pt cm\(^{-2}\)) cathode. Cell voltage data were recorded at 90°C with 0.75 M methanol \( \lambda_{\text{MeOH}} = 4.5 \) and pressurised air (30 psig, \( \lambda_{\text{air}} = 5 \)). In a second (pseudo half-cell diagnostic) experiment, the anode potential was determined by passing pure hydrogen across the cathode (instead of air) and the fuel cell was driven by an electric load. Hence, the anode and cathode potentials could be decoupled from the cell voltage. Current-interrupt measurements were used to determine the MEA resistance.

Under these conditions, the MEA with Nafion 112 had the better performance than with Nafion 117, especially at higher current densities. This was shown to be mainly a resistance effect – the resistance-corrected data for both MEAs were comparable (except that the cell voltage of the Nafion 112 MEA was about 10 mV lower at low current densities, probably due to enhanced methanol crossover). This observation was confirmed by the anode and cathode half-cell data for the MEAs. As expected, the anode half-cell potentials of both MEAs were very similar. In the Nafion 112 MEA the cathode potential was only about 10 to 20 mV lower than in the Nafion 117 MEA due to the enhanced crossover rate through the thinner membrane.

Figure 11 also shows the cathode potential for the same Nafion 112 MEA when it was operating...
Fig. II A comparison of Najion 117 and Najion 112 membranes in MEAs. Both MEAs have a 40 wt.% Pt, 20 wt.% Ru anode (1 mg Pt cm\(^{-2}\)) and a Pt black cathode (4 mg Pt cm\(^{-2}\)). The data were recorded in a 50 cm\(^2\) single cell at the operating temperature of 90°C with 0.75 M methanol fuel (\( \lambda_{\text{MEOH}} = 4.5 \)) and pressurised air (30 psig, \( \lambda_{\text{air}} = 5 \)).

In a pseudo half-cell experiment, pure hydrogen was passed across the cathode to help determine the anode potential. The Najion 112-based MEA had the higher performance (especially at higher current densities) due to reduced membrane resistance.

as a PEMFC. Instead of methanol and dry air, it was supplied with humidified hydrogen and humidified air, respectively, (both at 30 psig). The cathode potential in PEMFC-mode is only slightly higher (10 mV) than in DMFC-mode (but is slightly lower than the cathode potential for the Najion 117 MEA in DMFC-mode). This suggests that the Pt black-based cathode structure used in these MEAs has good methanol tolerance and indicates that the cathode structure can be optimised to make it essentially methanol tolerant. However, these experiments were carried out with relatively high air flows (\( \lambda_{\text{air}} = 5 \)) and at high pressures which reduce the effects of crossover to some extent.

Reducing the Cathode Air Flow

The air flow rate in the single cell shown in Figure 11 is too high for most practical fuel cell applications (large volumes of air require energy to pressurise them). The cathode exhaust gas from the fuel cell stack must also be cooled efficiently to remove any methanol (from crossover) and water vapour. This places a high energy demand on the fuel cell system. A lower air flow, preferably equivalent to a stoichiometry of 2 (\( \lambda_{\text{air}} = 2 \)) or less, is thus desirable.

Figure 12 shows the performance of a Najion 117-based MEA, of similar construction to that in Figure 11. Single cell measurements were carried out at 90°C with 0.75 M methanol fuel (\( \lambda_{\text{MEOH}} = 4.5 \)) and pressurised air (30 psig), but at the lower air flow rate, \( \lambda_{\text{air}} = 2 \). Under these conditions, the MEA performance was very similar to that of the MEA in Figure 11 which was operating with a high air flow (\( \lambda_{\text{air}} = 5 \)).

Pseudo half-cell experiments were carried out to decouple the anode and cathode half-cell potentials in the MEA. The cathode potential was found
Fig. 12 Data recorded at low air flows to the cathode, $\lambda_{\text{air}} = 2$, in a 50 cm$^2$ single cell with a Nafion 117 MEA. The anode is 40 wt.% Pt, 20 wt.% Ru (1 mg Pt cm$^{-2}$) and the cathode is platinum black (4 mg Pt cm$^{-2}$). The operating temperature is 90°C and the fuel supplied to the anode is 0.75 M methanol ($\lambda_{\text{MeOH}} = 4.5$); the air is pressurised (30 psig). The cell performance under the low air flow conditions is comparable to that at higher air flows. This demonstrates the good methanol/water tolerance of the cathode.

Reducing Cathode Electrocatalyst Loading

The DMFC anode electrocatalyst developments described so far have been aimed at reducing the Pt loading to 1 mg Pt cm$^{-2}$, while maintaining performance. This has been achieved with 40 wt.% Pt, 20 wt. % Ru/Vulcan XC72R. By comparison, in the PEMFC the typical Pt electrocatalysts used in the cathodes are also supported on Vulcan XC72R, but the loading is only 0.2 to 0.7 mg Pt cm$^{-2}$ which gives an excellent MEA performance (1).

All the DMFC single cell data described here have used MEAs containing high loaded cathodes (Pt black, 4 mg Pt cm$^{-2}$). To reduce this loading, work was undertaken to develop carbon-supported Pt electrocatalysts of much higher surface area than Pt black electrocatalyst (24 m$^2$ g$^{-1}$ Pt) (1). A reduction in Pt loading from 4 to 1 mg Pt cm$^{-2}$ was investigated, and providing that the methanol tolerance is comparable to that of Pt black, no impact on performance was expected. The new materials must also be able to cope with the high levels of water and methanol found at the DMFC cathode.

In Figure 13, data from a 25 cm$^2$ single cell measured at 90°C for three MEAs is shown, one is based on Pt black (4 mg Pt cm$^{-2}$) and two are based on carbon-supported Pt cathodes (1 mg Pt cm$^{-2}$). Methanol (0.5 M) was supplied to the anode ($\lambda_{\text{MeOH}} = 3$) and pressurised air to the cathode (30 psig, $\lambda_{\text{air}} = 10$). Cathode A was based on 40 wt.% Pt on carbon (ECA 60 m$^2$ g$^{-1}$ Pt) of similar construction to that used in the PEMFC. Cathode B was based on a 60 wt.% Pt on carbon (ECA 45 m$^2$ g$^{-1}$ Pt) and was optimised for DMFC operation. The performance of the MEA with cathode A was slightly lower than the Pt black cathode. The MEA with cathode B performed comparably to the Pt black cathode, showing that the cathode Pt loading to be only 5–10 mV lower under the low air flow conditions, showing the excellent water and methanol tolerance of the cathode. The cathode potentials were also compared in DMFC- and PEMFC-modes, and were found to be identical under the low air flow condition. Thus, the effects of methanol crossover can be significantly reduced by careful design of the cathode and the performance can be maintained at low air flows. Indeed, methanol-tolerant materials (6) may not be required under these conditions, especially with Nafion 117 membrane.
Fig. 13 Cell voltage data recorded in a 25 cm² single cell of the performances of three MEA cathodes at a 90°C operating temperature. The Pt black cathode is loaded at 4 mg Pt cm⁻². Cathode A (40 wt.% Pt/carbon) and Cathode B (60 wt.% Pt/carbon) are loaded at 1 mg Pt cm⁻². Methanol fuel (0.5 M) was supplied to the anode (λan=3), and pressurised air (30 psig) to the cathode at high flows (λ cath = 10). The anode was 40 wt.% Pt, 20 wt.% Ru/XC72R (1 mg Pt cm⁻²).

can be reduced significantly without performance loss. Further optimisation is expected to bring the Pt loading to the levels used in the PEMFC.

Portable DMFC Applications

Recently, the tremendous advances attained in power densities by the DMFC have prompted companies, such as Smart Fuel Cell (Germany); Manhattan Scientific, MTI and Motorola (U.S.A.); and Toshiba (Japan) to establish ambient micro-DMFC programmes to target the 1–100 W power range. While the power densities offered by the DMFC are considerably less than those from the PEMFC, the DMFC can still generate sufficiently high energy densities to make it an attractive alternative to secondary batteries for a wide range of applications. Miniaturisation of the DMFC system is also simpler. With liquid fuel, the main advantage is the convenience of almost instant recharging, by replacing a spent fuel cartridge – an advantage over rechargeable batteries. The DMFC is therefore being targeted at applications such as mobile phones, notebook computers and video cameras where rapid recharging is advantageous.

To date, the most efficient DMFC systems are almost all exclusively designed to operate at higher temperatures and pressures where the power densities are the highest. Most MEA development has focused on increasing the performance in the temperature range 80 to 130°C and little work has been done to increase the MEA performance at lower temperatures and pressure (20 to 60°C, ambient air pressure). Often, the MEAs used in portable ambient DMFC systems have been optimised for higher operating temperatures and pressures, which may not be the best option to maximise power density. Tailoring the MEA components, including the electrocatalysts, substrate and membrane, may improve the performance further and is a high priority for device developers, as improvements in the stack power/size ratio will allow more straightforward miniaturisation.

Miniaturising the Fuel Cell Stack

Figure 14 presents 50 cm² single cell data for an MEA based on Nafion 117 membrane, a 40 wt.% Pt, 20 wt.% Ru/XC72R anode (1 mg Pt cm⁻²) and a Pt black cathode (4 mg Pt cm⁻²). The data were measured at 40, 60 and 80°C with 0.5 M methanol (flow rate 6 ml min⁻¹) and ambient air (< 0.3 psig inlet pressure) at low flows (λ cath = 2). Although this MEA was optimised for higher temperatures and pressures, its performance under low pressure conditions was good. The data is summarised in Table III together with projected fuel cell stack volumes (cm³) for a range of devices.

The fuel cell stack volumes were calculated based on a 3 mm cell pitch (the thickness of one bipolar flow field plate and one MEA), 10 mm thick stack end plates and an MEA membrane.
Fig. 14 Single cell data for an MEA based on Nafion 117 with an anode of 40 wt.% Pt, 20 wt.% Ru/XC72R (1 mg Pt cm$^{-2}$) and a Pt black cathode (4 mg Pt cm$^{-2}$). The temperatures were 40, 60 and 80°C with 0.5 M methanol fuel supplied to the anode (flow rate 6 ml min$^{-1}$) and ambient air (< 0.3 psig inlet pressure) at flows ($\lambda_{in}$= 2) to the cathode. At 40°C, the cell voltage was 0.409 V and power density 21 mW cm$^{-2}$; at 60°C, the cell voltage was 0.419 V and power density 42 mW cm$^{-2}$; and at 80°C the cell voltage was 0.440 V and power density 66 mW cm$^{-2}$.

border of dimensions 5 mm × 5 mm × 5 mm × 10 mm for edge sealing (the 10 mm dimension includes provision for porting – the holes cut into the membrane to allow the gases and liquids to flow). The calculation does not include the volume of the fuel pump, the air blower or the fuel tank. The projected stack volumes are based on the power density of the MEA increasing by a factor of two.

The first example in Table III shows, that to generate 1 W of power at a stack voltage of 3.6 V (typical cell phone requirements) when operating at 40°C, 9 MEAs of active area 5.4 cm$^2$ are required, giving a projected stack volume ~ 63 cm$^3$ – far too large to fit a modern cell phone. Doubling the power density produced by the MEA would only modestly reduce the stack volume to ~ 42 cm$^3$ because the end plates and MEA edge seals are responsible for a large proportion of the stack volume. This demonstrates that miniaturisation of the DMFC to fit a cell phone will be challenging.

The other examples shown in Table III correspond to larger 30 W 10 V devices operating at 40, 60 and 80°C. The larger devices utilise volume more effectively, primarily because the end plates and edge seals represent a much smaller proportion of the overall volume of the stack. When operating at 40°C, the projected stack volume based on current MEA technology is 823 cm$^3$ (requiring 24 MEAs of active area 61 cm$^2$). If the temperature of the fuel cell stack is increased to 60 and 80°C, the volume of the stack decreases to 430 and 334 cm$^3$, respectively. Temperature thus has a large effect on stack volume. When the temperature is increased from 40 to 60°C the stack volume almost halves. The stack volumes are very attractive; when operating at 60°C, the approximate dimensions of a 30 W 10 V stack would be 5.5 cm × 5.5 cm × 14 cm. When operating at 40°C, with a doubled MEA power density, the projected stack volume is again significantly reduced from 823 to 441 cm$^3$. At 60 and 80°C, the impact on the stack volume is less marked, decreasing from 430 to 261 cm$^3$ and from 334 to 191 cm$^3$, respectively. Again, these are very attractive stack volumes and show why the DMFC is being rigorously developed as a secondary battery replacement device.

**Extending Upper Temperature Limit**

While the power densities produced by low temperature ambient pressure DMFC stacks have become attractive enough to drive its near term
commercialisation, some argue that longer term transport applications should be targeted. The DMFC system, and the reformer-PEMFC system, are considered to be good options for transport uses, but the DMFC efficiency is poor compared to the PEMFC. On the other hand, the PEMFC stack must be humidified so the hydrogen (reformer) and air are saturated with water vapour. Without humidification the MEA will dry out and eventually fail due to resistive heating and pin-holing of the membrane. In addition, the large amounts of low grade heat must also be removed from the stack and radiated to the surroundings. However, the size restrictions, for example, of an automobile make this difficult to achieve effectively, and has led some to believe that the fuel cell stack operating temperature must be increased beyond 100°C. Heat management would then be less critical.

This presents an ideal opportunity for the DMFC, with its dilute methanol fuel solution providing it with the necessary humidification. The

---

**Table III**

<table>
<thead>
<tr>
<th>Stack power, W</th>
<th>Stack voltage, V</th>
<th>Stack temp., °C</th>
<th>Current density, mA cm⁻²</th>
<th>Number of MEAs</th>
<th>MEA active area, cm²</th>
<th>Cell voltage, V</th>
<th>Power density, mW cm⁻²</th>
<th>Stack volume, cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.6</td>
<td>40</td>
<td>50</td>
<td>9</td>
<td>5.4 (2.8)**</td>
<td>0.409</td>
<td>20.5</td>
<td>63 (42)</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>40</td>
<td>50</td>
<td>24</td>
<td>61 (31)</td>
<td>0.409</td>
<td>20.5</td>
<td>823 (441)</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>24</td>
<td>30 (16)</td>
<td>0.419</td>
<td>42</td>
<td>430 (261)</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>80</td>
<td>150</td>
<td>23</td>
<td>20 (11)</td>
<td>0.440</td>
<td>66</td>
<td>334 (191)</td>
</tr>
</tbody>
</table>

* Data from a 50 cm² single cell for an MEA based on Nafion 117 membrane with an anode of 40 wt.% Pt, 20 wt.% Ru/XC72R (1 mg Pt cm⁻²) and a Pt black cathode (4 mg Pt cm⁻²). Methanol fuel 0.5 M (flow rate 6 ml min⁻¹) is supplied to the anode and ambient air (< 0.3 psig inlet pressure) at flow (λₐₐᵦ = 2) is supplied to the cathode.

**This value and all other values in brackets are projections based on increasing the power density of the MEAs by a factor of two.**

---

**Fig. 15** The effects of operating temperatures 90 and 130°C on a DMFC single cell with a Nafion 117-based MEA. The anode is 40 wt.% Pt, 20 wt.% Ru (1 mg Pt cm⁻²); the cathode is Pt black (4 mg Pt cm⁻²). Pressurised air (30 psig) flows (λₐₐᵦ = 2) to the cathode and 0.75 M methanol (λₑᵦᵦᵦᵦ = 4.5) is supplied to the anode. At 90°C the MEA performance is ~ 330 mA cm⁻² at 0.5V. At 130°C the MEA performance is ~ 530 mA cm⁻² at 0.5V (or 500 mA cm⁻² at 0.510 V).
large volumes of water circulated around the stack help to keep the membrane humidified at temperatures where the PEMFC membrane could not operate.

Figure 15 presents DMFC single cell data for a Nafion 117-based MEA employing 40 wt.% Pt, 20 wt.% Ru anode (1 mg Pt cm\(^{-2}\)) and a Pt black cathode (4 mg Pt cm\(^{-2}\)). The design of the MEA is more advanced than previously presented. It is supplied with 0.75 M methanol (\(\lambda_{\text{Meth}} = 4.5\)) and pressurised air at low flows (\(\rho_{\text{air}} = 2\)). At 90°C, the MEA performance is \(~330\, \text{mA cm}^{-2}\) at a cell voltage of 0.5 V, which is significantly higher than presented earlier. Due to the advanced design of the MEA, its performance increases dramatically at higher temperature. Hence, at 130°C the performance was about 530 mA cm\(^{-2}\) at 0.5 V (or 500 mA cm\(^{-2}\) at 0.510 V). The current-interrupt resistance was found to be unchanged at 130°C showing that the MEA was well humidified.

This level of performance brings the DMFC much closer to that of the PEMFC and strongly suggests that with further modest improvement in power density, the DMFC system could successfully compete with the reformer/PEMFC system.

Acknowledgements


References


The Authors

Martin Hogarth is a Senior Scientist at the Johnson Matthey Technology Centre and has worked in the area of DMFCs since 1992. His main interests are the development of new electrocatalyst materials and high-performance MEAs for DMFCs. He is also interested in novel high-temperature and methanol-impermeable membranes for the PEMFC and DMFC, respectively.

Tom Ralph is the Head of Electrochemical Engineering at the Johnson Matthey MEA manufacturing facility based at Swindon. His main interests are the development of MEAs for PEMFC and DMFCs.