A New Palladium-Based Catalyst for Methanol Steam Reforming in a Miniature Fuel Cell Power Source

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A novel palladium-based catalyst has been developed for use in a miniature fuel cell power source for portable applications, incorporating a polymer electrolyte membrane (PEM) fuel cell. Hydrogen, which is the fuel for the cell, is produced in a ceramic microreactor via the catalytic reaction of methanol steam reforming: $CH_3OH + H_2O \rightarrow 3H_2 + CO_2$. *The need for a new catalyst in this application is driven by the limitations of traditional particulate catalysts based on copper oxide, zinc oxide and alumina (Cu-Zn-Al catalysts), which have low thermal stability and high sensitivity towards air and condensing steam. These features result in a declining activity and mechanical integrity of Cu-Zn-Al catalysts under the frequent start-stop conditions typical of the operational mode of the miniature power source. The new Pd-based catalyst has activity and selectivity similar to those of Cu-Zn-Al catalysts, but is more durable and stable under the duty cycle conditions of a portable power source. In the microreformer, the catalyst is washcoated directly on the walls of the steam reforming section, providing favourable conditions for efficient heat transfer between the heat-generating catalytic combustion section of the microreformer and its heat-consuming steam reforming section.*

1. Introduction

Current trends in energy demand for portable electronics show that the power consumption in devices such as cell phones, personal digital assistants (PDAs), notebook computers and digital cameras continues to rise. Consumers demand small size, light weight, but long battery life. The batteries most commonly used in these devices are of the rechargeable (secondary) type. However, in certain applications such as those used by exploratory expeditions, first responders and the military, recharging a battery in the field is often difficult, if possible at all. Therefore a heavy load of disposable (primary) batteries must be transported to remote locations. One solution to this problem is to use a small portable battery charger powered by a fuel cell.

Due to the low energy density of compressed hydrogen, using it as a fuel for a portable fuel cell charger is not a viable option. Liquid fuel, in particular methanol, has a much higher energy density and is easier to transport and handle, which makes it practically attractive for this application.

Methanol is used as a fuel in two different types of fuel cells. In the direct methanol fuel cell (DMFC) (Figure 1), methanol is fed directly to the anode where it reacts with water, generating electrons which travel through the external circuit as electric current, Reaction (i):

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad (i)$$
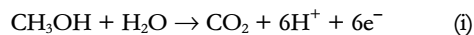
Protons travel through the proton-conducting polymer electrolyte membrane (for example, Nafion®) to the cathode where they react with oxygen from the atmosphere, to produce water.

The subject catalyst of this article was developed for use in a reformed methanol fuel cell, shown in Figure 2. In essence this is a classic type of fuel cell, invented in 1839 by William Grove. Here the fuel is hydrogen which is fed to the anode, where it splits electrocatalytically into protons and electrons, Reaction (ii):
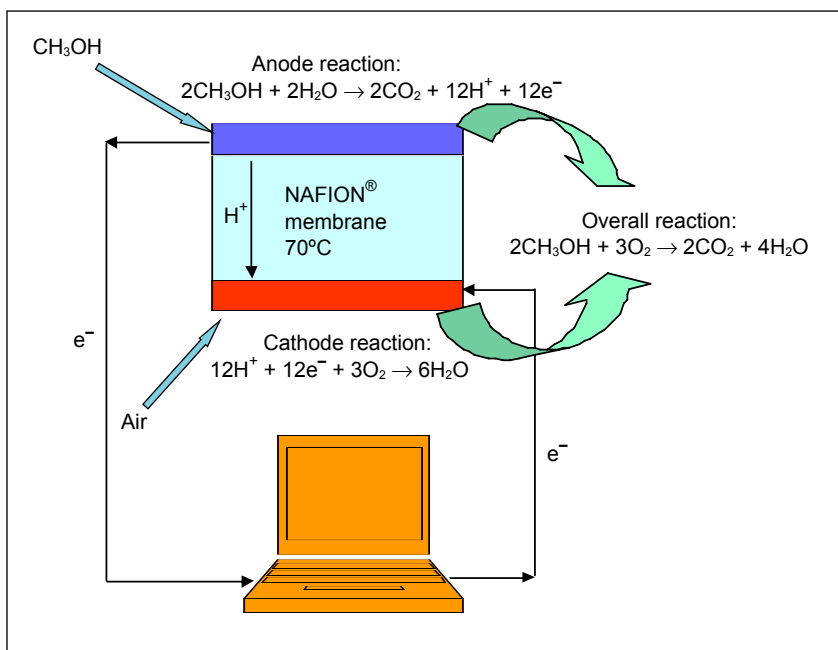
$$H_2 \rightarrow 2H^+ + 2e^- \qquad (ii)$$

CH$_3$OH

Anode reaction:
$2CH_3OH + 2H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$

NAFION$^{®}$
membrane
70ºC

H$^+$

Overall reaction:
$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$

Cathode reaction:
$12H^+ + 12e^- + 3O_2 \rightarrow 6H_2O$

e$^-$

Air

e$^-$

Hydrogen production *via* methanol steam reforming:
$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$

Anode reaction:
$2H_2 \rightarrow 4H^+ + 4e^-$

PBI/H$_3$PO$_4$
(Polybenzimidazole)
180ºC

H$^+$

Overall reaction:
$2H_2 + O_2 \rightarrow 2H_2O$

Cathode reaction:
$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

e$^-$

Air

e$^-$

In contrast to Grove's cell, however, in our application the hydrogen is produced by the catalytic steam reforming of methanol, Reaction (iii):

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \qquad \text{(iii)}$$
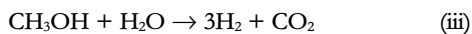
This reaction has received much attention in the last decades as an attractive route to hydrogen supply. An excellent review on methanol steam reforming (MSR) for hydrogen production has recently been published by Palo *et al.* (1).

The MSR reaction can be efficiently catalysed by copper-based catalysts (2–7), including the Cu-Zn-Al particulates otherwise used in methanol synthesis (8) and the water-gas shift reaction (9). These catalysts are commercially produced, and have been used successfully in industry for many years. By their nature they are quite sensitive to the process conditions. In particular, they are prone to sintering at temperatures above about 280 to 300°C, which results in a significant decline in activity, and also deteriorate both mechanically and in performance if steam condenses on them. Besides, a Cu-Zn-Al catalyst can develop dangerously strong exotherms if in its oxidised state it is exposed to a reducing environment, or, in its reduced (active) state, to an oxidising environment, such as ambient air (10). Therefore in industrial settings Cu-Zn-Al catalysts are operated under carefully controlled conditions. The operating cycle includes a lengthy start-up with slow reduction in syngas (H_2/CO) or hydrogen heavily diluted with nitrogen to minimise the reduction exotherm. The reduced and activated catalysts normally operate under steady-state conditions.

By contrast, the duty cycle anticipated for the MSR catalyst in the miniature fuel cell power source is much more demanding. The miniature power source will be operated with frequent starts and stops, during which liquid (reformate) will condense and may even freeze on the catalyst. Besides, slow reduction in dry gas with low concentrations of a reductant will clearly be unavailable, and the catalyst will have to be activated (reduced) upon direct contact with the methanol/water feed mixture. The properties of Cu-Zn-Al catalysts are incompatible with these requirements, and therefore a new application-specific catalyst had to be developed. This catalyst is a further improvement over the family of palladium-zinc-based catalysts which have been developed for fuel cell applications in recent years (11–16).

2. Experimental

The novel MSR catalyst has been developed using a combination of rapid catalytic screening and detailed parametric studies simulating the duty cycle of the miniature power source. The catalyst consists of Pd and Zn on an oxide support with proprietary additives. In the present paper this catalyst is designated as 'Pd-Zn/oxide support'. It is fabricated in a powder form, then slurried and used as a washcoat on the channels of the microreformer (Figure 3) to be incorporated into a miniature fuel cell power source.

The catalytic performance of a MSR catalyst is determined by two characteristics: activity and selectivity. A good MSR catalyst should provide high rates of conversion of methanol and water into hydrogen and carbon dioxide, while side reactions should be minimised. In the MSR process, in addition to the target steam reforming Reaction (iii), several undesired side reactions can occur. In particular, carbon monoxide can be formed *via* methanol decomposition, Reaction (iv):

$$CH_3OH \rightarrow CO + 2H_2 \qquad \text{(iv)}$$
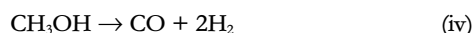
and/or reverse water-gas shift, Reaction (v):

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \text{(v)}$$
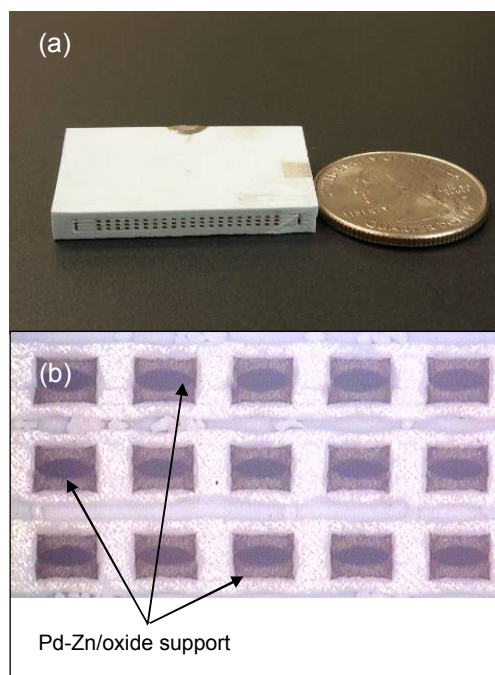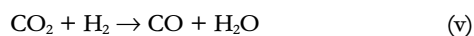

Pd-Zn/oxide support

Fig. 3 (a) The prototype microreformer (with U.S. quarter dollar coin for scale); (b) cross section of the microreformer with Pd-Zn/oxide support washcoated in the microchannels (Reproduced with permission from Motorola Energy Technologies Lab)

Carbon monoxide, a known catalytic poison, can only be tolerated by the fuel cell catalysts if its concentration in the reformate is low. Even for the fuel cells based on polybenzimidazole (PBI) membranes, which operate at elevated temperatures (~ 180ºC) and are more CO-tolerant than the fuel cells with Nafion® membranes which operate at ~ 80ºC, the CO level in the reformate must not exceed 1–2%.

Another possible side product is methane, which could be generated *via* methanation, Reactions (vi) and (vii), that consumes considerable amounts of hydrogen, while generating large amounts of heat:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (vi)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (vii)$$
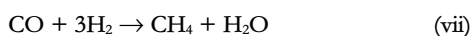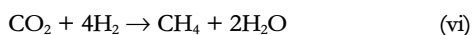
In the context of this article, the selectivity is understood as the ratio of the concentration of a given product at certain conversion of methanol to the sum of concentrations of all carbon-containing gas-phase products (in our catalytic tests no coke formation was observed), for example Equation (viii):

$$S_{CO_2} =$$
$$100 \times [CO_2]/([CO_2] + [CO] + [CH_4]) \qquad (viii)$$

where S_{CO_2} (%) is the selectivity towards CO_2, and [CO_2], [CO] and [CH_4] are the concentrations of the corresponding species.

3. Results
3.1 Performance Testing of the Cu-Zn-Al and 'Pd-Zn/Oxide Support' Catalysts in the Simulated Start-Stop Mode

The anticipated duty cycle of the miniature power source will include frequent starts and stops, with variable periods of steady-state operation. The catalysts to be used in the microreformer must be thoroughly tested under conditions simulating such operation, and a special laboratory test procedure has been developed for this purpose. The test consisted of the following elements as illustrated in Figure 4: (a) initial heat-up of the reactor to the reaction temperature, followed by starting the flow of the methanol/water feed mixture and (b) steady-state operation for approximately sixty hours; (c) multiple start-stop cycles consisting of (d) cooling down to 40ºC with the feed flow stopped (simulated shutdown of the power source); (e) heating up to the reaction temperature; (f) restarting the flow of the methanol/water feed mixture with steady-state operation for approximately two hours.
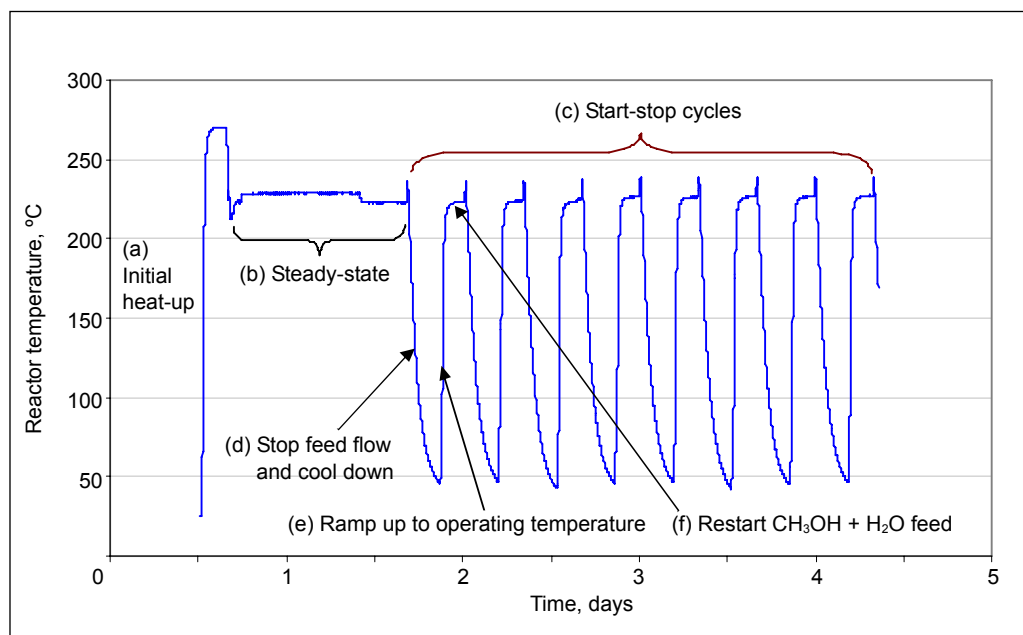

Fig. 4 Experimental temperature profile in methanol steam reforming reactor during the catalyst performance test

In the catalytic performance test using the above protocol, the commercial Cu-Zn-Al catalyst, initially run under steady-state conditions, showed stable activity for a period of about two weeks. However, soon after the onset of the start-stop temperature cycling the activity began decreasing, which continued for another two weeks of operation, showing no signs of stabilisation. However the CO_2 selectivity remained very high (in excess of 99%) throughout the test.

For the catalyst 'Pd-Zn/oxide support', tested using the same protocol, the activity under the steady-state conditions was also stable and close to that of Cu-Zn-Al catalyst. At the beginning of the temperature cycling, a slight drop in the methanol conversion was registered but the activity remained stable thereafter. The CO_2 selectivity was also stable throughout the test at 98 ± 0.6%.

The temperature dependence of the initial CO_2 selectivity (i.e. S_{CO_2} at low conversions of methanol) was further investigated in the range 230 to 320°C, and was found to decrease with the temperature from 98.2 to 94.2% (Figure 5). It was also observed that for the given reaction conditions CO_2 selectivity is fairly constant over a broad range of methanol conversions; however it decreases at high conversions (above ~ 95 to 97%).

3.2 Mechanical Strength of the Cu-Zn-Al and 'Pd-Zn/Oxide Support' Catalysts

It is known that exposure to a liquid can cause mechanical deterioration of particulate Cu-Zn-Al catalysts (9). This practically important aspect has not been sufficiently addressed in the open literature. Therefore in addition to catalytic performance we also analysed the Cu-Zn-Al catalyst for its mechanical strength before and after sixty temperature cycles, and found that the catalyst pellets lose about 80% of their initial strength as a result of the temperature cycling. The number of starts and stops of the future miniature power sources will certainly be much greater, and therefore a more significant negative impact on the mechanical strength and finally on the integrity of the catalyst should be anticipated. This is yet another reason why particulate Cu-Zn-Al catalysts cannot be used in the miniature fuel reformer, and why a new and more robust catalyst had to be developed.

The 'Pd-Zn/oxide support' catalyst was deposited on the walls of the prototype microchannel reformer, with the hydraulic diameter of a channel measuring a few hundred microns (Figure 3). The catalyst was successfully tested in the microreformer, producing hydrogen-rich reformate *via* MSR. The same catalyst on different support
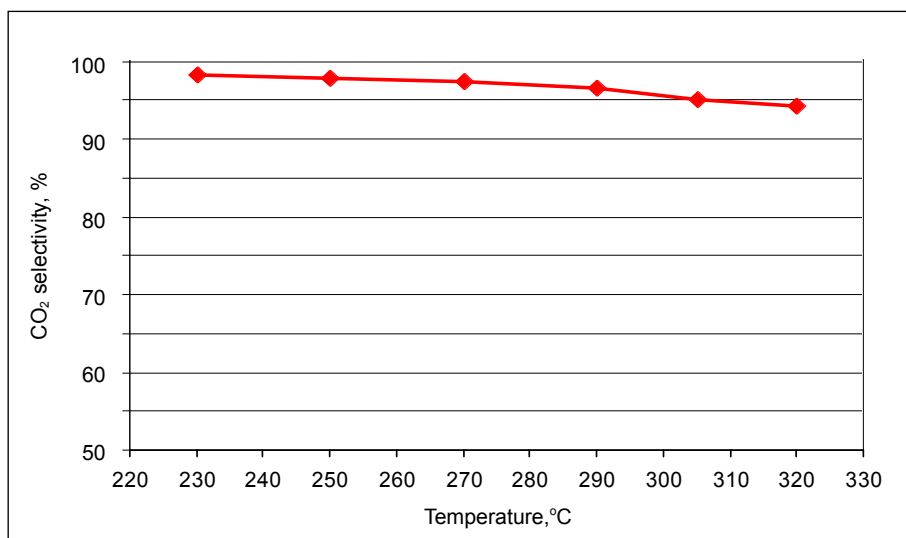

Fig. 5 Initial CO_2 selectivity versus the methanol steam reforming reaction temperature for the catalyst 'Pd-Zn/oxide support'. Test conditions: molar ratio of feed $CH_3OH:H_2O = 0.88$; gas hourly space velocity (GHSV) = 230,000 h^{-1} (powder catalyst); CH_3OH conversions within 11%

structures is now used commercially in other applications.

3.3 'Pd-ZnO/Oxide Support' Compared to 'Pd-ZnO/Al$_2$O$_3$', Pd/Al$_2$O$_3$ and Cu/CeO$_2$ Catalysts

High MSR activity with high CO$_2$ selectivity is well documented for Pd-Zn catalysts, which were first discovered by Iwasa *et al.* (17), and are now being extensively investigated for hydrogen generation in portable fuel cell power systems. The literature information pertaining to the MSR performance of the Pd-Zn catalytic system, and available to the authors, deals with catalysts composed of Pd supported on zinc oxide and also Pd-ZnO compositions supported on alumina (12–17).

Driven by a continuing interest in inexpensive non-precious metal catalysts for MSR applications, new copper-based catalytic compositions are also being developed (18, 19). To better understand the strengths and possible limitations of our Pd-based catalyst it is important to compare performance of this catalyst with that of other Pd- and Cu-based catalysts. To that end, following a procedure similar to those described in References (14) and (16), we prepared two Pd-ZnO catalysts on different supports: alumina and an oxide support material used in preparation of the new Pd-based catalyst, both catalysts having equivalent contents of Pd and ZnO. These catalysts are hereinafter referred to as 'Pd-ZnO/Al$_2$O$_3$' and 'Pd-ZnO/oxide support', respectively. For comparison, alumina-supported palladium catalyst (Pd/Al$_2$O$_3$) with the same amount of palladium as in Pd-ZnO samples was also prepared *via* the same procedure. In addition, a copper/ceria catalyst with 20 wt.% CuO (Cu/CeO$_2$), similar to that used in (18), was prepared by incipient wetness impregnation of ceria with aqueous copper nitrate solution followed by drying and calcining. All catalysts were compared in terms of their activities and selectivities, now at elevated temperatures typical for certain advanced applications. The samples (3 g of each) were tested in a laboratory flow reactor as granules 250 to 710 μm in size. This particle size ensures test conditions free of pore diffusion. The feed mixture

consisted of a reagent grade methanol (Aldrich) and deionised water in volume ratio MeOH:H$_2$O = 1:1 (molar ratio 0.88:1). The feed flow rates (from 0.3 cm^3 min^{-1} to 2.0 cm^3 min^{-1}) and the catalyst temperatures (375ºC to 475ºC) were programmed and controlled throughout the test as shown in Figures 6 to 9. The automated gas chromatographic analysis was conducted at twenty minute intervals by sampling the gas mixtures exiting the reactor. Performance of all of the catalysts described above is analysed below.

Methanol conversion and CO$_2$ selectivity for the catalyst 'Pd-ZnO/oxide support' are plotted in Figure 6 for temperatures 375ºC, 425ºC and 475ºC and a range of flow rates. It can be seen that the catalyst has stable activity (100% methanol conversion in the first and the last segments of the run, these segments having identical experimental conditions) with CO$_2$ selectivity ranging from around 70% at full conversion of methanol to around 82% at lower conversions.

Under the same experimental conditions the sample 'Pd-ZnO/Al$_2$O$_3$' is less active, and has much lower CO$_2$ selectivity (Figure 7). This catalyst ages, partially losing activity in the course of the run. This is illustrated by lower methanol conversion in the last segment of the run as compared with the first. The main product with this sample is CO; under the experimental conditions of the test, methane is also produced with selectivity ranging from 1 to 6%. This implies significantly less efficient production of hydrogen with 'Pd-ZnO/Al$_2$O$_3$', and also different reaction pathways for the two similar catalysts – 'Pd-ZnO/oxide support' and 'Pd-ZnO/Al$_2$O$_3$'.

The Pd/Al$_2$O$_3$ sample is even less active than 'Pd-ZnO/Al$_2$O$_3$', is more prone to ageing and has very poor CO$_2$ selectivity (Figure 8). CO and methane are the dominant carbon-containing products with the Pd/Al$_2$O$_3$ catalyst under the experimental conditions employed, rendering this catalyst composition unsuitable for hydrogen generation.

The Pd-free sample with Cu impregnated on ceria has high initial activity and relatively high CO$_2$ selectivity (up to about 75%); however it ages rapidly with a significant loss in activity (Figure 9).
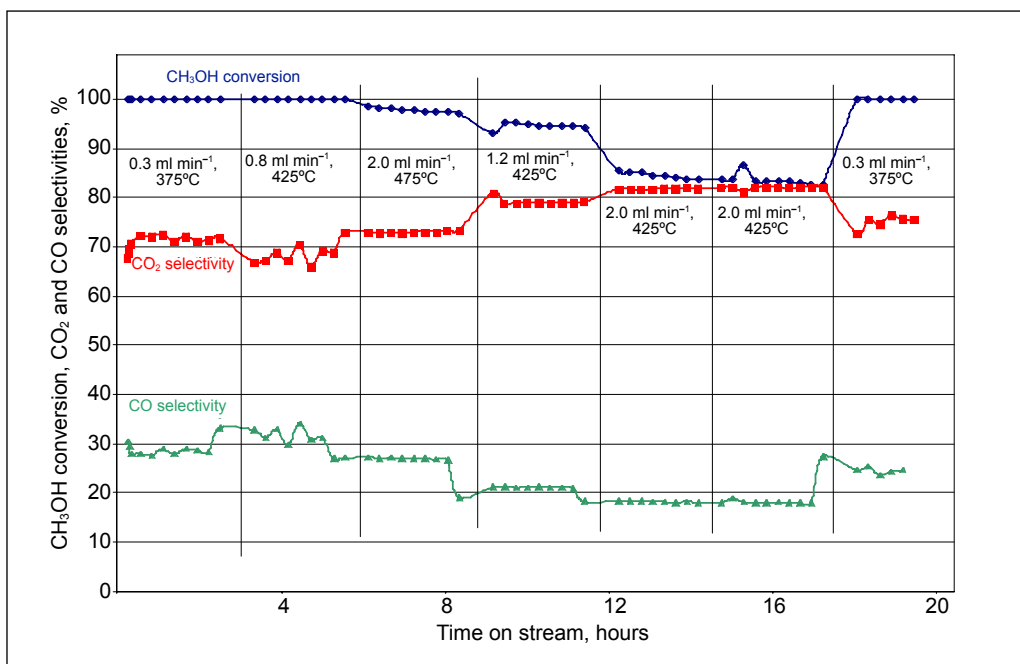
Fig. 6 Methanol steam reforming performance test of the catalyst 'Pd-ZnO/oxide support'
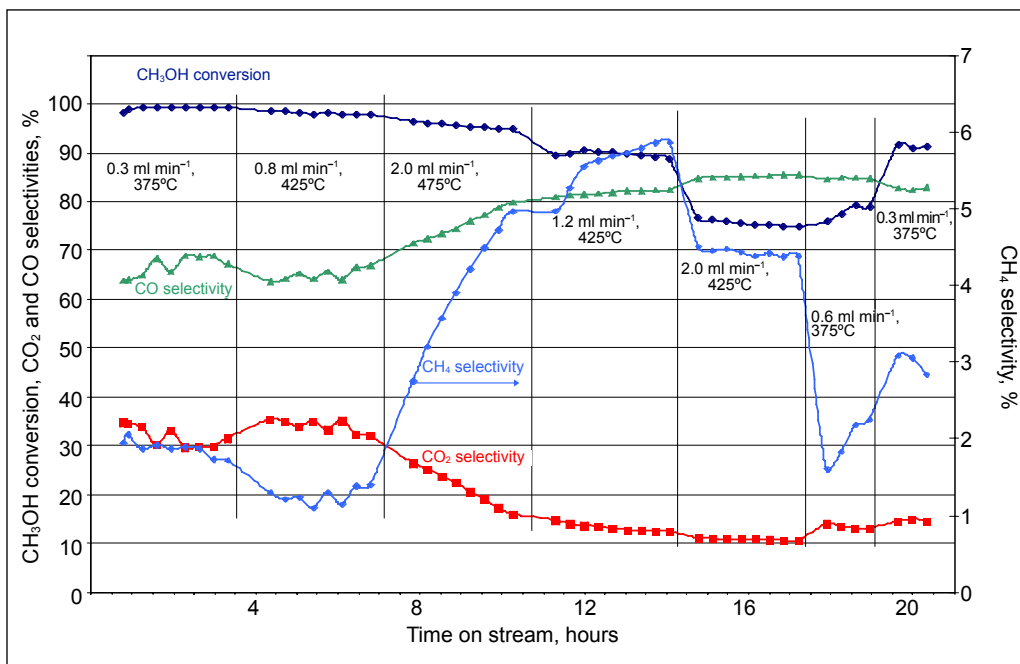

Fig. 7 Methanol steam reforming performance test of 'Pd-ZnO/Al₂O₃' catalyst

The ageing in this case is probably due to the thermal sintering of Cu (20). The fresh catalyst at high temperatures also produces small amounts of methane, but methanation stops as the catalyst ages.

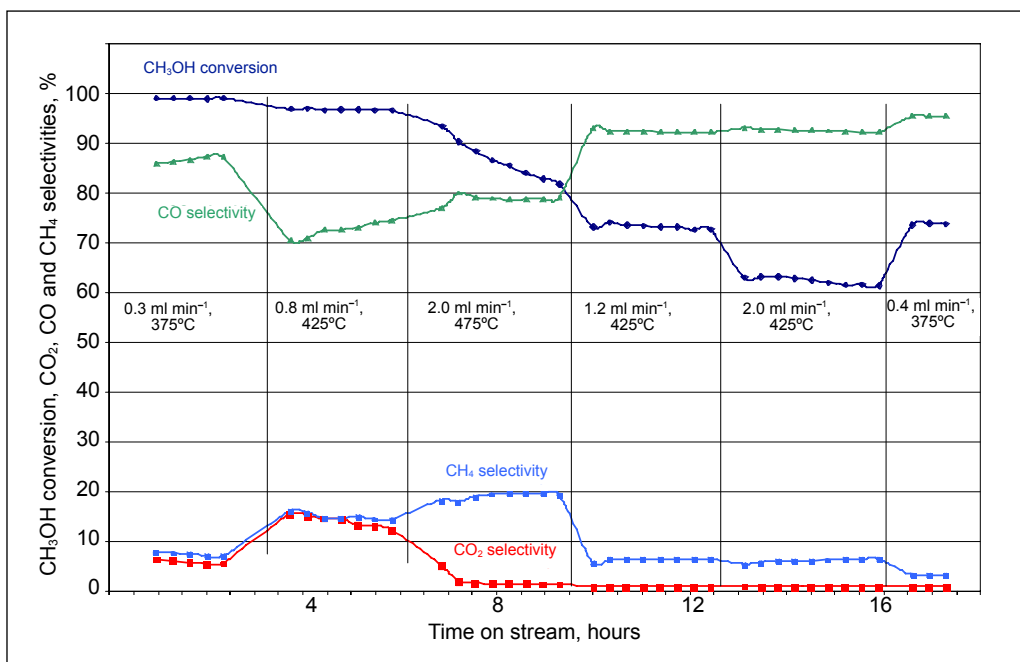The results of our comparative study show that the catalyst 'Pd-Zn/oxide support' has an

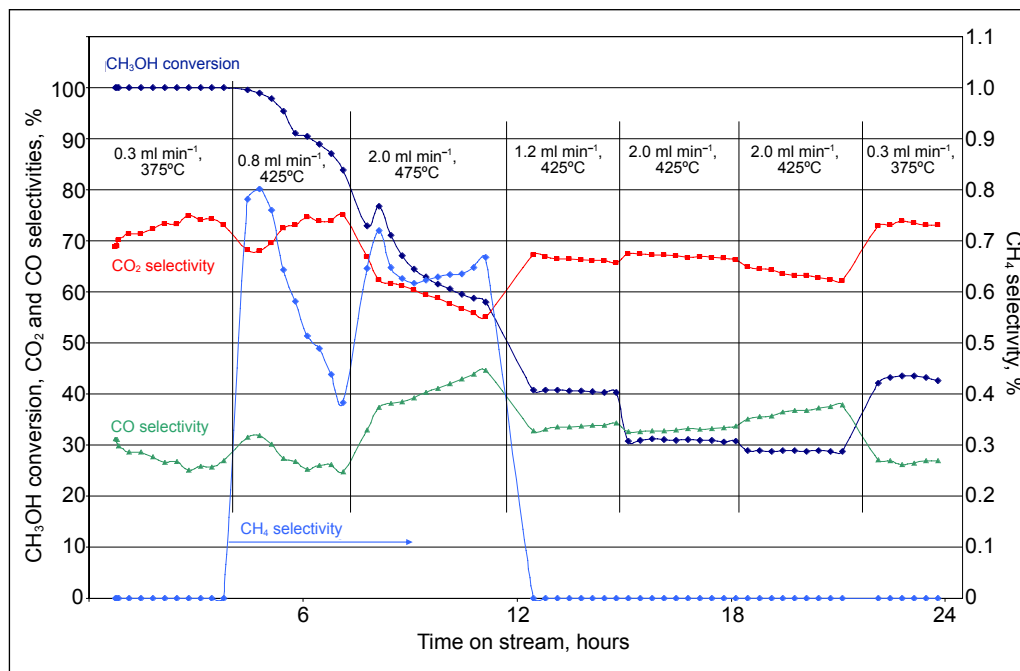*Fig. 8 Methanol steam reforming performance test of Pd/Al₂O₃ catalyst*

Fig. 9 Methanol steam reforming performance test of Cu/CeO₂ catalyst

optimum composition for the MSR reaction. It possesses high and stable activity, as well as the highest CO_2 selectivity over a broad range of MSR process conditions. The catalyst 'Pd-Zn/oxide support' is hence the most efficient among the catalysts tested in this study for hydrogen generation.

4. Conclusions

A new active Pd-based MSR catalyst has been developed for use as a washcoat in a microchannel reformer integrated to a miniature fuel cell power source. The catalyst 'Pd-Zn/oxide support' with proprietary additives shows stable performance under the frequent start-stop operating conditions typical of a portable fuel cell power source. The new catalyst is also thermally stable, which enables its extended operation over a broad range of temperatures and simplifies fabrication of the miniature power source.

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