

# Direct methanol–air fuel cells with membranes plus circulating electrolyte

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## Abstract

A new approach for direct methanol–air fuel cells (DMFC), with the advantage of reduced methanol crossover is discussed in this paper. Methanol traces in the circulated electrolyte are recovered and CO<sub>2</sub> bubbles in the cells are removed due to the forced methanol–electrolyte stream through the cell.

Degradation of the catalyst is reduced since fuel cell electrodes degrade on activated stand without load to a higher extent than under load because high voltage on open circuit promotes carbon oxidation, catalyst changes, etc. Therefore, life expectancy increases with circulating electrolyte by removing the electrolyte from the cells between operating periods. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Fuel cells with circulating electrolyte

The classical example of a fuel cell with liquid electrolyte is the alkaline fuel cell (AFC). The introduction of AFC for space applications led to the elimination of circulating electrolyte due to removal of any mechanical pumps, which were not reliable enough. The use of matrices (for instance, micro-porous asbestos) soaked with KOH became standard for NASA space fuel cells. The fact that liquid circulating electrolytes offered great advantages for heat management and water removal requirements was believed to be overcome by the disadvantage of creating parasitic shunt currents in cell assemblies connected in series. Delayed start-up procedures often led to the reversal of cells and irreversible cell failures. The advantages of combining fuel cells with rechargeable batteries in a hybrid system were not recognised. As a matter of convenience and for time saving, all the testing of fuel cells was (and is) done in a continuous operation mode. The need to operate fuel cells in an interrupted fashion, sometimes with long idle periods did not seem to be important — but surely it is. The fuel cell must be able to shut down completely for longer time periods, hours, days, weeks, etc. it must be safe in the garage, with

turned-off fuel supply, at ambient and even low temperatures. It should also be mentioned that on activated stand, without load, fuel cell electrodes and catalysts degrade more than under load. The high voltage on open circuit is the reason for carbon oxidation processes, catalyst changes, etc. [1–3].

Direct methanol fuel cells with KOH or NaOH as electrolytes have been built by Vielstich [4] and high current densities had been achieved with flow-through Raney type electrodes [5]. The air electrodes produced high voltages and good current densities due to the alkaline pH of the electrolytes. However, the anodic reaction products of the methanol are CO<sub>2</sub> and H<sub>2</sub>, and therefore, the KOH is used up, requiring an exchange of the electrolyte after use.

The historic alkaline direct methanol systems can be improved by using circulating electrolytes and separator systems designed to cut down the cross leakage and preventing the destruction of the hydrophobic property of the air cathodes by methanol. It will then be possible to use alkaline methanol–air fuel cells in the same way as zinc–air batteries with replaceable zinc anodes. Actually the procedure of emptying the spent electrolyte and filling up the tank again with a near stoichiometric methanol–electrolyte mixture instead of an equivalent methanol–water mixture would be quite simple.

Acidic fuel cell electrodes have been extensively developed for phosphoric acid fuel cells. Formulations for carbon activation and catalysts used in phosphoric acid cells [6]

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have been useful for acidic methanol cells. Acidic DMFCs have been investigated by Shell and Exxon using sulphuric acid, later also fluoroboric acid and bicarbonates have been tested. Though  $\text{CO}_2$  sensitivity was avoided, no solution was found to the problem of corrosion and performance reduction due to methanol crossover. The projects were suspended. No research is reported with circulating electrolyte [7–10].

## 2. Direct methanol fuel cell with circulating electrolyte

A new system of a direct methanol fuel cell with circulating electrolyte is suggested [11–13]. The DMFC with circulating electrolyte has the potential to solve the problem of methanol crossover and at the same time has the advantages of a circulating electrolyte. The liquid electrolyte is arranged between two matrices. The matrix could be a proton exchange membrane, but the goal is to find a more inexpensive material for the matrix to reduce methanol diffusion into the electrolyte. The circulating liquid electrolyte containing methanol leaves the cell and thereby prevents crossover (chemical short circuiting). Since the liquid electrolyte is pumped through the system, the fuel cell can easily be interrupted and deactivated. A loss of methanol between operating periods is avoided as well. The small amount of methanol in the electrolyte will be recovered and the electrolyte recycled into the cells.

Fig. 1 shows in principle how membrane DMFC systems can be modified by adding a liquid electrolyte, demonstrating the principle of an acidic DMFC with a circulating electrolyte. The out-flowing liquid carries any small amounts of permeated methanol out of the cell into a

recovery (distillation) unit. The fuel mix can now be fed even at a higher concentration as before and no damage to the air electrode will occur. Fig. 2 shows mass flows in a direct methanol fuel cell with liquid electrolyte and (optionally) with matrix or membrane on the anode or cathode (or on both sides). Several possible combinations of electrodes, membranes or separators and liquid flow fields are shown in Fig. 3. The optimal arrangements will have to be explored with performance and cost considered. Very promising to improve the cost situation, is a system arrangement without a polymer electrolyte membrane (Fig. 3a).

Presently the acidic DMFCs are built with PEM membranes. The introduction of an acidic liquid electrolyte in addition to PEMs will also change the membrane characteristics. This is expected also in hydrogen–air PEM systems. Especially the water transport (water is attached to the protons) can be influenced and changes in ionic mobility are expected. The  $\text{H}_2\text{SO}_4$  electrolyte for example has conductivities in the fractional Siemens ranges. The system can be completely shut down if needed, whereby the catalysts re-activate. Membranes are re-wetted immediately when the cells start again, no complicated wetting procedures are required. However, the biggest advantages are probably obtained in the higher temperature ranges where water vapour (relative humidity) control and cooling becomes a major effort. Performance criteria for PEMs, mechanical influences of cations on water content, gas permeability, cross leakages as function of thickness and current densities, ion exchange capacity versus resistances, differences between ac and dc resistance values, etc. [14–16].

The system built first (Fig. 4) was operated with hydrogen and oxygen using a 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte between the anode and cathode up to  $550 \text{ mA cm}^{-2}$  at 0.35 V.

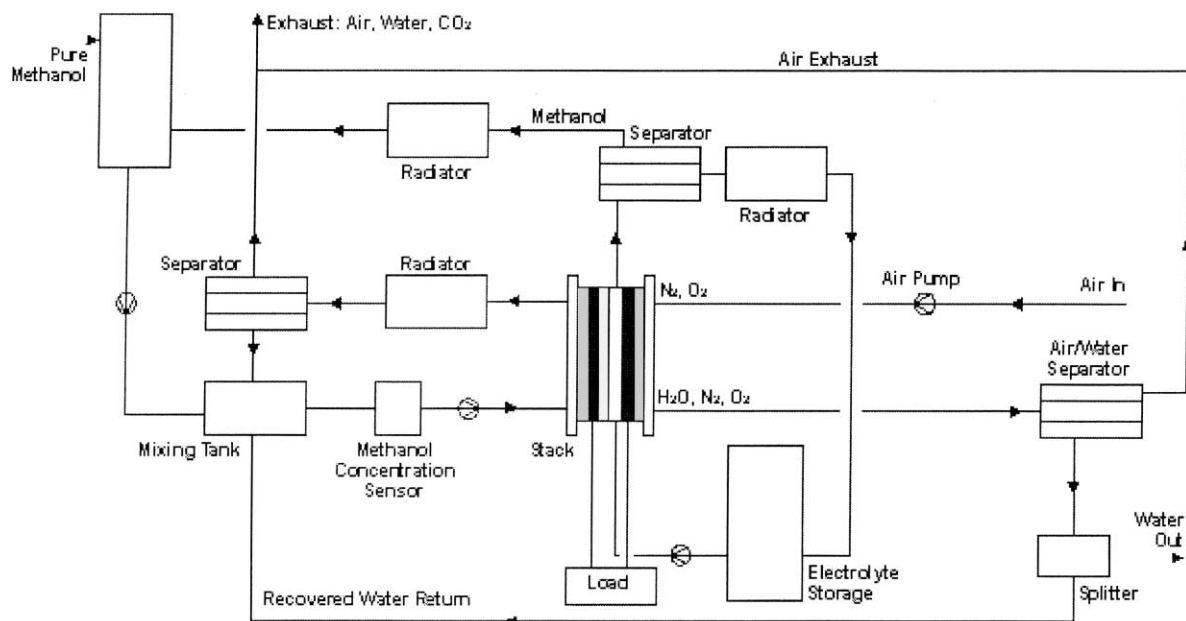


Fig. 1. Concept of a DMFC system with liquid acidic electrolyte, operating at 70°C.

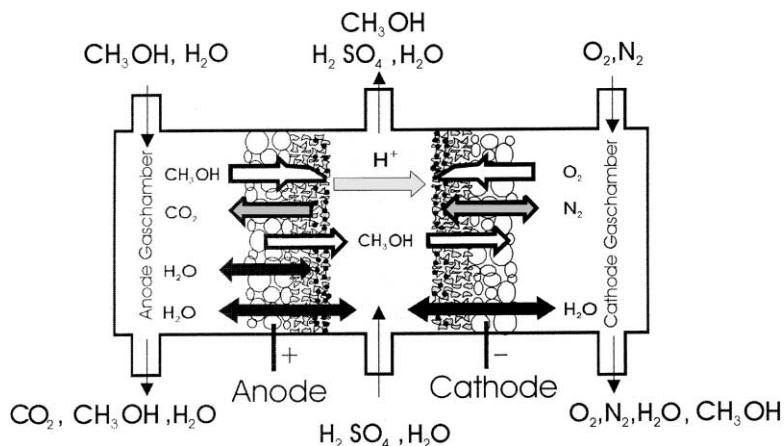


Fig. 2. Mass flows within a direct methanol fuel cell.

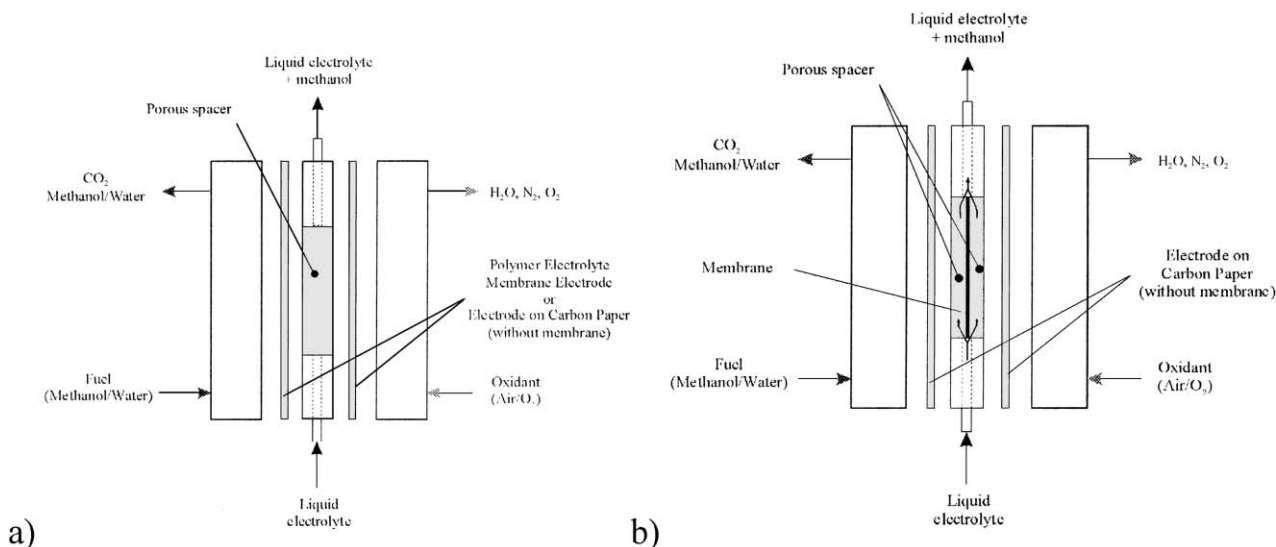
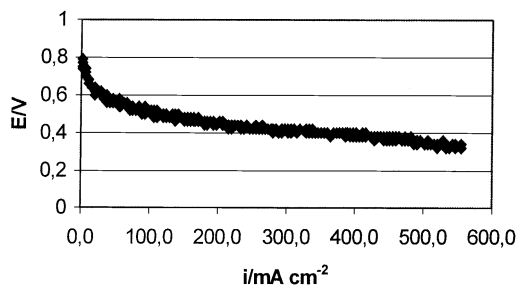


Fig. 3. Possible variations of direct methanol fuel cells with circulating electrolyte.

The result of a preliminary experiment with a single DMFC is shown in Fig. 5. It was done with E-TEK EFCG electrodes on TGPH-120 Toray Carbon (two PAFC electrodes with a catalyst loading of  $4 \text{ mg cm}^{-2}$  Pt/Ru). No membrane was used.

Fig. 4. Voltage/current density curve obtained with hydrogen and oxygen at  $20^\circ\text{C}$ , not under pressure and  $0.5 \text{ M H}_2\text{SO}_4$  as electrolyte.

The electrolyte ( $0.5 \text{ M}$  sulphuric acid) is pumped through the system by using a tubing pump. The electrolyte in the cell is being circulated at an exchange rate of approximately four times a minute. The experiment was done at ambient temperature. At the cathode pure oxygen, at the anode a  $10 \text{ M}$  methanol–water mixture, was used. As shown in Fig. 5, the open circuit voltage (OCV) reaches approximately  $0.8 \text{ V}$  in the starting phase. Thereafter, phase 1 shows that the OCV remains stable although methanol can easily go through the membrane because no PEM is used. At the beginning of phase 2 the circulation was stopped and the OCV falls rapidly. Summarising, it can be said that while pumping electrolyte through the system (phase 1) the OCV remains constant, while after interruption of the circulation of the electrolyte (phase 2) the OCV decreases by the effect of methanol crossover.

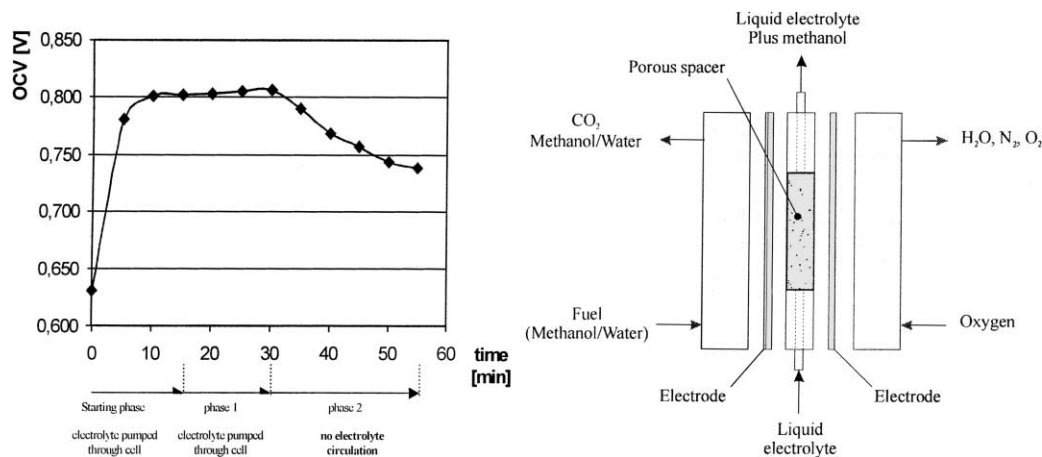


Fig. 5. Influence of electrolyte circulation on open circuit voltage of a DMFC cell (left), schematic of the system, which had an active electrode area of  $4.5 \text{ cm}^2$  (right).

### 3. Conclusion and future work

Preliminary test results confirm the assumptions that a circulating electrolyte helps to avoid methanol crossover in DMFCs. Experiments with different systems of DMFC with circulating electrolytes and at different temperature levels are planned whereby it is expected that the combination of a liquid electrolyte with a polymer electrolyte membrane controls drying and humidification and also makes it possible to influence the water transport via the protons of the membrane and that heat management of the stack will be eased.

Operation at higher temperature becomes possible by using different electrolytes. For cost reduction, a replacement of the polymer electrolyte membrane will be sought.

From the experiences with acidic electrolyte fuel cells it can be concluded that life expectancy for DMFC with circulating electrolyte can be increased by emptying the electrolyte between operating periods since this shuts down the system and eliminates all parasitic currents.

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