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Alkaline methanol–air system

A historical survey and some new work

Abstract Methanol is a promising fuel for power devices such as fuel cells because it has a high theoretical capacity per volume and weight, is relatively easy to handle and is easy to store. Many studies on the alkaline methanol fuel cell system were made in the 1960s and 1970s. The article gives a brief summary of these studies and shows some results of the new work started recently at the TU Graz, Austria

Keywords Historical survey · Methanol · Alkaline system · Fuel cell · Non-noble catalyst

Introduction

Portable energy is one of the hottest issues in the consumer electronics market. New generations of cellular phones, laptop computers, PDAs and portable cameras with more and more features need more and more energy.

Metal–air batteries are one of the possible devices to satisfy the increased energy hunger.

The use of zinc–air and zinc–aluminium cells with exchangeable electrolyte and replaceable metallic anodes has been suggested for many purposes, ranging from military power sources to electronic equipment and electric vehicles. In recent versions, zinc metal pellets and dry KOH powder mixes were inserted and only water had to be added. All these procedures are mechanical in nature and not too efficient if the energy needed for the regeneration is considered.

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The mechanical features are avoided by using methanol as fuel in a caustic liquid electrolyte.

This is not new [1] and high current densities have been reported [2], with only one major trouble: the cross leakage of—the methanol to the air cathode damages the noble metal catalyst. One way to avoid the crossleakage problem is to use silver as the catalyst, while another way is to use special cathode structures which are not sensitive to the methanol cross leakage.

The chemical reactions of a direct methanol–air fuel cell operating in alkaline electrolyte are as follows:

$$CH_3OH + 1.5O_2 + 2KOH \rightarrow K_2CO_3 + 3H_2O$$

lf the alkali electrolyte is not regenerated, it can be considered consumable in the cell reaction and 2 mol of KOH are required per mole of fuel.

A advantage of methanol as a fuel is the high theoretical capacity per volume and weight. The capacity of 1 kg methanol is 5,025 Ah. With a density of $\rho = 0.79$ kg/m^3, the capacity per volume is about 4,000 Ah/l.

The compact stage of stored energy offers the possibility of using methanol not only in continuously working fuel cells but also in "primary" type cells. The capacity of such a primary cell depends on the fuel concentration and the volume of the electrolyte used. For 6-M methanol and 12-N KOH 1,000 Ah/l can be achieved assuming an operating voltage of 0.5 V. Primary cells are normally used only once. Methanol–air cells with liquid electrolytes can be used for longer periods of time if the electrolyte mixture is replaced. The number of refill and discharge cycles depends on the stability of the air electrode. This is very similar to Zn–air batteries.

A historical survey [3]

In the 1960s and 1970s many efforts on developing optimal catalysts for the methanol oxidation, good air

electrodes and reducing methanol crossover with more or less good results were made.

Vielstich [4] reported in 1965 some laboratory cells with an electrolyte–fuel mixture of 10-N KOH and 4.5-M methanol. KOH was chosen because cells with NaOH have higher polarizations, particularly on the air side. Platinum with a load of 2–5 mg/cm^2 has been used as catalyst on the fuel electrode. On the air side electrochemically active carbon electrodes (250 cm^2), which were made hydrophobic with polyethylene, were used. The open circuit voltage of these methanol–air cells was about 0.9 V; at a current drain of 0.5 A the terminal voltage dropped to 0.6–0.75 V (see Fig. 1).

On the basis of laboratory investigations Brown Boveri a.Cie. built a 6-V, 10-A battery for a flashing buoy (Fig. 2). The module contains ten cylindrical cells, each cell had 18 pairs of electrodes connected in parallel. From 400 l of fuel–electrolyte mixture, 180 kWh can be obtained.

John Perry Jr. [5] reported in 1976 a fuel cell system that used a silver amalgam catalyst on the air electrode, which was virtually inert to direct methanol oxidation. 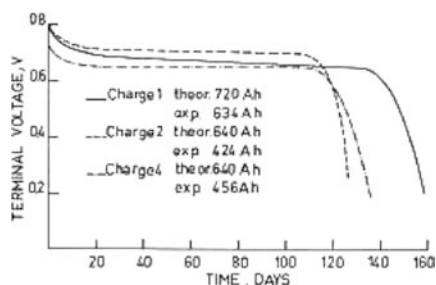Therefore, no membrane was needed. The air catalyst was bonded on an expanded silver current collector using PTFE to form a hydrophobic gas diffusion electrode. The catalyst loading was 20 mg/cm^2. The fuel electrodes consisted of an expanded silver current collector and a catalyst layer, 10 mg/cm^2, of 30% platinum and 70% palladium. The anode was bonded by PTFE, but not sintered and therefore hydrophilic. The anolyte consisted of 6 M methanol and 11 M KOH. Fig. 3 shows the voltage/current characteristics of such a cell and Fig. 4 shows a flashlight equipped with methanol–air fuel cells.

Figure 5 shows the basic construction of a liquid fuel–air D-size cell that Vielstich suggested in 1969 [6]. The cell had a stainless steel housing. The fuel electrode consisted of sintered nickel foil and was pressed against the wall of the housing by a perforated nickel screen (see Fig. 5). The sintered nickel was electroplated with 5 mg/cm^2 platinum/palladium in a ratio of Pd:Pt = 9.1.

A hydrophobic active carbon air electrode, which was fixed in the cap of the cell, was used.

Compared with a D-size dry cell, whose capacity was 3.5 Ah, the capacity of a liquid fuel battery was 7–8.5 Ah (with formate as fuel) and 20–23 Ah (with
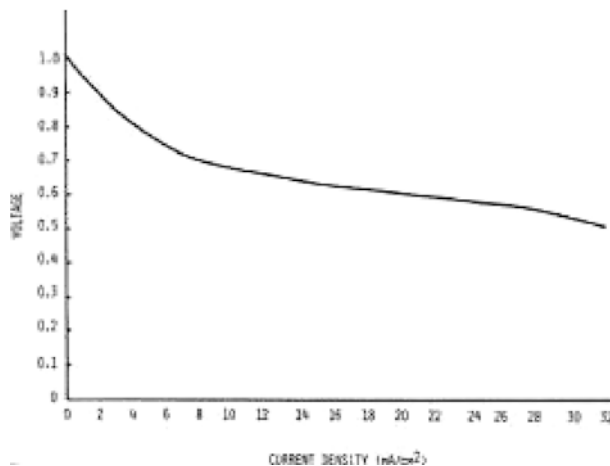

Fig. 1 Terminal voltage at periodic loads of a methanol–air cell, temperature 10–20 °C [4]

Fig. 3 Voltage–current characteristics of methanol–air fuel cell [5]

Fig. 2 Three coils of a 10-cell, 60-W methanol–air battery with cylindrical air diffusion electrodes for a flashing sea buoy [4]
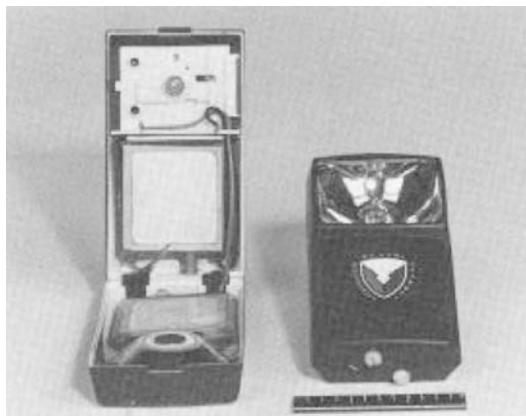

Fig. 4 Flashlight equipped with methanol/air fuel cells [5]

methanol as fuel). The discharge voltages of the formate and the methanol cells were between 0.7 and 0.5 V, whereas the terminal voltage of the dry battery ranges from 1.5 V to 0.7 V.

The liquid-fuel batteries showed a very good performance at low temperature. In comparison with a dry cell and with a zinc–air cell it showed a much smaller temperature dependence.(see Fig. 6).

New work on the alkaline methanol–air system

In August 2002 a new project on alkaline methanol–air systems started on the Institute for Chemical Technology of Inorganic Materials of the Graz University of Technology, Austria. The aim of the project is to develop new kinds of anodes and cathodes for the alkaline methanol air system with monopolar construction.

Anodes

The starting point in anode development was the common anode as it is used in the alkaline fuel cell. It is a typical gas diffusion electrode consisting of two diffusion layers with high PTFE content and an active layer without PTFE. Materials used for this kind of electrode are carbon, graphite, PTFE and organic binders such as PE or polysulfone. As current collector a common
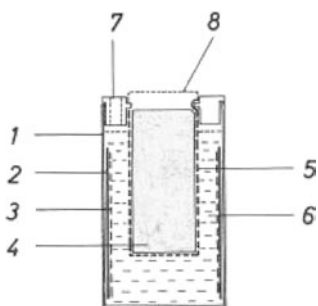
Fig. 5 Liquid fuel air cell [6]: 1, metal housing; 2, fuel electrode; 3, perforated nickel screen; 4, carbon air electrode; 5 silver plated nickel grid; 6, electrolyte; 7, opening; 8, positive terminal
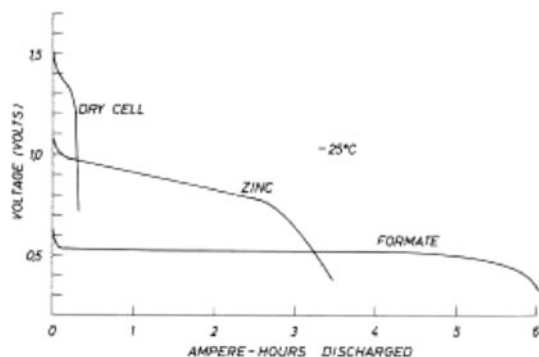
Fig. 6 Discharge voltages of different cells at −25 °C [6]

expanded metal (Ni) was used. The anode is made in a special rolling process as it is described by Cifrain [7]. The normal catalyst for an alkaline fuel cell anode is a mixture of platinum and palladium. For the methanol oxidation the catalyst has to be changed to the common Pt:Ru (1:1 atomic ratio) catalyst.

It turned out quickly that this kind of three phase electrodes are not usable for the oxidation of methanol because of its high resistance. One reason for this high resistance is the organic binder used. Another reason is the whole structure of the electrode which was not optimized for a liquid fuel.

Changing the binder resulted in a better performance but changing the structure resulted in very good performance. A new nickel structure was used as current collector and the production method was changed to a coating process. Figure 7 shows the comparison between the conventional anode and the anode with the new structure and it shows clearly the significantly lower resistance of the new structure. The red curves show the performance of the conventional anode described above (red points with white background = resistance included). The blue curves are showing the performance of the anode with the new structure (blue points with white background = resistance included).

Figure 8 shows the performance of our best anode. It is a two phase electrode with a new nickel structure as current collector. At lower current densities the high overpotential of the methanol oxidation can be seen. At higher current densities the curve gets very flat; the resistance is low. The curve is measured against zinc which has a potential of −0.47 V against the RHE. The catalyst loading is about 2 mg/cm^2 Pt:Ru.

Cathodes

Like with anodes the starting point for the development of cathodes was the common alkaline fuel cell cathode. These kind of cathodes are multilayer electrodes. Each layer has an different content of PTFE. The active layer
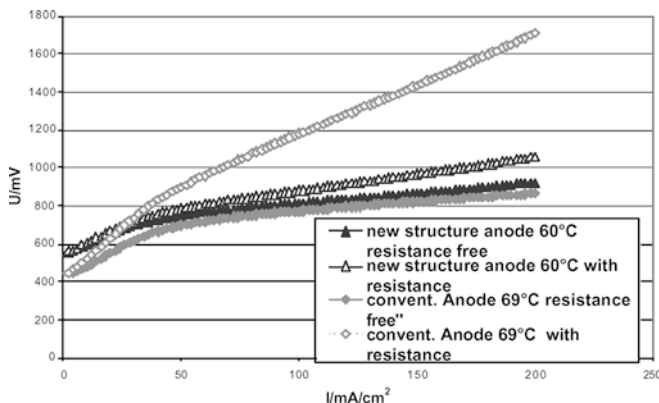
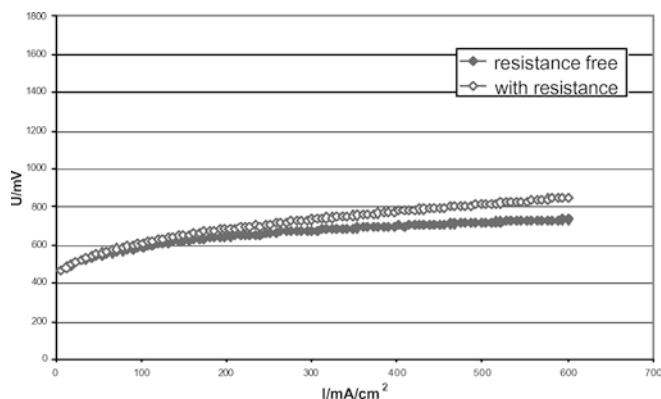**Fig. 7** Comparison of the anode with new structure—conventional anode against zinc in 6-M KOH

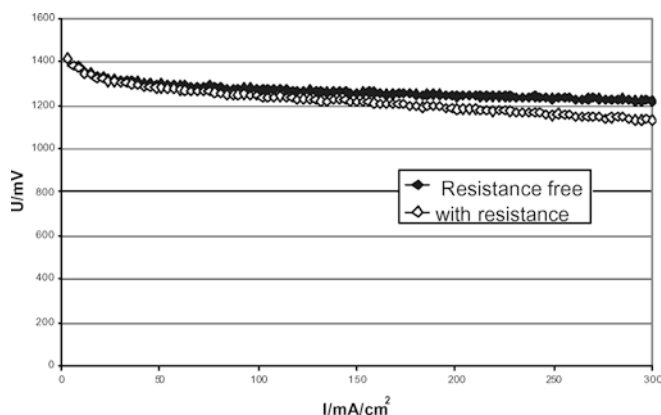**Fig. 8** Anode with a very good performance versus zinc at 80 °C and 6-M KOH

Fig. 9 Cathode with new nickel structure as current collector at 80 °C with 9-M KOH

Fig. 10 Behaviour of a cathode with platinum as catalyst in presence of methanol (80 °C, 9 M)
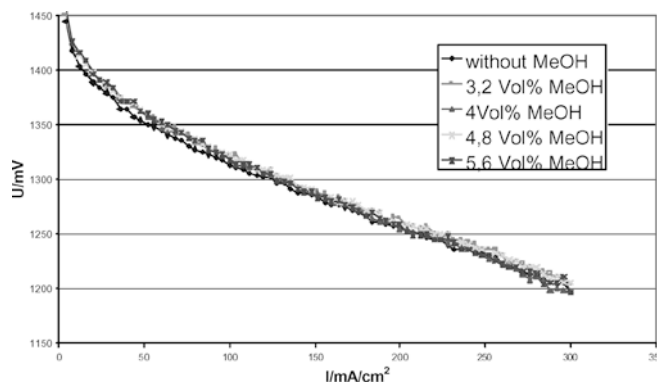
Fig. 11 Behaviour of a silver catalysed cathode in the presence of methanol (80 °C, 9 M KOH)

is bonded by an organic binder such as PE or PSU or a small amount of PTFE. In alkaline fuel cells usually catalyst loadings in the range from 0.5 mg/cm^2 to 1 mg/cm^2 are used. In the case of the methanol–air system the amount of catalyst had to be increased because of the expected crossleakage of the methanol. As current collector the same expanded metal as at the anodes is used.

Unfortunately the resistance was also relatively high. So a new approach with a new nickel structure as current collector and a different binder content was tested. As in the case of the anode the resistance could be decreased significantly. Figure 9 shows the performance of the cathode with the new structure.

In initial single cell tests it turned out that the methanol crossover causes a drastic drop of the potential of the cathode.

Using a membrane and circulating the electrolyte can minimize this problem but using a catalyst which cannot oxidize the methanol will be the better way. In alkaline solutions the use of silver for the oxygen reduction is well known.

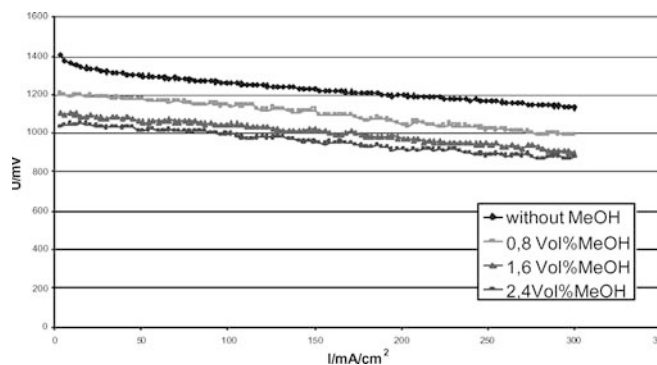In Fig. 10 the influence of the methanol on a common cathode with 2 mg/cm^2 platinum as catalyst can be seen. There is a significant drop of the potential even at low methanol content. The same experiment was made with a cathode with silver as catalyst. The result can be seen in Fig. 11. It shows clearly that there is no influence of methanol on the catalyst, even at high methanol contents. The amount of silver catalyst ranges from 1 to 5 mg/cm^2 and is, compared with older work [5], very low.

The problem with the carbonate

A problem is the formation of carbonate caused by the reaction of the CO_2, as product of the methanol oxidation, with the electrolyte KOH.

A new kind of filter system will be tested in the near future to filter out the carbonate from the system.

Summary

In the past many efforts on the alkaline methanol–air system were made but in the middle of the 1970s the work on these systems was completely cancelled. The reason is not really known.

A new start with new kinds of cathodes and anodes was made in 2002 at our institute. The first results are very encouraging: the use of silver as catalyst is a good

answer to the methanol crossover. Despite the good results many efforts are required.

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