

# Can refillable alkaline methanol–air systems replace metal–air cells?

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## Abstract

A new start in development of the alkaline methanol/air system was made at the Graz University of Technology. A comparison between the metal/air system and the methanol/air system, some new work on the electrodes for the methanol/air system and silver as catalyst for oxygen reduction is given in this paper.

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## 1. Introduction

Many different types of metal/air batteries, like primary, reserve, electrically rechargeable, and mechanically rechargeable battery configurations, have been explored and developed over the last decades.

Several metals have been considered for use in metal/air batteries like, Li, Ca, Mg, Al, Zn and Fe. Zinc has received the most attention of the potential metal/air battery candidates because it is the most electropositive metal that is relatively stable in aqueous and alkaline solution. The first applications of the zinc/air batteries were large batteries using alkaline electrolytes for railroad signaling, remote communications and ocean navigational units requiring long-term, low rate discharge. As thin electrodes were developed, the technology was applied to small, high capacity primary cells, which are used in hearing aids, pagers, and similar applications.

## 2. Rechargeable zinc/air batteries

Zinc is also attractive for electrical rechargeable metal/air systems because of its relative stability in alkaline media and also because it is the most active metal that can be electrodeposited from an aqueous electrolyte. Problems of dendrite formation, nonuniform zinc dissolution and depo-

sition, limited solubility of the reaction product, and unsatisfactory air electrode performance (bifunctional electrode is required) have slowed progress toward the development of a commercial rechargeable battery.

Mechanically rechargeable zinc/air batteries are designed with a means to remove and replace the discharged anodes or discharge products. This kind of battery was seriously considered for powering military electronic equipment in the late 1960s because of its high specific energy and ease of recharging. This battery contained a number of bicells (Fig. 1) connected in series to provide the desired voltage.

The anode, which was a highly porous zinc structure enclosed in an absorbent separator, was inserted between the cathodes. KOH was used as electrolyte. It was contained in a dry form in the zinc anode and only water was needed to activate the cell. Recharging was accomplished by removing the spent anode, washing the cell, and replacing the anode with a fresh one.

These batteries were never deployed because of their short activated life, poor intermittent operation and the development of new high-performance lithium batteries which were superior in rate capability and ease of handling in the field.

A design similar to the portable mechanically rechargeable zinc/air battery has been considered for electric vehicle applications.

In 1994 a large project using Zn and ZnO in replaceable cassettes was supported by the German postal service. It was finally abandoned (Fig. 2).

Fig. 3 shows the cell and electrode performances of a zinc/air battery with replaceable zinc anodes as it is described from Knapp [3].

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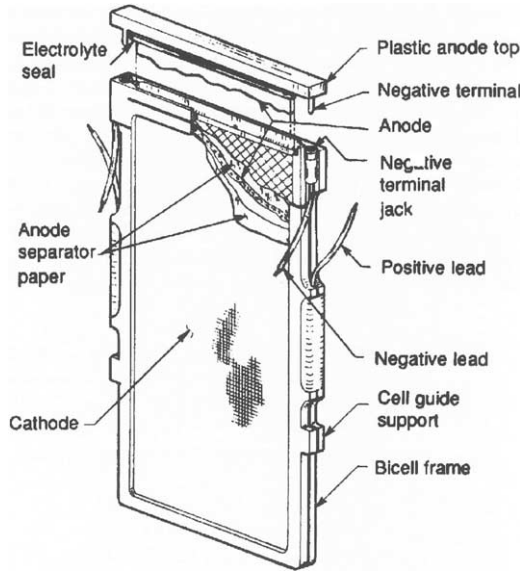


Fig. 1. Zinc/air bicell [1].



Fig. 2. German postal vehicle with zinc/air battery [2].

As can be seen, the zinc anode is the limiting electrode. Another kind of mechanically rechargeable zinc/air battery involves zinc powder replacement. Fig. 4 shows the Sony car powered by zinc/air batteries with a circulating

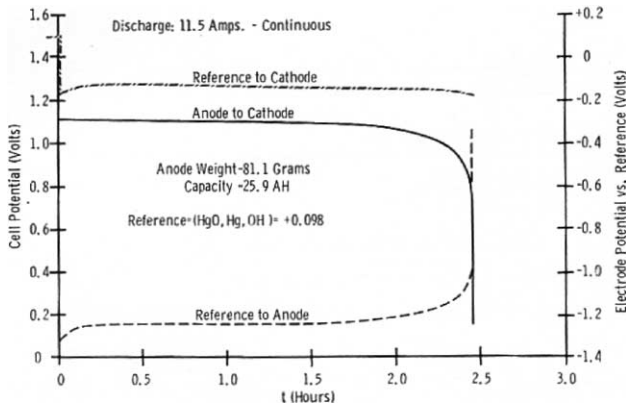


Fig. 3. Performance of a zinc/air battery with replaceable zinc anodes [3].

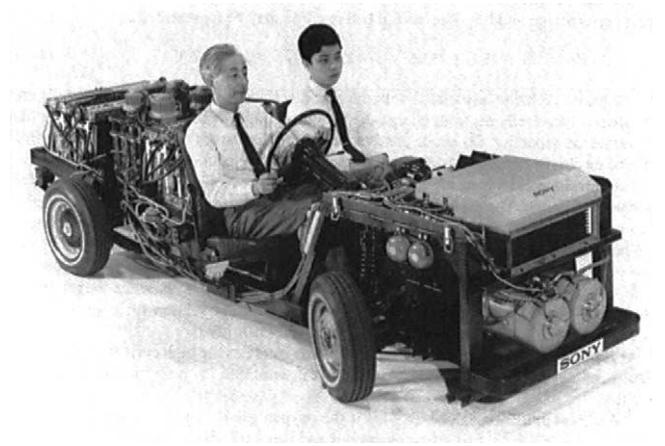


Fig. 4. The Sony car with mechanically rechargeable zinc/air batteries built 1971. Hideo Baba is the driver. SEA paper No. 710237 (1971) Courtesy of Sony [4].

powder zinc electrolyte [4]. The used electrolyte used was externally regenerated.

### 3. The alkaline methanol/air system

All these procedures are mechanical in nature and not too efficient if the energy needed for the regeneration is considered. The mechanical features are avoided by using methanol as fuel in a caustic liquid electrolyte.

This is not new [5] and high current densities have been reported [6] A historical survey of such systems is given in [7].

Already in 1951 Kordesch and Marko [8] suggested an alkaline methanol/air cell with Pt-catalysed carbon tube on the air side (Fig. 5).

The only major trouble is that the cross-leakage [6] of the methanol to the air cathode damages the noble metal catalysts.

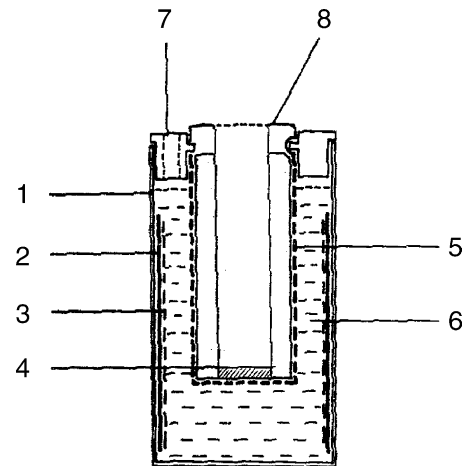


Fig. 5. Alkaline methanol/air R20 (D sized) cell [8]. (1) Can (negative); (2) Pt-fuel electrode; (3) screen, (4) Pt-catalyst/carbon tube; (5) separator; (6) CH<sub>3</sub>OH + KOH; (7) filler; (8) metal cap (positive).

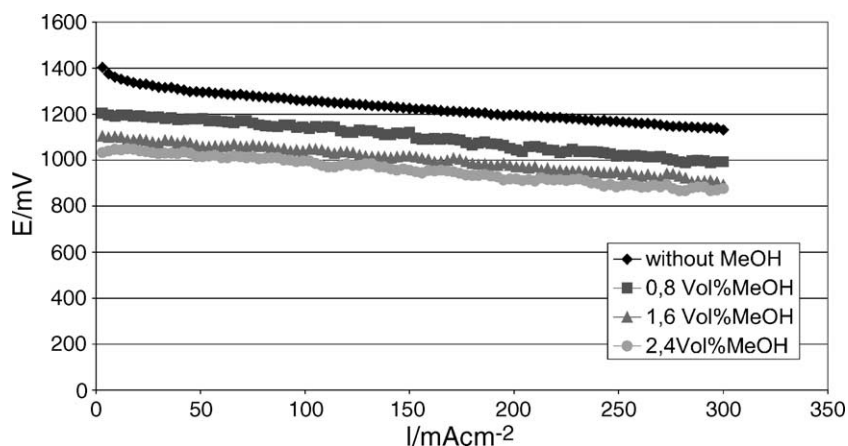


Fig. 6. Behaviour of a cathode with platinum as catalyst in presence of methanol (80°C, 9M KOH).

There are several methods to avoid this problem. One of them is to use effective membranes which are not permeable to the methanol, another is to use a flowing electrolyte system which carries away the methanol before it can interact with the catalyst on the air side. A combination of both methods is described in [9]. A smart solution for the crossover problem is to use a methanol oxidation-insensitive catalyst on the air side. In caustic media silver is such a catalyst, which shows excellent electrochemical behaviour for the oxygen reduction and insensitivity against the methanol oxidation.

Fig. 6 shows the behaviour of a cathode with a common Pt catalyst (carbon supported platinum from ETEK, 2 mg/cm<sup>2</sup>) in the presence of methanol. There is a significant drop of the potential even at low methanol content.

The same experiment was repeated with silver as catalyst. The result can be seen in Fig. 7.

It shows clearly that there is no influence of the methanol on the performance of the silver catalyst, even at high amounts of methanol.

The loading of silver catalyst ranges between 1 and 5 mg/cm<sup>2</sup> and is in comparison with older work [10], very low.

Last year a new project in alkaline methanol/air systems was started on the Institute for chemical technology of inorganic materials of the University of Technology Graz, Austria. The aim of the project is to develop new kinds of anodes and cathodes for the alkaline methanol–air system with monopolar construction. The Starting point in electrode development was the common electrodes as they are used in the alkaline fuel cell and the old hydrazine fuel cell [11].

### 3.1. Anode development

It turned out quickly that the performance of a usual alkaline fuel cell anode, which has the structure of a conventional gas diffusion electrode, was not satisfactory. One reason for this is that it was not optimized for a liquid fuel. Therefore a new two-phase structure was developed. The composition of such electrodes includes carbon, graphite and an organic binder. A new nickel structure was used as current collector. As catalyst the conventional mixture of Pt:Ru (1:1 atomic ratio) was used, with loading ranges between 1 and 4 mg/cm<sup>2</sup>. The production method was changed from a rolling process as is described from Cifrain [12] to a coating process with ensuing pressing step. The performance can be seen in Fig. 8.

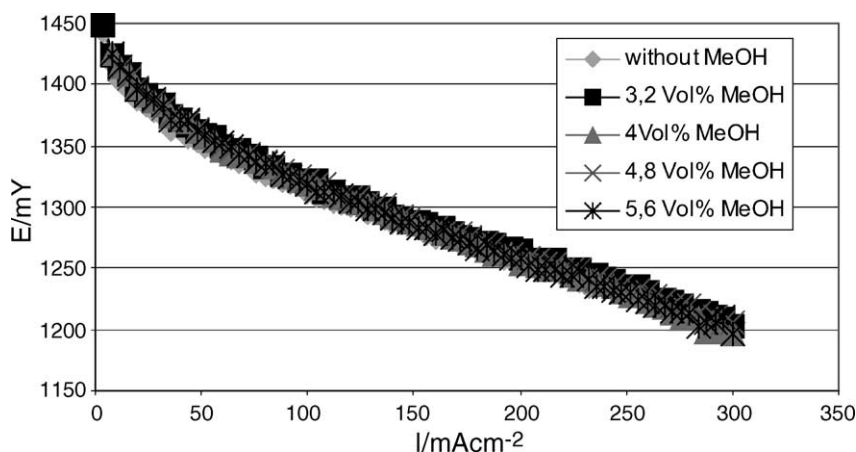


Fig. 7. Behaviour of a silver catalysed cathode in presence of methanol (80°C, 9M KOH).

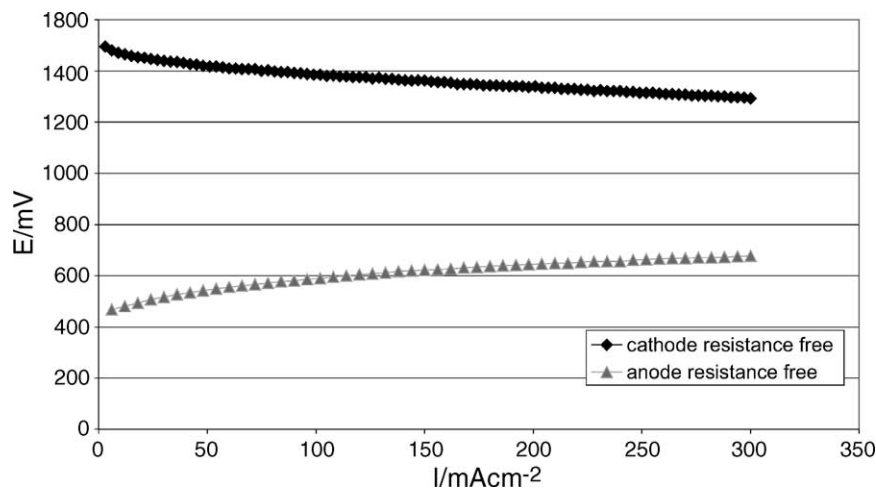


Fig. 8. Half cell performances of anode and cathode vs. zinc at 75 °C, 9 M KOH.

### 3.2. Cathode development

As with anodes, the starting point of the development of cathodes was the common alkaline fuel cell cathode. The normally used expanded metal was changed to a new nickel structure and the catalyst was changed from platinum to silver because of the problems with the platinum catalyst described above. The cathode is a normal three-phase gas diffusion electrode made of PTFE, carbon, graphite and an organic binder. Fig. 8 shows the performance of the cathode.

In Fig. 8, a comparison of the anode and the cathode resistance-free half cell performance is shown. The theoretical cell voltage amounts 0.79 V at 100 mA/cm<sup>2</sup>; 0.69 V at 200 mA/cm<sup>2</sup> and 0.61 V at 300 mA/cm<sup>2</sup>. The practical achievable cell voltage should be nearly in the same range because of the small resistance of the electrodes.

### 3.3. The problem with carbonate

A problem is the formation of carbonate caused by the reaction of the CO<sub>2</sub>, as product of the methanol oxidation,

with the electrolyte KOH:



In the case of the primary methanol/air cell the products could be easily changed with new fuel and electrolyte. For bigger applications a new kind of filter system will be tested in the near future to filter out the carbonate of the system.

## 4. Summary

Table 1 gives a comparison of the advantages and disadvantages of both systems.

A big advantage of methanol as fuel is the high theoretical capacity per volume and weight. The capacity of 1 kg methanol is 5035 Ah. With a density of  $\rho = 0.79 \text{ kg/m}^3$ , the capacity per volume is about 4000 Ah/l. The capacity of a primary cell depends on the fuel concentration and the volume of the electrolyte used. For 6 M methanol and 12 N KOH, 1000 Ah/l can be achieved assuming an operating voltage of 0.5 V. Primary cells are normally used only

Table 1  
Advantages and disadvantages of Zinc/air [1] and methanol/air system

Zinc/air	Methanol/air
<b>Advantages</b> High energy densities Flat discharge voltage Long shelf life (dry storage) No ecological problems Capacity independent of load and temperature when within operating range	Theoretical capacity 5035 Ah/kg, 4000 Ah/l Practical capacity 1000 Ah/kg; 800 Ah/l Long shelf life (dry storage) Capacity independent of load Good low temperature behaviour Easy refilling primary, secondary cells and fuel cells possible
<b>Disadvantages</b> Dependent on environmental conditions Drying-out limits shelf life once opened to air Limited power output Limited operating temperature range H <sub>2</sub> from anode corrosion Carbonation of alkali electrolyte	Fuel is toxic Drying-out limits shelf life once opened to air Lower operating voltage than zinc/air

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.

A disadvantage is the lower operating voltage compared with a zinc/air cell. Several cells in serial connection are necessary to get the required voltage.

Overall, the new alkaline methanol/air cell has absolutely the potential to replace the metal/air system in many applications. First results were very encouraging but some further investigations, such as life time tests, are necessary.

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