

Can Refillable Alkaline Methanol-Air Systems replace Metal-Air Cells?

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Direct Methanol Fuel Cells (DMFCs) use membranes (PEMs) which are acidic in nature. The air electrode polarization is high [1]. Therefore we looked at the alkaline Methanol-Air Cells and discovered that they could actually replace Metal-Air cells.

The use of Zinc-Air and Zinc-Aluminum cells with exchangeable electrolyte and replaceable metallic anodes has been suggested for many purposes, ranging from military power sources to electronic equipment to electric vehicles. In recent versions, Zn-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. In 1994 a large project using Zn and ZnO in replaceable cassettes was supported by the German postal service. It was finally abandoned.

The mechanical features are avoided by using methanol as fuel in a caustic liquid electrolyte. The methanol in the KOH is kept at a low level by sensing it and injecting it when needed. Finally, the nearly used up, highly carbonated electrolyte is exchanged. This is not new [2] and high current densities have been reported [3], with only one major trouble: the cross-leakage [4] of the methanol to the air cathode damages the noble metal catalysts. Now, very effective membranes like in Ag-Zn cells can be used. In Graz a system design like the alkaline hydrazine fuel cells is developed. The reversed T-3 type air electrodes of Union Carbide Corp. used (1975) in the motorcycle hydrazine batteries of Kordesch [5] reduced the fuel cross leak considerably and the same way minimize now the unwanted chemical reaction of the methanol at the air electrode. The circulating electrolyte allows a complete shut during longer idle times. It serves also as thermal management system. The voltage of the alkaline methanol-air system is lower than that of the Zn-air cells, but the very high Ah capacity of methanol makes up for it [6].

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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 which 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.

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 deposition, 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 batteries were seriously considered for powering military electronic equipment in the late 1960's because of their high specific energy and ease of recharging. This battery contained a number of bicells (see [figure 1](#)) connected in series to provide the desired voltage.

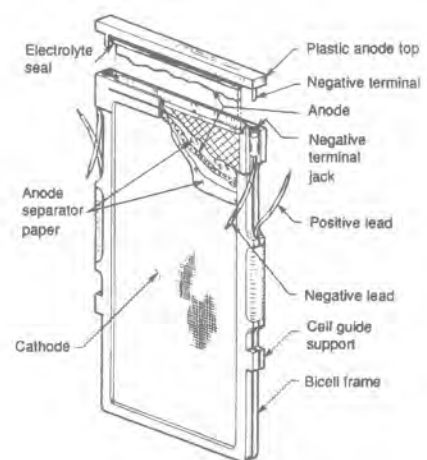


Figure 1: Zinc/air bicell [1]

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 zin/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.



Figure 2: German Postal Vehicle with Zinc-Air Battery [2]

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

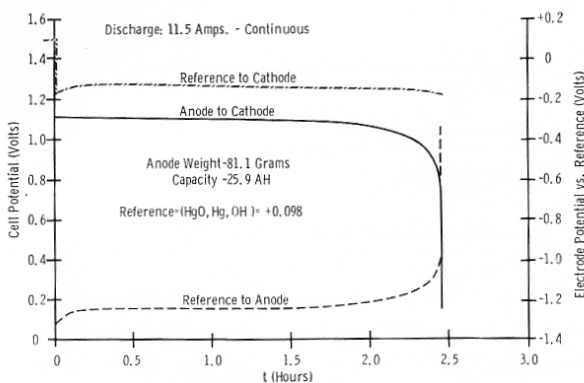


Figure 3: Performance of a zinc/air battery with replaceable zinc anodes [3]

As it can be seen, the zinc anode is the limiting electrode.

Another kind of mechanically rechargeable zinc/air battery are those with zinc powder replacement. **Figure 4** shows the sony car powered by zinc/air batteries with a circulating powder zinc electrolyte [4]. The used electrolyte was externally regenerated

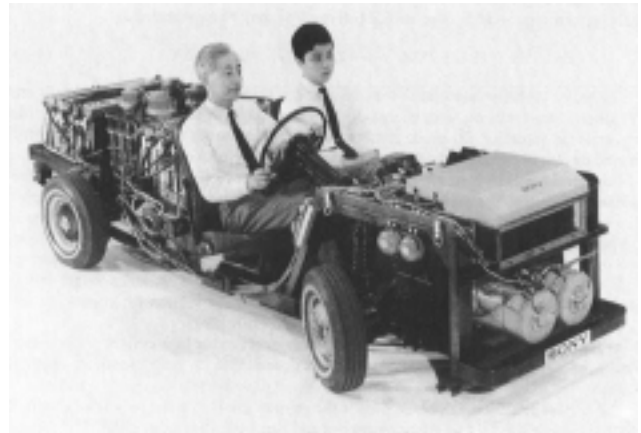


Figure 4: The Sony car with mechanically rechargeable zinc/air batteries from 1971[4]

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 [8] suggested an alkaline methanol/air cell with and Pt-catalysed carbon tube on the air side (see **figure 5**)

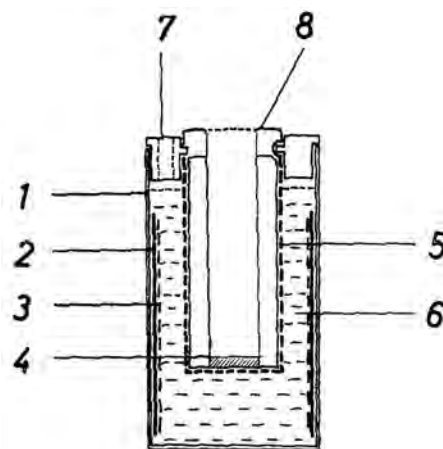


Figure 5: Alkaline methanol/air D-cell
 1. Can (-), 2. Pt-Fuel electrode,
 3. Screen, 4. Pt- cat. Carbon Tube,
 5. Separator, 6. CH₃OH + KOH,
 7. Filler, 8. Metal Cap (+) [8]

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

There are several methods to avoid this problem. One of them is to use effective membranes which are not permeable for 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.

Figure 6 shows the behaviour of an cathode with a common Pt catalyst (carbon supported platinum from ETEK $2\text{mg}/\text{cm}^2$) 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 *figure 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 $1\text{--}5\text{ mg}/\text{cm}^2$ and is, compared with older work [10], very low

Last year a new project on 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. Starting point in electrode development were the common electrodes as they are used in the alkaline fuel cell and the old hydrazine fuel cell [11].

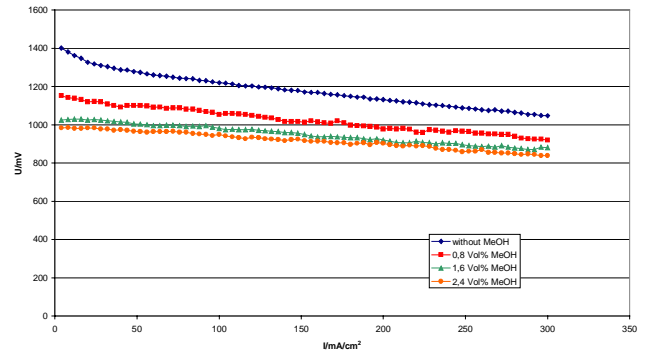


Figure 6: Behaviour of an cathode with platinum as catalyst in presence of methanol (80°C 9M KOH)

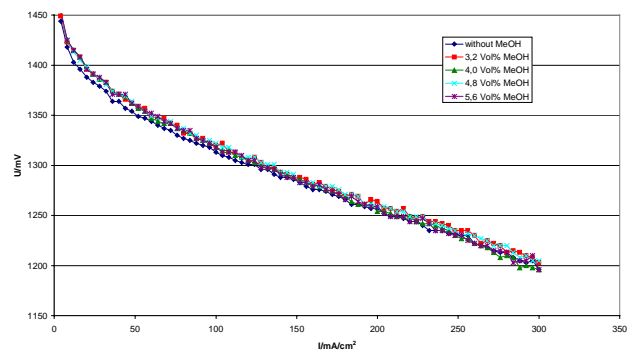


Figure 7: Behaviour of a silver catalysed cathode in presence of methanol (80°C 9M KOH)

Anode development:

It turned out quickly that the performance of a usual AFC anode which has the structure of a conventional gas diffusion electrode, was not satisfying. 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. The loading ranges between 1 and $4\text{ mg}/\text{cm}^2$. The producing method was changed from a rolling process as it is described from Cifrain [12] to a coating process with ensuing pressing step. The performance can be seen in *figure 8*.

Cathode development:

Like 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 platin to silver because of the problems with the platin catalyst described above. The cathode is a normal 3-phase gas diffusion electrode made of PTFE, carbon, graphite and a organic binder. Figure 8 shows the performance of the cathode.

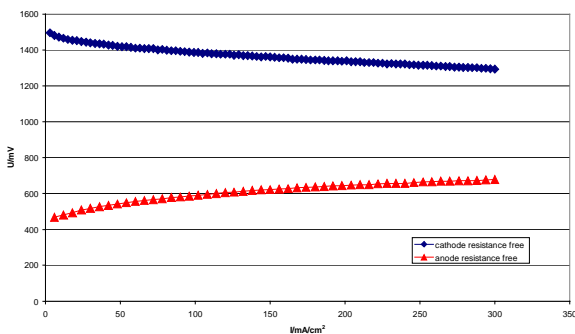


Figure 8: Half cell performances of anode and cathode vs Zinc at 75 °C and 9m KOH

In figure 8 a comparison of the anode and the cathode resistance free half cell performance is shown. The theoretical cell voltage amounts 0,79V at 100 mA/cm²; 0,69V at 200 mA/cm² and 0,61V at 300mA/cm². The practical achievable cell voltage should be nearly in the same range because of the small resistance of the electrodes.

The problem with the carbonate:

A problem is the formation of carbonate caused by the reaction of the CO₂ , as product of the methanol oxidation, with the electrolyte KOH



In case of the primary methanol/air cell the products could be easily changed

with new fuel and electrolyte. For bigger applications new kind of filter system will be tested in the near future to filter out the carbonate of the system.

Summary:

In tabel 1 a comparison of the advantages and disadvantages of both systems is given.

	Zinc/Air	Methanol/Air
A	High energy densities	theoretical cap. 5035Ah/kg, 4000 Ah/l
d	Flat discharge voltage	practical cap. 1000Ah/kg; 800 Ah/l
v	Long shelf life (dry storage)	Long shelf life (dry storage)
a	No ecological problems	Capacity independent of load
n	Capacity independent of load and temperature when within operating range	good low temperature behaviour
t		easy refilling
a		primary, secondary cells and fuel cells possible
g		
e		
s		
D	Dependent on environmental conditions	fuel is toxic
i	Drying-out limits shelf life once opened to air	drying-out limits shelf life once opened to air
s	Limited power output	lower operating voltage as zinc/air
a	Limited operating temperature range	
v	H ₂ from anode corrosion	
a	Carbonation of alkali electrolyte	
n		
t		
a		
g		
e		
s		

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

A big advantage of methanol as fuel is the high theoretical capacity per volume and weight. The capacity of 1kg 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 6M methanol and 12N KOH 1000 Ah/liter 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.

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 like life time tests are necessary

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