

AN ALKALINE METHANOL-AIR PRIMARY BATTERY SYSTEM

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A primary battery system operating on methanol dissolved in KOH, and air, has been developed to the laboratory hardware stage. Fuel-electrolyte solution flows by gravity through palladium-activated porous nickel electrodes. Teflon waterproofing and semi-permeable separators minimize fuel and electrolyte loss through the cathode. Condensed in a chimney, water is recycled from the emerging air stream. Extensive tests carried out on a battery rated at 30 W (one-third max. power) indicate that in series, 24 cells, individually about one-fourth sq. ft. in area, deliver 12 V. At rated output, utilization of 5 molar $\text{CH}_3\text{OH}/6$ molar KOH fuel is ca. 55 Wh/lb. Single cells have been operated one year at room temperatures, and cells in test batteries have maintained 3000 hours of satisfactory output. A preliminary cost analysis indicates that the system can be competitive with existing primary and secondary batteries.

INTRODUCTION

The advantages of a methanol fuel and an alkaline electrolyte are well known in fuel cell lore. The two in combination suffer the disadvantage that alkali is consumed in the fuel cell reaction. Thus, for long term operation either a large reservoir must be provided or the electrolyte must be continuously purified of formate, carbonate and other reaction products.

Three fairly comprehensive studies of alkaline methanol systems have been reported in the literature. Murray and Grimes (1) describe a methanol-oxygen system in which methanol is metered into a circulating electrolyte. Temperature of the battery is controlled by a heat exchanger in the electrolyte loop. No means of reformation of carbonate ion to hydroxide ion was provided, so that the size of the electrolyte reservoir limits the operating time - about five hours in the system described. Electrodes are of a bipolar design. The anode consists of a sintered nickel plaque impregnated with a palladium-platinum catalyst, and the cathodes are fabricated from porous nickel plaques containing silver catalyst and Teflon waterproofing. Considerable methanol is lost through evaporation, but that which is oxidized goes to carbonate.

Vielstich (2) describes a methanol-air fuel battery and its application in a signaling device. In this case, the electrodes are immersed in a container of

fuel-electrolyte solution, the spent solution being replaced as required. Platinum catalyst on an unspecified porous carrier serves as the anode, and the cathodes consist of wetproofed porous carbon activated with silver. Natural convection and diffusion serve to provide an adequate supply of air to open-topped cathodes. A 28-cell battery of this design, fabricated by Brown, Boveri, Ltd. (Baden, Switzerland), was tested as a power source for a river navigation buoy over a six month period. About a 10% loss in methanol (presumably by evaporation) was experienced. Oxidation of fuel consumed is to carbonate ion.

An alkaline methanol system in which dissolved sodium chlorite is used as the oxidizer has been reported by Boies and Dravnieks (3). The development was not carried past the single cell stage. A fuel solution approximately 5M in methanol and 5M in KOH is circulated past an anode which consists of a platinized substrate of flame-sprayed Raney nickel. The oxidant solution (4M in sodium chlorite and 5M in KOH) similarly flows through a cathode chamber. The cathode is flame-sprayed Raney nickel-silver and fuel and oxidant chambers are separated by a dialysis membrane. External heating of the reactant solutions is used to maintain a cell operating temperature of 55°C. An output of 144 mA/cm² at 0.6 V is reported. Methanol is not oxidized past the formate stage, and a considerable parasitic loss due to chemical oxidation of methanol by chlorite occurs.

This paper describes a study of a continuous flow alkaline-methanol fuel battery system which has been carried through the laboratory model stage. The work was carried on as part of a joint research and development program of the Pure Oil Company and Gould-National Batteries, Inc. A primary design objective was a reliable system capable of unattended operation over periods of several months. Only slightly less important were first cost and operating cost. A minimum of power-operated controls and auxiliaries are used. Natural forces, i.e., gravity and surface tension, serve to effect and control the flow and distribution of reactants.

CELL DESIGN

Cell design is shown schematically in Figure 1. A nickel sheet forms one side of the anode compartment, and a diaphragm forms the other side. The anode is a standard sintered-nickel battery plaque in which palladium catalyst has been deposited. The cathode contains silver catalyst bonded to nickel screen by Teflon particles in the sub-micron size range. In single-cell tests, electrode size has been two or four inches square, while in batteries the electrodes have been as large as one-fourth square foot in area.

The diaphragm separating the electrodes may be either a semi-permeable membrane or a more porous separator such as asbestos. In most of the cells constructed to date, we have used Permion 300 or 320 type membranes such as have been used in experimental silver-zinc batteries.

Electrical connection between cells is provided by a corrugated nickel screen which serves also to maintain sufficient separation between cells to permit air convection.

Electrolyte containing dissolved fuel is admitted to the cell at the top of the anode, flowing down under the influence of gravity through the anode compartment and dripping out of the cell into a collecting trough.

SYSTEM DESIGN

Cells are stacked three per inch and are held in place by compression between end plates connected by tie bolts. Fuel-electrolyte solution is distributed to the cells in parallel flow by means of a system of wicks and manifold which is operable over a wide range of flow rates.

The battery and fuel distributor are enclosed in a cabinet as shown in Figure 2 of a 24-cell system. Natural draft over the height of the battery cabinet is sufficient to provide adequate air convection past the cells. Controls and design features are provided to maintain flow rates and temperatures within the limits of satisfactory operation over a range of environmental conditions.

Air enters the cabinet through a thermostatically controlled opening near the bottom. Air leaves the cabinet through an opening near the top, entering a chimney of narrow rectangular cross section. Some water is condensed on the walls of the chimney and returned to the battery through the fuel distributor. To provide auxiliary cooling at high ambient temperature, metallic fins extend from each cell through the back wall of the cabinet into a secondary air chamber through which natural air flow is thermostatically controlled. To prevent excessive heat loss in a cold environment, the cabinet and secondary air chambers are covered with a layer of polyurethane foam insulation.

The feed rate of fuel-electrolyte solution is controlled automatically in response to battery output by means of a controller developed by Honeywell. Several types of valves and positioners have been tried. One type which resulted in good control characteristics consisted of a needle valve having a stem with a one-degree taper which was turned by a small reversible DC motor.

OPERATING CHARACTERISTICS

A polarization curve for a typical natural-flow cell at room temperature is shown in Figure 3. In order to permit comparison with other types of cells in which electrolyte concentration changes are negligible, the data in Figure 3 were obtained at a high feed rate. Maximum power output at these conditions was about 10 W/ft².

Ordinarily, if this natural-flow system is to be operated with once-through flow of electrolyte, feed rate will be very slow in order to provide good utilization

of reactants. The effect of feed rate on output voltage is shown in Figure 4. These data were obtained with a six-cell uninsulated battery with natural convection of air. Voltage dependence shows two markedly different regions. At feed rates between about 170-300% of the theoretical methanol rate (100-180% of theoretical potassium hydroxide rate), voltage is roughly proportional to feed rate. At higher feed rates voltage increases only slightly with feed rate, and at very high rates voltage would decrease because of the cooling effect of the feed.

The explanation for this operating characteristic lies in the influence of reactant and product concentrations on reaction rate. At low fuel rates concentration changes in the electrolyte are extensive, and a voltage gradient is observed through the cell along the path of the electrolyte. The potentials of anode and cathode vs. a reference electrode both become more positive as the reference electrode is moved from the electrolyte inlet to the electrolyte outlet. Single-cell data illustrating this effect are shown in Table I. At a feed rate of 275% of theoretical methanol, the change in potential between inlet and outlet amounted to 0.14 V.

TABLE I. EFFECT OF FEED RATE ON ELECTRODE POTENTIALS

Feed: 5M CH₃OH - 6M KOH
 Current Density: 10 mA/cm²
 Cell Temperature: 30°C

Feed Rate, % of Theoretical Methanol	Electrode Potentials vs. SCE in:				Measured Cell Voltage
	Feed		Effluent		
	E _{Anode}	E _{Cath.}	E _{Anode}	E _{Cath.}	
750	-.83	-.34	-.83	-.33	.51
470	-.80	-.32	-.80	-.32	.49
345	-.81	-.35	-.79	-.32	.46
295	-.80	-.36	-.74	-.29	.44
275	-.78	-.39	-.65	-.24	.40

Utilization of fuel, in terms of specific power output of the fuel solution in Wh/lb, can be derived from the voltage dependence and is plotted in Figure 4. If output voltage were strictly proportional to fuel rate in the low rate region, then fuel utilization would be independent of fuel rate in this region. However, Figure 4 shows that fuel utilization does increase slightly as fuel rate is decreased.

Maximum fuel utilization with 5M CH₃OH-6M KOH fuel was about 55 Wh/lb. It was limited largely by methanol loss occurring by evaporation through the

diaphragm but also by electro-osmotic flow of electrolyte through the diaphragm and cathode. These losses could be reduced through the use of a more retentive diaphragm. Concentration of formate in the spent electrolyte is less than 0.05 mole/liter, indicating high selectivity to carbonate formation.

Battery temperature is a function of current and of the flow rates of feed solution and air. Table II lists operating temperatures of the 24-cell battery shown in Figure 2 at a fuel rate of about 300% of theoretical based on methanol content of the 5M CH₃OH-6M KOH feed solution used; however, if the fuel rate were calculated on the basis of potassium hydroxide rather than methanol, it would be 180% of the theoretical rate required by the current. In these experiments air was forced through the cabinet at a metered rate rather than being allowed to flow by natural convection.

TABLE II. OPERATING TEMPERATURE OF 24-CELL BATTERY

Ambient Temperature: 25°C

Feed: 5M CH₃OH-6M KOH

Feed Rate: 300% of Theoretical CH₃OH

<u>Current Density</u> mA/cm ²	<u>Air Rate,</u> % of Theoretical	<u>Battery</u> <u>Voltage</u>	<u>Temperature, °C</u>
10	200	10.8	61
10	500	11.2	58
20	200	8.6	79
20	500	12.0	63

At an ambient temperature of 75°F, battery temperature is roughly 60-65°C at current densities of 10-20 mA/cm² and at the air rates and feed rates ordinarily used. At a low air rate the boiling point of the fuel can be exceeded, resulting in severe reduction of output voltage. Cell voltages at these currents are ordinarily between 0.4 and 0.5 V.

USE AS A POWER SOURCE WITH INTERMITTENT LOAD

One possible application of this primary fueled-battery system is as a power source for signalling devices, many of which operate intermittently. A load of this type was simulated by means of a timer operating for one second on and nine seconds off in series with a 250 W, 12 V lamp. Since the current surge required to operate this load was greater than could be supplied directly by the fueled battery, a storage battery was connected in parallel with the fueled

battery. The storage battery was a 12 Ah, 10 V assembly of sealed nickel - cadmium cells*. A schematic diagram of the system is shown in Figure 5.

This system operated automatically for a three day test period, during which time the voltage under load remained within the range of 9.0 to 9.7 V. Although the storage battery was operated under severe overcharge conditions for most of the test period, it performed satisfactorily.

LIFE TESTS

Single cells have been tested at room temperature for periods up to one year under a continuous drain of 10 mA/cm². Voltage decline has occurred mainly at the anode, amounting to 10 to 30% of the initial voltage output. Cracks in epoxy edge seals have required some increase in feed rate during the progress of the test in order to maintain cell performance at this level.

Cells in test batteries have maintained satisfactory output for 3000 hours of operating time accumulated in successive test batteries. The longest time which a battery has been operated thus far is 2000 hours; the battery was utilized in system tests rather than battery life tests and was subjected to more extreme operating conditions than would be expected in an optimum system design.

In some early batteries containing cells with thin-membrane diaphragms, cell reversals resulted in deposition of palladium and silver in the diaphragms to the extent that electrical shorting occurred. The problem was eliminated by removing the cause of cell reversal, namely, unequal feed rate to individual cells which resulted in excessive fuel depletion in some cells.

OTHER FUELS

Since the major cause of low methanol utilization in this system is the high volatility of methanol, one might expect less volatile fuels to overcome this difficulty. Ethyl alcohol, for example, boils 14°C higher than methyl alcohol. In a single cell test, however, fuel loss was not reduced by the substitution of ethyl alcohol. Ethylene glycol is not an acceptable fuel because it forms an insoluble oxidation product which plugs the cell passages.

COSTS

Based on a specific power output of 50 Wh/lb of fuel solution and a cost of \$0.10/lb of methanol and potassium hydroxide, fuel cost would amount to \$0.80/kWh.

Catalyst cost is about \$3/W, most of which is recoverable. Cost of the complete system would be many times this amount in small scale production.

* Manufactured by Alkaline Battery Division, Gould-National Batteries, Inc.

Even so, with a life of only one year the alkaline methanol-air system might be economically competitive with existing primary and secondary batteries.

CONCLUSIONS

Because a natural-flow fueled-battery system can operate with a minimum of moving parts, it should be inherently reliable. The system can operate automatically and unattended, giving power on demand and maintaining itself in standby condition under no load.

Power capability can be substantially higher than is practical with air-depolarized primary batteries or with secondary batteries. The system is simply recharged for a new period of use by refilling the fuel-electrolyte reservoir with fresh solution. Life tests of single cells indicate a useful life of at least one year and possibly considerably longer.

Costs may be competitive with existing low-energy power sources.

ACKNOWLEDGEMENTS

This work was conducted under a joint fuel cell research program of Gould-National Batteries, Inc. and Pure Oil Company. The assistance of Messrs. E. L. Burkholder, P. S. Chow and W. G. Howard in various phases of battery construction and testing is gratefully acknowledged.

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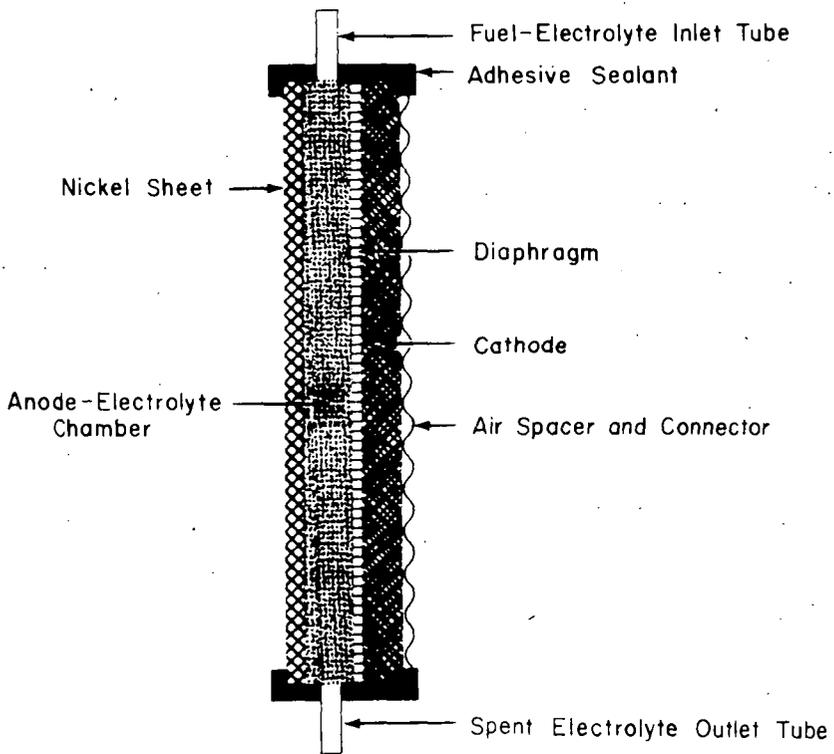


FIGURE 1. CONSTRUCTION OF DISSOLVED-FUEL CELL WITH NATURAL FLOW

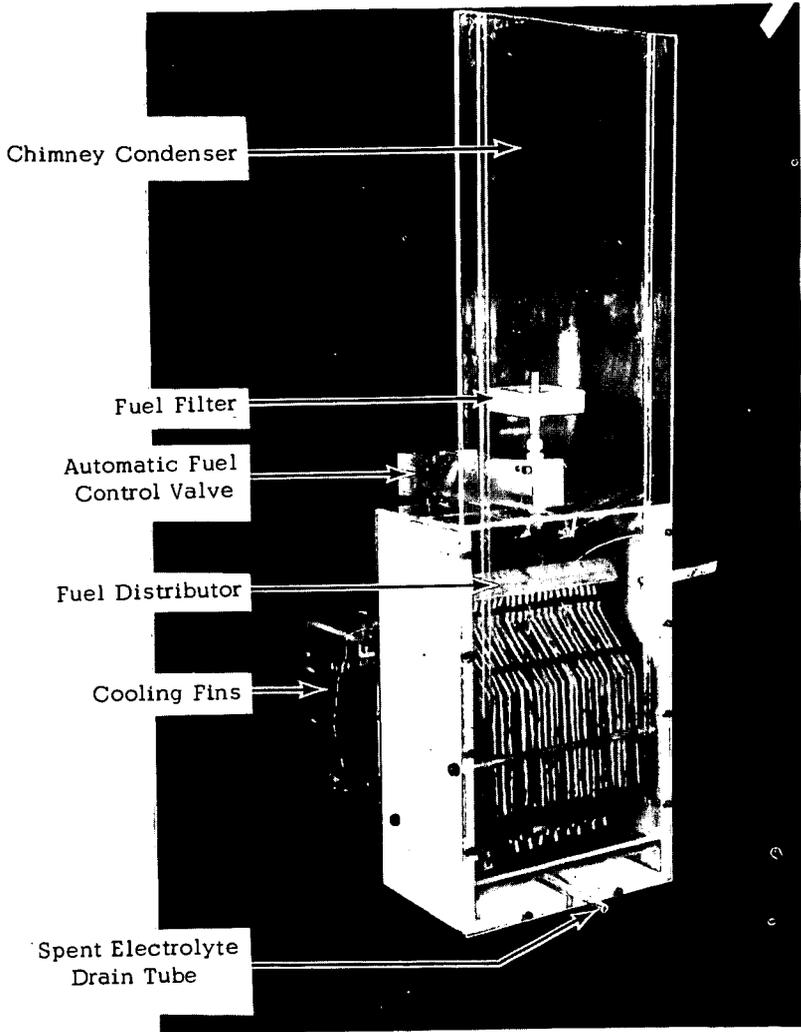


FIGURE 2. NATURAL FLOW ALKALINE METHANOL-AIR SYSTEM

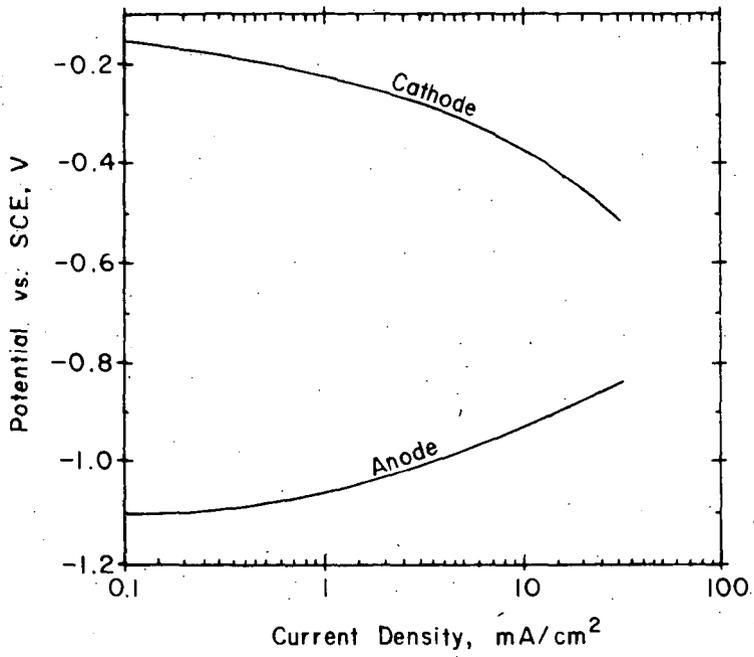


FIGURE 3. POLARIZATION CURVES FOR NATURAL-FLOW CELL

Temperature: 30°C
Fuel Rate: High

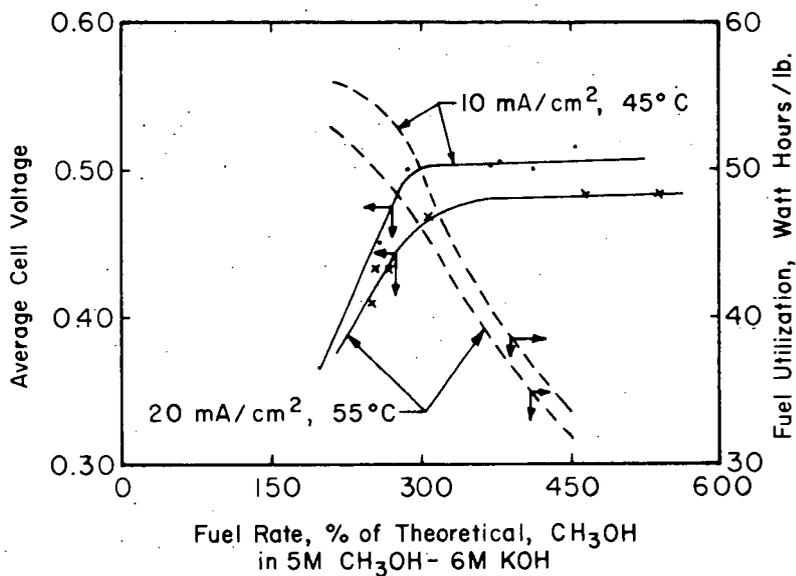


FIGURE 4. EFFECT OF FEED RATE ON AVERAGE CELL VOLTAGE AND ON FUEL UTILIZATION

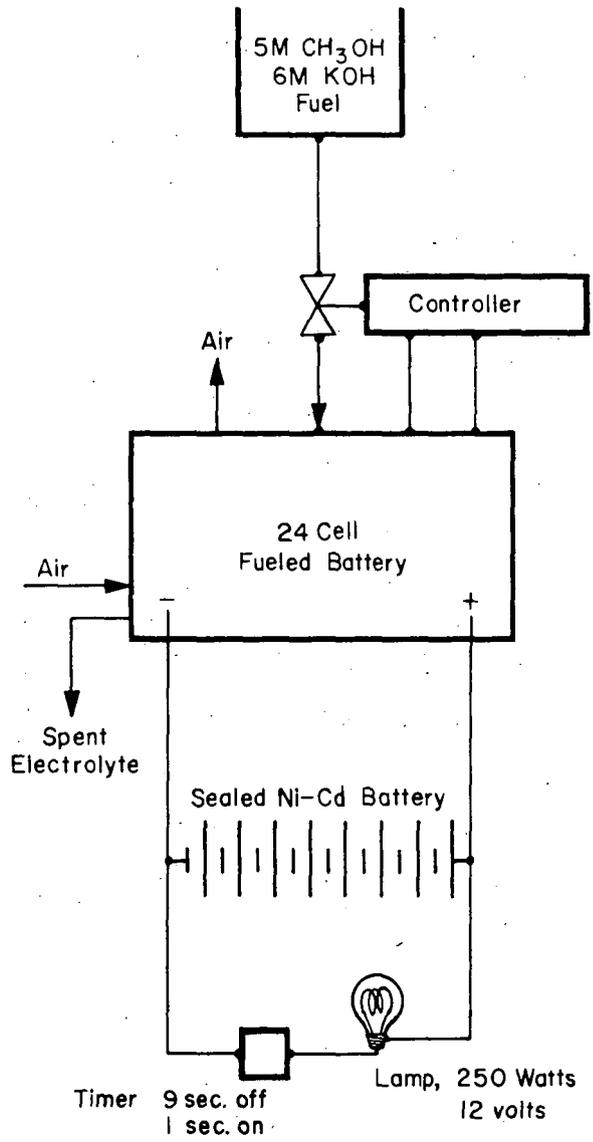


FIGURE 5. SCHEMATIC DIAGRAM OF COMPLETE POWER SYSTEM INCLUDING AN INTERMITTENT LOAD