ELECTRIC CURRENT FROM THE DIRECT CONVERSION OF LOW MOLECULAR WEIGHT C,H,O-COMPOUNDS

C. H. HAMANN* and P. SCHMÖDE

Institut für Physikalische Chemie der Universität Bonn, D 53 Bonn 1, Wegelerstrasse 12 (BRD)

(Received January 3, 1976)

Summary

This paper gives a report on the results obtained in the development of formate/air fuel cells, and of formate/air, glycol/air and formic acid/air rechargeable elements, in the years 1971–75.

A current density of 50 mA cm^{-2} can be drawn continuously from formate/air fuel cells using alkaline electrolyte. Corresponding formate/air rechargeable elements achieve an energy density of 71 Wh kg^{-1} at 10 mA cm^{-2} in a single duty cycle. Due to the multiple rechargeability of these elements an energy density of up to 170 Wh kg^{-1} can be obtained (in this case the potassium formate used as fuel and the potassium hydroxide used as electrolyte have to be stored in solid form and to be dissolved in non-pretreated water). In consequence the costs per kWh can be reduced to 5 US $.

By replacement of the formate fuel by ethylene glycol an energy density of 101 Wh kg^{-1} (single duty cycle) is obtained, and the cost decreases to 2 US $ per kWh (based on multiple recharge). These data show that the formate/air and glycol/air rechargeable elements combine exceptionally good values of energy density with a cost efficiency up to now not achieved by primary batteries.

A considerable number of these elements has already been built and tested; the shift to a small series production appears to be possible immediately. A rechargeable element with an acid electrolyte and formic acid as fuel is, however, still in an early state of development (323 Wh kg^{-1} formic acid; cost *ca.* 3.50 US $ per kWh).

Zusammenfassung

In der vorliegenden Arbeit wird über den in den Jahren 1971–75 mit Formiat–Luft-Brennstoffzellen sowie mit Formiat–Luft-, Glykol–Luft- und Ameisensäure–Luft-Füllelementen erzielte Ergebnisse berichtet.

Alkalischen Formiat–Luft-Brennstoffzellen können im Dauerbetrieb 50 mA cm^{-2} entnommen werden. Alkalische Formiat–Luft-Füllelemente

---

*To whom correspondence should be addressed, now at: Universität Oldenburg, Fachbereich IV, D29 Oldenburg, Postfach 943 (BRD).

erreichen bei 10 mA cm^{-2} Gesamtenergiedichten von 71 Wh kg^{-1}, wenn man sich auf eine einzelne Arbeitsperiode bezieht. Rechnet man die mehrfache Reaktivierbarkeit des Elements durch Neufüllung mit Betriebsstoffen ein, so resultiert eine Grenzenergiedichte von bis zu 170 Wh kg^{-1} (bei Speicherung des Brennstoffs Kaliumformiat und des Elektrolyts KOH in fester Form und Lösen in nicht vorbehandeltem Wasser). Die Kosten pro erzeugter kWh können bei Ausnutzen der Reaktivierbarkeit bis auf *ca.* 5 US $ kWh^{-1} absinken. Bei Ersatz des Brennstoffs Formiat durch Äthylenglykol erhält man eine Energiedichte von 101 Wh kg^{-1} (einzelne Arbeitsperiode) und die Kosten gehen (bei Zugrundelegen häufiger Reaktivierung) auf 2 US $ kWh^{-1} zurück. Diese Daten weisen aus, dass Formiat–Luft- und Glykol–Luft-Füllelemente ausserordentlich gute Energiedichtwerte mit von Primärsystemen bisher nicht erreichter Preiswürdigkeit verbinden. Die zuvor genannten Elemente wurden bereits in beträchtlicher Stückzahl hergestellt und erprobt, der Übergang zu einer Kleinserie scheint unmittelbar möglich. Demgegenüber befindet sich ein Füllelement mit saurem Elektrolyten und Ameisensäure als Brennstoff (323 Wh kg^{-1} Ameisensäure, Kosten *ca.* 3.50 US $ kWh^{-1}) noch in einem frühen Entwicklungsstadium.

A. Introduction
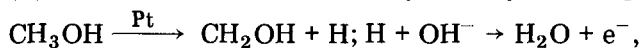
Basic aspects of the electrochemical oxidation of low molecular weight C,H,O-compounds

The electrochemical oxidation of low molecular weight C,H,O-compounds both with alkaline and with acid electrolytes has already been the subject of considerable research. Using mostly platinum catalysts, a wide range of results has been obtained. The following mechanisms are discussed in particular:
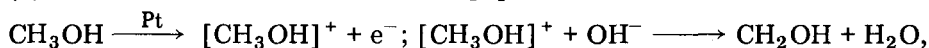
(a) Oxidation by oxygen-chemisorption layers formed on the surface of the electrocatalyst [1 - 3]
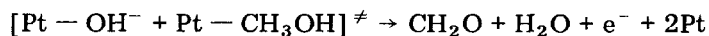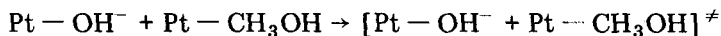
$$Pt + OH^- \rightarrow Pt - OH + e^-; \; 2\,Pt - OH + CH_3OH \rightarrow CH_2O + 2H_2O + 2Pt^*,$$

(b) Oxidation starts with a catalytic dehydration [1, 4, 5]

$$CH_3OH \xrightarrow{Pt} CH_2OH + H; \; H + OH^- \rightarrow H_2O + e^-,$$

(c) Direct electrochemical oxidation [6]

$$CH_3OH \xrightarrow{Pt} [CH_3OH]^+ + e^-; \; [CH_3OH]^+ + OH^- \longrightarrow CH_2OH + H_2O,$$

(d) Oxidation according to a reaction pair-mechanism (formation of an activated complex between the adsorbed C,H,O-molecule and an adjoining adsorbed OH$^-$ ion or an H$_2$O molecule)

$$Pt - OH^- + Pt - CH_3OH \rightarrow [Pt - OH^- + Pt - CH_3OH]^{\neq}$$

$$[Pt - OH^- + Pt - CH_3OH]^{\neq} \rightarrow CH_2O + H_2O + e^- + 2Pt$$

---

* The examples shown refer to alkaline electrolyte, CH$_3$OH fuel and a platinum electrocatalyst respectively.

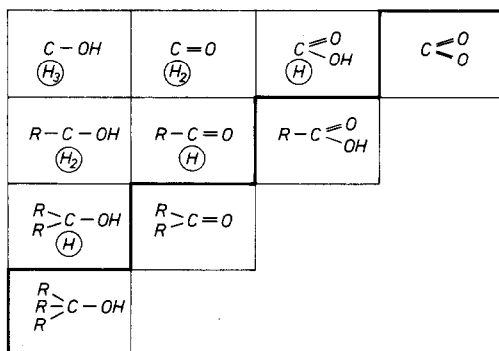|			
$C-OH$ (H_3)	$C=O$ (H_2)	$C\lessgtr^O_{OH}$ (H)	$C\lessgtr^O_O$
$R-C-OH$ (H_2)	$R-C=O$ (H)	$R-C\lessgtr^O_{OH}$	
$R{>}C-OH$ (H)	$R{>}C=O$		
$R{>}C-OH$ (with three R)			

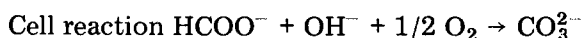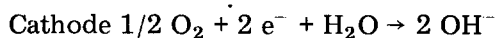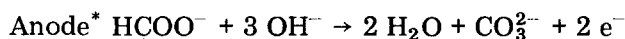Fig. 1. Electrochemically active and inactive C,H,O compounds.

Which of the mechanisms mentioned really takes place in each case and what kind of intercombinations are formed during the further reactions of intermediate products cannot generally be determined exactly. This is particularly so because of a lack of work on the unambiguous identification of short-lived intermediate products, and since the course of reactions may be influenced by electrochemically inert, *i.e.* surface poisoning, reaction products. On the other hand a recent report [7] has clearly shown which of the hydrogen atoms in a C,H,O-molecule is oxidised. It was found in experiments with an acid electrolyte and a platinum electrode that the differences in the electrochemical behaviour of some alcohols are solely due to the number of hydrogen atoms bound to α-carbon: these differences do not depend on the nature and the arrangement of functional groups within the molecule. The C—H binding of the α-C atom must therefore be regarded as the only reactive spot of the molecule.

Thus it can be predicted that the compounds listed in Fig. 1 to the left of the diagonal must be electrochemically oxidizable, and that those listed to the right are inactive. This is exactly what has been observed in experiments, *i.e.*, CH_3OH, CH_2O, $HCOOH$ and $HCOO^-$, as well as higher alcohols containing α-hydrogen atoms (*e.g.* $(CH_2OH)_2$), are especially suitable for electrochemical oxidation in galvanic elements.

B. Experimental

B. 1. Alkaline formate/air fuel cells

For the actual experiments we decided to use formate (in the form of HCOOK) dissolved in KOH as a fuel for the conversion of C,H,O compounds in air-breathing galvanic fuel cells.

Anode* $HCOO^- + 3\ OH^- \rightarrow 2\ H_2O + CO_3^{2-} + 2\ e^-$

Cathode $1/2\ O_2 + 2\ e^- + H_2O \rightarrow 2\ OH^-$

Cell reaction $HCOO^- + OH^- + 1/2\ O_2 \rightarrow CO_3^{2-}$
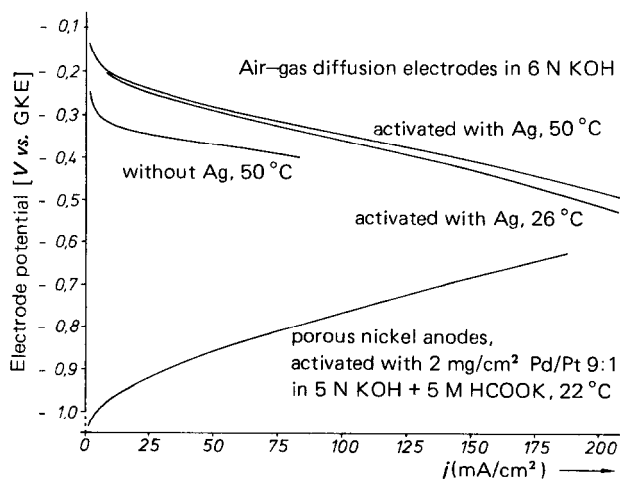
—————

* Main electrode processes.

Fig. 2. Voltage curves in 6 M KOH (air electrodes) and in 5 M KOH–5 M HCOOK mixtures (formate anode, measured in half cell arrangements).

Sheets of 70% porous nickel sinter, 1 mm thick, were used as the anode material. 2 mg of a palladium–platinum catalyst per cm^2 geometrical surface were used to activate the sheets by a soaking and precipitation process. The finished electrode weighs $ca.$ 200 mg cm^{-2}.

The active layer of the air cathodes consists of Teflon-bonded activated carbon with the addition of 30 weight % of silver. This material is pressed together with a thin silver mesh (current collector) to obtain a foil, which is then pressed once more, this time onto a commercially available porous Teflon foil to give the finished electrode. This electrode is $ca.$ 0.3 mm thick, very flexible and weighs about 0.1 g cm^{-2}.

Figure 2 shows the voltage curves resulting from the electrodes described above (measured in a half-cell arrangement). It can be seen that the air cathode is quite efficient even when no silver catalyst is being used.

As with other C,H,O-compounds, formate does not react with carbon or silver activated carbon; thus the formate anode and the air cathode can be combined to form a galvanic element without inserting a diaphragm. As we are working with a highly concentrated, chemically stable fuel solution, no dosage apparatus is needed. Thus, the system remains very simple (as can be seen in Fig. 3), where the 12V–12A setup consists of 30 cells in which the formate anodes are each 11 cm × 11 cm. The anode in the single cell is placed between two air cathodes, leaving 1 mm clear space for the circulation of the fuel–electrolyte mixture. The cathodes of two adjoining cells are separated by a plastic lattice (air inlet). For current densities >30 mA cm^{-2} a miniature blower is added. Power consumption of the electrolyte circulating pump and the blower is 2 W each.

Figure 4 is a photograph of a similar fuel cell with 24 elements and Fig. 5 shows the voltage curve of a 30-element fuel cell. It can be seen from Fig. 5 that a terminal voltage of 650 mV is obtained from a single cell using oxygen
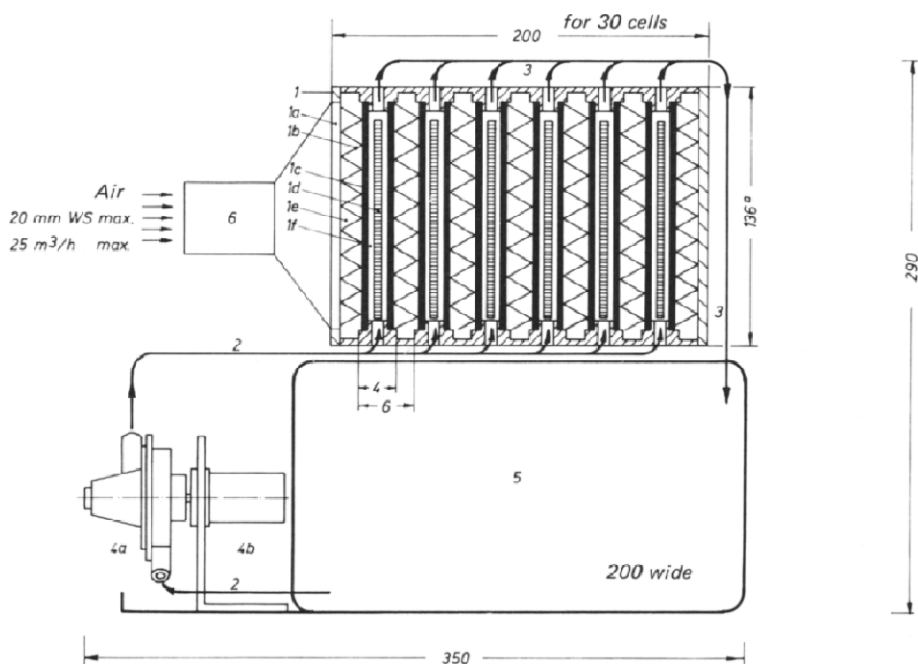
Fig. 3. Diagrammatic view of a 30-cell 12 V–12 A formate/air fuel cell. 1, single cell; 1a, terminal plate of the module; 1b, supporting net; 1c, air electrode; 1d, formate anode; 1e, air space; 1f, electrolyte/fuel space; 2, electrolyte/fuel input; 3, return; 4a, centrifugal pump; 4b, driving motor; 5, electrolyte/fuel tank; 6, blower; (all dimensions given in mm).
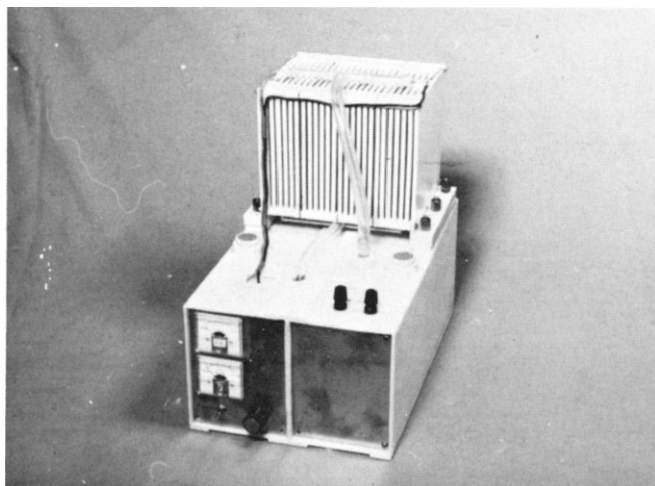

Fig. 4. Photograph of a 24-cell formate/air fuel cell.

and an equimolar 5 M KOH–5 M HCOOK mixture at 10 mA cm^{-2} and 400 mV at the maximum current of 50 mA cm^{-2}, (with air these values are 600 and 350 mV respectively). With a theoretical Ah-capacity of 268 Ah l^{-1} for the
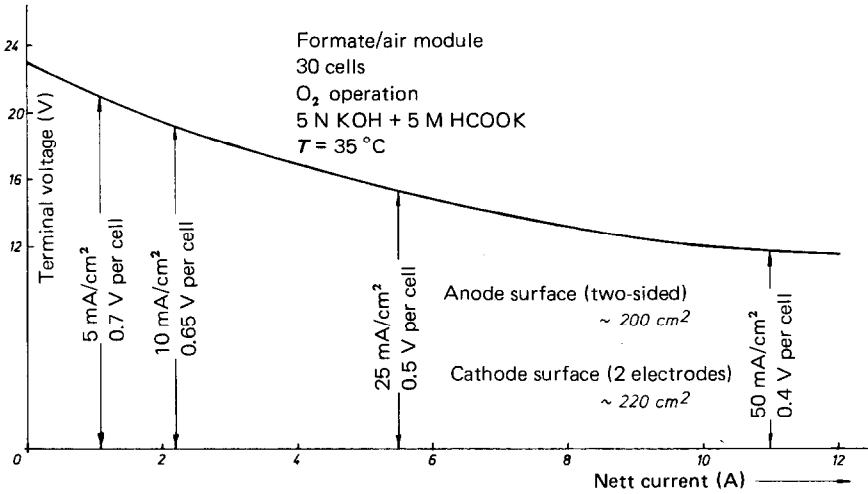
Fig. 5. Voltage characteristic of the 30-cell formate/air fuel cell run with oxygen.
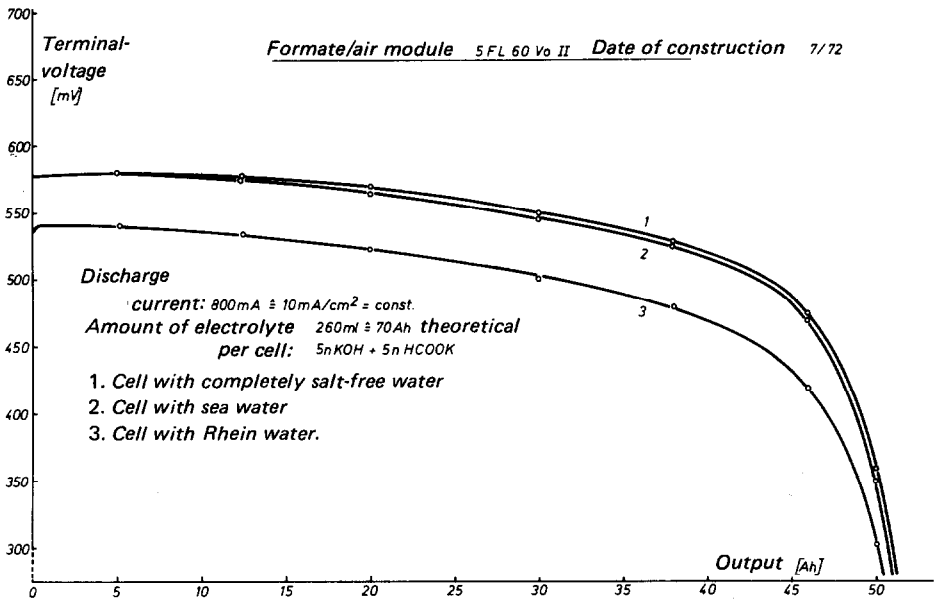

Fig. 6. Dependence of the discharge characteristic of a formate/air single cell, with a fuel supply for 50 Ah operated with air, on the kind of water.

given mixture, energy density values of 174 Wh l^{-1} (124 Wh kg^{-1}; $\rho = 1.40$) and 107 Wh l^{-1} (76.6 Wh kg^{-1}) are obtained for the electrolyte–fuel mixture (when operated with air oxygen, the results are 114 and 67 Wh kg^{-1} respectively). About 80% of these values can be achieved in practice. The unladen weight of the complete apparatus shown in Fig. 4 is 4 kg; including the fuel
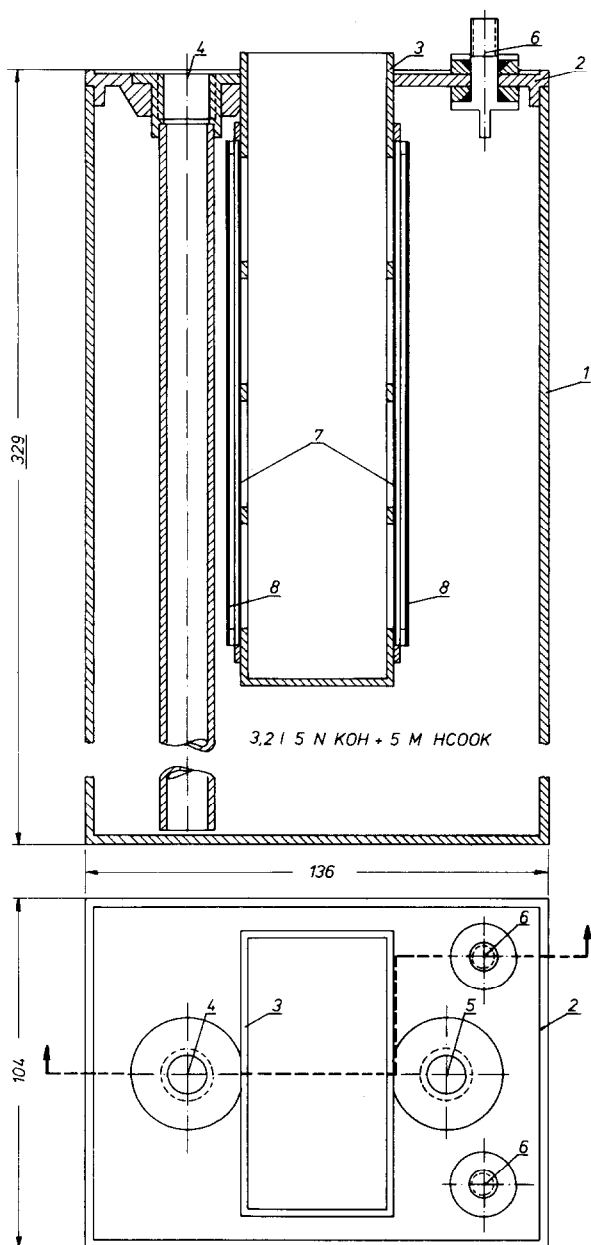
Fig. 7. Diagrammatic view of a formate/air rechargeable element (700 Ah capacity).
1, polystyrol cell casing; 2, cell lid; 3, ventilating shaft; 4, exhaust rising pipe; 5, feed cock; 6, pole-terminals; 7, air electrodes; 8, formate anodes; (all dimensions given in mm).

for running 2.5 h at full power the unit weighs 10 kg. The total energy density relative to 2.5 h full power operation (with air) is about 32.2 Wh kg^{-1}, the power density is *ca.* 10 W kg^{-1}.

The fuel cell described here can be used, amongst other things, as a power source for electronic appliances or as a mobile charging apparatus. Another advantage not mentioned up to now is that no pre-treated water is needed as a solvent to produce a ready-to-use HCOOK–KOH mixture, as the cell's capacity is only slightly influenced by the use of tap, sea, or even dirty river water (from which the suspended particles have been separated; Fig. 6). Thus HCOOK and KOH can be taken along in solid form, leading to 170 Wh kg^{-1} for the solid fuel (HCOOK + KOH equimolar) assuming an 80% power yield and 0.6 V average terminal voltage (10 mA cm^{-2}, operated with air).

B. 2. Alkaline formate/air rechargeable elements

Air breathing rechargeable elements fueled by formate have already been constructed in various forms [1]. When rather small electric or electronic appliances are being used in isolated places, very often only low currents but, on the other hand, the highest possible energy densities are required. This is a case in which the formate/air system may be yet further simplified by switching to a so-called rechargeable element.

Rechargeable elements are galvanic systems, which may be recharged by replacing a fuel–electrolyte mixture or by refilling with fuel (this is also known as a "discontinuous fuel cell").

Figure 7 shows the set-up of such a formate/air rechargeable element. It consists mainly of a battery casing for the fuel–electrolyte mixture (again 5 M KOH–5 M HCOOK), a ventilating shaft with the air cathodes glued on to it and the formate anodes (see section B.1.). The latter are fixed about 2 mm behind the cathodes by means of short spacers.

Figure 8 shows a photograph of such a formate/air rechargeable element. The cell shown, can hold 3.2 l of the fuel–electrolyte mixture and has a total weight of 5.38 kg. The surface of the electrodes used is 2 cm × 90 cm (cath-
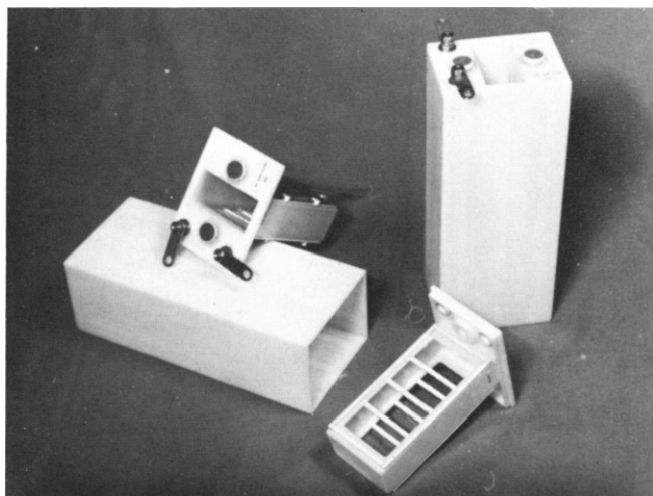

Fig. 8. Photograph of a formate/air rechargeable element (700 Ah capacity).

odes) and 2 cm × 100 cm (anodes). Thus the total current at 10 mA cm^{-2} is *ca.* 2 A, the terminal voltage *ca.* 600 mV (Fig. 9). A maximum of 6 A can be drawn from the cell. The fuel supply corresponds to a capacity of 268 Ah l^{-1} × 3.2 l = 860 Ah. In reality about 700 Ah are obtained, leading to 385 Wh, or 71.6 Wh kg^{-1} at an average discharge voltage of 550 mV and a total weight of 5.38 kg.
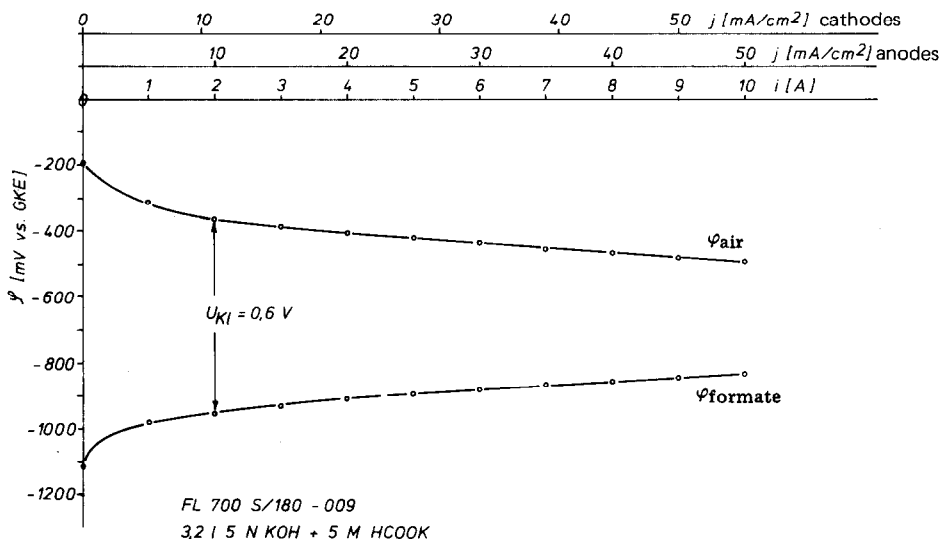

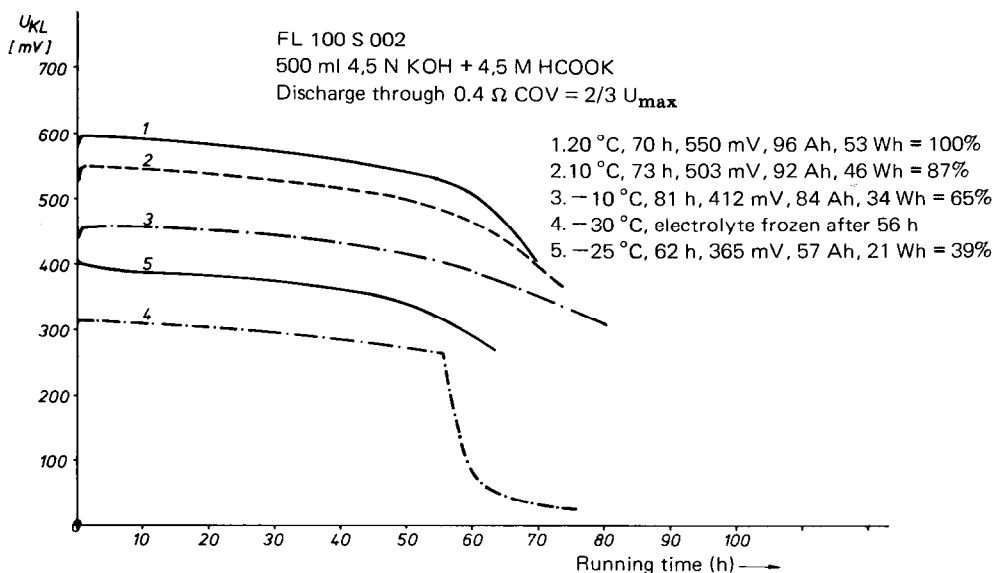Fig. 9. Dependence of the electrode potentials of a formate/air rechargeable element on the power load.

Fig. 10. Discharge curves of a formate/air rechargeable element at various surrounding temperatures.

Figure 10 shows the change in discharge characteristics of formate/air rechargeable elements with temperature. The level discharge characteristic is quite remarkable as is also the high efficiency even at temperatures below zero.
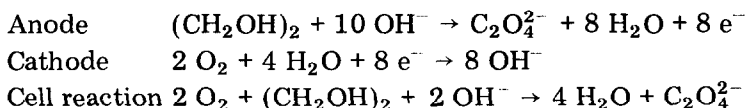
The cells described here were put into operation as a power supply unit in 1973 on a sailing yacht (12 cells — 6 V module). The cells survived the wear and tear and even the fact that the ventilating shafts got waterlogged with sea water. A 3 V module consisting of 5 smaller cells of 55 Ah capacity (together with a voltage transformer and a Ni–Cd accumulator as a hybrid system) has been in use continuously since 1971 acting as a power supply for a radio telephone in a sail plane. This module has survived more than 4000 take-offs and landings and has been refilled 16 times with the electrolyte–fuel mixture. Its electrical characteristics have however hardly deteriorated (20 - 30 mV voltage loss at 10 mA cm^{-2}). All in all, a great number of proto-types in sizes from 6 Ah (same external shape as a monocell) to 700 Ah (Fig. 7) have been manufactured.

Formate/air rechargeable elements can generally be used where there is a need for a reliable supply of electric energy of up to 100 W at low cost, over a long period of time, mains electricity not being available (*e.g.* radio beacons, light buoys, TV transposers, etc.). A cost analysis as well as a com-parison of cost and performance with other systems is to be found in the discussion following this section.

The above-mentioned advantage of a possible maximum energy density of 170 Wh kg^{-1} when the fuel is stored in the solid state and dissolved in un-treated water, also holds for rechargeable elements. One possible problem with this construction is, however, the fact that the solution may flow out of the cell's filling aperture when the atmospheric humidity is very high (as in the tropics; humidity enters the hygroscopic solution through the cathode). Problems arising from carbonization (CO_2 in the air going into solution in the same way) have not yet been encountered. (The longest use of an element without a fuel change was 2 years.)

B. 3. Alkaline ethylene glycol/air rechargeable elements

In an attempt to develop the air breathing rechargeable elements de-scribed above with a higher energy density, an attempt will be made to re-place the formate fuel by a C,H,O compound with a higher number of hydro-gen atoms bound to the α-carbon atom. (See introduction). Methanol (CH_3OH) is a possible choice, but the current densities reached with a reason-able amount of noble metal catalysts on the methanol anodes, as well as the low temperature behaviour of the latter, are not satisfactory. Moreover, a methanol–oxygen fuel cell has been described in 1972 by Gugenberger and Spahrbier [8]. For this reason, ethylene glycol ($CH_2OH)_2$ was investigated as a fuel. (As to the earlier use of glycol fuel, *e.g.* by Spengler and Grüneberg, see [1].)

Anode $\quad (CH_2OH)_2 + 10\ OH^- \rightarrow C_2O_4^{2-} + 8\ H_2O + 8\ e^-$

Cathode $\quad 2\ O_2 + 4\ H_2O + 8\ e^- \rightarrow 8\ OH^-$

Cell reaction $2\ O_2 + (CH_2OH)_2 + 2\ OH^- \rightarrow 4\ H_2O + C_2O_4^{2-}$
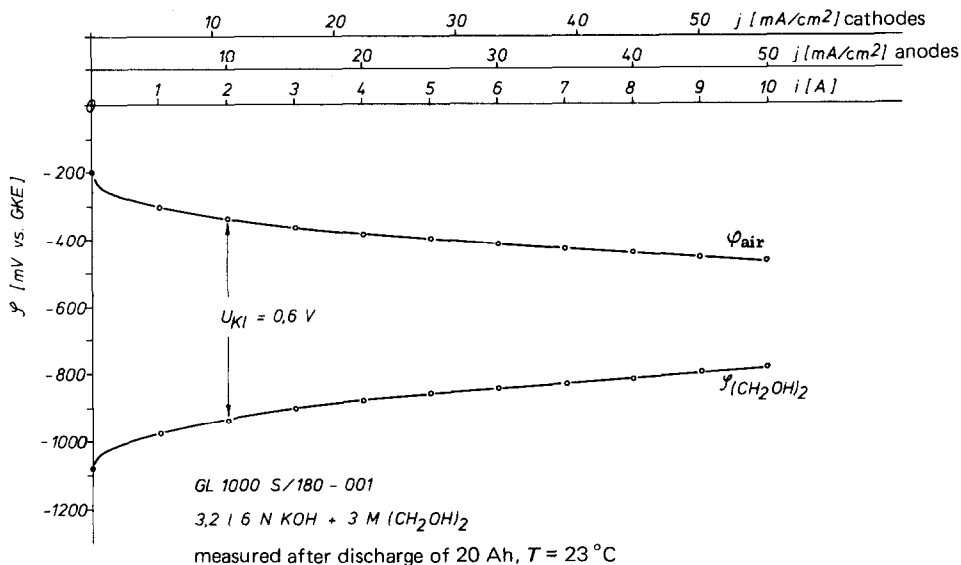
Fig. 11. Dependence of the electrode potentials of an ethylene glycol/air rechargeable element on the power load.

When producing a glycol/air rechargeable element, the previously mentioned cell set-up (Figs. 7 and 8) remains the same, as well as the construction of the electrodes as described in Section B.1.. 4 mg platinum cm^{-2} have turned out to constitute the best catalyst layer for the glycol anode. When making the cathodes it proved necessary to increase the hydrophobicity of the electrode's active layer in order to avoid "weeping". This is the formation of beads of liquid on the gas side of the air electrode, which flow towards the lower end in the course of time (mixtures of glycol and KOH possess a lower surface tension than formate–KOH mixtures). This does not impair the operation of the electrode, but fuel is lost after some time.

Figure 11 shows the current–potential characteristic of a glycol/air rechargeable element when using a mixture of 3 M glycol and 6 N KOH and it can be seen that the overall behaviour of such a cell is only slightly different from that with formate fuel: the terminal voltage is practically the same at 10 mA cm^{-2} (about 600 mV). The potential of a glycol anode though is not as stable over time as that of a formate anode: during a single discharge the over voltage goes up by about 100 mV and thus the terminal voltage is lowered. This process is accompanied by an increasing yellowing of the electrolyte–fuel mixture. Both effects are due to an ever increasing formation of glycol oxidation products. After replacing the spent fuel mixture the original starting potential is immediately re-established.

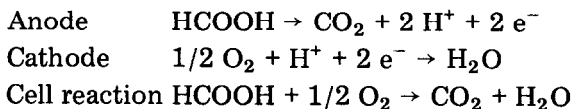The theoretical Ah capacity of a mixture of 3 M glycol and 6 N KOH is 643 Ah l^{-1}, i.e., 510 Ah kg^{-1} (ρ = 1.26). But in reality only 50% of these values are obtained (($CH_2OH)_2$-oxidation products seem to be at least partly electrochemically inert). For the 3.2 l-size cell shown in Figs. 7 and 8 these values lead to a capacity of ca. 1000 Ah. This corresponds to 500 Wh at an

average discharge voltage of 500 mV. Considering the total weight of 4.93 kg, this results in an energy density of 101 Wh kg^{-1} (with formate, for example, these figures were 700 Ah, 385 Wh and 71.6 Wh kg^{-1} respectively).

Air breathing rechargeable elements with ethylene glycol fuel have been functioning well. They may be used in the same instances as the quoted examples for formate/air rechargeable elements. The higher capacity more than compensates for the slightly lower terminal voltage. A further increase in the capacity seems doubtful though, since the Ah yield (and thus the economic performance) decreases with the use of higher glycol concentrations. This problem might be solved with a suitable catalyst. On the other hand, it is quite difficult to produce active air cathodes with $(CH_2OH)_2$ concentrations >4 M that do not "weep". As to the comparison of the efficiency and economic performance with competing systems see section C.

B. 4. The technical conversion of low molecular C,H,O compounds in acid solutions (the formic acid/air rechargeable element)

Low molecular C,H,O compounds like CH_2O, CH_3OH and $(CH_2OH)_2$ may also be oxidized anodically in acid solutions, just as HCOOH (see *Introduction*). This possibility leads to rechargeable elements in which, unlike the alkaline systems, the electrolyte (OH$^-$ ions in the alkaline system) is not used up and therefore does not enter into the economic considerations:

Anode $HCOOH \rightarrow CO_2 + 2\ H^+ + 2\ e^-$

Cathode $1/2\ O_2 + H^+ + 2\ e^- \rightarrow H_2O$

Cell reaction $HCOOH + 1/2\ O_2 \rightarrow CO_2 + H_2O$

(*e.g.* formic acid). The final products are gaseous CO_2 and water; there is no danger of carbonization, and to recharge such an element a simple replacement of the spent fuel is required.

By using formic acid fuel and storing it in concentrated form in the rechargeable elements, these will possess an extremely high energy density. Pure HCOOH possesses an Ah capacity of 1407 Ah l$^{-1} \triangleq 1153$ Ah kg^{-1}. If a working terminal voltage of 0.4 V and a material conversion of 70% is assumed, this results in an energy density of 323 Wh kg^{-1}.

A special anode is necessary for the direct conversion of concentrated formic acid, the active layer of which consists of platinized carbon — still with a 10% Pt content. Figure 12 shows the current density–potential curve obtained with such a special anode, from which it can be seen that 10 mA cm^{-2} can be obtained with an overvoltage of only 350 mV against the reversible hydrogen potential. At 5 mA cm^{-2} this potential value has been up until now maintained for 24 h.

By combining a formic acid anode with an air cathode (which has been made suitable for use in acid surroundings by using platinum activated carbon and noble metal current collectors), an experimental element was obtained with a 10 cm^{-2} electrode surface from which 100 mA could be drawn at a terminal voltage of 400 mV (normal temperature).
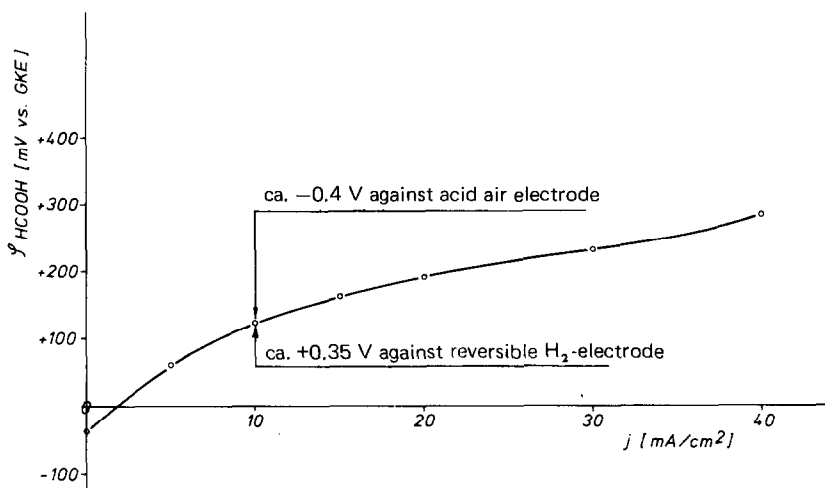
Fig. 12. Anodic oxidation of concentrated formic acid on a special anode.

A lot of research still has to be done on catalysts, on the resistance of the cell components to acid and on cheaper materials for current collectors, etc., before the $HCOOH/H_2SO_4$/air rechargeable element is ready for practical use.

C. Discussion

C. 1. Cost analysis and comparison with other battery systems.

The material costs for a formate/air or a glycol/air rechargeable element of the size shown in Fig. 8 are given in Table 1. The production cost is *ca.* 20.- DM per cell (assuming series production, according to information from a West German battery manufacturer). Thus a formate/air cell would cost *ca.* 50.00 DM (700 Ah) and a glycol/air cell 60.00 DM (1000 Ah).

The running costs for the fuel/electrolyte mixture are (in DM):

	formate/air	glycol/air
per filling (3.2 l)	5.47	2.50
per kWh	14.21	5.00

These figures are based on energy densities of 71.6 Wh kg^{-1} for a mixture of 5 M KOH–5 M HCOOK and 101 Wh kg^{-1} for a 6 M KOH–3 M $(CH_2OH)_2$ mixture, which are obtained when cells are discharged at 10 mA cm^{-2}. The price for the chemicals was taken as 1.04 DM for 1 kg 86% KOH, 3.20 DM for 1 kg 98% HCOOK, and 1.96 DM for 1 kg 99% glycol (wholesale prices).

A total price of 145 DM per kWh (formate/air element) and 125 DM per kWh (glycol/air) is reached for one filling of elements with the above discussed capacities (385 Wh with formate fuel and 500 Wh with glycol). For the formic acid/air element discussed in Section B. 4., running costs are about

TABLE 1

Material costs for rechargeable elements (of size shown in Fig. 8)

(DM per cell, 1975)

	formate/air	glycol/air
Casing and accessories		
Cell casing (production type accumulator casing, 3.2 l)	5.00	5.00
Connectors, channels, battery plugs, sealing rings, piping	4.20	4.20
Cathodes (2 cm × 91 cm each)		
Silver mesh	9.60	9.60
Activated carbon, PTFE and Ag	1.00	1.00
Teflon foil	1.20	1.20
Anodes (2 cm × 100 cm each)		
Sintered nickel	4.80	4.80
Platinum catalyst[*]	0.65	12.70
Palladium catalyst[*]	1.95	—
Sum (DM per cell)	28.40	38.50

[*] 0.4 g Pt/Pd 1:9 per 200 cm^2 for formate/air elements; 0.8 g Pt per 200 cm^2 for glycol/air.

9.30 DM per kWh (approximate energy yield 323 Wh kg^{-1} formic acid, price per kg 3.00 DM). The low material costs of the formate and glycol/air cells will only be attained when it is possible to use smaller amounts of the noble metal-electrocatalyst (which does not, however, appear probable in the near future) or to leave out the noble metal of the catalysts completely.

The values mentioned correspond to a load of 10 mA $cm^{-2} \triangleq 1.8$ A and to discharge times of 390 and 550 h respectively. The corresponding costs for commercial primary cells are 140.00 to 320.00 DM per kWh (Leclanché monocells), 225.00 to 360.00 DM per kWh (alkaline manganese monocells) and 54.00 to 120.00 DM per kWh (large air breathing zinc primary cells around 1000 Wh). (These are the selling prices quoted by the manufacturers.)

For a single duty cycle, therefore, these figures show that formate/air or glycol/air elements are not cheaper than the usual primary systems. This changes rapidly though, when the possibility of recharging and exchanging exhausted electrolyte–fuel mixtures is considered. The cost per kWh goes down with every filling until it approaches the cost of the fuel electrolyte mixtures (14.21 and 5.00 DM respectively). Thus these elements are the cheapest of all the primary systems known up to now.

These relationships are summarized in Fig. 13. The limiting values are 16.30 and 5.60 DM per kWh for formate/air and glycol/air respectively. It should however be noted that in Fig. 13 production costs are shown for the rechargeable elements whilst selling prices have been used for the competing systems. The length of operation after which it becomes more economical to
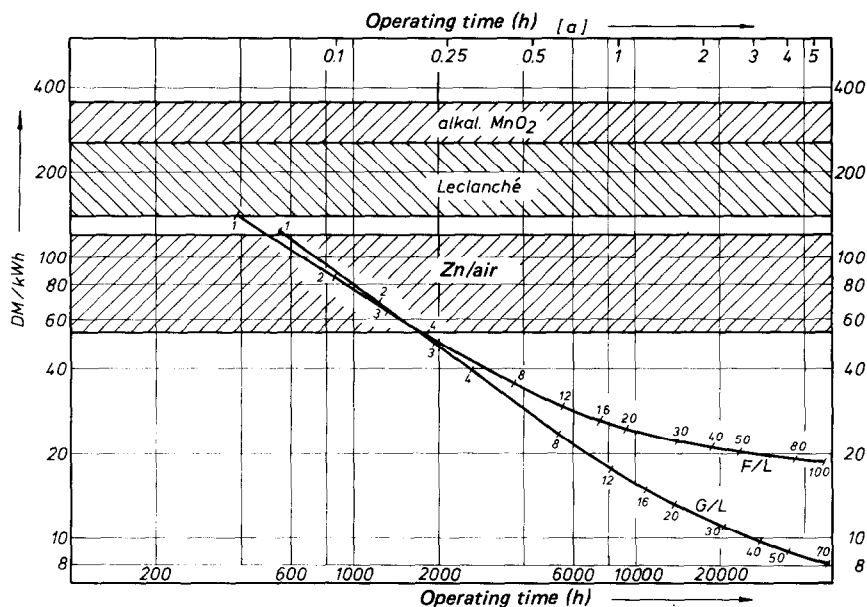
Fig. 13. Time dependence of the cost of the electric energy produced by formate/air (F/L) and glycol/air (G/L) rechargeable elements.

When calculating the curves shown, the de-activation of the electrodes through usage over a long period of time was taken into consideration, by assuming a reduced terminal voltage. (From the second discharge onwards, 315 instead of 385 Wh per 3.2 l formate filling and 410 instead of 500 Wh per 3.2 l glycol filling respectively were assumed.) Discharges took place through 0.4 Ω, leading to discharge times of 470 and 690 h respectively. The figures on the curves correspond to the necessary recharges in each case. The running costs of commercially available primary batteries are listed for comparison.

use formate/air and glycol/air elements depends therefore on the trading costs and margins. It can be assumed though, that the limiting values mentioned above will hardly be influenced since the investment in the cell itself is of minor importance for long-term operation (more than 10 refillings).

C. 2. Energy density - power density
Finally Fig. 14 shows the ranges of energy density–power density of the systems compared. The power densities of 40 W kg^{-1} for the formate/air element were obtained with high power rechargeable elements not described in this paper, which have an accordingly greater electrode surface/total volume and are therefore more expensive. Similar glycol/air cells are also possible.
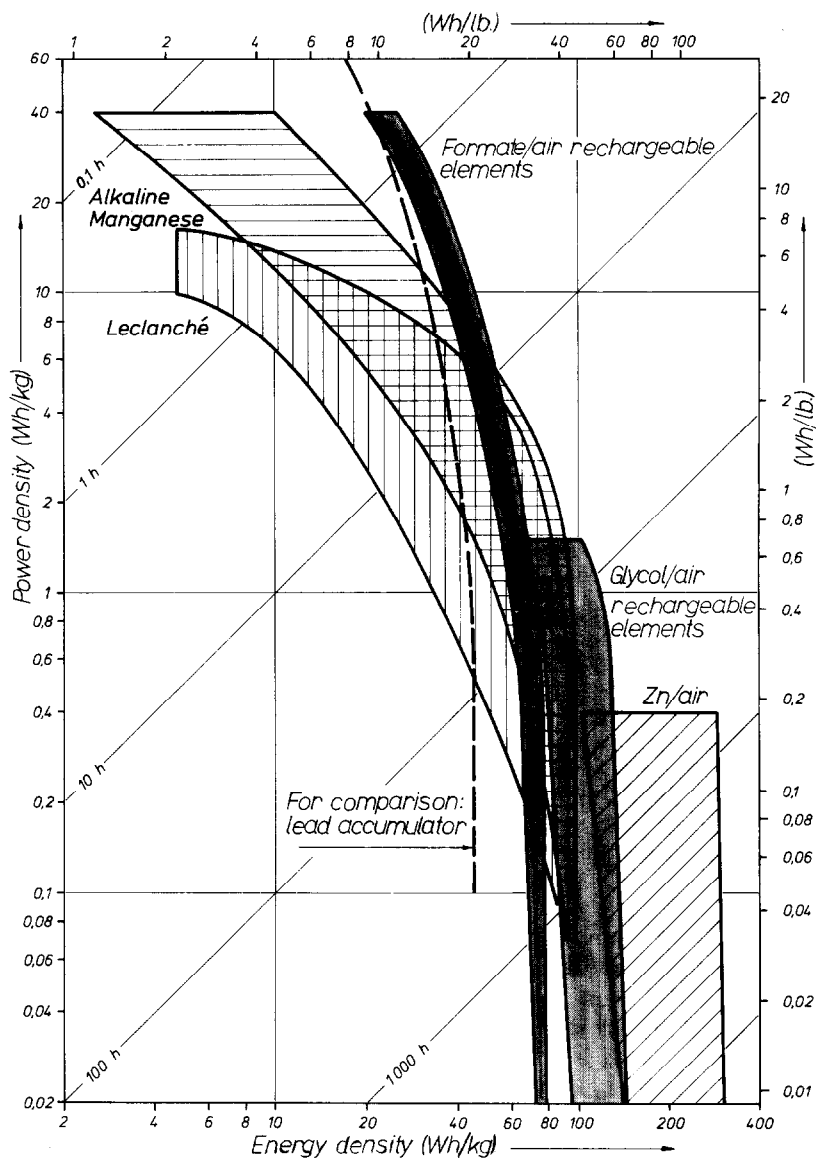
Acknowledgements

Fig. 14. Energy density–power density area of formate/air and glycol/air rechargeable elements as well as commercially available primary batteries. The area for the formate/air element is identical (up to 1 to 2 W kg^{-1}) with the rechargeable elements described in Section B. 2. The fuel cell described in Section B. 1. achieved up to 10 W kg^{-1}, the area above 10 W kg^{-1} pertains to high power rechargeable elements (see Section C.2).

References

1 W. Vielstich, Fuel Cells, Wiley-Interscience, New York, 1970, (see also the references mentioned there).

2 F. G. Will and C. A. Knorr, Z. Elektrochem., 64 (1960) 258, 270.
3 J. Giner, Z. Elektrochem., 63 (1959) 386.
4 S. S. Beskorovainaya, Ju. B. Vasil'ev and V. S. Bagotzkii, Elektrokhimiya, 2 (1966) 167, 1439; 4 (1968) 315; 8 (1972) 376.
5 V. E. Kazarinov and V. N. Andreev, Elektrokhimiya, 9 (1973) 506.
6 G. A. Bogdanovskii and A. I. Schlygin, Zh. Fiz. Khim., 31 (1957) 2428; 33 (1959) 1769; 34 (1960) 57.
7 E. Sokolova, Electrochim. Acta, 20 (1975) 323.
8 Th. Gugenberger and D. Spahrbier, in D. H. Collins (ed.), Power Sources 4, Oriel Press, Newcastle upon Tyne, 1973.