FUEL CELL ASSEMBLIES WITH AN ACIDIC ELECTROLYTE

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Summary

The application of fuel cells in the lower power range up to 10 kW depends on the use of commercially available liquid fuels like gasoline, diesel oil or methanol. This means a fuel conditioning to produce a hydrogen containing crude gas, which can best be consumed by a fuel cell with an acidic electrolyte.

The possibilities for fuel conditioning are described. The crude gas can be oxidized at different non-noble metal catalysts, *e.g.* WC, which are not poisoned by crude gas components such as CO. This report also reviews various cathode catalysts. A conceptual design of a battery able to operate in diluted acids at higher temperatures is described.

Zusammenfassung

Die Anwendung von Brennstoffzellen des unteren Leistungsbereiches bis 10 kW setzt die Verwendung von handelsüblichen, flüssigen Brennstoffen wie Benzin, Dieselkraftstoff oder Methanol voraus. Diese Brennstoffe müssen zu einem wasserstoffhaltigen Rohgas aufbereitet werden, das am günstigsten in einer Brennstoffzelle mit saurem Elektrolyten umgesetzt werden kann.

Es werden die verschiedenen Möglichkeiten einer Brennstoffaufbereitung diskutiert. Das Rohgas kann an Nichtedelmetallkatalysatoren, vor allem WC, anodisch oxidiert werden, ohne dass eine Vergiftung des Katalysators durch einzelne Rohgaskomponenten wie CO eintritt. Weiter wird über verschiedene Kathodenkatalysatoren berichtet und der Aufbau einer Batterie mit saurem Elektrolyten beschrieben.

1. Introduction

The advanced state of technical development of fuel cells* has already been demonstrated by their use in supplying energy for space craft [1, 2].

^{*}For basic information on fuel cells reference may be made to [1, 57 - 60].

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However, despite this, due to the unsatisfactory economics, terrestrial utilisation of these fuel cell assemblies has not been achieved.

The most essential feature in a terrestrial application of fuel cells is the use of a cheap, liquid fuel which is readily obtainable commercially, such as a hydrocarbon (petrol or diesel oil) or methanol, which can be produced from oil or coal [3, 4]. The desired direct conversion of these liquid fuels is not vet possible, since, with the exception of methanol in an alkaline medium [5] suitable electrocatalysts are not available, causing the loss of electrolyte through the formation of carbonate. Apart from a few substances which are uneconomic for energy production, such as hydrazine and formic acid, the only suitable working materials for fuel cells are hydrogen and oxygen, both relatively expensive gases which also give rise to transport and storage problems. A crude gas containing hydrogen must therefore be produced from commercially available liquid fuels, in a preparatory stage coupled to the fuel cell battery. For financial reasons, air is used as the oxidizing agent. Under these conditions, it is advisable to choose a fuel cell with an acidic electrolyte, since in this case the CO_2 content of the fuel gas and air does not cause the formation of carbonate, and the troublesome purification process can then be omitted.

The following is a report on such batteries with an acidic electrolyte, in the lower output range of up to about 10 kW.

2. Fuel reforming

The possibilities for converting commercially available liquid fuels into fuel gas containing hydrogen are sufficiently well-known [6-9]. In large scale production, hydrogen is made from petrochemical raw materials; the processes used are well established. In connection with fuel cells, difficulties are caused by the need to adjust the fuel conditioning to the comparatively low hydrogen requirement of a fuel cell battery. In addition to being light and compact, the reformer unit, including the control and monitoring apparatus, should be of robust and simple construction, to guarantee low maintenance during operation over a long period of time. These factors should be considered both in the construction of the reforming unit and in the choice of the initial fuel.

2.1. Hydrocarbons

If hydrocarbons such as petrol, diesel oil, JP-4, liquid gas etc. are to be used as the initial fuel, the following processes may be considered: partial oxidation, steam reforming, and thermal cracking.

Of these, partial oxidation for fuel preparation can be excluded, since using air, with its high proportion of nitrogen, as an oxidizing agent results in a crude gas with a relatively low hydrogen content.

Both steam reforming and catalytic thermal cracking can be used. However temperatures of 800 °C or 1000 °C to 1100 °C are necessary: only in [10] does one find a description of steam reforming at an operational temperature of 500 $^{\circ}$ C.

The sulphur content [11] or the presence of higher-boiling fractions reduces the activity of the catalysts used in fuel conditioning. The long-term behaviour is also unfavourably influenced. One must in addition take into account the fact that discontinuous process operation for thermal cracking increases apparatus and investments [12, 13].

However the main problem with fuel cell assemblies of the range under consideration (up to 10 kW) remains the high temperatures which are necessary for the conditioning of hydrocarbons. This gives rise to:

-higher insulation requirements for the reactor, with the associated disadvantages of increased specific weight and volume;

-a considerable start-up time at the beginning of the operation,

 $-{\rm and}$ the necessity of cooling the fuel gas before conducting it into the fuel cell.

In addition, further preparatory stages such as desulphurization, gas purification, or hydrogen enrichment are scarcely acceptable for these relatively small assemblies, because of the negative effects on size, weight and performance level: the simple construction of the assembly and hence the operation at low maintenance would also suffer. This means in effect that the hydrocarbons can only be used when one succeeds in developing a simple straight-forward conditioning process.

2.2. Methanol

The use of methanol as the initial fuel results in decidedly fewer problems. Methanol is a synthetic fuel, and therefore contains, apart from higher alcohols, hardly any impurities. The second positive and extremely important aspect is the low reforming temperature for methanol. Both steam reforming

 $\rm CH_3OH + H_2O \rightarrow \rm CO_2 + 3H_2$

and thermal cracking

 $CH_3OH \rightarrow CO + 2H_2$

take place, with the corresponding catalysts, at temperatures below or around 300 °C. For both processes, catalytic systems based on zinc oxide-chromium oxide, copper oxide-zinc oxide, or copper-zinc oxide-aluminium oxide can be used.

The methanol:water ratio is chosen between 1:1 and 1:3 for steam reforming. Both reactions are endothermic, so that it is necessary to heat the reactor. This can be done as shown in Fig. 1 by burning the waste gas from the fuel cell. In the case of thermal cracking the CO content of the cracked gas is sufficient to produce the heat required for decomposing the methanol [14]. In the fuel cell battery, the best possible conversion rate of the hydrogen can be achieved through cascading (series connection) the gas flow.

For steam reforming, on the other hand, a certain portion of hydrogen must be left in the fuel cell waste gas to ensure the heating of the reactor.



Fig. 1. Schematic diagram of an indirect methanol/air fuel cell assembly with an acidic electrolyte.

According to [15] there is hardly any difference in the thermal efficiency of the two methods of methanol conditioning.

In selecting the process for conditioning the methanol the composition of the fuel gas in relation to the fuel-cell battery employed, and the availability of the fuel components-in one case CH_3OH , in the other CH_3OH and water-constitute the determining factors. Methanol cracking seems on this basis a somewhat better process.

Our experiments have shown that the cracking can be done in a simple tubular reactor (Fig. 2). Here the heating in the central tube is caused by burning the exhaust gases from the fuel cell, whilst the catalyst is situated between the two concentric tubes. The efficiency of this fairly small unit is presented in Fig. 3. Gas chromatography studies show that, above 300 $^{\circ}$ C, the composition of the cracked gas is independent of gas output (Fig. 4).



Fig. 3. Performance characteristics of the methanol cracker: cracked gas yield as a function of amount of methanol used (parameter: cracking temperature).



Fig. 2. Reactor for cracking methanol.

The reactor illustrated in Fig. 2 for a 1-1.5 kW assembly has been in operation for more than 4 months, without any loss of performance. Nor does the presence of resin or condensed products (from the recycling of the unconverted methanol) cause any impairment of the copper/zinc-oxide/ aluminium-oxide catalyst, obtained from Imperial Chemical Industries.

3. Fuel cell

The conditioning processes described above always result in gas mixtures which contain not only hydrogen, but also CO and CO_2 in differing propor-

100 1 T=280°C T = 320°C % 80-=CŌ =Rest HC HO , CO2 , CH3 OH 60 40 20 400 800 ò 400 800 0 l/h ---

Fig. 4. Percentage composition of the cracked gas as a function of the amount of crude gas at 280 $^{\circ}$ C and 320 $^{\circ}$ C.

tions, and small amounts of other substances. In choosing the type of fuel cell, one should ensure that the hydrogen in the gas mixtures will be electrochemically oxidized without any reduction occurring in the activity of the anode catalyst.

There are two means of achieving this:

-cells with Pt-anodes and working temperatures of 150 °-180 °C, or

-cells with catalysts made from non-precious metals, which are resistant to catalyst poisoning.

In cells with Pt-anodes, the CO content has a particularly negative effect on the catalyst [16, 17]. To prevent this, precious metal alloys are used, or the working temperature is raised to $150^{\circ}-180^{\circ}$ C. Since the blocking action is based on an extremely stable adsorption of the CO on Pt, an appreciable reduction of the poisoning effect can be achieved by this temperature increase.

Furthermore, when using cells with Pt-anodes, conditioning processes which produce a fuel gas with the lowest possible CO content should be considered: namely, steam reforming of CH_3OH and of hydrocarbons, in the latter case providing for a conversion of the CO with steam to H_2 and CO_2 . The disadvantage of the required high operating temperature for the fuel cell lies in a continuous loss of activity of the Pt catalyst through recrystallization [18–20].

This line of research is being pursued chiefly in the U.S.A.-especially by Pratt & Whitney, Engelhard Industries and Energy Research Corporation. In the process, the phosphoric acid matrix cell with Pt-electrodes has been developed, operating at temperatures up to $180 \degree C$ [21 - 23].

It does not lie within the scope of this report to give further details of this method: attention will be focused on the second possibility mentioned above, whereby the conversion of the conditioned fuel gas takes place in cells with non-precious metal anodes, at temperatures below 100 $^{\circ}$ C, in an electrolyte of dilute sulphuric acid.

3.1. Catalysts

In contrast to the U.S.A., efforts in Europe have been concentrated on replacing the precious metals with non-precious metals, not only because of the sensitivity to CO, but also for cost considerations.

Since in the meantime it has become possible to greatly reduce the Pt content of the electrodes [24], these cost considerations and the argument of availability are only relevant if large numbers of fuel cells are being made: the sensitivity of platinum to CO therefore becomes the main factor.

A number of demands are made of an electrocatalyst used in an acidic electrolyte:

-highest possible catalytic activity;

-stability in acid electrolytes under the conditions in fuel cells;

-electrical conductivity;

-immunity to catalyst poisons;

-availability and low price.

The second point in particular limits the number of elements and compounds that could be considered suitable, since, with the exception of the precious metals, most substances are not sufficiently stable in hot sulphuric acid over long periods of time. Nevertheless a few catalysts made from nonprecious metals have been developed, which can be used as electrode materials in fuel cells.

3.1.1. Anode catalysts

The first non-precious metal catalyst to be found was tungsten carbide [25]. Of the large group of hard materials tungsten carbide was the sole member to show noticeable activity [26, 27]. The commercial grade tungsten carbide displays however only a low activity in H₂-conversion. Firstly by the development of a suitable production process we were able to improve significantly the catalytic properties of WC (Fig. 5). Then reduction of the



Fig. 5. Developments in the WC-catalyst with time: current-voltage curve for WC-anodes under H₂ at 60 $^{\circ}$ C in 2N H₂SO₄.

carburizing temperature, the use of carbon monoxide as the carburizing gas, and a partial oxidation of the carbide [28], which might form tungsten oxides on the surface, all had a favourable effect on the activity of the material. The rate determining step in the oxidation of the hydrogen is either the dissociation of the hydrogen or the adsorption of the hydrogen molecule, dependent on the activity of the material [29–31]. The resistance of tungsten carbide to catalyst poisons is particularly worthy of note [32]; and the behaviour with regard to CO is of special importance. When CO is present in the fuel gas, only the polarization increases, to an extent corresponding to the reduction in partial pressure of the hydrogen: a poisoning effect is not evident.

The life-time of a tungsten carbide catalyst is exceptionally long. We were able to operate tungsten carbide electrodes in a small test battery for more than 40,000 hours, without any loss of performance: the life-time was limited by the carbon cathode and the contact to it.

It is perhaps also useful to mention that organic substances, such as aldehydes and formic acid, can also be converted at tungsten carbide [33], but that the direct conversion of methanol or other alcohols is not possible.

The sulfides of tungsten and molybdenum, WS_2 and MoS_2 , can also catalyze H_2 conversion [34]. For these substances, one should note the high activity, in comparison to hydrogen, for CO conversion. The same current densities under H_2 and CO can be achieved with suitably prepared charges [35]. However, the activity with at most 20 mA cm⁻² at 200 mV polarization is too low for use in fuel cells. A mixed catalyst made from molybdenum oxides and sulfides has also been described as catalytically active [36]. A further catalyst for H_2 conversion is cobalt carbide [37], which however is not sufficiently stable for long operating times.

Catalytic activity for hydrogen oxidation is also shown by various binary phosphides and arsenides, as well as by some ternary compounds (FePS, CoPS and CoAsS) [38]. Of these compounds, CoP₃ is described as the most active: at 100 mV polarisation, a current density of 180 mA cm⁻² can be maintained with hydrogen in 2.5 M H₂SO₄ at 70 °C. Since however this value is measured without taking the IR-drop into account, a direct comparison of the catalyst CoP₃-which is deposited on activated carbon as a carrier-with other catalysts cannot be made.

 CoP_3 , too, is not irreversibly altered by carbon monoxide; but a larger reduction in current density, for a CO content of 2%, is evident than is the case with tungsten carbide. Whilst only a change in current density corresponding to the reduction in H₂ partial pressure is observed for tungsten carbide, CoP_3 seems to adsorb carbon monoxide rather more strongly: in which case CoP_3 would be classified as lying between tungsten carbide and Pt with regard to CO.

3.1.2. Cathode catalysts

As for anode materials, attempts have also been made to develop nonprecious metal catalysts for cathodes. However, this is a much more difficult task, since cathode materials must be stable at the high potential of oxygen electrodes in an acidic electrolyte.



Fig. 6. Organic electrocatalysts for oxygen reduction in acid solution.

A possible catalytic material is activated carbon. Carbon is not only cheap and easily available, but also stable at the potentials used [39]. Different activated carbons manifest different activities for O₂ reduction in an acid medium. The activities found are however relatively low, but an improvement in the catalytic properties can be achieved by a further activation with ammonia at high temperatures (900 °C - 1000 °C) [40]. (A similar activation process has already been reported for carbon electrodes used in an alkaline medium [41].) The current density can be increased by as much as a factor of 2 using such a process: at a potential of $U_{\rm H} = 600$ mV, electrodes of NH₃activated carbon could be loaded with 120 mA cm⁻² (60 °C, 2N H₂SO₄). The effect of the NH₃-activation apparently depends on the incorporation of nitrogen containing groups on the carbon surface.

Activity similar to that of carbon catalysts can also be arrived at by thermal degradation of plastics containing nitrogen, such as polyacrylonitrile [38].

Possibly one is dealing in both cases with carbon catalysts of the same or of similar composition: in the first case, nitrogen is incorporated, whilst in the second, the nitrogen content of the PAN is reduced by the thermal treatment.

Inorganic compounds, particularly resistant to acid are the tungsten bronzes. According to [42], it should be possible to use tungsten bronze as a cathode material.

The activity of the specimens was however caused by traces of platinum [43]. Pure sodium tungsten bronzes even of large specific surface area, show hardly any O_2 reduction activity; a synergistic effect using a tungsten bronze/ platinum catalyst can also be discounted [44, 45].

Similarly, oxygen could be reduced on sulphides [46], but the activity is not sufficient.

Besides the inorganic substances, a number of organic complex compounds are used as cathode catalysts: monomeric and polymeric phthalocyanines [47], tetra aza annulenes [48] and substituted porphyrines [49]. As can be seen from the formulae in Fig. 6, these are all structurally similar compounds. Essential factors for the activity are the central atom, the method of preparation-the complexes are deposited onto carbon as a conducting carrier-and, in the case of porphyrines, the substituents of the benzene ring [49]. The adsorption of the O_2 -molecule on the central atom is assumed to take place. This is confirmed by the low activity of the non-metallic complexes. An attempt to explain the activity with the help of the MO-theory has been made [49].

Although the complex compounds manifest very noticeable activity, their application has hitherto failed due to insufficient stability. A continuous reduction of activity must be taken into account, particularly at high temperatures. For Fe-phthalocyanine at 30 mA cm⁻² and 70 °C in 4.5 N H₂SO₄ a reduction of the potential from about 700 mV to 500 mV within 500 hours is reported [50].

There is, therefore, no known non-precious metal cathode catalyst, with the exception of activated carbon, which can only be used for cells with a low power density. One is, then, forced to use the precious metals, trying however to keep the precious metal content per cm² of the electrode as low as possible [24, 51, 52]. With the help of radioactively marked platinum, it was shown that the oxygen conversion on hydrophobic electrodes takes place on the electrolyte side in a layer only 100 - 150 μ m thick [53]. It is, then, possible to concentrate the Pt content in a layer of this thickness only, or to use cathodes of only this thickness. According to [24], more than 200 mA cm⁻² can be obtained with O₂ and about 40 mA cm⁻² with air from electrodes with a Pt content of only 0.25 mg cm⁻² in 20% H₂SO₄ at 70 °C at a potential of 700 mV against the H₂ electrode in the same solution. The platinum is deposited onto activated carbon as carrier. The measurements were made in a half-cell assembly.

3.2. Cells

Considering the various possibilities which result from the presently known catalysts, a WC/C(Pt)-cell would seem to be the most suitable for converting the impure hydrogen produced from methanol conditioning in batteries with outputs up to 10 kW.

Figure 7 shows the current-voltage characteristics of a WC/C(pt)-cell with a cathode containing 4 mg Pt cm⁻² in comparison with a WC/C-cell with NH₃-activated carbon. These results were obtained from test cells with small electrodes of 5 cm² surface area.

3.3. Batteries

In the case of cells and batteries with large surface area electrodes in an acidic medium, it is particularly difficult to obtain an even contact over the whole electrode surface. Good conducting materials such as the metals cannot, with the exception of the precious metals and tantalum, be used for current collection because of corrosion; and both the precious metals and tantalum



Fig. 7. Current--voltage and performance curves of WC/C and WC/C(Pt)-test cells using H₂ and O₂ at 60 $^{\circ}$ C (2N H₂SO₄); electrode area 5 cm².

are too expensive for consideration. The only effective solution known to date is the use of graphite as a contact material. Since hydrophobic electrodes possess, because of their plastic content, only a fairly low surface conductivity, the electrode must make contact with the conducting element at as many places as possible. This should not, however, hinder the gas supply to the electrode, and one can ensure this by using a contacting element with a ribbed surface.

In addition to the contact element, all of the other components of the battery, such as the gaskets, end plates and frames, must be stable under the operating conditions of a fuel cell. The requirement of resistance to acid greatly limits the number of plastics that can be used. The polyolefin types and the phenol-formaldehyde resins are the only ones which have proved suitable, apart from a few mixed polymers and rubbery polymers.

The batteries are generally constructed according to the bipolar concept.

Construction using electrodes with current collectors could also be considered, in which case, due to the low conductivity of the graphite, the contact element should be made from a perforated metal foil coated with graphite [14]. It has however become apparent that the graphite coating can only be made absolutely acid-proof in individual cases: faults invariably occur in large scale production-partly through damage in the subsequent processing-so that the metal foil corrodes during operation of the battery.

With the bipolar concept, the whole cross-section of the battery serves as a connection from cell to cell, rendering the use of metal foil redundant. Ribbed graphite plates [20] or plates of graphite/plastic compounds are used as contact elements. Graphite/plastic compounds are much more flexible than pure graphite plat s, so that any danger of breaking when assembling the battery is avoided.

The construction of our bipolar battery is presented in an explosion diagram (Fig. 8). Various characteristics of this battery have proved particularly advantageous. The use of special rubber O-rings as cell frames makes the battery absolutely leak-proof. The demands made by temperature changes



Fig. 8. Explosion diagram for bipolar batteries.

do not cause any loss of electrolyte. Gas losses were prevented by changing the main gas channels from the cell frames to the electrolyte chambers [54]. The reaction water formed is carried away from the cathode by the air flow. To maintain the water balance, the amount of air flow must be controlled in relation to the current density or, alternatively, the excess water carried away must be condensed and returned to the system. The heat due to energy losses is brought out by the electrolyte circulation in connection with a heat exchanger.

The current-voltage curves of a WC/C(Pt)-cell with an electrode area of 150 cm^2 for H_2/O_2 and crude gas/air are shown in Fig. 9. Since short circuit losses can be practically ignored as a result of the extremely narrow cell channels to the individual electrolyte chambers, additive values, corresponding to the number of cells, can be taken for the batteries.

When using gas mixtures such as crude gas and air, the limitation on diffusion causes a reduction in power in comparison to H_2/O_2 values. This reduction is mainly due to the air cathode, both the low partial pressure and the diffusion coefficient of oxygen playing decisive roles. At the anode, on the other hand, the high partial pressure of the hydrogen and the good diffusion characteristics of H_2 have positive effects. In both cases, however, one must work with a correspondingly high gas flow, to prevent H_2 or O_2 impoverishment of individual electrode areas. In Fig. 10, the dependence of the cell voltage at constant current (5A) on the amount of crude gas flowing through is shown. The measurements were made for a 10-cell battery with 260 cm² electrode area; oxygen was supplied to the cathodes. It is obvious from the diagram that only a slight increase in polarization occurs at the WC-anodes when the supply of crude gas is sufficient.

Figure 11 is a photograph of the new construction of a 40-cell battery with 260 cm² electrodes, which operates at 60 °C to 70 °C with circulation of $2N H_2SO_4$ electrolyte. The life-time of the WC/C(Pt)-batteries is satisfactory.



Fig. 9. Current–voltage and performance curves of a fuel cell with 150 cm² WC-anodes and C(Pt)-cathodes at 60 °C in 2N H₂SO₄.

Fig. 10. Dependence of the voltage of a 10-cell battery on the gas flow at 5A.

A battery has up until now been in operation for more than 4,300 hours, without any decline in power [55]. This result was expected, following the successful operation of a test battery with small electrodes (5 cm²) for 40,000 hours.

However, despite these positive results, the WC/C(Pt)-battery must be further improved. Particularly important is the transfer of the good half-cell values that have been achieved with small electrodes to the large 260 cm^2 electrodes. In addition, the difference in output between operating with hydrogen/oxygen and with crude gas/air should be reduced. One possibility is by decreasing the thickness of the electrodes-particularly the cathodeswhich at the moment are 0.8 mm, and thereby decreasing the diffusion limitation.

4. Applications of fuel cell assemblies with acid electrolytes

The use of fuel cells is particularly interesting because of their mobility, low maintenance, long life, low noise and very low emission of air pollutants. However despite these positive characteristics, fuel cells will only stand a real chance in technical applications when they can compete economically with conventional systems.

Applications of assemblies in the lower power ranges can be categorized into three groups: the so-called "island" application, mobile uses, and emergency plants. "Island"-applications are those in which, due to lack of a mains supply system, other sources of electrical energy must be found. These include signal facilities, warning systems, radio link systems, TV-transposers,





Fig. 11. WC/C(Pt)-battery of 40 cells; electrode area 260 cm², weight 7.5 kg, volume 7.5 l.

weekend cottages etc. Mobile uses refer only to special applications, such as the slow heavy transport with electric utility trucks, or fork-lift trucks. The idea of using fuel cells in private cars, often mentioned in the context of city traffic, is at the moment, on the basis of the technical specifications of fuel cells, particularly on account of the power to weight rate, a purely utopian one. A comparison of costs for fuel cells with electric motors and the internal combustion engine also clearly favours the conventional solution.

Emergency plants should, in the case of a breakdown in the mains supply, be able to supply electrical energy reliably to the consumers: this should be realisable with a suitably designed fuel cell assembly.

In all three areas of application, the main competitors to fuel cells are accumulators or the combination of combustion engine and generator [56] reports on an assessment of the economics of fuel cells in comparison with conventional systems in three particular types of application. As the examples of the electric freight truck, fork-lift truck and radio link system show, based on the realisation of the given assumptions, possibilities do indeed exist for the economic application of a fuel cell operating on methanol, as the primary fuel, and air.

References

- 1 H. A. Liebhafsky and E. J. Cairns, Fuel Cells and Fuel Batteries, Wiley, New York, 1968.
- 2 B. J. Crowe, Fuel Cells, A Survey, National Aeronautics and Space Administration, Washington D.C., 1973.
- 3 M. Schwarzmann, Chem.-Ing.-Tech., 47 (1975) 56 61.
- 4 Chem.-Ing.-Tech., 45 (1973) A 351.
- 5 H. Schmidt and W. Vielstich, Chem.-Ing.-Tech., 41 (1969) 701.
- 6 F. Fischer and H. Pichler, Brennst.-Chem., 13 (1932) 421.
- 7 H. Pichler, Erdöl Kohle, 11 (1958) 515.
- 8 N. C. Updegraff, Pet. Refiner, 38 (1959) 175.
- 9 G. W. Bridger, Chem. Process. Eng. (Bombay), 47 (1966) 12, 39.
- 10 A. R. Khan, J. Meck and B. S. Baker, Proc. A.E.Ch.E., 58th Annual Symposium on Fuel Cell Processes and Systems, Philadelphia, Dec. 5 9, 1965.
- 11 R. Engdahl and E. S. Tillman, Final Report, U.S. Army Contract DAAB 07-70-C-0153, Energy Research Corp., Bethel, 1971.
- 12 E. A. Gillis, Proc. 5th Intersociety Energy Conversion Engineering Conference, Las Vegas, 1970.
- 13 M. A. Callahan in G. Sandstede (ed.), From Electrocatalysis to Fuel Cells, University of Washington Press, Seattle and London, 1972, p. 189.
- 14 L. Baudendistel, H. Böhm, J. Heffler, G. Louis and F. A. Pohl, Proc. 7th Intersociety Energy Conversion Engineering Conference, San Diego, 1972, p. 20.
- 15 H. Böhm and R. Fleischmann, Proc. Elektrochemische Stromquellen, Prag, 1975, p. 159.
- 16 L. W. Niedrach, D. W. McKee, J. Paynter and J. F. Danzing, Report Nr. 66-C-394, General Electric, Schenectady, Nov. 1966.
- 17 P. Stonehart and G. Kohlmayr, Electrochim. Acta, 17 (1972) 36.
- 18 K. Kinoshita, K. Routsis, J. A. S. Bett and C. S. Brooks, Electrochim. Acta, 18 (1973) 953.
- 19 A. C. C. Tseung and S. C. Dhara, Electrochim. Acta, 20 (1975) 68.
- 20 B. Angelé and M. Jakubith, Chem.-Ing.-Tech., 47 (1975) 678.
- 21 O. Adlhart, Proc. 3 Intern. Tagung für das Studium der Brennstoffzellenbatterien, Brüssel, 1969, p. 227.
- 22 A. J. DeCasperis and L. H. Ferguson, Final Report, U.S. Army contract DAAK 02-70-C-0518, Pratt & Whitney Aircraft, East Hartford, 1973.
- 23 R. N. Camp, A. Nowotka and B. S. Baker, Semi-annual Report, DAAK 02-72-C-0247, Energy Research Corporation, Bethel (1972).
- 24 H. R. Kunz and G. A. Gruver, J. Electrochem. Soc., 122 (1975) 1279.
- 25 H. Böhm and F. A. Pohl, Wiss. Ber. AEG (Allg. Elektricitaets-Ges.)-Telefunken, 41 (1968) 46.
- 26 F. A. Pohl and H. Böhm, Proc. 3 Intern. Tagung für das Studium der Brennstoffzellenbatterien, Brüssel, 1969, p. 180.
- 27 J. Heidemeyer, D. Baresel, W. Gellert and P. Scharner, Collection Czech. Chem. Commun., 36 (1971) 944.
- 28 H. Böhm and W. Diemer, Angew. Chem., 83 (1971) 894.
- 29 H. Böhm, Electrochim. Acta, 15 (1970) 1273.
- 30 D. V. Sokolsky, V. Sh. Palanker and E. N. Baybatyrov, Electrochim. Acta, 20 (1975) 71.
- 31 H. Böhm, Chem. Ing. Tech., 45 (1973) 1043.
- 32 H. Böhm and F. A. Pohl, Proc. 3 Intern. Tagung für das Studium der Brennstoffzellenbatterien, Brüssel, 1969, p. 183.
- 33 K. von Benda, H. Binder, A. Köhling and G. Sandstede in G. Sandstede (ed.), From Electrocatalysis to Fuel Cells, University of Washington Press, Seattle and London, 1972, p. 87.

- 34 H. Böhm, W. Diemer, J. Heffler, F. A. Pohl and W. Sigmund, Energy Convers., 10 (1970) 119.
- 35 H. Böhm, Nature (London), 227 (5257) (1970) 483.
- 36 W. R. Wolfe, D. Patent DAS 1 671 873, App. Dat. 17.1.1968.
- 37 K. Mund, G. Richter and F. V. Sturm, Tagung CITCE, Prag, Sept. 1970.
- 38 G. Luft, K. Mund, G. Richter, R. Schulte and F. V. Sturm, Siemens Forsch. Entwicklungs Ber., 3 (1974) 177.
- 39 H. Binder, A. Köhling, K. Richter and G. Sandstede, Electrochim. Acta, 9 (1964) 255.
- 40 H. Böhm, Wiss. Ber. AEG-Telefunken, 43 (1970) 241.
- 41 J. Mrha, Collection Czech. Chem. Commun., 32 (1967) 708.
- 42 D. B. Sepa, A. Damjanovic and J. O'M. Bockris, Electrochim. Acta, 12 (1967) 746.
- 43 J. O'M. Bockris, A. Damjanovic and J. McHardy; Proc. 3. Intern. Tagung für das Studium der Brennstoffzellenbatterien, Brüssel, 1969, p. 15.
- 44 J. Heffler and H. Böhm, Metalloberfläche-Angew. Elektrochem., 27 (1973) 77.
- 45 J.-P. Randin, J. Electrochem. Soc., 121 (1973) 1029.
- 46 H. Behret, H. Binder and G. Sandstede, Electrochim. Acta, 20 (1975) 111.
- 47 H. Jahnke, Ber. Bunsenges. Phys. Chem., 72 (1968) 1053.
- 48 F. Beck, W. Dammert, J. Heiss, H. Hiller and R. Polster, Z. Naturforsch., 28a (1973) 1009.
- 49 A. Alt, H. Binder, W. Lindner and G. Sandstede in G. Sandstede (ed.), From Electrocatalysis to Fuel Cells, University of Washington Press, Seattle and London, 1972, p. 113.
- 50 C. Kretzschmar and K. Wiesner, Proc. Elektrochemische Stromquellen, Prag, 1975, p. 144.
- 51 R. N. Camp and B. S. Baker, Proc. 7th Intersociety Energy Conversion Engineering Conference, San Diego, 1972, p. 7.
- 52 K. V. Kordesch, R. F. Scarr, Proc. 7th Intersociety Energy Conversion Engineering Conference, San Diego, 1972, p. 12.
- 53 V. Hartmann, M. Reese and H. Böhm, Ext. Abstr. 25th Meeting of ISE, Brighton, 1974, p. 242.
- 54 G. Louis and H. Böhm, 4th Intern. Symp. on Fuel Cells, Antwerpen, 1972.
- 55 H. Böhm and K. Maass, Proc. 9th Intersociety Energy Conversion Engineering Conference, San Francisco, 1974, p. 836.
- 56 H. Carl, H. Böhm and F. A. Pohl, Wiss. Ber. AEG (Allg. Elektricitaets-Ges.)-Telefunken, 46 (1973) 109.
- 57 E. Justi and A. Winsel, Kalte Verbrennung, Steiner, Wiesbaden, 1962.
- 58 K. R. Williams, An Introduction to Fuel Cells, Elsevier, Amsterdam, 1966.
- 59 F. v. Sturm, Elektrochemische Stromerzeugung, Verlag Chemie, Weinheim, 1969.
- 60 W. Vielstich, Fuel Cells, Wiley-Interscience, New York, 1970.