

Alkaline fuel cells: a critical view

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Abstract

Low-temperature fuel cells constitute an important element in pollution-free energy conversion. Although many groups have stopped working in the field of alkaline fuel cells (AFCs) in recent years in Germany, a few groups in Europe continue. Recent important projects are presented here. The mathematical simulation of fuel cells and a few examples of fundamental research on catalysts are shown. It is concluded from these fundamental investigations, that poisoning of electrocatalysts in AFCs with rolled electrodes due to carbon dioxide does not take place. A brief view of calculations of the costs of well known fuel cell systems is also presented. The calculations show that the AFCs are as cheap as other small fuel cell systems. AFCs are as suitable for mobile applications as other low-temperature fuel cells.

Keywords: Alkaline fuel cells; Electrodes

1. Introduction

In 1902 Reid [1] and in 1904 Noel [2] described fuel cells using aqueous KOH electrolyte. The history of the present alkaline fuel cell (AFCs) begins 63 years after Grove's invention of the acid fuel cell. During this long time, however, a lot of problems have been solved and many problems have been described in the literature.

AFCs are easy to handle, have very high electrical efficiency and an excellent suitability for alternating loads. They can be built in small compact systems as well as in large power plants. However, many groups in Europe have stopped working in the field of AFCs. In this paper the problems and the disadvantages of AFCs are explained, and false opinions on this type of cell that appear in the literature will be mentioned and their advantages stated.

2. Alkaline fuel cells

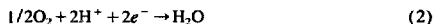
A fuel cell is an electrochemical device that can convert the chemical energy of hydrogen and oxygen directly into electric current. In principle, the direction of the electrode reactions in alkaline water electrolysis is reversed in AFCs. Thus, the thermodynamic fuel cell voltage at 25 °C is 1.23 V, equivalent to a theoretical energy conversion efficiency of 83%.

The anode and cathode reactions are:

(i) anode:



(ii) cathode:



The working temperature ranges from 20 to 90 °C. The electrolyte is a KOH solution (30–35%). There are four different cell types: (i) cell with a free liquid electrolyte between two porous electrodes; (ii) ELOFLUX cell with liquid KOH in the pore-systems; (iii) matrix cell where the electrolyte is fixed in the electrode matrix [3–5], and (iv) the falling film cell will be described separately in this paper. All types of AFC have porous electrodes.

Many problems concerning AFCs are described in the literature. The most important problems are:

(i) *preparation method of the electrodes.* The electrodes consist of porous material which is covered with a layer of catalyst. In general, it is very difficult to distribute the catalyst at the surface and to produce a defined pore system for the transportation of the reactants.

(ii) *costs of the electrode, stacks and fuel cell systems.* The preparation of electrodes with noble metal catalysts is very expensive. In general, the electrodes are manufactured in a small-scale production with high overhead costs.

(iii) *life time of the electrode/degradation.* The electrolyte is very corrosive and the catalyst materials are sensitive to high polarization. Using nickel and silver as catalysts, in order to reduce the costs of the fuel cell, leads to a high degradation of these catalysts.

(iv) *diaphragm made of asbestos.* The diaphragm of low-temperature fuel cells is made of asbestos. But this material is hazardous for health and in some countries its use is even

Table 1
Research groups working in the field of AFCs

Company name	Status
Siemens, Erlangen stopped working on the AFCs; still working on the development of PEFC	terminated
VARTA AG, Kelkheim stopped working on preparation of technical electrodes and technical fuel cell stacks	terminated in 1993
GH, Kassel stopped working on preparation of technical electrodes and technical fuel cell stacks; still working on the field of PEFC	terminated in 1994
ISET, Kassel stopped working on technical AFC systems	terminated in 1994
DLR-ITT, Stuttgart stopped working on the investigation of the degradation of technical electrodes, the development of new catalysts for AFC and the theoretical simulation of stacks and systems; still working on the field of PEFC	terminated in 1994
ELENCO, Antwerpen stopped working on electrodes, stacks and systems	terminated in 1995
Royal Institute of Technology, Stockholm working on the field of stationary fuel cells powered by bio-fuels	regular projects
Hoechst AG, Frankfurt stopped working on AFC electrodes and stopped development of the falling film cell	terminated
Technical University, Graz planning an investigation of degradation effects	new plans

banned. Therefore, new diaphragms should be developed, but it is difficult to find a material with a similar behaviour in KOH.

(v) *CO₂-contaminated fuel gases (carbonating of electrolyte and electrodes)*. It is well known, that CO₂ intolerance is the most important disadvantage of air-breathing AFCs. Thus, alkaline technology is commonly not considered in mobile fuel cell applications.

Research groups are working on the development of technical AFC systems to solve the problems mentioned above, see Table 1. The activities in the countries of the former USSR are not considered.

3. Demonstration projects of AFC systems

Most of the research groups have stopped their work, but in the field of AFCs many projects finished successfully. A list of some selected technical applications and demonstration projects is given in Sections 3.1. to 3.4.

3.1. Space applications

The space applications are the development of an AFC system for the European space shuttle HERMES (Siemens, ELENCO, VARTA/GHK), and the bipolar matrix AFC system Photon for space applications (Ural Electrochemical Integrated plant).

3.2. Vehicles

Applications of AFCs in vehicles are: fork-lift truck of VARTA AFC; VW Van, 14 kW ELENCO AFC and battery; VW Van, 17.5 kW Siemens AFC; submarine, 100 kW Sie-

mens AFC, and EUREKA-Bus 80 kW ELENCO AFC and battery.

3.3. Decentralized energy supply

These supplies comprise: a meteorological station, 5 W, VARTA AFC for long-term operation; a TV-transmitting installation Ruppertsshain, 100 W VARTA AFC, and a mobile current supply unit for the Belgian Geological Service, 40 kW, ELENCO AFC.

3.4. Energy storage

The solar hydrogen-demonstration plant in Neunburg vorm Wald, 6.5 kW Siemens AFC and the solar hydrogen system at Fachhochschule Wiesbaden, 1.2 kW ELENCO AFC are typical examples.

4. Investigations at DLR

AFCs are being investigated at the German Aerospace Research Establishment (DLR), focusing on a cheap production of perfluorinated tetrafluoroethylene (PTFE)-bonded gas-diffusion electrodes. The target is an electrochemical system for a mobile application with hydrogen fuel.

4.1. Preparation of rolled electrodes

The production of these gas-diffusion electrodes at DLR is based on the principles developed at the Kassel University [6–9]. The electrodes are produced with a cold-rolling machine, no solvents are used.

The material for the production of anodes is Raney nickel. This catalyst is a nickel–aluminium alloy containing 50 wt.%

of each metal. The powder is activated by adding a KOH solution for dissolving the aluminium. After this procedure, the dissolution process is continued at a constant temperature of 80 °C in order to remove further aluminium. Then the powder is washed and dried. It is important to prevent the powder from burning in the presence of air, because the catalyst contains hydrogen [10]. Then the catalyst is passivated stepwise with air to build up a thin layer of nickel oxide on the surface. Once the electrode has been produced, this oxide layer is removed by a final electrochemical reactivation. The powder is mixed, in a powder grinder, with PTFE and additives using the 'reactive mixing process'. This means that the individual Raney nickel granules are covered with PTFE and thus stuck to each other [9]. During mixing the catalyst mass is formed. The catalyst mass is thickened between two rolls turning in opposite directions and thus formed into a self-carrying strip. This strip is rolled onto a metal net to increase mechanical stability and to obtain a homogeneous current collection. The production method for the silver cathode is nearly the same. Only the material is a powder of silver oxide, which is reduced after rolling.

This preparation procedure is well known and proven in the battery industry to produce electrodes.

4.2. Reactivation of gas-diffusion electrodes

The electrochemical reactivation of the gas-diffusion electrodes is a reduction of the hydrogen electrode in the cell stack. Hydrogen is evolved at low current densities and constant temperature. It is supposed that the oxide layer, built up during passivation, will be removed.

This procedure has been investigated in detail at DLR. With the optimization of the parameters, the electrochemical reactivation is an important step to achieve good current densities and minimum degradation behaviour of the electrodes.

During reactivation a significant change in porosity was found, correlating with an enlargement of the active surface area. The pore-size distribution of the catalyst is measurable during reactivation [11].

4.3. Degradation of gas-diffusion electrodes with pure and poisoned fuel gas

An essential problem often mentioned in the literature is the carbonating of electrodes using air instead of oxygen. The DLR studies have been carried out concerning this topic. Electrodes (anodes and cathodes) were operated with pure and with CO₂-contaminated fuel gases and investigated after operation. The tests were always brought to an end without problems at 3500 h of operation time.

In order to investigate the degradation of the electrodes the following methods were used: porosimetry (BET), X-ray photoelectron microscopy (XPS), energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD), scanning electron microscope (SEM), voltammetry and electrochemical impedance spectroscopy (EIS).

The degradation experiments were carried out in half-cells. The cells were operated with pure and CO₂-contaminated reactants; the cell temperature was kept constant at 70 °C. For recording and monitoring the electrochemical data, a computer-controlled experimental setup was available. Thus, it has been possible to adjust the load of the electrodes and keep it constant (up to 5000 h) and to record stationary cell characteristics.

In a first series of experiments, pure hydrogen-consuming PTFE-bonded nickel gas-diffusion electrodes were stressed with a current density of about 100 mA/cm² after a standard re-activation (18 h, mA/cm²). The internal source conductivity per unit of area is a characteristic indicator for the capacity or maximum current density. This indicator, calculated from voltage-current characteristics, is a function of current density and polarization. The dependence on time of the internal source conductivity per unit of area is shown in Fig. 1.

In this plot the characteristics of samples 1 and 2 have been normalized to a current density of 100 mA/cm² for the first 500 h. At the beginning of the operation time there is a fast decrease for all samples. After 250 h the degradation effects decrease, thus indicating a stabilization of the electrodes. As a result of fitting procedures of these curves, two different degradation effects have to be considered. The first effect (0–250 h) depends on the current density and the second effect (after 250 h) depends on the time of operation. The detailed mechanisms of these degradation effects are not known.

In order to determine the influence of CO₂ poisoning on the fine pore system, a series of hydrogen-consuming nickel electrodes with a characterized fine pore system was investigated. Only the degradation of the electrodes, by blocking the pores due to carbonate precipitation, was investigated in these experiments. Thus, hydrogen-consuming electrodes were used, where a poisoning of the catalyst due to CO₂ is not expected. The electrodes were operated for 1000 h with a CO₂-containing fuel gas (5% CO₂ in H₂) and a load of 100 mA/cm². From gas-chromatographic experiments we found that CO₂ was absorbed by the electrode and penetrated the

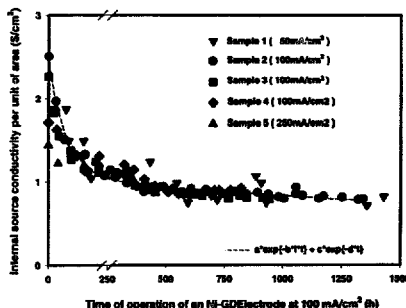


Fig. 1. Raney nickel anode.

electrodes, finally being detected as carbonate in the electrolyte.

With the BET method the pore-size distribution and the specific area were determined. Raney nickel has a fine pore system, about 2 nm [9,11], which also builds up the pore system in the gas-diffusion electrodes. During fuel cell operation the surface area did not change within 1300 h. However the pore-size distribution did change. The peak of the pore frequency increased. SEM investigations show that the nickel particles crumpled, so the pore frequency increased.

The comparison of the CO₂-exposed electrodes with the contamination-free reactant-exposed electrodes during long-term measurements shows that the source conductivities per unit area are not affected by CO₂ contamination in the reactant gases.

No evidence for the blocking of the fine pore system by carbonate precipitation has been found on the hydrogen-consuming nickel electrodes.

These experiments indicate that the presence of carbonate within the electrolyte due to the utilization of CO₂-containing oxidants, e.g. air, at the oxygen-consuming air electrode will not influence the reaction on the hydrogen-consuming electrode.

Two identical oxygen-consuming silver electrodes were operated under comparable conditions (70 °C, 30 wt.% KOH). However, the first sample was operated with oxidants contaminated with 5% CO₂ (5% CO₂ in O₂) and the second electrode was operated in a monitor experiment with pure oxygen. The CO₂ contamination of 5% corresponds to a 150-fold CO₂ concentration in air. Since the silver electrodes show no distinct fine pore system as known from Raney nickel electrodes, a detailed investigation of the modifications in pore-size distribution was not performed. The degradation excess of oxygen-consuming electrodes due to CO₂ is related to the poisoning of the catalysts, but not to the blocking of the fine pore system by carbonate. The long-term experiments were extended to operating periods of 3500 h at a constant load of 150 mA/cm².

During the operation with CO₂-contaminated oxidants the K₂CO₃ concentration of the electrolyte increases up to 450 g/l. This carbonization of the electrolyte was monitored during the long-term experiment and we found a linear dependence on operating time. The OH⁻ concentration of the electrolyte was kept constant to 30–32% by adding water. Other kinds of electrolyte treatment were not performed.

After 3500 h of operation, the long-term experiments were terminated since an overall charge transfer of 525 Ah/cm² was achieved at CO₂ contamination corresponding to the 150-fold CO₂ concentration of air. The electrodes were fully operable when terminating the long-term experiment.

During long-term operation stationary current-voltage characteristics were recorded in order to control the degradation of the electrodes and to investigate the influence of CO₂ contaminations on degradation behaviour. In Fig. 2 the potential characteristics of the Ag electrodes with reference to the Hg/HgO electrode are shown. These data are IR-drop

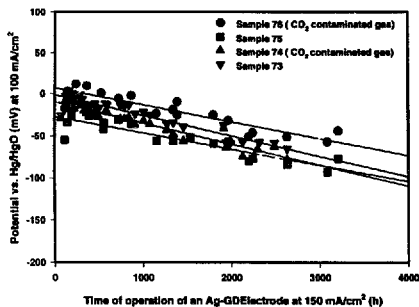


Fig. 2. Silver cathode.

corrected. The slope of the curves in Fig. 2 (investigation time: 5000 h) indicates a potential drop of 17 μ V/h which is caused by the degradation of the electrodes. This degradation effect is nearly equal for all electrodes considered. Mutual differences in the behaviour of the different electrodes are found to be within the usual range normally observed for different electrodes. Thus we found no evidence for an additional degradation mechanism caused by CO₂ contamination.

Summarizing the investigations of the degradation of anodes operated with pure hydrogen, the following results are obtained:

- (i) two different degradation mechanisms: first mechanism depending on charge transfer (0–25 Ah/cm²), and the second mechanism depending on operation time (25–500 Ah/cm²);
- (ii) investigations using XPS measurements show decomposition of PTFE during life time, and
- (iii) life times are longer than 5000 h.

Summarizing the investigations using CO₂-contaminated reaction gases, the following results for the operation of AFCs are gained:

- (i) no blocking of the fine pore system due to carbonate precipitation on the nickel electrode surface;
- (ii) the CO₂ content of the fuel gases does not influence the degradation behaviour of silver and nickel electrodes;
- (iii) the CO₂ contamination of the electrolyte does not affect cell performance, and
- (iv) no carbonate formation on the silver electrode surface.

4.4. Alkaline technical mobile system

The data found above in half-cell experiments have been transferred to a technical system. The model system was an AFC system of the Institute for Solar Energy Technology (ISET Kassel, Germany). The system was constructed for a load of 3.5 kW. It was developed for a mobile application. The technical data are given in Table 2.

Both systems contain similar gas-diffusion electrodes (anode: Raney nickel, cathode: silver) [12].

Table 2
Alkaline technical mobile systems

	Half-cell: experiment	ISET fuel cell system
Life time (h)	3500	15000
Temperature (°C)	80	80
Pressure (bar)	1	3
Electrolyte (ml/W)	18	4

The following deduction can be made: the half-cell experiment, without electrolyte circulation and with an operation time of about 3500 h, shows that the operation time with the ISET-fuel cell system can be about 800 h. After an operation time of about 800 h, the electrolyte probably has to be changed. When the solubility of the carbonate is reached, it is possible to have an operation time of at least 1600 h and, using optimistic parameters, of about 7000 h.

4.5. Simulation of AFCs

In recent years, an essential problem of high power density devices is the rejection of a considerable amount of waste heat. Since the cell stacks have become highly compact, energy conversion in electrochemical power devices is closely correlated with high chemical waste heat generation. Thus, the understanding of the thermal behaviour of fuel cells during operation is growing in importance. In particular, knowledge about the temperature distribution within the fuel cell stack is required in order to avoid thermal damage. In order to predict the heat dissipation and the electrochemical conversion rates within fuel cells, a three-dimensional simulation of their stack operation has been developed. Since no probes can be integrated into the compact electrode stack, simulation of the stack thermal behaviour is essential to gain a better understanding of the heat generation and dissipation processes.

The model theory allows the investigation and assessment of the influence of changes concerning the construction and electrochemistry of fuel cell operation [13]. The system simulation shows that the electrode temperature depends closely on the heat and mass transport in the fuel cell and the electrochemical conversion rates depend on the electrode temperature. The understanding of these mutual interactions is essential to avoid damage by progressive processes during fuel cell operation.

4.6. Investigations on fuel cells at DLR

Today's investigations at DLR in the field of low-temperature fuel cells are focused on the PEFC (proton-exchange membrane fuel cell). DLR hopes that PEFCs will be built into simple systems. The development of this system has not yet gone very far. Despite the fact that not all problems are yet solved, many institutes believe that fuel cells with solid polymer electrolyte are easier to handle in mobile applications.

At DLR investigations in the field of PEFC started in 1993. The target is a rolled electrode with cheap and simple catalysts. We are trying to use the experience of the alkaline system. The first developments are finished successfully [14,15].

5. Falling film cell

A new type of fuel cell stack is the falling film fuel cell of Hoechst. The first falling film process was used in 1981 in chlor-alkali electrolysis in order to save electric power [16]. In the falling film fuel cell, the electrolyte flows from the top to the bottom through the cells. The hydrostatic pressure is compensated by an equally large, but opposing hydrodynamic pressure drop [17]. The pressure difference between the electrolyte on the front-side of the electrode and the gas on the other side remains constant over the whole area of the vertical electrode. This is important in order to work without a diaphragm. The gap between the electrodes is 0.5 mm. The cell, therefore, operates at very high current densities of more than 25 kA/m². The costs of this new type of stack are very low and the power densities are very high [18].

The largest cell of this new technology is 0.25 m wide and 1 m high and has been tested as an electrolyzer. From 1990 onwards, a large number of gas-diffusion electrodes has been operated successfully in half-cells as fuel cells.

This example shows that, as with other types of low-temperature fuel cells, there are new ideas in the field of AFCs, for reaching higher current densities.

6. Costs of an AFC system

An Otto engine costs US \$150/kW in the large-scale production. This price must be matched for fuel cells if they are to be used in individual cars. Calculations were made of the costs of fuel cells and systems by DLR and other institutions: (DLR (Germany), LBST (Germany), ZSW (Germany), Hoechst (Germany), Royal Institute of Technology (Sweden)) [18–20].

All calculations show that the stack costs are similar to all other low-temperature systems. The production costs for the AFC systems seem to be the lowest. A price of about US \$400–500/kW was calculated using today's technologies and today's knowledge in large-scale production. Small-scale production cost will lead to 5–10 times higher production costs than the large scale.

7. Important problems mentioned above and their solutions

1. *Preparation method of the electrodes.* At VARTA AG and University of Kassel a low-cost preparation was devel-

oped. Together with DLR the electrode preparation method has been investigated.

2. *Costs of the electrode, the stacks and fuel cell systems.* At VARTA AG and the University of Kassel a low-cost preparation for modular stacks was developed and at ISET Kassel an alkaline system was built.

3. *Life time of the electrode/degradation.* At DLR the degradation of low-cost gas diffusion electrodes is being investigated. The degradation mechanisms are understood. The operation time of low-cost electrodes is more than 5000 h.

4. *Diaphragm made of asbestos.* ISET Kassel is investigating diaphragms to build the 3.5 kW system. They have found materials which can be used successfully in AFCs and electrolyzer stacks [8,21,22].

5. *CO₂-contaminated fuel gases (carbonating of electrolyte and electrodes).* At DLR a new pretreatment was developed to prepare CO₂-resistant electrodes.

8. Conclusions

Only a few research groups are still working on AFCs in Europe. It was shown that the well-known problems have been solved and that there are new ideas for constructing technical systems.

Concerning fundamental research, we may conclude that a poisoning of electrocatalysts in AFCs with rolled electrodes by CO₂ does not take place and that this fuel cell is as suitable for mobile applications as other low-temperature fuel cells.

Calculations show that all kinds of low-temperature fuel cells are in the same range of costs.

Thus, the AFC is as suitable for mobile applications as other fuel cells.

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