Another Chance for Classic AFCs? Experimental Investigation of a Cost-Efficient Unitized Regenerative Alkaline Fuel Cell, Using Platinum-Free Gas Diffusion Electrodes

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Abstract

The big challenge of global phase-down of carbon dioxide emissions leads us to alternatives in storing electric energy from renewable sources. For the worldwide use of batteries and fuel cells very high amounts of precious electrode materials are needed. Batteries require rare earth metals and environmentally harmful Lithium, PEM fuel cells require noble platinum and iridium. Thus, an economical and eco-friendly alternative to lithium-ion-batteries should be found, especially for the use in domestic homes. In the on-hand work, a well-known type of fuel cell is revised and considered in the new context of global material usage. Therefore, an alkaline fuel cell with the classic design of an electrolyte gap in-between the electrodes is observed. Gas-diffusion-electrodes are used, based on Raney-nickel. Results are given for different catalysts: Raney-nickel, Raney-silver, manganic-oxide, carbon and ruthenium. For the analysis current-voltage-characteristics, chronopotentiometry and SEM micrographs are used. The results are discussed in comparison to a unitized reversible PEM fuel cell. At low current density, the alkaline cell is obtaining round-trip efficiencies close to 70%, while the PEM cell achieves only 60% efficiency. With Silver-catalyst clear higher efficiencies up to 80% are presentable. The PEM fuel cell shows obvious better performance at high current densities.

Keywords: Alkaline Fuel Cell, Bi-functional Catalyst, Gas Diffusion Electrodes, Raney-Nickel with Stable Carbon, Unitized Regenerative Fuel Cell

1 Introduction

The report of the Intergovernmental Panel on Climate Change, IPCC, sees immediate need for action, to limit the global warming to 1,5 degrees Celsius. Therefore, the carbon dioxide emissions must be halved until 2030 and total decarbonization must be accomplished until 2040 [1]. This means not less than a comprehensive worldwide change of our whole energy infrastructure. For the global traffic, electric battery cars will be the first choice, at least for smaller short-range vehicles. Additionally, in our residential buildings more and more batteries will be installed, to save the electric energy from photovoltaics for the night. But, for such a restructuring of billions of vehicles and houses, immense quantities of rare metals must be produced – while their disposal means toxic waste. For batteries rare earth and lithium are needed, which are produced in only a few mining areas worldwide, in regions which might be politically not stable. Germany, for example, who has no access to these materials, will become dependent on foreign suppliers again like during the fossil decades. Additionally, the mining industry causes enormous

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quantities of toxic waste – pure entropy – which must be disposed of in these areas. Thus, we should be attentive, that we do not fabricate the next ecological and political disaster, when producing and disposing these raw materials. It is absolute necessary, that we present the problem in its entirety and save natural and financial resources – especially when dealing with such huge quantities.

Definitely, one of the biggest advantage of rechargeable batteries is the high energy storage efficiency. While lead-acid accumulators have storage efficiencies of only 60–70%, modern lithium-ion-batteries provide more than 90% of the electric energy, which was used for charging. In [2] for example, an energy efficiency of around 95% is reported. Lithium-ion batteries designed for residential homes are discussed in [3], where a round-trip efficiency between 82–89% is reported. Current issues of Lithium-ion batteries are discussed in [2], [4] and [5]. On the other hand, there is one general problem of all batteries: here, the whole electric energy is stored inside the mass of the electrochemical material, directly in the cell. The more capacity you want to have – the more material must be used. In contrast to that, fuel cells have the big advantage that the energy can be stored outside of the electrochemical cell. The size of the hydrogen gas tank is independent from the electrical capacity of the fuel cell. In this way, the range of an electric vehicle can be easily expanded without increasing the raw materials, used in the electrochemical cell.

In the 1990s, nearly all R&D activities in fuel cell research were focused on the PEM fuel cell. The core element of this fuel cells is a polymer electrolyte membrane (PEM) based on a sulfonated and perfluorinated polymer with the trade name Nafion®. The charge transport inside these membranes takes place with protons (H⁺-Ions), why the setting is acidic. For this reason, the selection of the catalyst material, which is applied on both sides of the membrane, is clear restricted: only platinum and some other noble metals like gold and iridium can resist in this strong acid environment. However, since the membrane is chemically very stable, the thickness could be successive reduced and hereby the power density increased. While the thickness of Nafion®-N-117 was 183 μm, today the Nafion®-111-IP has a thickness of only 25 μm. In [7] results of different PEMS are presented, with current densities of around 1.5 A cm⁻² with a cell voltage of about 0.6 V. However, high power densities produce although very high heat flows, which can hardly be removed from the membrane. Thus, it must be assumed, that the reported current densities will only occur for short moments, e.g., during acceleration in electric driven vehicles. Further development and economic utilization of PEM fuel cells are amongst others presented in a comprehensive overview in [8].

In residential homes, an economical favorably alternative is given by unitized regenerative fuel cells. Herewith, water electrolysis with electric energy from photovoltaics is used for producing hydrogen. In the fuel cell mode, hydrogen is being consumed for the production of electric energy, while both directions are realized in the same cell design. In [9] an overview of different reversible fuel cell technologies is presented: reversible alkaline, reversible polymer electrolytic and reversible solid oxide fuel cells. Different concepts and cell designs are discussed. Solid oxide fuel cells seem to be favorable, but they are working at high temperatures of 600°C and they get along with considerable corrosion problems.

In [10], the authors researched different catalysts, which are stable in the very aggressive oxygen environment of acid PEM electrolyzers. They figured out, that Platinum and Iridium have been mainly proposed as bi-functional electrocatalysts. With PEM fuel cells, very high current densities can be obtained. But for designing a unitized reversible fuel cell, the PEM technology has also some disadvantages: the storage efficiency is only around 40 to 50% – without considering the energy for pumps, compressors, valves and control systems [11]. For switching over from electrolyzer to fuel cell mode, the water must be removed from the oxygen side and several vales, pumps and humidifiers must be activated and controlled. The system complexity is quite high, which is shown for example in an US patent [12]. Another crucial point are the materials in reversible PEM fuel cells. Since the oxygen side has a very high reduction potential, only high-grade metals will sustain. Thus, flow fields and gas diffusion layers must be produced from titanium, which is very strong and mechanical processing is dreadful. In the area of gas diffusion layers, some improvement could be made, using a Ti-felt GDL with a fiber diameter of 80 micron and PTFE treatment [13]. In [14] tita-nium felts with a high specific surface area are researched for regenerative fuel cells with acidic media. In [15] a unitized regenerative PEM fuel cell was researched during switching form fuel cell to electrolysis mode while water has been pumped into the oxygen gas channels. It was figured out that the rate of the two-phase volume flow and the water temperature have a big influence on a temporary voltage peak. The electrolysis voltage jumped from 1.6 V to about 2.0 V, while the duration of this peak lays between 36 and 72 s. Furthermore, in [16] an overview about current research status of regenerative PEM fuel cells is given. Therefore, a standard Nafion®-117 membrane was used and bipolar plates made of titanium. While platinum was the preferred catalyst at the hydrogen side, extensive studies were conducted to found the optimal bi-functional catalyst for the oxygen side. Here, a mixture of platinum and iridium is the first choice, but also additive ruthenium or oxides of iridium (IrO₂) and ruthenium (RuO₂) seem to have a positive influence. In the end, most of these noble materials are very costly and will distinctively increase the price of a reversible fuel cell system. This, in combination with very high production costs of milling titanium plates and the fact that reversible PEM fuel cells can only achieve a maximum round-trip efficiency of about 50%, lead us to a closer look of an alternative fuel cell system.

The alkaline fuel cell (AFC) was the first technology of this kind, which was developed for technical use, especially for the NASA space program APOLLO and for the Space Shuttle in the 1960s to 1980s [6]. AFCs have a liquid alkaline electrolyte, more or less fixed in-between the electrodes. Here, the biggest advantage is given by the kinetics of the oxygen reaction,
which is distinguished to run much faster and with less restraints than in acid media. Thus, lower overvoltage and clear higher energy efficiencies can be realized. The Siemens fuel cell for example is working with an immobile alkaline matrix electrolyte, fixed in an asbestos diaphragm, using platinum electrodes. A considerable performance with current density up to 500 mA cm\(^{-2}\) and remarkable high cell voltage above 900 mV is presented, e.g., in [17] and [18]. Another interesting benefit results from the fact, that catalysts are not restricted to noble platinum-group-metals. Also nickel, carbon and silver resist in the alkaline environment – partially although during electrolysis at higher potentials. Against the background of the widespread use of fuel cells, the alkaline fuel cell technology is again getting more interest these days. In [7] for example it is reported, that the number of published research papers about AFCs increases exponentially since 2010. Especially in east asia and in north america high activities are registered to find alternatives for PEM fuel cells without platinum catalysts. Current research activities are now focused on alkaline membranes, e.g., presented in [20]. One classic type, originally developed for water treatment (Fumatech Company) is based on a stable PBI-structure and is containing KOH aqueous solution, soaked into the hydrophilic membrane structure. Technical process problems are mainly caused by drying the membrane or leaking out of the KOH. On the other hand, they are quite stable even at higher temperatures up to 80 °C and more. One major issue of alkaline fuel cells is the performance degradation due to the precipitation of metal carbonate crystals (K₂CO₃), when the electrolyte comes in contact with the carbon dioxide of the air. Therefore, a new type of membrane has been developed, which is called anion exchange membrane (AEM). It is based on a solid polymer electrolyte (e.g., a polysulfone structure) with fixed positive ionic groups and mobile negative charged anions – usually hydroxide [7]. While these membranes are designed without metal cations, no carbonates can be formed and operation with air is possible. AEMs can be used like PEMs, but with some constraints. Since there is a general problem of decomposition of the molecular structure due to the presence of highly nucleophile OH\(^-\), the temperature range is typically limited to 50–60°C. The ionic conductivity is lower compared with PEMs and the diffusion coefficient of OH\(^-\) is twice less than that of H\(^+\) [7]. On the other hand, the power density can be quite high. In [20] different publications are summarized to present the power density of AEMs. With thin membranes of 25 μm thickness it is possible to achieve around 230 mW cm\(^{-2}\). With an AEM based on vinylbenzyl chloride (VBC) radiation grafted onto polyethylene-cotetrafluoroethylene (ETFE) with trimethylamine functional groups, a very impressive peak power density of 1.4 W cm\(^{-2}\) is published in [21]. The associated current density is nearly 3.0 A cm\(^{-2}\). One can imagine, that the resulting extreme heat power peaks will fuse the membrane within seconds, if not the perfect gas flows and humidities are regulated. After all, AEMs seem to become competitive to PEMs nowadays. On the other hand, nearly all research groups, which are presenting these high power densities of AEMs, are using platinum-group-metal catalysts for their experiments and costly, hard to machine titanium bipolar plates. The advantages over PEM fuel cells concerning to cell design and material costs, is then negligible.

At this point one should have a closer look to the classic AFC design – especially when not the highest power densities are required, for example in combination with photovoltaics in residential houses. Within a classic alkaline fuel cell, a liquid electrolyte, typically potassium hydroxide solution (KOH), is flowing through a gap in-between two electrodes. The catalysts are usually based on a porous Nickel-structure designed in form of gas diffusion electrodes (GDE). Here, a hydrostatic equilibrium exists between the electrolyte liquid phase at one side and the gas pressure at the other side – resulting in a high number of three-phase-contact lines at the catalyst surface. The reaction water and heat are fed and removed with the electrolyte flow. In [22], a university book of electrochemical fundamentals, it is mentioned, that current densities of 1–2 A cm\(^{-2}\) can be achieved with GDEs, when pure oxygen and hydrogen gases are applied. In technical application the current densities are much lower, to avoid high overvoltage. The SIEMENS fuel cell with mobile electrolyte get along without any platinum-group-metal: the hydrogen electrode is made of Raney-nickel, the oxygen electrode is made of silver, nickel and some titanium. At 200 mA cm\(^{-2}\) current density, the cell voltage is still above 900 mV, at 400 mA cm\(^{-2}\) it is at least around 800 mV [17, 18]. The preparation of gas diffusion electrodes (GDE) was amongst others developed by Prof. Winsel in the 1980\(^{th}\). The catalyst (Raney-Nickel) is mixed in a rotating knife mill with PTFE and then rolled onto a wire gauze in a continuous process [6, 18, 23]. Therewith, a theoretical endless band of electrodes can be produced and sold by the meter in an economic way. The funding of a new company Gaskatel, for the commercial production of these GDEs, was based on the group of Prof. Winsel at the University of Kassel and on the Varta Company development group of zinc-air batteries in 1997. A special type of alkaline fuel cell, the Eloflux cell developed by the team of this company. Here, 0.3 mm thick GDEs are pressed together on both sides of a hydrophilic polyolefin-separator and then embedded in an epoxide resin block. While 4 cells are combined and supplied with micro gas channels, the liquid electrolyte is pumped and flowing vertical to the electrodes. With silver and nickel GDEs a cell voltage above 800 mV can be processed at current densities of 200 mA cm\(^{-2}\) [6]. Another group was developing and researching the classic AFC at the German Center of Aerospace, DLR, until the last decade. In a similar process like the Gaskatel Company, a mixture of Raney-nickel and PTFE is produced by reactive mixing and then calendered on a metal gauze (“DLR process”). A silver GDE produced by this process is analyzed in [24] by REM micrographs, cyclic voltammetry, voltage current characteristics and impedance spectroscopy. Current densities of about 600 mA cm\(^{-2}\) could be achieved, with a potential of about 300 mV at the oxygen electrode vs. Hg/HgO [24] and [25]. Some other groups are reporting about experimental investigations of alkaline fuel cells. The group of Prof. Wendt at the Darmstadt University of Technology, e.g., was producing...
Raney-nickel for GDEs [26]. Some Articles are especially about the silver GDE for the oxygen reduction. In [27] the long term stability of silver GDE is researched. Silver Carbon catalyst for alkaline fuel cells is although researched in [28]. The influence of the PTFE content in silver GDE is shown in [29]. In [30] the problem of degradation of the performance of the oxygen electrode in alkaline solutions is answered by the design of a flooding-tolerant electrode on the base of a water-proof silicon-oil. Only one group is reporting about a bi-functional catalyst for alkaline fuel cells, which works in both directions – in fuel cell, as well as in electrolysis mode. In [31] different electrodes for a bi-functional alkaline fuel cell are researched. The catalysts were analyzed using cyclic voltammetry and rotation disc technology, with current densities up to 10 mA cm\(^{-2}\). In 0.1 molar KOH the best alternative catalyst for the oxygen reaction is a nickel carbon mixture (Ni/C). However, most of the experimental investigations mentioned above are working with tiny half-cells with only 1 cm\(^2\) active area. One group, who was developing a useable fuel cell system in the last decades, is the Ovonic Company [32]. In a small stack several alkaline fuel cells are combined to generate a useful power for small electric applications. The voltage of a single cell is about 800 mV with a current density of only 100 mA cm\(^{-2}\). It shows, how different the power density can be, when an appreciable active area must be supplied with gases and liquid electrolyte in a uniform way.

In summary, the classic alkaline fuel cell design has some appreciable advantages over membrane fuel cells:

(i) Appreciable cost-reduction by avoiding the use of platinum-group-metals
(ii) Cost-effective production of framed electrodes to avoid costly titanium bipolar-plates
(iii) Simple process control: no consideration of complex membrane humidification
(iv) Perfect cooling of the electrodes through electrolyte flow
(v) switching from fuel cell to electrolysis mode within seconds:
   – no fluid mechanical issues caused by 2-phase-flow in oxygen-channels
   – no technical expense for water fed and removal when switching operation mode

However, to realize these advantages in a fuel cell, some sophisticated design solutions must be developed. A bi-functional electrode catalyst must be found and optimized. Therefore, detailed experimental investigations must be conducted, to figure out, if there is a realistic chance for a wide technical use of an alkaline reversible fuel cell in the classic design. This should be the challenge for the present work.

2 Fundamentals

In opposite to polymer electrolyte membranes (PEM), alkaline water electrolysis works with concentrated KOH of about 40% weight, as liquid electrolyte. Instead of positive H\(^+\)-ions, negative charged OH\(^-\)-ions are moving in alkaline cells from the cathode to the anode. The water splitting takes place at the cathode:

\[
2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^- \quad (1)
\]

At the anode, 2 OH\(^-\)-Ions are consumed, when one molecule of water is formed:

\[
2 \text{OH}^- \rightarrow 1/2 \text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^- \quad (2)
\]

Thus, to produce one molecule oxygen, 4 molecules OH\(^-\) have to cross the electrolyte and in the opposite direction 2 molecule of H\(_2\)O has to flow.

For the design of gas diffusion electrodes, it is important to have a close look at the physics on the catalyst surface, where the actual reactions take place: three phases are here in close contact: solid metal, liquid electrolyte and gas. Since the reaction directly at the catalyst surface is very fast, the mass transportation is slowing down the reaction rate, especially at high current densities. The gases always must diffuse through a liquid layer (water and electrolyte) which is in general a slow process (see Figure 2a).

Another effect is comparable between boiling and electrolysis: the bubble grows. Since liquid pressure and surface tensions compress the bubble from the outside, the gas pressure must overcome the forces from the inside, before the bubble starts to grow.

The mechanical equilibrium of a bubble is given by the Young-Laplace-equation [6]:

\[
\Delta p = \frac{2\gamma \cdot \cos \theta}{r_B} \quad (3)
\]

where \(r_B\) is the bubble diameter, \(\gamma\) the surface tension and \(\theta\) the contact angle. \(\Delta p\) is the pressure difference between liquid and gas pressure around the bubble.

Therefore, the gas generation must work with an overheat in thermal case and with an overvoltage in the electrochemical case. The dynamics of bubble growth during nucleate boiling is directly associated with the temperature of the metal surface under the bubble, resulting in the typical saw-tooth pattern [33]. The same dynamic pattern of bubble grows over time is presented in [34] during electrolysis, while data from a mathematical model are validated with measured values. Since bubble grows seems to be a complex, fluctuating and energy consuming process – it should be avoided in micro-fluid-dynamics when designing technical systems. In thermal applications, the
heat pipe the means of choice, where micro-structured evaporators have a high number of 3-phase-contact-lines for direct evaporation without bubble formation. In electrochemical cells, gas diffusion electrodes have been developed for gas generation in micro-structured without bubble formation.

In Figure 1, a schematic sketch of a gas diffusion electrode (GDE) is given. The challenge is to regulate the hydrodynamic equilibrium within the porous structure of the catalyst material. For avoiding total flooding, the catalyst particles are blended with PTFE, to create hydrophobic pores for the gas diffusion (left side). Additionally, a PTFE membrane is rolled on the electrode at the gas side, to prevent leaking out of liquid electrolyte. At the right side of Figure 1, the electrolyte is flowing in a gap. As a barrier and to support the hydrodynamic equilibrium, a hydrophilic separator is pressed from the right side onto the electrode. Hydride ions and water must be exchanged through this, while diffusion and feeding liquid through micro-pores into the catalyst structure takes place. The smaller these pores, the higher is the gas pressure, the electrode can withstand. The idea is to create a maximum region of partly wetted catalyst particles with a very high number of 3-phase-contact lines. Generated gas diffuses through the structure without bubble formation. Hydride ions diffuse from the opposite side. The electric current is led through a wire gauze, which is rolled on the back side of the electrode as a conductor.

For a more detailed understanding of the physics within the above mentioned micro-pores, a model based on Young-Laplace-equation is illustrated in Figure 2. The model can be used for the explanation of two physical processes, running within gas diffusion electrodes. First, the mechanical equilibrium of the liquid meniscus. One can imagine that the boundary surface is hold from the solid material like a sail with an anchor. The gas is pressing from one side; the surface tension is holding against. Involving the Young-Laplace-equation, leads to the diagram at the right side of Figure 2b. The smaller the pore diameter, the higher has to be the internal gas pressure, before the bubble starts to grow. But, the raised pressure in the bubble works in turn against the electro-chemical equilibrium, which leads to an increase of the overvoltage needed for bubble evolution. For this reason, electrolysis on flat metal surfaces requires obvious higher voltages, than on micro-structured surfaces. In an ideal case, no bubbles are generated and the developed gas diffuses at the 3-phase-contact-line from the catalyst directly to the boundary surface. Thus, a high number of contact lines have to be designed during the operation of gas diffusion electrodes.

3 Experimental

An alkaline fuel cell with the classic design of an electrolyte gap in-between the electrodes has been developed at the Ennoble Power research laboratory [35]. It was also installed
in the laboratory of the Frankfurt University of Applied Sciences and improved in some points. Representative of this cell is a simple structure with cost-effective materials. No milling of complex metal parts is required. Instead of that, only flat materials are used, which can be easily produced by laser-cutting. The assembly of the cell is given in Figure 3.

The electrolyte gap in-between the electrodes is a crucial point of the design. It is defined by a frame (6) including a support structure (7). On the one hand side, it must be very thin, to minimize ohmic resistance. On the other hand, it must ensure a uniform liquid supply without any gas bubbles. It must be chemically stable against high concentrated brine and thermally stable up to 80°C. Additionally, flat gaskets must be considered with a resulting total electrolyte gap thickness of 1.7 mm. Several materials and designs were observed for optimization. Meshworks of polypropylene (PP) with different thread diameters and mesh openings were investigated with positive results (many thanks to the PVF Mesh & Screen Technology GmbH, Germany, for supporting the team with samples). Another promising approach was made by 3d-printing of CAD-models. Frame and support structure could be produced in one pass (with many thanks to the student Marius Botta for implementation). The experiments were conducted using KOH with about 30% concentration (by weight).

For all experiments gas diffusion electrodes from the Gaskatel Company in Kassel were installed. The electrodes are edged with metal frames produced from 0.3 mm thick nickel sheet metal by laser cutting. Soldering the overlapping wire gauze from the electrodes on the nickel frames results in optimal electrical contact and good handling of each electrode. The active area in this cell is 25 cm². Alkaline membranes from the Fumatech Company (8) were pressed on the electrolyte side of the GDEs and tightened in-between the nickel frames and flat sealing (6). The flow fields (2) are simple flat gaskets with 2 mm thickness including a meander structure. The gaskets are made by water jet cutting from Silicone plates. The components are enclosed in-between two 10 mm thick end-plates (9) made of stainless steel, with heating foils at the outside for temperature control. Insulated screws (10) and compression pipe fittings (11) are completing the fuel cell assembly.

In Figure 3 the experimental setup is shown. The fuel cell is mounted vertical since the electrolyte flow is important in this case. It is pumped from the bottom side through the support structure in-between the electrodes. On top of the cell, the out flowing electrolyte is led back to the electrolyte tank. The tank was fabricated from stainless steel. Flange and bottom plate were made by waterjet cutting and then fixed onto a tube of 42 mm diameter, using tungsten-inert gas welding. A heating foil is glued around the outside of the tank and then covered with an insulating foam. The temperature of the tank is measured with resistance thermometer of 4 mm diameter, enclosed into a stainless-steel tube. The set temperature is being adjusted with an electronic temperature controller. The gases oxygen and hydrogen are produced in a small external electrolyzer to ensure gas supply during electrolyzer and fuel cell mode. Over pressures are avoided with pressure regulator valves at the gas outlets of the cell. In electrolyzer mode, the electrode frames are conducted to a direct current power supply from the VoltaCraft Company. In fuel cell mode a load resistor bank was conducted, for gradual increase of the resistance and thereby increase of load and electric current. The electrolyte pump is adjustable and powered with about 6 V direct current.

4 Results and Discussion

At first, the electrolysis mode was observed. For nearly all experiments, at the hydrogen side a Raney-Nickel GDE (NiH 33) from Gaskatel Company were used. One series of experiments were conducted with a fine nickel mesh at the oxygen side, which was totally flooded with liquid electrolyte. Herewith, bubble evolution takes place at the surface of the metallic structure, bubbling through the liquid and resulting in a two-phase flow out of the cell. Voltage-current characteristics were recorded at different electrolyte temperatures, for visualizing the above mentioned effect of bubble growth. In a second series of experiments, a GDE made of Raney-nickel mixed with a stable carbon catalyst (NiC) was installed at the
oxygen side. A hydrophilic separator prevented the electrode from flooding. In this case, no bubbles were formed and the produced oxygen gas diffused directly into the dry gas channels to the outlet of the cell.

In Figure 5 two things are apparently visible: first, the gradients of the curves with the nickel-mesh are distinctively higher than with the GDE; second, a little gradient variation is observable for different temperatures. There are different effects which lead to the observed behavior. The electrochemical reaction at the catalyst is given by the overvoltage. The electrons have to tunnel through a layer of water molecules, adhering directly at the catalyst surface. This is a temperature dependent process. Typically, the activation energy can be interpreted by reading the gradient in voltage current characteristics at very low current flow. At higher current densities, additional effects overlay the electrochemical reaction: The ohmic resistance of the electrolyte is one, which is obviously a function of temperature. If gas bubbles are generated at the catalyst surface, additional effects with complex physics have to be considered, which are also dependent on temperature. When a tiny bubbles have to grow on a flat metal surface, which is totally flooded with liquid, high internal pressure must be applied to work against the effect of surface tension at high curvature. Therefore, a high overvoltage is necessary which leads to a comparative high cell voltage around 3.5 V at 100 mA cm\(^{-2}\) current density. When using a GDE, the laborious bubble formation can be avoided and the generated gas diffuses directly into the gas channels. Additionally, porous gas diffusion electrodes made of Raney-Nickel have an immense higher internal surface area, than flat metal sheets. Thus, much more reactive regions are available for the electrochemical reactions.

Subsequent, with the use of GDEs, considerable performance of the cell in fuel cell mode can be presented. The following experiments are all conducted with GDLs and hydrophilic separators at both sides.

In the fuel cell mode, it is beneficial to work with a little higher gas pressure at the electrodes. On the other hand, the hydrostatic equilibrium in GDEs, as described above, is a very sensitive thing. If the pressure is too high, gas is pressed through the GDE to the electrolyte side - with major implications. Bubbles will occur in the electrolyte outlet. But, if a gas layer accumulates in-between the GDE and the separator, the function of the electrode can be totally disturbed. Then, liquid electrolyte cannot reach the GDE in an efficient way and almost no electric current can be realized. If no separator is used, the bubble point through the electrode is around 400 mbar, which was researched in a former study of the author [36]. From experiments with the differential pressure a narrow pore size distribution between 4 and 9 µm was assumed. In the on-hand work this was confirmed by the interpretation of SEM pictures.

In Figure 6, scanning electron micrographs microscope (SEM) pictures are presented which were recorded at the laboratory of the Frankfurt University of Applied Sciences. Many thanks to Prof. Hektor Hebert for providing the instruments and help. In Figure 6, pictures of a manganese mixed oxide (MOC) GDE are given at different magnifications. With a magnification of 100 times, a more or less flat surface can be recognized (first picture). With a magnification of 500 times, some bigger openings of about 70 µm are visible in a superficial way (second picture). A closer view into one of these pores, with a magnification of 5,000 times, is given in the third picture. Here, one can imagine, that a real pore, which has kind

Fig. 5 Temperature influence on current-voltage characteristics during electrolysis for simple nickel-mesh and for NiC GDE, at different temperatures.

Fig. 6 SEM picture of a gas diffusion electrode (MOC). Magnification: 100 times (a), 500 times (b), and 5,000 times (c).
of tunnel connection to deeper regions, can be assumed with only some microns in diameter. This agrees roughly with the bubble point experiments presented in [36]. Comparing this with the calculations given in Figure 2, in a hydrophobic electrode structure a pore diameter of about 1 micron should be assumed to hold a gas pressure of some hundred millibars. Recent experiments with a Fumatech-separator have shown, that a gas pressure of 200 mbar could be established during electrolysis and fuel cell mode. The pore size in this hydrophilic separator is assumed with a diameter of about 0.2 m. However, for working with higher gas pressures, more effort must be invested in the cell design to seal the separator against the frames. For the fuel cell experiments it has shown, that a stable operation is beneficial with a low overpressure of about 30–50 mbar.

In the following, the fuel cell mode was researched using different GDEs at the oxygen side. The hydrogen electrode was for all experiments a NiH 33 electrode, consisting of Raney-nickel and PTFE. The hydrogen oxidation and reduction is running fast and with very low overvoltage at the nickel catalyst. On the other hand, it has to be considered, that the Raney-nickel must first be deoxidized and activated, before the characteristics can be recorded. Therefore, the temperature should be clear above 50°C and hydrogen gas has to flow along the electrode for several hours. After the cell voltage is above 800 mV, a little load can be connected to realize a small current density. Using a potentiostat is very helpful in this phase, since the cell voltage should not fall lower that 700–750 mV. After activating, the cell can be loaded with higher current densities.

The oxygen side of an alkaline fuel cell works much more difficult and the higher overvoltage is caused here. While Raney-nickel is a very efficient catalyst for the electrolysiss, it is nearly unfeasible in fuel cell mode. Coming from electrolysis it holds quite a high voltage around the theoretical value of 1,200 mV. But if current is applied, the voltage breaks down immediately. Therefore, different oxygen catalysts were researched during a series of experiments.

Looking at the characteristics in Figure 7, it is obvious that the Ag-GDE shows the best performance. As mentioned above, it is reported from several research groups, that silver is a very good catalyst for the oxygen-reduction in alkaline fuel cells [17,18,24,27]. In the on-hand work, a GDE made of Raney-silver and PTFE were used. It is remarkable, that voltages above 1,000 mV can be achieved at low current densities up to 30 mA cm⁻². A cell voltage of 900 mV was recorded at 50 mA cm⁻². Thus, the silver GDE is a promising option for designing an alternative storage system with high energy efficiency. On the other hand, silver is questionable in electrolysis, it is nearly unfeasible in fuel cell as well as in electrolysis mode, also at higher potentials. In a Fundamental research paper about bi-functional catalyst in alkaline solution, a Ni/C mixture was recommended as the best alternative to platinum-group-metal catalysts [31]. In Figure 7 the characteristic of the NiC electrode made by the Gaskatel Company is given. In comparison to the other electrodes, NiC shows only the lowest performance. With a current density of 50 mA cm⁻², just 600 mV cell voltage was measured. This is quite a low value, especially against the background of energy efficiency. On the other hand, the NiC-GDE allows actual stable operation during electrolysis and fuel cell mode, also at higher current densities. Last but not least, it is a low price alternative to noble material electrodes. By the way, the curve progression is quite parallel to the curve of the silver-GDE. This is a good indication of the reproducible operation of the cell design. While the gradient
of the curves is essentially caused by the ohmic resistance of the electrolyte and other cell components, this seems to be equal. The parallel shifting to lower potentials is caused by the high overvoltage of the NiC catalyst. However, there are some options to improve this behavior.

In the following, characteristics of electrolysis and fuel cell mode are combined in one diagram to discuss the usability for a regenerative unitized fuel cell. Some sentences should be said to the word “regenerative”; this may imply that a reverse function is possible while energy is “generated”. Actually, both process directions are involving ohmic losses and therewith heat production. This means that the processes are not reversible from thermodynamic point of view. To avoid misunderstanding, in the following the word “bi-function” should be used, which means that both functions, fuel cell and electrolysis, are performable with the same electrodes. The round-trip or energy efficiency will be displayed later on; it is the ratio of cell voltage in fuel cell mode to voltage in electrolysis mode, at the same current density.

In Figure 8 the current-voltage characteristics of three bi-functional electrodes, operating in the AFC, are given for electrolysis and fuel cell mode. For comparison, the characteristics of a bi-functional PEM fuel cell from the Fraunhofer ISE are displayed, which has a Nafion® membrane, platinum catalyst at the hydrogen side and platinum/iridium catalyst at the oxygen side [11]. Both fuel cells are working at similar conditions (atmospheric pressure and 50°C/60°C temperature). It is apparently that the PEM fuel cell has higher overvoltage at low current densities, observable by an exponential curve progression. The electrolysis starts above 1.4 V cell voltage, the fuel cell below 1.0 V. The alkaline electrolysis starts much lower, only a little above the reversible cell voltage of 1.23 V. A special case is given by the characteristics of the silver electrode. It seems to work without any overvoltage; the characteristic during electrolysis starts around 1.2 V open circuit and increases almost linear with increasing current density. This behavior should be handled with care. It must be assumed, that not an actual electrolysis takes place, but more or less a battery function. Silver will start oxidizing at a potential above 1.2 V. When 1.45 V is exceeded a second oxidation state will happen. The evolution of gas bubble will occur not before all silver has been oxidized. Thus, the characteristic of the silver electrode is more or less the characteristic of a silver battery. It shows in a demonstrative way, why batteries have a much higher energy efficiency: here the energy is stored by a chemical conversion of the electrode material. In contrast to that, during electrolysis and fuel cell mode, the charge carriers have to go an obstructive way. They have to tunnel through a static double layer of solvated water molecules sitting at the catalyst surface (Helmholtz-Model). This effect causes the overvoltage in an important way and is recognizable by the exponential curve progression. It is also distinctive at the characteristics of the NiC electrode. While the open circuit voltage is close to the reversible cell voltage of around 1.2 V, it turns in an exponential way into a remarkable voltage difference when current is applied. With increasing current densities, the curve progression is almost parallel to the curve of the silver electrodes. Here, ohmic resistances of electrolyte and cell components are responsible for the gradient. A much lower gradient is given by a PEM fuel cell which is displayed for comparison in dashed line. Due to the comparative lower electrolyte resistance of the Nafion®, the curve of the PEM fuel cell has a wide area with almost linear progression. This, can be explained by the ohmic resistance of the different electrolytes: while the thickness of the PEM membrane is only one tenth of the alkaline electrolyte gap, the ohmic resistance of the AFC is clear higher. This results in a stronger decline of the voltage with increasing current. On the other hand, it should be completed that the production costs of the reversible PEM fuel cell with machined titanium plates and noble catalysts was more than 2,000 €. The alkaline fuel cell, researched in this article, had production costs of only little more than 200 €, which is one-tenth. With this low costs it is conceivable to build an alkaline fuel cell stack which includes some cells for the electrolysis and some cells for the fuel cell mode. With the unipolar design, the single cells can be connected in different ways, depending on the hydrogen or electricity demand. However, this attempt will increase the costs anyway. Thus, it is preferred to design a cell that works in both directions with the same electrodes.

In Table 1, the different catalysts researched in the on-hand work are listed and discussed for their usability in a bi-functional cell. Raney-nickel without any additives is not functional in fuel cell mode, while MOC is not able to work with high potentials during electrolysis. Silver would be a very good catalyst for the fuel cell, but it is only limited suitable for the electrolysis. The problems of oxidation as mentioned above is one thing, but it is also reported, that silver is dissolving over time, especially at higher potentials. Raney-nickel with an addition of ruthenium could be a feasible alternative. Indeed, Ruthenium also belongs to the platinum-group-metals, but its price is much lower than platinum or iridium. In fact, it is only about one-hundredth of the price for platinum, thus it is more comparable with the silver price. On the other hand, the long-term stability and the dynamics during switch-
Another Chance for Classic AFCs?

Research into in-between electrolysis and fuel cell mode should be researched, especially by cyclic voltammetry. The only catalyst which nowadays is stable in both operation directions and cost-efficient seems to be the NiC. To resolve the problem of high overvoltage, the catalyst was researched more detailed in the laboratory of the Gaskatel Company.

Using a half-cell with 1 cm² active area, a NiC gas diffusion electrode was implemented working against a standard hydrogen electrode of platinum. The carbon of the NiC was originally developed for alkaline batteries and is very stable even at high potentials, high temperature and high concentration. In the following the results of chronopotentiometry with NiC are presented.

In Figure 9, the voltage characteristics over time are given, for different concentration of potassium hydroxide (KOH). Thereby, the current of the cell is switched between –10 mA and +10 mA, while is cell voltage is measured over time. First, it is noticeable, that in some cases it takes quite a long time until the cell is reaching stable operation. One reason for that is the internal energy storage due to the capacitor effect. Since the electrodes consist of a noteworthy amount of metal in form of a thin plate (electrode thickness approximately 0.3 mm) it acts like a plate capacitor. After switching the current direction, first, a kind of charging process takes place until the electrode turns into the stable electrochemical operation. All fuel cell and electrolysis experiments discussed above were conducted using KOH with 30% by weight, which corresponds to a molarity of 7.64 mol L⁻¹. For the experiments in Figure 9, the concentration was one time very low (1 mol L⁻¹) and then significantly increased to a molarity of 20 mol L⁻¹. With the high concentration the overvoltage could be clearly decreased. But within the cyclic time of the experiments no stable operation could be obtained. With 20 mol L⁻¹ KOH at 80 °C quite good performance could be achieved. In fuel cell mode around 0.9 V and in electrolysis mode around 1.37 V were recorded which is quite better than in the experiments described above (FC: 0.78 V/EL: 1.4 V). Little degradation is observable after 50 h.

Furthermore, another very interesting thing, can be discussed with the measurements, given in Figure 9. The assumption was made, that water dipoles are hindering the ion transport and lead to higher overvoltage. Thus, one experiment was done with an eutectic mixture of water and potassium hydroxide (KOH-H₂O), which is melting at around 60 °C. With this, a kind of molten electrolyte fuel cell was realized. This molten electrolyte has almost no overvoltage, which can be seen in Figure 9. In fuel cell mode, around 1.0 cell voltage was reached, which leads to an energy efficiency above 70%. After 50 h the catalyst was destroyed. More similar experiments should be conducted to evaluate the long term stability of the different electrodes.

Finally, the round-trip energy efficiencies for the different GDEs were calculated and displayed in Figure 10, at different current densities. The energy (storage) efficiencies were calculated by the ratio of fuel cell voltage to electrolysis voltage, respectively at a certain current density. The values for the calculation are taken from the characteristics in Figure 8. It must be mentioned, that these energy efficiencies are only the efficiency of the single cell. Additional system components like pumps, valves, controllers and compressors are not included.

Looking at Figure 10 it is obvious that the silver GDE shows by far the highest round trip-efficiency. Values close to...
90% are usually known for rechargeable accumulators like Lithium-ion batteries. As mentioned above, this is due to the fact that internal redox-reactions of the metal dominates the conversion and not a real fuel cell or electrolysis process. The second-best is the nickel-ruthenium GDE, which shows efficiencies up to 70% at low current densities of 10 mA cm\(^{-2}\) and around 50% at 50 mA cm\(^{-2}\). Unfortunately, the stable NiC-GDE shows comparable low efficiency of less than 40% at 50 mA cm\(^{-2}\). But, it is foreseeable, that with higher concentrations and higher temperature the energy efficiency can be cleared increased. At current densities above 75 mA cm\(^{-2}\) nearly all alkaline GDEs shows significant decrease of the efficiency. Looking further, some improvements are expected, when the gas pressure at the electrodes will be increased. The PEM fuel cell has a lower maximum efficiency at small current density, but shows a more stable progression with increasing current densities. The maximum efficiency is about 60% the average more or less around 40%.

5 Conclusion

The challenge of the on-hand work was to research an eco-friendly and economical alternative to Lithium-ion batteries, especially for the use in domestic homes, where low current densities are acceptable. Therefore, a bi-functional unitized alkaline fuel cell has been developed, which is simple and cost-effective in production. With the classic design of an electrolyte gap in-between two gas diffusion electrodes it is possible to switch from electrolysis to fuel cell mode and back with in seconds. Different catalysts and GDEs have been researched in this technical application. In summary, the alkaline fuel cell has the potential to realize a cost-effective storage application with high energy efficiencies, especially at low current densities up to 50 mA cm\(^{-2}\).

The fuel cell design works very well during all experiments. Keeping the electrolyte temperature was possible without complaints. The gas channels were absolute dry and no electrolyte was leaking out – a general issue of alkaline fuel cells. From the design point of view, some aspects of the fuel cell should be reviewed. The actual flow fields are very easy to produce and cost only a few Euros. They are sealing well, but the consistence is too soft. Some improvements concerning to the utilization of the active area should be made in this point. In the near future, higher gas pressure should be applied for the experiments.

Concerning to the GDEs and catalysts, it is actual challenging, to find the perfect solution between the oppositional requirements of electrolysis and fuel cell mode. Remarkable is the very high energy efficiency with silver catalyst in alkaline media. On the other hand, this should be handled with care in electrolysis mode, since it works here more or less like a battery. The silver catalyst should be researched more in detail during electrolysis.

A promising bi-functional catalyst is given by Raney-nickel with a stable carbon additive (NiC). But currently, the energy efficiency is too low for an efficient storage application. Some improvements are expected when using higher temperature, concentration and gas pressure. First experiments with an addition of ruthenium are given in this work. Ruthenium belongs to the platinum-group metals, but the price is much lower and more comparable with silver. It shows an effective way of optimizing the energy efficiency of Raney-nickel. Further experiments should be conducted with a mixture of NiC with an addition of ruthenium. The long term stability of ruthenium catalyst must be proved.

In summary, nearly all experiments with GDEs in the alkaline fuel cell shows too low current densities, comparing with data from literature. A closer look to the different mechanisms is required, which can be realized by impedance spectroscopy. Herewith, the different internal dynamic resistances of the electrodes, conductor frames, the electrolyte and separators can be apportioned. This should give clear understanding of the current internal weaknesses of the fuel cell. Since investigations with impedance spectroscopy has now started at the Gaskatel Company and at the Frankfurt University of Applied Sciences, new results will follow soon.

Since the production costs of the presented alkaline fuel cell are only one-tenth of the costs for a reversible PEM fuel cell, further design studies should be discussed. An integrated solution should be considered, with different cells for electrolysis and fuel cell mode, in mono-polar design, combined in one stack. Herewith, an energy efficiency around 70% will be achievable at low current densities. In comparison with a reversible PEM fuel cell, which obtains only about 50% efficiency, this would be a feasible improvement in saving energy.

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List of Symbols

Ag Silver
$e^-$ Electrons
H$_2$ Hydrogen
H$_2$O Water
H$^+$ Protons
O$_2$ Oxygen
OH$^-$ Hydroxide ions
$r_b$ Bubble/pore diameter
$\Delta p$ Pressure difference between liquid and gas
$\gamma$ Surface tension
$\theta$ Contact angle

Abbreviations

AFC Alkaline fuel cell
GDE Gas diffusion electrode
MOC Manganese oxide electrode
NiC Raney-nickel electrode with stable carbon
NiH$_3$ Raney-nickel hydrogen electrode
NiRu Raney-nickel ruthenium electrode
PEM Polymer electrolyte membrane

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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