

Long-term operation of AFC electrodes with CO₂ containing gases

E. Gülzow, M. Schulze*

Institut für Technische Thermodynamik, Deutsches Zentrum für Luft- und Raumfahrt e.V., Pfaffenwaldring 38–40, D-70569 Stuttgart, Germany

Abstract

Low temperature fuel cells represent an important component in pollution-free energy conversion for mobile application. Alkaline fuel cells are an interesting alternative for polymer electrolyte membrane fuel cells (PEFC), because they do not need expensive membranes and catalysts. It is commonly accepted, that carbon dioxide intolerance is the most pronounced disadvantage of air breathing alkaline fuel cells. Thus, alkaline technology is commonly not considered for mobile fuel cell application. In this study, the long-term influence of carbon dioxide containing reaction gases on electrodes manufactured by a rolling process were investigated. To investigate the mechanisms of carbon dioxide poisoning, gas diffusion electrodes (GDEs) which were designed for alkaline fuel cells had been operated in a half cell configuration up to several thousand of hours with a constant load of 150 mA/cm². The reactants were contaminated with 5% CO₂. The experiments were performed with both electrodes, anode and cathode. Control measurements were performed by operating electrodes with pure reactants. During these long-term experiments, the *V–I* curves were recorded daily. Recently also the chemical surface compositions of the gas diffusion electrodes were investigated by X-ray-induced photoelectron spectroscopy (XPS) after long-term operation. In addition to the characterization of the electrode, the carbonate concentration in the electrolyte was determined after different operation times. The electrochemical performance of the electrodes, anodes and cathodes, decreases during the operation time in both operation modes, operated with pure gases as well as with CO₂ containing gases. The decreases in both modes are comparable; this means the CO₂ neither enhances the degradation process nor induces a new, detrimental degradation process. The XPS characterization of used cathodes operated with pure and with CO₂ containing oxygen yielded no significant difference. A slightly higher carbon concentration was observed on the surface of the anodes which was operated with CO₂ containing hydrogen than on surfaces of anodes which were operated with pure hydrogen. The carbonate concentration in the electrolyte increases during fuel cell operation with CO₂ containing gases. The long-term behavior of the investigated alkaline fuel cell (AFC) electrodes supplied with CO₂ containing gases gives no evidence that CO₂ affects significantly the degradation process.

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Keywords: Gas diffusion electrodes; AFC electrode; Polymer electrolyte membrane fuel cells; Carbon dioxide; Degradation

1. Introduction

Alkaline fuel cells (AFC) are an interesting alternative to polymer electrolyte membrane fuel cells (PEFC). Nickel can be used as catalyst in the anodes and on the cathode silver can be used as catalyst, because the alkaline electrochemical environment in AFC is not so strongly corrosive as in acid fuel cells. In addition, liquid alkaline solution is used as electrolyte. Both, catalysts and electrolyte, represents a big cost advantage with AFC in comparison to PEFC and, therefore, considering only the cost, the AFC has a much higher potential for the commercialization of fuel cells. Nevertheless, very recently a fuel cell company specialized to AFC finished its activity [1]. The advantages of AFC are not limited to the cheaper components, AFC has also advantages

in the system technique, because no process gas humidification is needed for AFC operation, which is a significant problem of the present PEFCs, and due to the fact that the electrolyte is liquid the temperature management of AFC can be performed with the electrolyte. Some one will see the liquid electrolyte as disadvantage, because AFC needs a circuit for the electrolyte; a similar circuit for liquids is also needed for high efficient PEFC systems for the temperature management, whereby the electrolyte circuit in AFC may be more expensive because of the higher corrosivity of the electrolyte compared with water of other cooling media in the PEFC. The alkaline solution in the AFC must be reconcentrated during long-term operation, but this is very simple in comparison to the water management in a PEFC.

Low temperature fuel cells represent an important element in pollution-free energy supply for mobile applications. It is a commonly opinion, that carbon dioxide intolerance is the most important disadvantage of air breathing alkaline fuel cells [2,3], this was one of the reasons that in the beginning

* Corresponding author. Tel.: +49-711-6862-456;
fax: +49-711-6862-332.
E-mail address: mathias.schulze@dlr.de (M. Schulze).

of the 1990, the activities in alkaline fuel cell research were terminated or drastically reduced in most companies and as consequence caused by the decreasing financial support also in the research institute [4]. Thus, alkaline technology is commonly not considered in mobile fuel cell applications. In contrast, in more recent publications, the carbon dioxide tolerance of AFC is confirmed [5,6].

The life time of fuel cells is a decision factor for their commercialization. The degradation of fuel cell components is investigated with increasing activities mainly focussed on PEFC [7–18]. For alkaline fuel cells several studies of degradation processes exist [6,19–28], they are focussed on the electrodes, because the electrolyte in AFCs can be easily exchanged. The investigation of the carbon dioxide influence can only be studied in long-term experiments and comparing with and without carbon dioxide loading.

2. Experimental

2.1. Sample preparation

The electrodes investigated are gas diffusion electrodes (GDE) consisting of a metallic catalyst and polytetrafluorethylene (PTFE) on a metal web. The preparation technique based on a development of Sauer [29] and Winsel [30] has been further developed for electrodes of different low-temperature fuel cell types, alkaline fuel cells [22,31–36] and polymer electrolyte membrane fuel cells [13,37–41].

The investigated anodes consist of a mixture of a size selected Raney-nickel catalyst with an addition of copper powder and PTFE powder onto a copper web. The nickel catalyst is a highly porous metallic catalyst which is formed from an aluminum–nickel alloy by dissolving the aluminum. The basic alloy used for the catalyst and the PTFE powder is the same in all electrodes. The preparation of the electrodes is described in more detail in [19]. The electrodes were activated in a standard procedure by hydrogen evolution at 5 mA/cm^2 for 18 h in a 30% KOH [26]. During this activation procedure, the oxidized nickel was reduced to metallic nickel, the copper was partially dissolved, the specific surface area increased and the pore size distribution changed [26].

The preparation of the cathodes was performed in an analogous way by rolling the electrode powder, a silver catalyst supported by PTFE or a silver powder mixed with PTFE, onto a silver web. The cathodes were reduced by hydrogen evolution before insert into the electrochemical cells [42].

2.2. Electrochemical operation and characterization

The electrodes, anodes and cathodes, were electrochemically stressed and characterized in an electrochemical half cell configuration consisting of the electrode in a holder manufactured from plexiglass, a nickel counter electrode and a Hg/HgO reference electrode. In the experimental setup,

the electrodes were supplied with gases without overpressure from the backside (the side with the metallic web). The electrode holder was inserted into a temperature controlled vessel (353 K) containing 30% KOH. The vessel contains approximately 1.5 l electrolyte. The electrode has an active area of 6 cm^2 . The gas diffusion electrodes were operated up to several thousand hours with a constant loading of 100 mA/cm^2 or 150 mA/cm^2 . The advantage of the half cell tests compared to long-term experiments in full cell configuration is that the electrodes and their degradation can be investigated individually.

To investigate the mechanism of carbon dioxide poisoning, the measurements were performed by operating electrodes with gases containing 5% CO_2 and also with pure gases as reference. Before operation with CO_2 containing gases all electrodes have operated with pure gases for 100 h. The CO_2 content in the gases is 150 times higher than for the CO_2 content of air, the high concentration was used to enhance potential effects of the carbon dioxide.

For the electrochemical characterization V – I curves were recorded and corrected by I – R drop measurements to compensate the ohmic losses in the measured potential. The V – I curves were recorded every 24 h. A characteristic parameter for the electrochemical performance of the anodes is the slope of the V – I curve (surface specific conductivity) as described in [19]. The electrochemical performance of the cathodes can be described in the same way.

Parallel to the electrochemical characterization, the CO_2 content of the gases was investigated by gas chromatography and the carbonate concentration in the electrolyte was determined after various operation times with CO_2 containing gases.

2.3. Physical characterization

In addition to the electrochemical experiments, electrodes were characterized by physical methods before and after operation. For this, the electrodes were split into several parts for the different applied characterization methods.

The electrodes were investigated by scanning electron microscopy (SEM) [43] to investigate the structure of the electrodes and the changes of the structure induced by the electrochemical stressing. In addition, the pore systems in the nickel anodes were investigated by nitrogen adsorption measurements [44]. The investigation of the pore systems of the cathodes with nitrogen adsorption results in low pore volume values for analysis and an investigation with mercury penetration is impossible due to the formation of amalgam. The chemical composition of the electrodes was mainly investigated by energy dispersive X-ray spectroscopy (EDX) [43] and additionally by X-ray photoelectron spectroscopy (XPS) [43]. By alternating steps of XP spectra measurement and ion etching of the surface, depth profiles were recorded.

Prior to the physical characterization all electrodes were rinsed with distilled water and dried. For XPS and nitrogen adsorption measurements, the electrodes were dried

in vacuum at elevated temperature. The specific sample preparation for the XPS measurements is described in more details in [19,23], the SEM/EDX equipment and equipment for nitrogen adsorption is described in [19].

3. Results

All investigated cathodes show very similar initial electrochemical performance. Also the electrochemical performance of the anodes are very similar, but they differ from the electrochemical performance of the cathodes. The electrochemical performance of the electrodes decreases during the electrochemical experiments.

Fig. 1 shows the electrochemical performance during the long-term experiments performed with the silver cathodes. The decrease of electrochemical performance for all cathodes are similar independent if the experiments were performed with pure or with CO₂ containing oxygen. This indicates that the carbon dioxide does neither influence the electrochemical performance nor accelerate the degradation process. The slope of the time-dependent electrochemical performance shows a decrease of 17 $\mu\text{V}/\text{h}$ for the cathode. Electrochemical impedance spectroscopy measurements recorded during a long-term experiment with silver cathodes in pure oxygen [27] have shown that the decrease of the electrochemical performance is induced by a decrease of the active surface and an increasing transport hindering [42]. The decrease of the electrochemical performance could be explained by alteration or decomposition of the PTFE. PTFE is necessary for the gas transport and influences the extension to the three phase zone [42].

Physical characterization methods are powerful tools in the investigation of degradation mechanisms and can detect degradation effects before their influence is obvious with decrease electrochemical performance in fuel cell operation [13,16,19,23,42]. Therefore, XPS measurements were performed after operation of the silver anodes for more than 2600 h. The element distribution in the depth profile measurements of the electrodes operated with pure and with CO₂ containing oxygen are equal. Especially, the carbon signal in the XP spectra is of interest, because the carbon dioxide can form carbonates which may be deposited on or in the electrodes. Fig. 2 shows the C1s spectra recorded during depth profile measurement of the electrodes. Two main peaks can be observed in both spectra. The C1s signal at higher binding energies (approximately 292 eV) is related to the carbon bounded in the PTFE, the carbon signal at a binding energy of approximately 285 eV is related to carbon black or carbon in CH_x configuration [45,46] and may be induced by organic impurities. The C in the carbonates should yield an signal in the binding energy range of 288–290 eV [45]. The C1s spectra of both electrodes, which were operated with pure oxygen and operated with CO₂ containing oxygen are identically. The increasing intensity during the depth profiling in the binding energy range, where the carbonate-induced signal would appeared, is also observed for the electrode operating with pure oxygen. This signal is related to the fluorine depleted PTFE fragments, which were formed by the radiation-induced decomposition of the PTFE [47,48]. The XPS investigations show that no carbonate was deposited on the cathodes, and no other degradation mechanisms were induced or enhanced on the AFC cathodes.

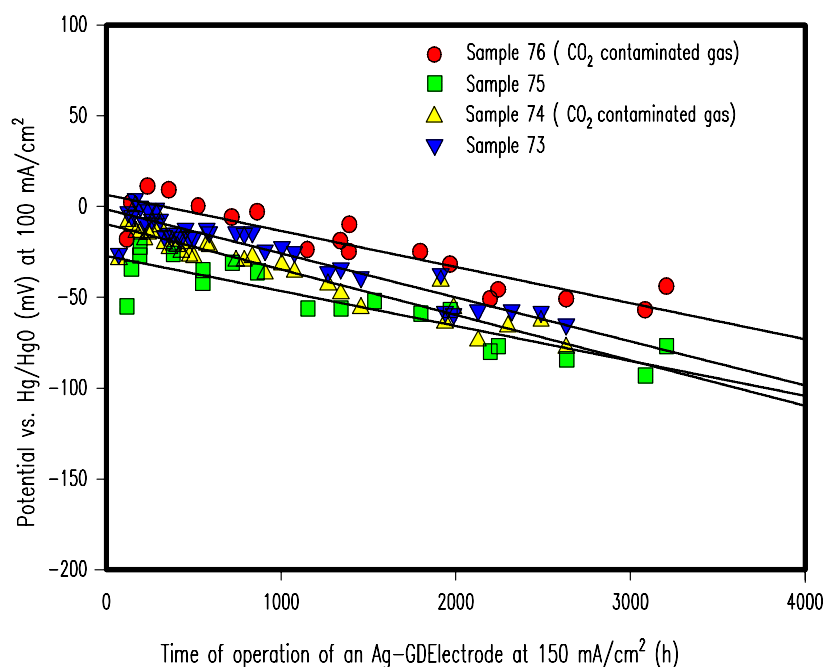


Fig. 1. Change of the electrochemical performance of the silver cathode during operation with pure oxygen and oxygen containing 5% CO₂.

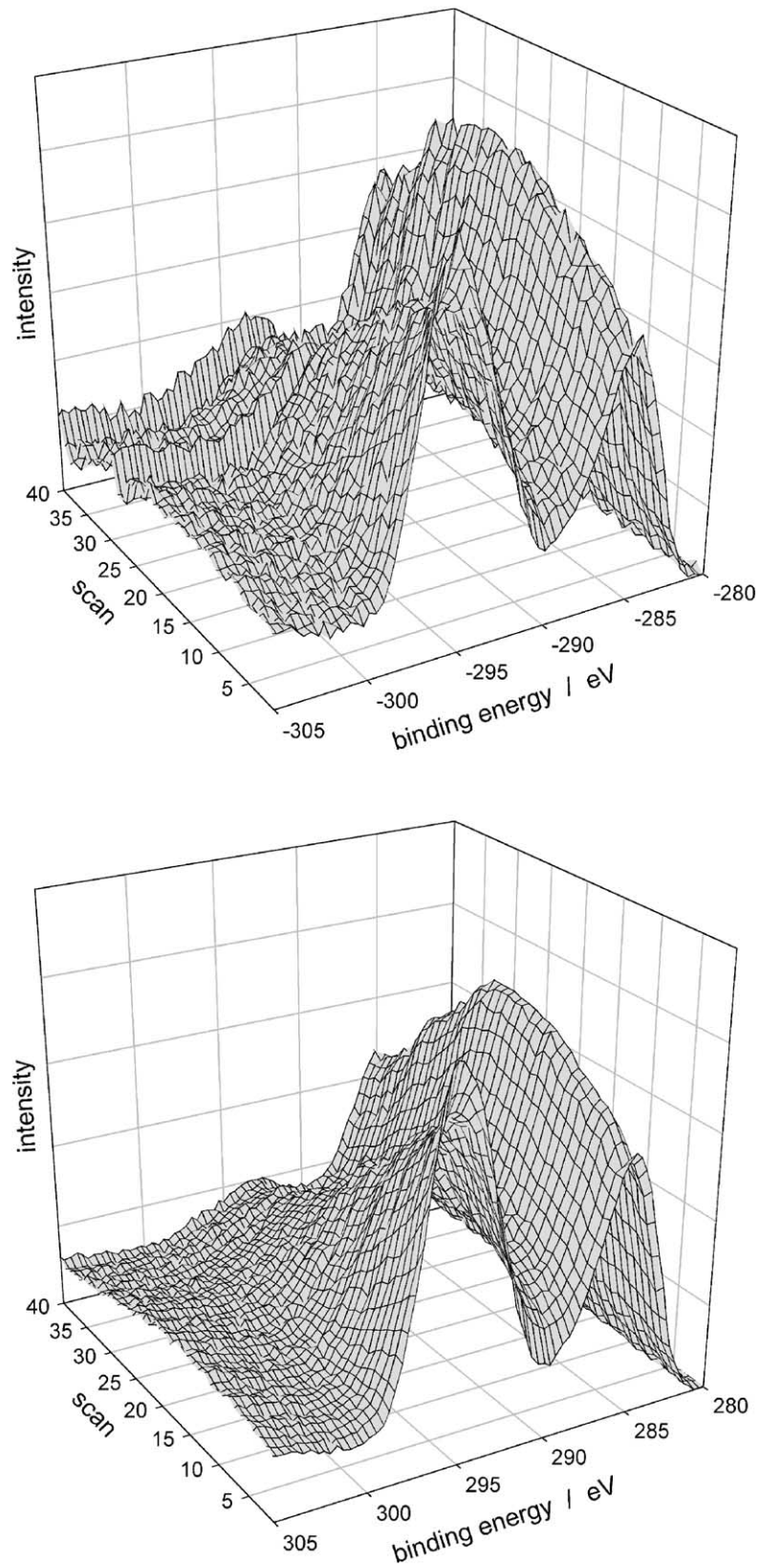


Fig. 2. XP spectra of the carbon C1s signal recorded during depth profile measurements of a cathode operating 2633 h with pure oxygen (on top) and of a cathode operating 2682 h with oxygen containing 5% CO₂.

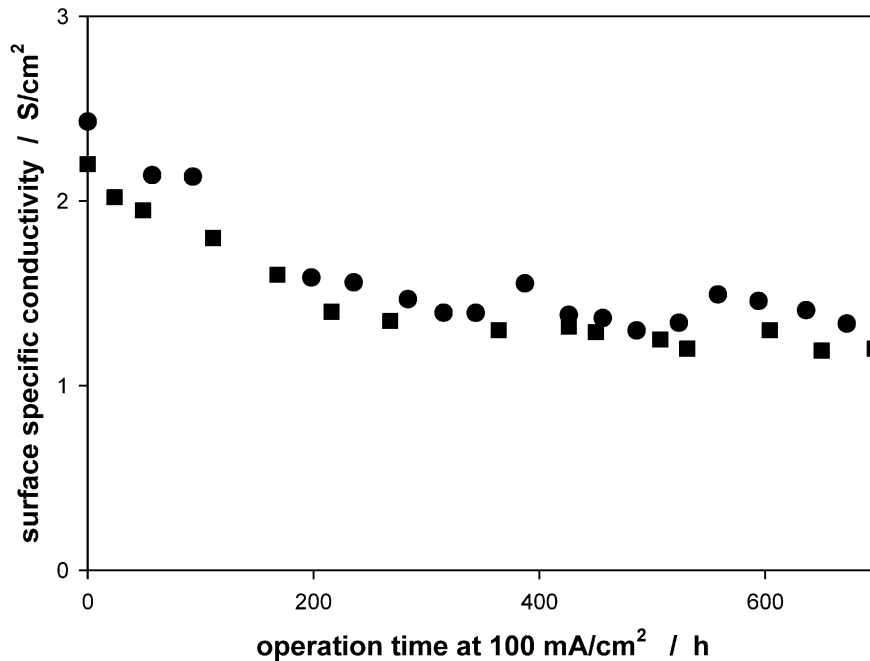


Fig. 3. Change of the electrochemical performance of the nickel anodes during operation with pure hydrogen (circles) and hydrogen containing 5% CO₂ (squares).

The decrease of the electrochemical performance of the anodes during operation with pure and CO₂ containing hydrogen is shown in Fig. 3. The electrochemical performance decreases as described in [19] under both operating conditions. The decrease is very similar; therefore the shape of decrease of the electrochemical performance does not indicate any influence of carbon dioxide.

The carbonate in the alkaline electrolyte forms CO₃²⁻ ions, which should be moved in the electrical field to the

anodes. Therefore, the investigation of the anodes is also necessary for the assessment of the CO₂ influence in AFC. If carbonates are deposited on the anode, they could close the pores in the electrode. Hence, the pore system and the specific surface of the nickel anodes were investigated by nitrogen adsorption measurements. Fig. 4 shows the specific surface area of anodes operated with pure hydrogen and with CO₂ containing hydrogen for various periods. Fig. 4 shows that the specific surface is nearly constant and no change

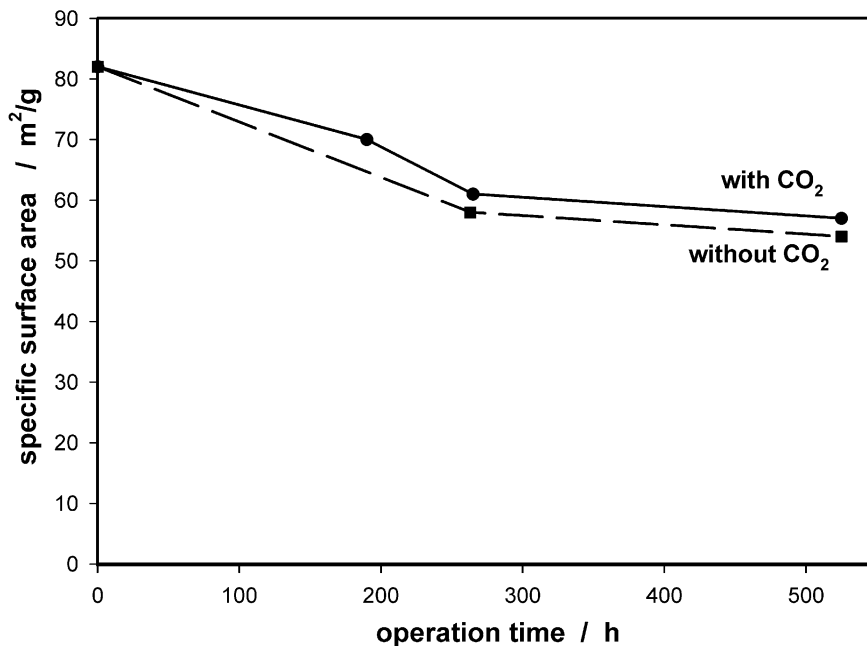


Fig. 4. Change of the specific surface area of the anodes after various times of operation with pure and with CO₂ containing gases.

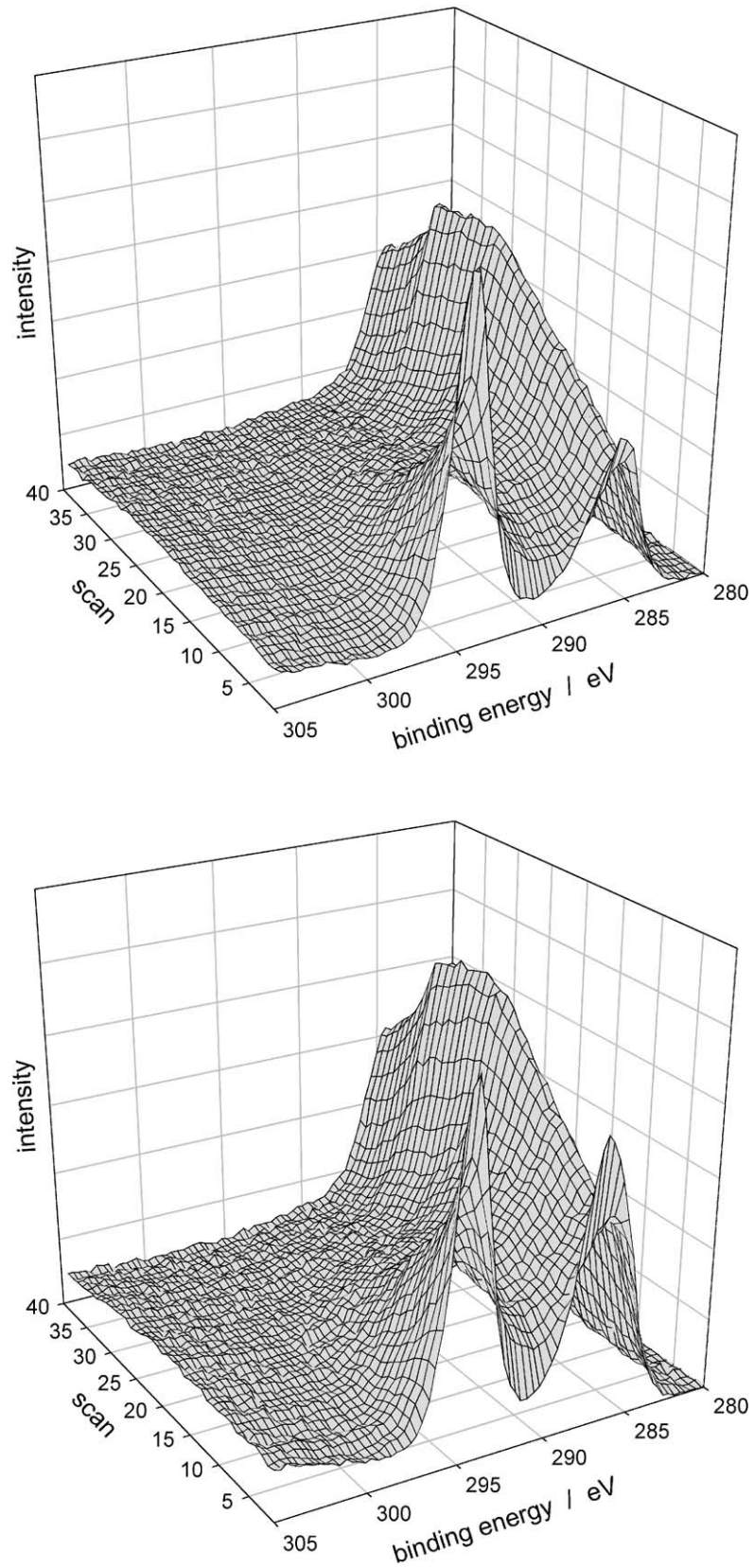


Fig. 5. XP spectra of the carbon C1s signal recorded during depth profile measurements of an anode operating 2633 h with pure hydrogen (on top) and of an anode operating 2682 h with hydrogen containing 5% CO₂.

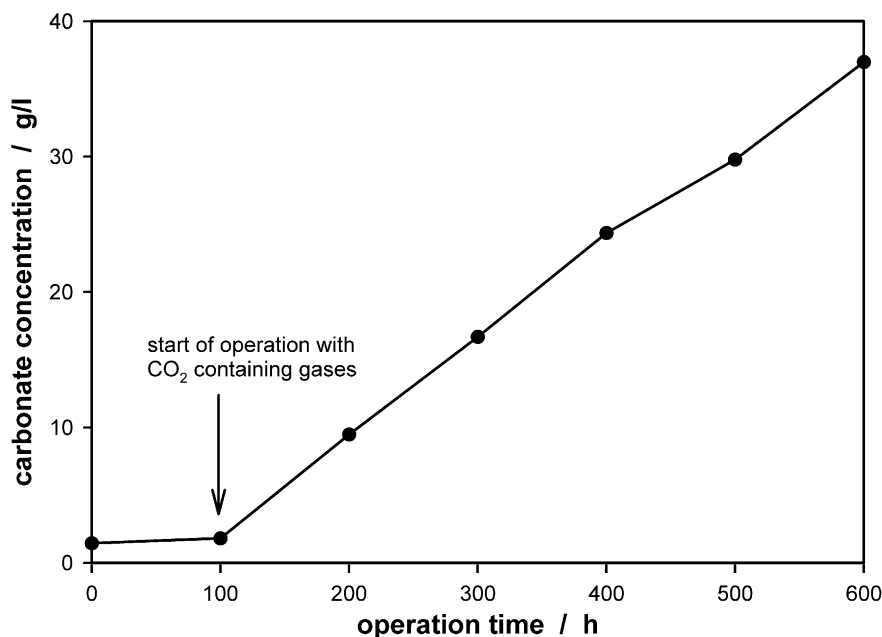


Fig. 6. Carbonate content in the electrolyte after various operation times with CO₂ containing gases.

induced by the carbon dioxide can be observed. Also in the pore size distribution only a maximum at 2 nm defined by the nickel catalyst can be observed, whereby the pore frequency depends on the operation time as displayed in Fig. 5 of [19] for the electrode named type 3 in this paper. The measurements show no effect caused by the CO₂.

In addition, anodes were investigated by XPS after operation over 2600 h in pure and in CO₂ containing hydrogen. Like the XPS analyzing of the silver cathode, also for the nickel anodes depth profiles were recorded. The depth profiles of both anodes are very similar. To show the effect of the carbon dioxide the C1s signals in the XP spectra recorded during depth profile measurements are displayed in Fig. 5. The spectra are very similar to the C1s spectra recorded during depth profile measurements of the cathodes. The same two carbon binding states can be observed in the spectra. In the change of the C1s spectra during the measurement the radiation-induced decomposition can be observed. The main difference in the spectra of the electrode running with pure hydrogen compared to the spectra of the electrode operated with CO₂ containing hydrogen is the initially higher C1s signal at lower binding energy. This carbon state is related to carbon in a CH_x configuration and not to carbonate, which would yield a signal at a binding energy of 288–290 eV. Therefore, like the XPS investigations on the cathode no deposited carbonate can be observed. The increased intensity at the binding energy of 285 eV must be related to other organic impurities and it cannot be explained why it is enhanced by the operation with CO₂ containing hydrogen.

In addition, SEM measurements were also performed for the electrodes operated with pure and CO₂ containing gases.

Like the porosimetry and the XPS measurements, no effects of the carbon dioxide were observed by SEM.

The electrochemical performance and the physical characterization of both, anodes and cathodes, show no significant influence of the carbon dioxide on the electrodes. The third electrochemical component in the AFC besides the two electrodes is the liquid electrolyte. Measurements of the CO₂ content in the residual gas by gas chromatography behind the fuel cell electrodes shows that the residual gas of the anode contains approximately 10% of the CO₂ in comparison to the feed gas and that the residual gas of the cathodes contains approximately 20% of feed gas. This indicates that most of the CO₂ are dissolved in the alkaline solution by forming K₂CO₃. Therefore, the carbonate concentration in the alkaline electrolyte increases as shown in Fig. 6. As expected, the carbonate concentration increases linearly during the operation time with CO₂ containing gases, whereby no difference between anode and cathode operation can be observed. In long-term experiments with increased K₂CO₃ concentration up to 450 g/l, the conductivity of the electrolyte is reduced but the electrodes are not effected. The solution limit of K₂CO₃ is between 50 and 60 wt.% in the temperature range used [49]. Therefore, in the shown experiments the solution limit was not reached.

4. Conclusions

The electrochemical performance and the decrease of the electrochemical performance of anodes as well of cathodes with the long-term experiments show no effect induced by CO₂. Only a decrease can be observed which is also

observed in long-term experiments with pure gases. In addition, the physical investigations of the electrodes show no effect or components caused by the carbon dioxide. Summarizing, the carbon dioxide content in the feed gases has no influence on the electrodes.

In contrast to the electrodes, the electrolyte is influenced by the supply of the electrodes with CO₂ containing gases. During operation with CO₂ containing gases the carbonate concentration increases linearly with operation time. 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 times higher CO₂ concentration of air. The electrodes were fully operable when terminating the long-term experiment. This operation time corresponds to an average time life of about 3000 h of internal combustion engines, whereby an electrolyte exchange after few hundred hours seem as acceptable, because of the fact that an electrolyte exchange is very simple.

Taking all the results into account, it must be concluded that the CO₂ in the air is not really a problem for AFCs, therefore AFCs can also be used for mobile applications. A real problem of the AFC is the normal long-term stability of the electrodes, the decrease of the electrochemical performance is presently too high. In contrast to the PEFC systems, the degradation mechanisms in the AFC components are much better understood and therefore the direction of research for the developing of long-term stable electrodes is clear.

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