

Chip integrated fuel cell accumulator

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Abstract

A unique new design of a chip integrated fuel cell accumulator is presented. The system combines an electrolyser and a self-breathing polymer electrolyte membrane (PEM) fuel cell with integrated palladium hydrogen storage on a silicon substrate. Outstanding advantages of this assembly are the fuel cell with integrated hydrogen storage, the possibility of refuelling it by electrolysis and the opportunity of simply refilling the electrolyte by adding water. By applying an electrical current, wiring the palladium hydrogen storage as cathode and the counter-electrode as anode, the electrolyser produces hydrogen at the palladium surface and oxygen at the electrolyser cell anode. The generated hydrogen is absorbed by the palladium electrode and the hydrogen storage is refilled consequently enabling the fuel cell to function.

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1. Introduction

The chip integrated fuel cell accumulator is a new approach to implement a rechargeable microenergy source on a silicon substrate. Miniaturising all the components of a microsystem is mandatory in order to realise energy self-sufficient microsystems that are, for example, nodes of sensor network projects such as “e-grain” or “smart dust” [1,2]. However, all components of autonomous microsystems except the power supply have been miniaturised in the past few years. Accordingly, scaling down conventional batteries causes various problems. The most common technology, the lithium ion accumulator, has to be sealed hermetically since intruding ambient air or humidity causes failure of the device [3,4]. Additionally the lithium compounds are toxic. Other energy systems like the nickel metal hydride batteries are utilising caustic potash solution. This corrosive medium is harmful and in addition to that incompatible to the silicon substrate because silicon is solubilised by this base.

By developing chip integrated fuel cells, a CMOS-compatible microenergy system was invented that complies with all requirements of being reducible in size for the integrated use in an autonomous microsystem [5]. Since the fabrication process of the system is CMOS-compatible a large-scale production is possible, for example, in a MEMS foundry. Besides its numerous benefits the chip integrated fuel cell has a major disadvantage; its functional principle is similar to that of primary batteries. In fact, the entire microsystem including the chip integrated fuel cell which powers the system is not rechargeable and has to be replaced after the hydrogen storage is empty.

Consequently within the scope of this project it was planned to eliminate this weak spot in the chip integrated fuel cell conception. Our approach was to additionally integrate an electrolyser cell creating a chip integrated fuel cell accumulator. By implementing this extension the chip integrated microenergy system acquires the ability to recharge the hydrogen storage. The schematic set up of the fuel cell accumulator is displayed in Fig. 1. Simplifying the fuel cell accumulator’s development process, the realisation was not planned as an enhancement of the CMOS process on the silicon substrate. The chip integrated fuel cell’s assembly with CMOS-compatible clean room processes implies various expensive and time-consuming fabrication steps.

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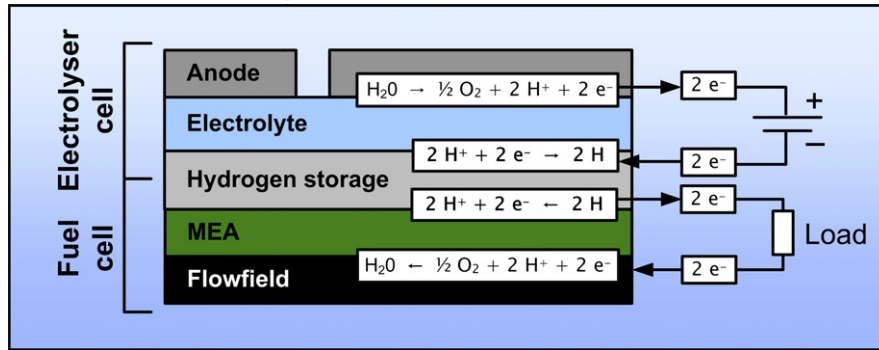


Fig. 1. Principle set-up of the fuel cell accumulator.

Reducing the development time and expenses the first stage laboratory prototype of the fuel cell accumulator was designed as a macroscopic system.

2. Experimental

2.1. Proof of principle—macroscopic fuel cell accumulator

In order to analyse and confirm the accumulator principle the fabrication was constructed and realised utilising simplified, conventional tooling methods.

2.1.1. The set-up of the macroscopic fuel cell accumulator

The accumulator was set up as a stack design; all the components have a diameter of 20 mm and a thickness in the range of 20 μm to 2 mm. The macroscopic set-up components' principle assembly, the electrolyser cell anode with integrated electrolyte reservoir as well as the aluminium oxide isolator, the palladium hydrogen storage, the polymer electrolyte membrane and the graphite flow field are illustrated (Fig. 2.). For both set-ups, the macroscopic and the chip integrated, the same materials were

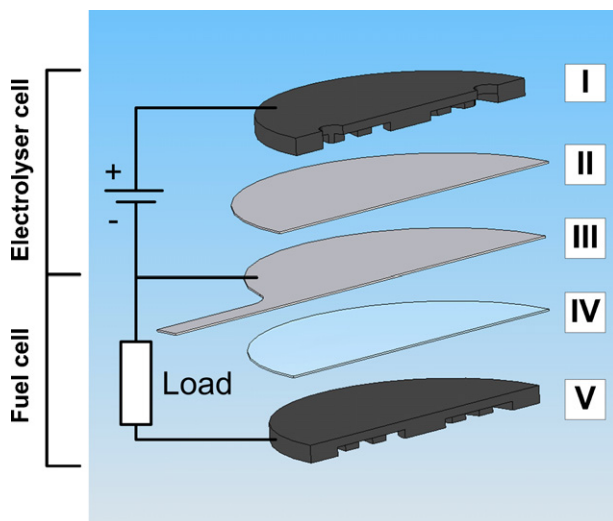


Fig. 2. Sectional view of the macroscopic fuel cell accumulator: electrolyser cell anode with integrated electrolyte reservoir (I), aluminium oxide isolator (II), palladium hydrogen storage (III), polymer electrolyte membrane (IV) and graphite flow field (V).

utilised as far as possible to assure the ability to transfer the experimental experiences and results. Thus, the hydrogen storage material, the electrolyte to recharge the fuel cell accumulator, the composition of the polymer electrolyte membrane and the fuel cell anode catalyst are identical in both systems. The hydrogen storage was cut out of a 100 μm thick palladium metal sheet by WEDM. The electrolyser cell anode was fabricated by CNC milling out of a 2-mm thick graphite plate. Additionally, a cavity to store the electrolyte was milled out of the electrolyser cell anode. Ensuring electrical isolation between the electrolyser's electrodes an interjacent porous aluminium oxide plate was used. The electrolyser cell was assembled using a polymer blend solution. The features of this polymer blend solution were optimised with regard to high proton conductivity and good adhesion to the electrodes.

This polymer blend solution was reused for the fabrication of the fuel cell's polymer electrolyte membrane. By CNC milling the graphite flow field was fabricated. Activating the flow field catalytically platinum particles were sprayed onto it. By pressing the flow field onto the polymer film the membrane electrode assembly (MEA) of the fuel cell was completed. Completing the set-up of the macroscopic fuel cell accumulator electrolyte, consisting of 0.1 M sulphuric acid, was filled into the cavity of the electrolyser cell anode.

2.1.2. Operating the macroscopic fuel cell accumulator

The measured mass of the accumulator's palladium hydrogen storage was $m_{\text{Pd}} = 368.4 \text{ mg}$. The standard atomic weight of palladium is $M_{\text{Pd}} = 106.42 \text{ g mol}^{-1}$, this correlates to an amount of palladium $n_{\text{Pd}} = 3.46 \text{ mmol}$ (Eq. (1)).

$$n_{\text{Pd}} = \frac{m_{\text{Pd}}}{M_{\text{Pd}}} = \frac{368.4 \text{ mg}}{106.42 \text{ g mol}^{-1}} = 3.46 \text{ mmol} \quad (1)$$

Utilizing Avogadro's constant $N_{\text{A}} = 6.02 \times 10^{23}$ the quantity of palladium atoms is 2.08×10^{21} (Eq. (2)).

$$\begin{aligned} N_{\text{Pd}} &= n_{\text{Pd}} N_{\text{A}} \\ &= 3.46 \text{ mmol} \times 6.02 \times 10^{23} \\ &= 2.08 \times 10^{21} \text{ palladium atoms} \end{aligned} \quad (2)$$

Since the maximum amount of hydrogen that can be incorporated within the palladium lattice is $\text{H/Pd} = 0.8$ [4], the

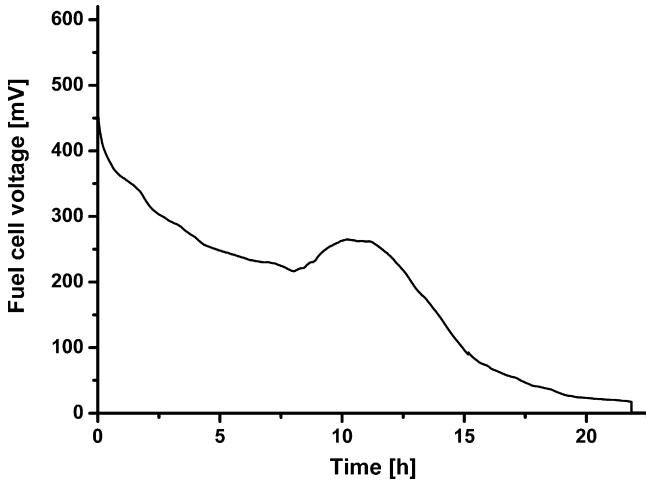


Fig. 3. Voltage graph of the macroscopic fuel cell accumulator discharged with a load of 330 Ω.

amount of hydrogen that can be stored within the palladium sheet is 1.66×10^{21} hydrogen atoms. Assuming each electron of the charge current generates a hydrogen atom that is incorporated within the palladium 1.66×10^{21} electrons are needed for the accumulator's full charge. Generating an amount of $n_e = 1.66 \times 10^{21} e^-$ using the elementary charge of $1.602 \times 10^{-19} C$ per electron, this amount of electrons is equivalent to an electric charge of 267.08 C (74.19 mAh) (Eq. (3)).

$$Q = n_e \times e$$

$$= 1.66 \times 10^{21} \times 1.602 \times 10^{-19} C = 267.08 C \quad (3)$$

Atomic fractions of hydrogen incorporated within the palladium higher than $H/Pd=0.5$ are causing plastic deformation of the palladium sheet. Avoiding delamination of the macroscopic fuel cell accumulator a maximum state of charge of 80 C ($H/Pd=0.25$) was determined. Additionally, the formation of hydrogen bubbles at the palladium surface has to be avoided during the charge process since these bubbles also cause delamination. Preventing bubble formation, charge current densities have to be lower than $1 mA cm^{-2}$. Since the active surface area of the palladium electrode is $3.14 cm^2$ a charge current of 2.5 mA was predefined. The charge time of the macroscopic fuel cell accumulator was 8 h. The generated electric charge resulted in 72 C (20 mAh). Afterwards the macroscopic fuel cell accumu-

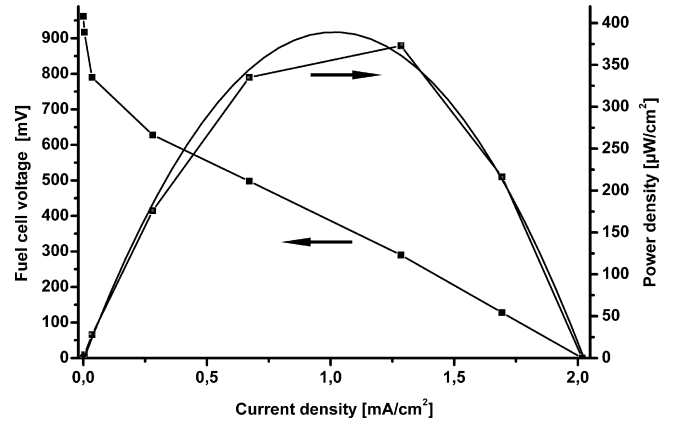


Fig. 4. Polarisation and power density plot of the macroscopic fuel cell accumulator.

lator was discharged using a load of 330 Ω. The graph of the recorded fuel cell voltage is shown in Fig. 3. By integration of the generated current flow during the discharge process an electric charge of 46.8 C (13 mAh) could be deduced. The over all charge efficiency (quotient of recovered charge by the fuel cell and the deployed charge during the charge process) of this non-optimised, tentative fuel cell accumulator stack is 65%. Afterwards an electrical characterisation of the set-up was performed. The results are displayed in Fig. 4. Therefore the macroscopic fuel cell accumulator could be proved as a rechargeable energy source and the working principle could be verified.

2.2. Proof of concept—chip integrated electrolyser

The promising result gained by the characterisation of the macroscopic fuel cell accumulator showed up this set-up principle's potential and encouraged the miniaturisation of the electrolyser. As shown in Fig. 5 the chip integrated electrolyser and the chip integrated fuel cell have one component in common, the metal hydrogen storage that consists of palladium is the connecting piece between the fuel cell and the electrolyser cell. The palladium hydrogen storage functions as the cathode of the electrolyser cell and the anode of the fuel cell. Therefore, the electrolyser part of the chip integrated system including the palladium hydrogen storage was planned and fabricated with CMOS-compatible processes. Proving the feasibility of the chip integrated charge concept the chip integrated electrolyser also prepares the planned combination with the chip integrated fuel cell.

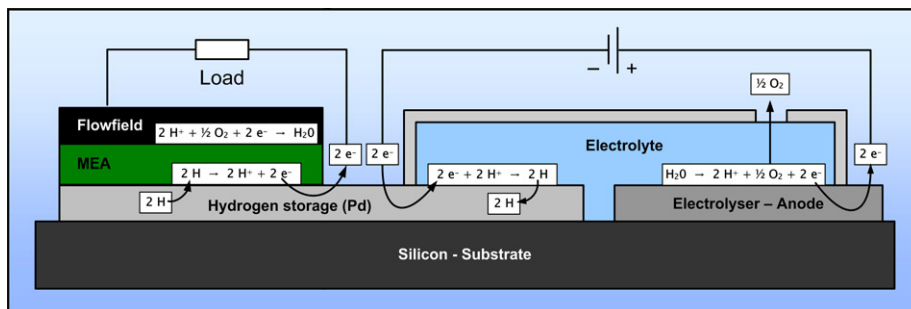


Fig. 5. Schematic set-up of the chip integrated fuel cell accumulator.

2.2.1. The set-up of the chip integrated electrolyser

The chip integrated electrolyser's design comprises two stages: clean room processing to fabricate metallic layers as well as the fluidic structures and laboratory assembly steps to complete the set-up.

Clean room fabrication steps: A 500 nm thick palladium layer, functioning as hydrogen storage, was deposited by physical vapour deposition (PVD) and structured by lift-off technique. The gold tracks that electrically connect the palladium cathode and the electrolyser's platinum anode were also structured by lift-off processes. In order to conduct electrolyte to the electrolyser cell's electrodes a frame for mounting the electrolyte reservoir chip was fabricated utilising a lithographic SU-8-process. The SU-8 resin was applied to the wafer by a spin-coating process and structured by UV-lithography. Concluding the clean room work the wafer was diced into single accumulator chips since the subsequent fabrication steps are serial, non-standard processes accomplished outside the clean room. The dimensions of the clean room processed electrolyser chip are 19 mm × 19 mm × 0.5 mm.

Laboratory assembly steps: The electrolyte reservoir chip that is mounted on top of the SU-8 structures was fabricated by a CNC milling process. A cavity was milled into the PMMA chip that forms the reservoir which conducts the electrolyte to the electrolyser cell's electrodes. Avoiding the electrolyte's depletion during the measurement electrolyte was continuously pumped through the chip. For this purpose two holes were drilled into the chip that serve as an in- and out-flow of the electrolyte. Mounting the electrolyte reservoir chip onto the SU-8 structures and attaching the electrolyte pump to the chip the set-up of the chip integrated electrolyser was completed.

2.2.2. Monitoring the state of charge of the hydrogen storage

The resistance of the palladium layer is a function of the atomic fraction of hydrogen incorporated within the palladium, the loading ratio H/Pd [6]. Therefore the state of charge of the palladium hydrogen storage can be determined by a resistive measurement. The square shaped palladium layer was connected by gold tracks deposited by physical vapour deposition processes. Minimizing the electrolyte concentration's influence during the experiments a continuous flow of electrolyte by an external pump was realised. The palladium layer's quiescent resistance R_0 was measured for a period of 1 min, its mean value was 8.255 Ω. Subsequently charging of the palladium layer was started, a constant current of 150 μA was applied and the change of resistance was monitored. The resistance curve ascends steeply within minutes since all the generated hydrogen is absorbed by the palladium hydrogen storage. Afterwards a flattening of the curve can be observed. The palladium hydrogen storage is almost completely charged, only small amounts of hydrogen are still being incorporated. Having reached a stationary state of charge the charge process was stopped. Due to diffusion processes, the hydrogen escapes out of the palladium layer causing the measured resistance's decline. Reaching a constant resistance level after the discharge process a new charge cycle was started. Typical charge and discharge cycles

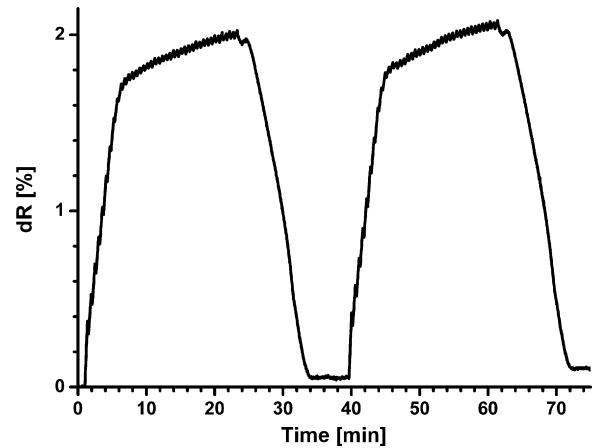


Fig. 6. Ohmic resistance variations during two charge and discharge cycles of the chip integrated electrolyser.

(Fig. 6) and the whole measurement graph with more than 200 accomplished cycles (Fig. 7) are displayed. The typical shape of the charge and discharge curve is congruent, but the resistance's absolute level, the level of the quiescent resistance R_0 , shows a growing tendency. Formation of stress-induced cracks in the palladium layer was the assumed reason for the ascending resistance values. After finishing the charge discharge cycles the surface of the palladium layer was examined by scanning electron microscopy (SEM). As shown in Fig. 8 the formation of cracks in the palladium surface is obvious. Thus the suspected reason for the ascending resistance values could be proved. In spite of the stress-induced cracks in the palladium layer no delamination between the hydrogen storage and the silicon wafer or corrosion of the electrolyser's electrodes could be observed. Thus the long-term stability of the chip integrated electrolyser components could be demonstrated. Since the typical shape of the resistance curve is constant, a state of charge sensor can be implemented into the system. Finally, hydrogen generation at the surface of the palladium and incorporation of hydrogen within the palladium layer could be verified.

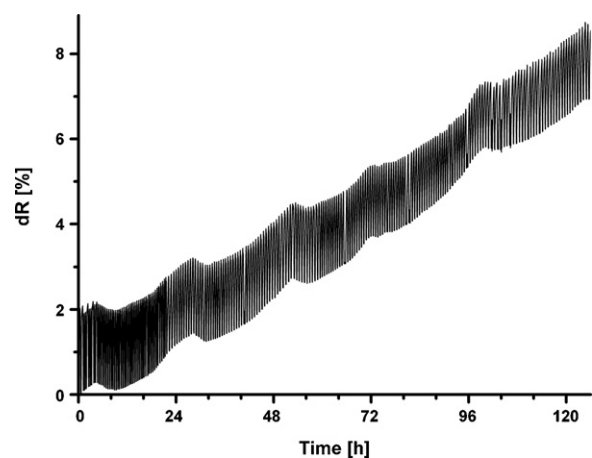


Fig. 7. Measurement graph of ohmic resistance variations during more than 200 charge and discharge cycles of the chip integrated electrolyser.

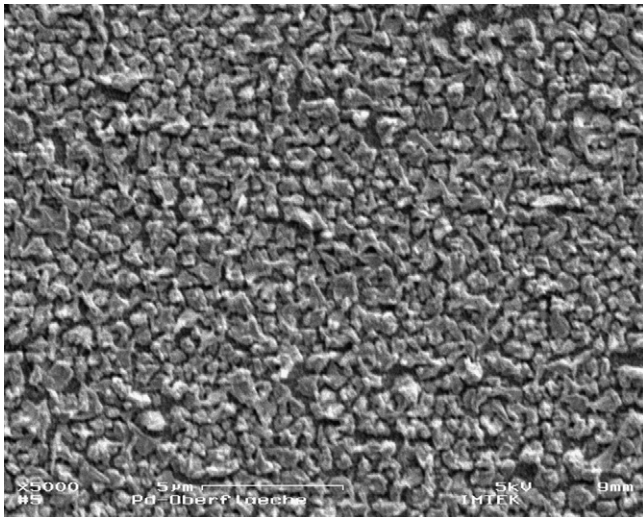


Fig. 8. SEM image of the palladium surface after completion of charge and discharge cycling tests.

2.3. Setting-up a laboratory prototype accumulator

The realisation of a simplified chip integrated fuel cell accumulator based on the chip integrated electrolyser's set-up with vapour deposited thin film palladium hydrogen storage was designed and fabricated.

Clean room fabrication steps: According to the process steps described in Section 2.2.1 the chip integrated electrolyser was fabricated. Furthermore, the SU-8 process was modified, in addition to the electrolyte reservoir's frame capillary structures that conduct electrolyte to the electrodes were implemented. Since the fuel cell's components are sensitive structures the dicing of the silicon wafer was accomplished before setting up the fuel cell. The dimensions of the diced clean room processed chip are $19\text{ mm} \times 19\text{ mm} \times 0.5\text{ mm}$. Fabricating the fuel cell's polymer electrolyte membrane (PEM) the polymer blend solution as described in Section 2.1.1 was utilised. The solution was applied to the palladium surface by a dispensing machine. Curing the polymer electrolyte membrane the film formation was thermally initiated. A clean room processed chip integrated fuel cell accumulator is displayed in Fig. 9.

Laboratory assembly steps: Having completed the clean room processing, the electrolyte reservoir chip was mounted on top of the SU-8 structures. This PMMA chip was fabricated by CNC milling. Realising an electrolyte storage capacity of 30 mm^3 a cavity was cut into the $8\text{ mm} \times 5\text{ mm} \times 3\text{ mm}$ sized chip. Additionally three openings were drilled into the chip enabling feeding of the electrolyte and the outlet of evolving oxygen and hydrogen gas. In order to enhance the polymer electrolyte membrane's proton conductivity it was activated by immersing the whole chip in 1 M sulphuric acid at 80°C . Afterwards the fuel cell accumulator chip was dried and the fuel cell part of the accumulator was set up. The fuel cell's flow field was cut out of a carbon fleece. Catalytically activating the cathode of the fuel cell the flow field's surface that contacts the polymer electrolyte membrane was coated with platinum particles. The flow field was positioned on the polymer electrolyte membrane completing

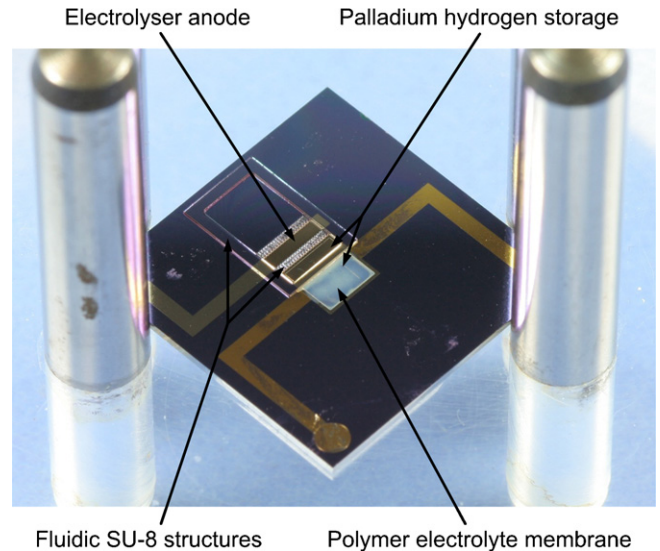


Fig. 9. Clean room processed laboratory prototype of the chip integrated fuel cell accumulator (chip dimensions: $19\text{ mm} \times 19\text{ mm} \times 0.5\text{ mm}$).

the membrane electrode assembly (MEA) of the fuel cell. Completing the laboratory prototype's set-up the electrolyte reservoir chip was filled with 0.1 M sulphuric acid. In Fig. 10 an unfilled laboratory prototype of the chip integrated fuel cell accumulator is shown.

2.3.1. Enhancements for the next generation prototype chip integrated fuel cell accumulator

Due to the prototype's set-up direct contact of the electrolyte with the palladium surface could not be avoided. However wetting of the palladium surface, as shown by experiments [7], increases hydrogen diffusion out of the palladium layer by orders of magnitude. Therefore the active area of the hydrogen storage, forming fuel cell anode and electrolyser cathode, has to be completely covered by the polymer electrolyte membrane. Hindering

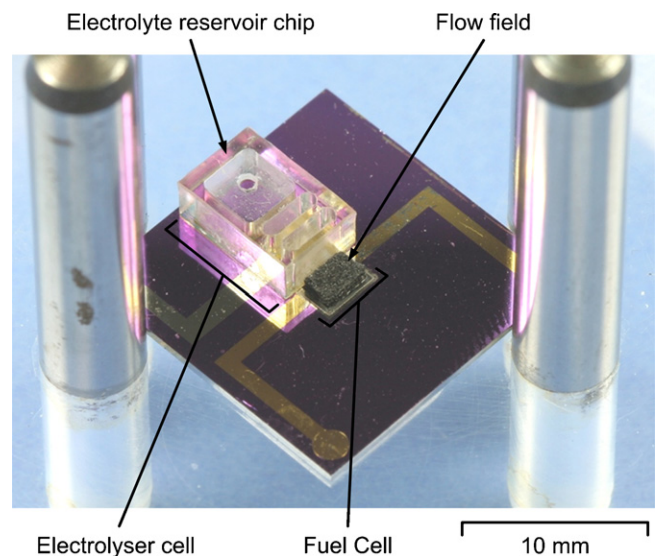


Fig. 10. Completed laboratory prototype of the chip integrated fuel cell accumulator (chip dimensions: $19\text{ mm} \times 19\text{ mm} \times 3.5\text{ mm}$).

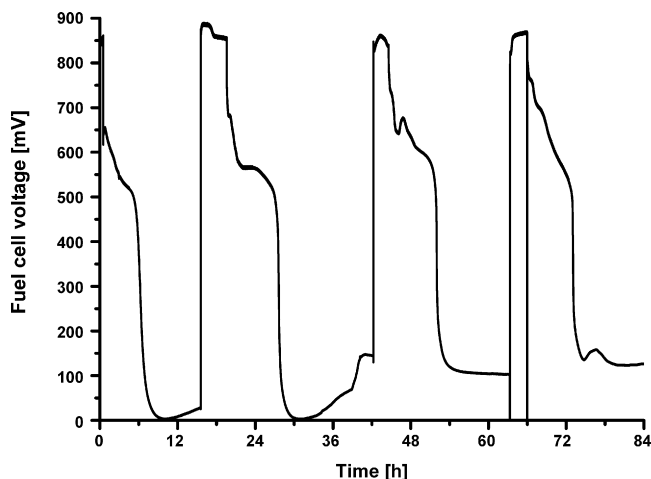


Fig. 11. Open circuit voltage graph of the chip integrated fuel cell accumulator laboratory prototype.

the unused escaping of hydrogen to the environment the incorporated hydrogen within the palladium hydrogen storage will only be consumed actively by the fuel cell.

Additionally the built-in optimisations of the chip integrated fuel cell will also be implemented into the chip integrated fuel cell accumulator set-up. On the backside of the chip integrated fuel cells hydrogen storage diffusion barriers were deposited. These hydrogen diffusion barriers avoid escaping of hydrogen due to diffusion through the silicon substrate. A further optimisation already implemented into the chip integrated fuel cell is the palladium hydrogen storage with a thickness of 100 μm . This palladium layer was deposited by electroplating in an etched cavity of the silicon substrate. Since the hydrogen storage capacity scales proportionally with the thickness of the layer this enhancement offers the potential of significantly increasing the runtime of the chip integrated fuel cell accumulator.

The laboratory prototype's fuel cell is built as a hybrid set-up. The cathode of the fuel cell is set up by spray coating of platinum particles onto a flow field carbon fleece. The fuel cell is assembled by positioning this conventionally fabricated component onto the polymer electrolyte membrane. Electrical contacting of the fuel cell's cathode up to now is realised by a spring contact. Implementing the deposition of catalyst layer and cathode current collector by clean room processes makes the flow field redundant and results in a more reproducible and increased fuel cell performance. Additionally this process offers the ability of directly connecting the fuel cell's cathode to the surface of the semiconductor substrate. Therefore the monolithic integration of chip integrated fuel cell accumulator and CMOS technology on a single silicon chip is made possible.

2.3.2. Operating the laboratory prototype accumulator

Utilising a constant current source the fuel cell accumulator was charged with the electrolyser by a current of 30 μA . The prototype's palladium layer size is 4 mm \times 4 mm \times 0.001 mm. Since the density of palladium is 12.02 g cm^{-3} this volume of palladium is equivalent to 192.3 μg . In theory, such mass of pal-

ladium has the ability of storing an electrical charge of 139.4 mC (38.7 μAh) at an atomic fraction of H/Pd = 0.8 (see calculation in Section 2.1.2). Neglecting hydrogen losses during the charge process the charging of the palladium hydrogen storage would be completed after 78 min. The palladium storage was charged for several hours, assuming the storage was fully loaded. Afterwards the open circuit voltage was measured, each measurement showed a reproducible voltage characteristic. The recorded voltage graph of the prototype is shown in Fig. 11. While charging the accumulator the fuel cell's open circuit voltage reached a level of 850–900 mV. Having finished the charge process open circuit voltage declined to a level above 500 mV which could be measured for up to 8 h. Although the optimisations mentioned in Section 2.3.1 were not yet implemented in the first generation laboratory prototype the achieved runtime of the device showed up promising results.

3. Conclusion

The development process of novel kind of chip integrated microenergy system was described. As proof of principle the design, fabrication and characterisation of a macroscopic fuel cell accumulator was realised. This tentative set-up revealed a charge efficiency of 65%. Therefore evidence was provided that the fuel cell accumulator principle is working. These promising results encouraged the realisation of a chip integrated electrolyser. The electrolyser components including a palladium thin film, functioning as metal hydrogen storage, were fabricated on a silicon substrate. By resistive measurements the concept of generating hydrogen at the palladium surface and the hydrogen's incorporation within the palladium layer could be verified. The chip integrated electrolyser further on was utilised to prove the long-run stability of the set-up. Having accomplished more than 200 charge and discharge cycles no corrosion or delamination of the electrolyser electrodes could be observed. Combining a thin film electrolyser and a self-breathing polymer electrolyte membrane fuel cell a first generation laboratory prototype of the chip integrated fuel cell accumulator was realised. The performed electrical characterisations showed up promising results. Therefore proof of concept for the realisation of a novel kind of chip integrated microenergy system could be adduced.

4. Outlook

Integrating the above-mentioned enhancements already implemented in the chip integrated fuel cell a significant improvement in runtime and electrical performance of the microenergy system is expected. The next step will be the set-up and the detailed electrical characterisation of the chip integrated fuel cell accumulator's second generation laboratory prototype. Prospectively the combination of a miniaturised energy harvesting device and a CMOS compatibly fabricated chip integrated fuel cell accumulator creates a microenergy system with high energy density and long lifetime. Such a novel microenergy system would open up the possibility of realising energy self-sufficient autonomous microsystems.

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References

- [1] B. Warneke, in: M. Ilyas, I. Mahgoub (Eds.), *Smart Dust: Sensor Network Applications, Architecture and Design, Miniaturizing Sensor Networks with MEMS*, CRC Press, 2006, pp. 5-1–5-15.
- [2] M.J. Wolf, R. Schacht, H. Reichl, The “e-Grain” Concept, *Building Blocks for Self-Sufficient Distributed Microsystems*, vol. 58, *Frequenz*, 2004.
- [3] B.J. Neudecker, N.J. Dudney, J.B. Bates, *J. Electrochem. Soc.* 147 (2) (2000) 517–523.
- [4] N.J. Dudney, *Mater. Sci. Eng. B* 116 (2005).
- [5] Erdler, et al., *Sens. Actuators A* 132 (2006) 331–336.
- [6] Y. Sakamoto, K. Takai, I. Takashima, M. Imada, *J. Phys.: Condens. Matter* 8 (1996) 3399–3411 (Nr. 19).
- [7] L. Grasjö, G. Hultquist, K.L. Tan, M. Seo, *Appl. Surf. Sci.* 89 (1995) 21–34.