

Design and fabrication of miniaturized PEM fuel cell combined microreactor with self-regulated hydrogen mechanism

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Abstract. In this work we present the design and fabrication of the miniaturized PEM fuel cell combined microreactor system with hydrogen regulation mechanism and testing of prototype microreactor. The system consists of two components (i) fuel cell component and (ii) microreactor component. The fuel cell component represents the miniaturized PEM fuel cell system (combination of screen printed fuel cell assembly and an on-board hydrogen storage medium). Hydrogen production based on catalytic hydrolysis of chemical hydride takes place in the microreactor component. The self-regulated hydrogen mechanism based on the gaseous hydrogen produced from the catalytic hydrolysis of sodium borohydride (NaBH_4) gets accumulated as bubbles at the vicinity of the hydrophobic coated hydrogen exhaust holes. When the built up hydrogen bubbles pressure exceeds the burst pressure at the hydrogen exhaust holes the bubble collapses. This collapse causes a surge of fresh NaBH_4 solution onto the catalyst surface leading to the removal of the reaction by-products formed at the active sites of the catalyst. The catalyst used in the system is platinum deposited on a base substrate. Nickel foam, carbon porous medium (CPM) and ceramic plate were selected as candidates for base substrate for developing a robust catalyst surface. For the first time the platinum layer fabricated by pulsed electrodeposition and dealloying (EPDD) technique is used for hydrolysis of NaBH_4 . The major advantages of such platinum catalyst layers are its high surface area and their mechanical stability. Prototype microreactor system with self-regulated hydrogen mechanism is demonstrated.

1. Introduction

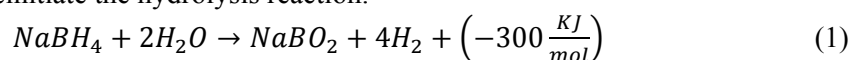
Though there are existing research understanding in the field of low temperature Proton Exchange Membrane (PEM) fuel cell for small scale portable or stationary applications, the main reason which hinders its commercialization is the fuel source (hydrogen, H_2). PEM fuel cell driven with H_2 paves the way for an energy source which can operate as a primary source or as secondary sources in combination with batteries. Speaking about the low temperatures fuel cell systems there are acidic and alkaline fuel cell systems. PEM fuel cells belong to the acidic fuel cell category where the redox reaction of hydrogen-oxygen happens at the anode and cathode forming electricity, water and heat. Protons are transported through the PEM layer and the electrons are transported across the external circuit. H_2 driven PEM fuel cell system provides many advantage over batteries in terms of increased energy density, instant recharge eco friendliness. As mentioned before the H_2 fuel storage is still an existing challenge from an engineering stand point. There are various H_2 storage techniques



available such as, compressed hydrogen gas (700 bar), liquefied hydrogen (approximately -200 °C), adsorption on metal organic frameworks (MOFs), reformation of hydrocarbons and metal-chemical hydrides. The possibilities of using the first two options are ruled out for portable applications due to its practical feasibility. The above mentioned other possibilities are extensively researched from both engineering and material stand points. Recently many works have been reported with on-board hydrogen generation as reliable alternates for the hydrogen fuel storage for PEM fuel cells which can be adapted in portable applications. The on-board hydrogen generation is based on metal hydrides and chemical hydrides. The metal hydride (also intermetallic compounds and alloys) represent the materials that can form metal-hydrogen compounds. This attributed to very specific lattice structure and the electronegativities of the element. The hydrogenation (adsorption) and dehydrogenation (desorption) process are reversible making them very attractive for portable applications. It is known that hydrogen actively reacts with metals at elevated temperature forming hydrides and these metals are called transition metals. Palladium is well-known for its hydrogen adsorption-desorption behaviour at ambient temperature and low pressures of hydrogen (1 bar) forming palladium hydride which is represented as $\text{PdH}_{0.7}$. Other intermetallic compounds and alloys such as TiFe , CeNi_3 , TiMn_2 and LaNi_5 are also been studied in order to adapt them for low temperature portable applications. The term chemical hydride is general representation which is further sub classified as following [1]

- binary saline hydrides: NaH , CaH_2 , MgH_2
- aluminium-based complex hydrides: LiAlH_4 , NaAlH_4
- boron-based complex hydrides: LiBH_4 , KBH_4 , NaBH_4

One of the most preferred chemical hydride is NaBH_4 due to its high stability at ambient atmosphere, capability to produce hydrogen at ambient conditions, relatively low exothermic in nature when compared to other hydrides and its eco friendliness. The hydrolysis reaction of NaBH_4 is shown in equation (1). The stoichiometric amount of hydrogen that can be generated according to equation (1) is 10.8 mass%. The self-hydrolysis of NaBH_4 is controlled by increasing the pH of the solution and then using an active catalyst to reinitiate the hydrolysis reaction.



The other mentioned hydrides are very unstable at ambient air which has significant risk in handling. It is worthwhile mentioning one other hydride which has gained significant interest; MgH_2 due to its stability at ambient air. A novel approach was presented with PEM fuel cell integrated palladium based hydrogen storage and an air breathing cathode fabricated on a silicon substrate [2]. The difference between the conventional PEM fuel cells and the chip integrated fuel cell accumulator is the absence of the gas diffusion layers and flow fields, which eventually leads to a simplified system design and easy fabrication. One other major advantage of such system is the ability to integrate CMOS for regulation of the output voltage. Figure 1 shows a fully fabricated chip integrated fuel cell accumulator.

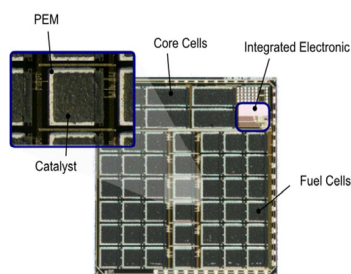


Figure 1. Chip integrated fuel cell accumulator with on-board palladium based H_2 storage and integrated CMOS electronics.

In the above mentioned system the PEM layer and the cathode layers were screen printed whereas the palladium layer was realized by sputtering and electroplating process. Major drawback of this system is the limited run time of the system which is due to the amount of hydrogen stored in the palladium. Simply increasing the layer thickness of bulk palladium causes irreversible damage to the substrate

due to the volumetric expansion of palladium on hydrogen adoption. In order to overcome this drawback an approach was presented in [3], where the bulk palladium layer was replaced by a palladium-polymer composite (chip integrated fuel cell accumulator with palladium-polymer composite H_2 storage will be hereon depicted as miniaturized PEM fuel cell). Using this approach the challenge related to the volumetric expansion of bulk palladium is overcome and simultaneously an increased hydrogen storage volume is achieved thereby an increased run time of the system. For further increasing the run time of the miniaturized PEM fuel cell system it was combined with the hydrogen production reactor (on-board range extender) [4]. The hydrogen was produced by the catalytic hydrolysis of alkaline $NaBH_4$ solution. The challenging aspect of the miniaturized PEM fuel cell combined on-board range extender system was the controllability of hydrogen production and its regulation. There are numerous approaches presented in the literature to generate hydrogen on-board using chemical hydrides and then stream the produced hydrogen into the flow fields of the PEM fuel cell after passing through a gas-liquid phase separator (regulation is done by conventional approach; external pumps and valves driven by parasitic energy) [5]. The hydrogen supply to the fuel cell is controlled by pumping speed of chemical hydride solution on to the catalyst surface. Our motivation is to address this challenge in the miniaturized PEM fuel cell combined microreactor system by using passive components; hydrophobic surface based gas venting technique [6].

1.1. System concept

In this work we present the design, fabrication process chain of miniaturized PEM fuel cell combined microreactor system with self-regulation hydrogen mechanism. A schematic view of the system design is shown in Figure 2. The system consists of two components (i) fuel cell component and (ii) microreactor component. The fuel cell component represents the miniaturized PEM fuel cell system (combination of screen printed fuel cell assembly and an on-board hydrogen storage medium).

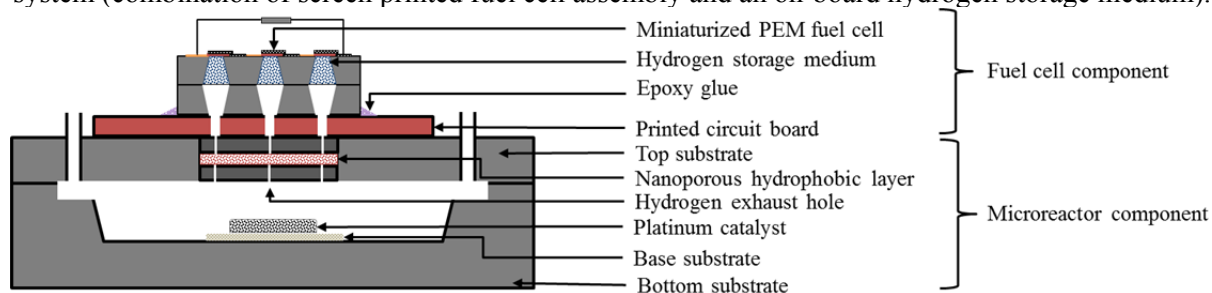


Figure 2. Schematic view of miniaturized PEM fuel cell combined microreactor with integrated self-regulation hydrogen mechanism

Hydrogen production based on catalytic hydrolysis of chemical hydride takes place in the microreactor component which comprises of top and bottom substrate (fabricated by micromilling on a polymer substrate). The top substrate houses the hydrogen exhaust hole; through which the hydrogen is transported outside the reactor. The bottom substrate houses a porous platinum layer. The gaseous hydrogen produced from the catalytic hydrolysis of sodium borohydride ($NaBH_4$) accumulates (bubbles) at the hydrogen exhaust holes. The built up hydrogen bubbles at the surface of hydrogen exhaust holes collapse when the pressure inside the hydrogen bubble overcomes the burst pressure of the hydrogen exhaust holes. This collapse causes a surge of fresh $NaBH_4$ solution onto the catalyst surface leading to the removal of the reaction by-products ($NaBO_2$) formed at the catalyst active sites of the catalyst.

2. Experimental

The system consists of two major components; (i) fuel cell component and the (ii) microreactor component. The fabrication of the fuel cell component involves both clean room and back end process. The polymer substrate based microreactor component is realized by micromilling.

2.1. Fabrication and characterization

The fuel cell component comprises of the miniaturized PEM fuel cell and the printed circuit board. A detailed description about the fabrication of the miniaturized PEM fuel cell with palladium-polymer composite hydrogen storage medium is presented elsewhere [4]. The microreactor component consists of top and bottom substrates; top substrate houses a sandwich of hydrogen exhaust holes and nanoporous hydrophobic layer. The hydrogen exhaust holes are realized by high aspect ratio dry etching (ICP) on silicon substrate followed by hydrophobic layer coating. The sandwich of the two silicon chips and the nanoporous hydrophobic layer were glued together resulting in one chip; hydrogen exhaust hole. The bottom substrate consists of the platinum catalyst layer deposited on to a base substrate. Initially two base substrates were adapted; nickel foam and CPM. Platinum catalyst was deposited by standard electroplating technique but there were considerable drawbacks such as, bad coverage of the 3 dimensional surface area of the base substrate, mechanical stability of the deposited platinum on to the base substrate (violent hydrogen production during the catalytic hydrolysis rips off the platinum from the base substrate causing a degradation in hydrogen production behavior of the system when used continuously, these results are not presented here). In search of solution for the above mentioned drawbacks the novel technique of electropulsed deposition and dealloying (EPDD) technique was adapted for nickel foam, CPM in addition to the ceramic plate base substrate [7]. Major advantages of such platinum catalyst layers are high surface area and high mechanical stability and the definition of the coating area, which is difficult to achieve using conventional electroplating. Figure 3 shows all three base substrates coated with platinum by EPDD.

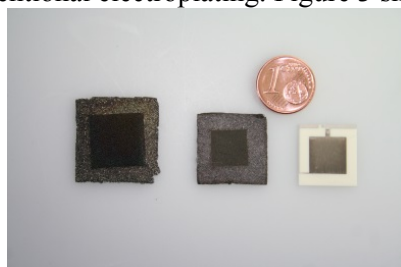


Figure 3. Base substrates coated with platinum layer by EPDD technique; the left most in the figure is nickel foam followed by CPM and the ceramic plate. The dark shade (colour version) at the centre of each sample is the deposited platinum.

Since ceramic plate was nonconductive in nature it was first patterned and sputtered with platinum thin film followed by the EPDD process. Same EPDD process parameters were applied for all the three base substrates. SEM micrographs of all the 3 base substrates are shown in Figure 4. The high voltage used for SEM micrographs were 5 KV, the magnification for the nickel foam and CPM samples are 100 X and for the ceramic plate was 1000 X. This difference is attributed to less visibility at 100 X magnification on the ceramic plate.

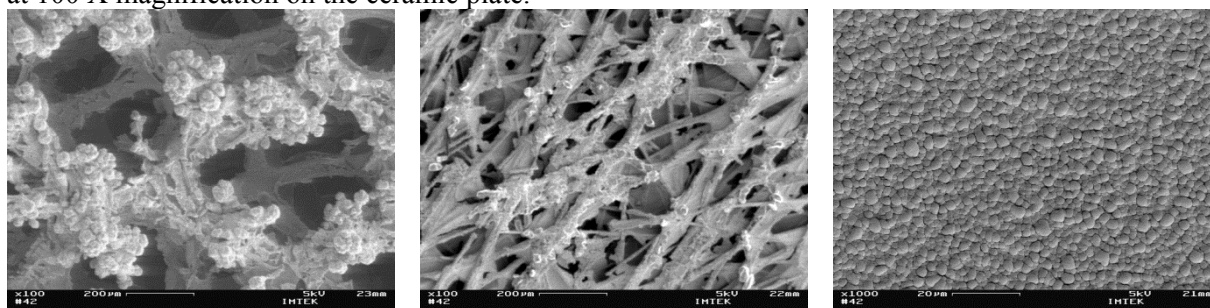


Figure 4. SEM micrographs of the base substrates deposited with platinum by EPDD technique. The left most image is nickel foam, middle is the CPM and the right most is the ceramic plate.

The proof of concept and functionality of microreactor with self-regulated hydrogen mechanism is demonstrated by a prototype microreactor; small reactor volume with single hydrogen exhaust hole

(500 μm diameter) coated with PTFE layer. Hydrogen concentration sensor was used to measure the produced hydrogen from the microreactor (CarboSen 1.000 from LAMTEC GmbH). The NaBH_4 stock solution was inserted into the prototype microreactor system with the nickel foam coated platinum catalyst and the change in hydrogen concentration was recorded with respect to time.

3. Result & discussion

The hydrogen produced from the catalytic hydrolysis of 800 μl of 0,7 wt% NaBH_4 and 4 wt% NaOH solution is shown in figure 5. The reactor initially produced hydrogen at a consistent rate followed by a pulsed release of H_2 . The peaks can be observed in the figure 5 which represent the unique behaviour of the self-regulated hydrogen mechanism of the prototype microreactor. When the measurement was repeated similar peaks were observed, which represent the self-regulated hydrogen release. This kind of H_2 release behaviour is advantageous for the miniaturized PEM fuel cell system. The pulsed H_2 could be further enhanced by implemented the silicon based hydrogen exhaust holes.

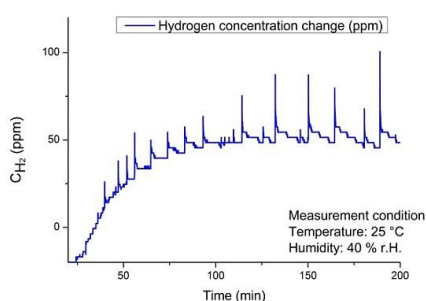


Figure 5. Functionality of the microreactor with integrated hydrogen self-regulation mechanism was tested by producing hydrogen by catalytic hydrolysis of 800 μl of stock solution. The microreactor was placed inside the measurement chamber and the change in hydrogen concentration inside the measurement chamber was measured with the hydrogen conc. sensor (ppm) with respect to time.

4. Conclusion & outlook

Design and fabrication of the miniaturized PEM fuel cell system combined microreactor with self-regulation hydrogen mechanism is presented. The prototype testing of the microreactor system is demonstrated with the self-regulation hydrogen mechanism. EPDD plated platinum on a ceramic base substrate is used for the hydrolysis of NaBH_4 . Work in progress includes the prototype testing and characterization of the miniaturized PEM fuel cell combined microreactor system (see Figure 6) and the optimization of EPDD deposited platinum for hydrolysis reaction of alkaline NaBH_4 . Advantages of miniaturized PEM fuel cell combined microreactor system include increased hydrogen storage possibilities, instant refilling and on-board energy conversion; this paves a platform for the development of new generation of energy sources for various applications.

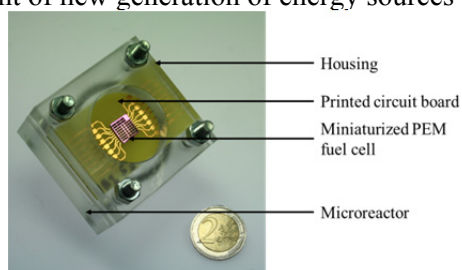


Figure 6. Miniaturized PEM fuel cell combined microreactor system. This system is the realization of the schematic diagram shown in figure 1. Microreactor and the housing is fabricated with PMMA (transparent and stable against alkaline solutions)

5. Reference

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