

Micro reactor integrated μ -PEM fuel cell system: a feed connector and flow field free approach

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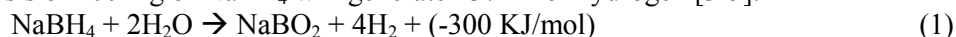
Abstract. A system level microreactor concept for hydrogen generation with Sodium Borohydride (NaBH_4) is demonstrated. The uniqueness of the system is the transport and distribution feature of fuel (hydrogen) to the anode of the fuel cell without any external feed connectors and flow fields. The approach here is to use palladium film instead of feed connectors and the flow fields; palladium's property to adsorb and desorb the hydrogen at ambient and elevated condition. The proof of concept is demonstrated with a polymethyl methacrylate (PMMA) based complete system integration which includes microreactor, palladium transport layer and the self-breathing polymer electrolyte membrane (PEM) fuel cell. The hydrolysis of NaBH_4 was carried out in the presence of platinum supported by nickel (Ni-Pt). The prototype functionality is tested with NaBH_4 chemical hydride. The characterization of the integrated palladium layer and fuel cell is tested with constant and switching load. The presented integrated fuel cell is observed to have a maximum power output and current of 60 mW and 280 mA respectively.

1. Introduction

In the recent decades the need for energy sources with high energy density and extended operation period had been increased for various applications in the micro and millimetre scale. As a response many types of micro fuel cell have been under research, like Direct Methanol Fuel Cell (DMFC), Solid Oxide Fuel Cell (SOFC) and Polymer Electrolyte Fuel cell (PEMFC), out of which the hydrogen driven PEMFC has acquired a wide interest owing to its ambient condition performance whereas the formers have the drawback of high temperature working conditions of fuel cell hydrogen based, micro Polymer electrolyte membrane Fuel Cells (μ -PFCs) have been the same or more promising candidate than the miniaturised lithium ion accumulators and other energy systems due to its high volumetric energy density in smaller area for autonomous microsystem, eco-friendliness e.g. [1-2]. The energy carrier hydrogen for the PEMFC has various ways of storing namely compressed, liquefied and hydrides. Hydrides are further classified as metal alloy hydrides and chemical hydride. The major requirements for portable micro power sources are its functionality at ambient conditions and its practical feasibility in terms of stability. Based of storage materials, chemical and metal alloy hydrides have the advantages of its high volumetric storage density. Chemical hydrides (e.g. NH_3 , $\text{NH}_2\text{-NH}_2$, H_3NBH_3 , LiH , NaAlH_4 , NaH , CaH_2 , MgH and NaBH_4) have been identified as potential



hydrogen carrier for micro power source. In particular NaBH_4 had gained more popularity among other due its high gravimetric density, easy handling, non-toxic and other storage capabilities. The exothermic hydrolysis reaction of NaBH_4 at ambient conditions results in pure gaseous hydrogen (equation (1)), the reaction and shelf-life is controlled the pH of the solution; under ideal ambient conditions hydrolysis of 100 mg of NaBH_4 will generate 237 ml of hydrogen [3-5].



Many researchers have been developing micro reactors using various technologies and base materials (e.g. silicon, photosensitive glass, ceramics, polymers, metals and plastics etc.). One of the major issues with the micro reactor technology is the complexity of the fully integrated system; every component introduced into the system increases the chance of arising a new issue. There is relatively less research focus, on reduction of the complexity of the system also not compromising the quality and system performance. This has given us the motivation to develop new concept which is able to fulfil the above mentioned two important factors.

1.1. New concept

In this work, a system with fully integrated microreactor and PEMFC is presented, eliminating the external hydrogen feed connectors and flow field for the fuel cells. The schematic view of the concept shown in figure 1, system in which the produced hydrogen from the microreactor (1) is transported and evenly distributed[6] with the help of a thin palladium layer (2) to the fuel cell anode (3) without any external hydrogen feed connectors and flow fields; all integrated in one system. The conceptual design proof, fabrication and functionality evaluation is carried out with PMMA substrate. The implementation of the presented concept on a silicon substrate, fabricated by MEMS technology is also discussed. Some of the major advantages of the presented system design are that we are able to eliminate components like gas liquid phase separators, filter membranes and external hydrogen feed connectors from the microreactor to the flow field of the PEMFC system.

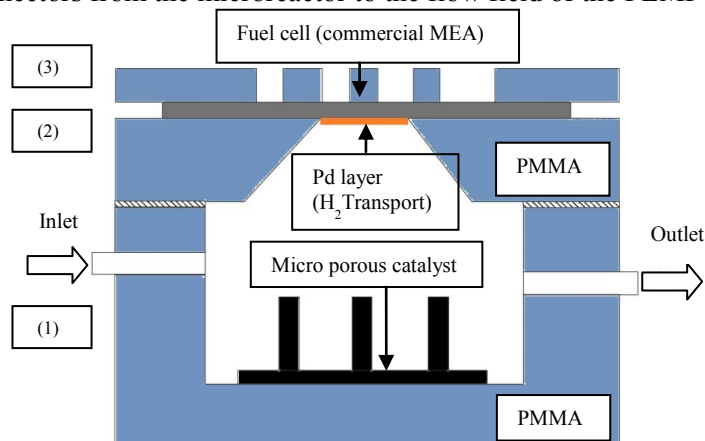


Figure 1. Schematic view of the system concept (prototype with PMMA substrate) with the 3 major components (1) base reactor (reactant inlet/outlet and micro porous catalyst layer), (2) Pd layer (H_2 transporter), (3) fuel cell component

2. Experimental

The prototype design for verifying the functionality of the presented approach is demonstrated in figure 1. The prototype system is a 3 modular system namely, base microreactor, palladium layer as the hydrogen transporter and the fuel cell. The fabrication of these components is done by CAD aided micro milling technique.

2.1 Fabrication

The base micro reactor has a reaction chamber which includes micro porous catalyst and an inlet/outlet for the reactant. The micro porous catalyst layer is fabricated with 95% porous nickel foam as a support followed by electroplating of platinum on it. The electroplating of platinum on a cleaned nickel foam is performed in a commercially available, Umicore Platina® RT electrolyte operating at a

temperature of 30°C and a current density 8 mA/cm². The module with the pd layer is fabricated by first milling a through hole conical structures on a PMMA plate ures and then a palladium thin membrane is glued. Palladium thin membrane is also fabricated by electroplating process; one side protected thin copper sheet (30-45 μm thick) is used as a seed layer for electroplating the palladium on the side exposed to the electroplating electrolyte. The copper layer is selectively etched off resulting in a thin free standing palladium layer (approximately 4-5 μm thick), schematic view of the fabrication process is shown in figure 2 (a) and the fabricated palladium layer in figure 2 (b). The electroplating of palladium is performed in commercially available, DODUCO Doduform® Palladium electrolyte operating at a temperature of 45°C and current density of 4 mA/cm². The membrane thickness is optimized to about 5 μm, owing to the fact of stability and the possibility of achieving a closed membrane surface. The fuel cell component is an assembly of two nickel mesh current collectors and conventional membrane electrode assembly (MEA) of area 9 cm². A sandwich of nickel current collectors and MEA is inserted between a pair of patterned PMMA sheets. Both the PMMA sheets had patterned openings which act as a window for the fuels to come in contact with the MEA, but on the anode side of the setup there is the palladium membrane which acts as a filter, flow field and a buffer storage for hydrogen, shown in figure 3. The sealing is done by applying instant polymer sealant at the side of the two PMMA sheets. The individual modules are mechanically clamped together constituting one complete system. The inlet/outlet of the system is connected with polymer tubing in which the reactant is pumped. The complete assembly shown in figure 4 constitutes; catalyst embedded micro reactor (1), palladium membrane (2) and fuel cell stack with external contacts (3) to the measurement system.

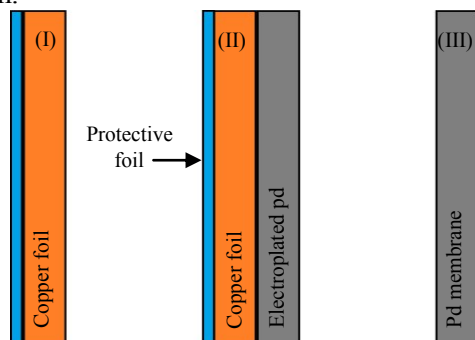


Figure 2 (a). Schematic view of 3 step fabrication of palladium membrane, (I) copper foil with one side covered with protective foil, (II) electroplating of pd on the exposed side of copper foil, (III) selective etching of the copper foil



Figure 2 (b). Picture of the palladium membrane after the selective etching of copper foil for the back side, resulting in a free standing & mechanically stable palladium membrane.

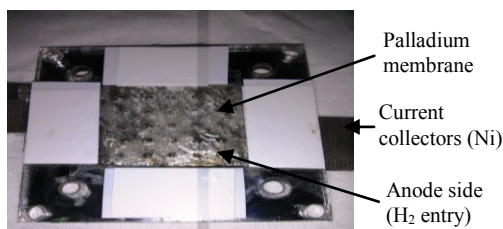


Figure 3. These two figures have been placed side-by-side to save space. Justify the caption.

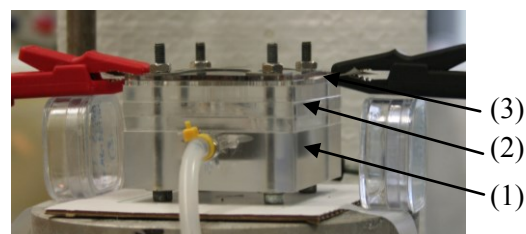


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2.2 Performance measurement

The assembled system is tested for its performance using an experimental set up, consisting of syringe and a computer controlled potentiostat. The system is tested with pure hydrogen source for characterization of the fuel cell module before using the chemical hydride. The chemical hydride, NaBH_4 solution is supplied to the reactor using the syringe. The reactant NaBH_4 solution is prepared by dissolving in high concentration sodium hydroxide (NaOH) and a small amount of 99% pure sodium dodecyl sulphate (surfactant). The reason for using the surfactant is to reduce the surface energy of the catalyst ultimately reducing the by-product clogging effect on the catalyst active sites. The micro reactor setup is tested with pure hydrogen flow for obtaining the performance characterization of the fuel cell module; polarization characterization. Then the system is then tested with 20 ml chemical hydride solution as a source of hydrogen; current and voltage values of the fuel cell are recorded under fixed electrical load (set based on the information obtained from polarization characteristics).

3. Result & discussion

The experiments are performed as described in the above section, the performance characteristics of the fuel cell module is tested with pure hydrogen flow to the anode side and ambient air on the cathode side. In figure 6 (a) shows the polarization characterises, on observation the maximum power output of the system is relatively small; on detailed examination of the setup the issue is identified that the structured PMMA plate (system 1) causes lack of air on the cathode side. The partnering of the PMMA plate was modified in such a way that there is enough air able to reach the cathode of the fuel cell (system 2). Replacing the PMMA plate design 1 with the PMMA plate design 2, the system 2 is again tested with pure hydrogen flow; as expected the polarization characterization of the system 2 shows a factor of 6 higher maximum power output measured and a factor of approximately 4 higher in the maximum current than system 1, the polarization characterization is shown in figure 6 (b). The system 1 & 2 is tested for its performance with the hydrolysis of NaBH_4 (20 ml) in the presence of Ni-Pt catalyst. A constant electrical resistance act as a load and the corresponding drop in the output voltage from the open circuit voltage is recorded. There are two variations; one with constant load and other with switching load. Figure 7 (a-b) shows the systems performance for the above mentioned types of load; figure 7 (a) shows that system 1 (PMMA plat design 1) response for constant load and figure 7 (b) shows the system 2 (PMMA plat design 2) response for switching load. The electrical load resistance are set in such a way that it is same or close to the internal resistance, obtained from the polarization characteristic of the respective systems (e.g. for system 1 it is approx. 10 ohm and for system 2 it is approx. 3 ohm). The system 1 response for constant electrical load is shown in figure 7 (a), a load sweep from 40-160 ohm is done showing a step change in the measured output voltage. The system 2 response for switching load is shown in figure 7 (b), where a 3 ohm electrical resistance is set for 2 minutes with an interval of 1 minute followed by a 5 ohm resistance was set for 1 minute with an interval of 5 minutes. The load response of the chemical hydride driven fuel cell system with an integrated palladium layer for hydrogen transport is very satisfactory, and seems to be promising for longer periods of operation.

4. Conclusion & outlook

An integrated microreactor-fuel cell system is fabricated eliminating external feed connectors, fuel cell flow fields and filter members but only using a thin palladium membrane instead. The system functionality (proof of concept) of using such an approach is demonstrated using the PMMA prototype system. The system behaviour with pure hydrogen source and chemical hydride source is clearly demonstrated. The characterization of the integrated fuel cell is demonstrated by the polarization characteristics (external supply of pure hydrogen) followed by the system performance for constant and switching electrical load resistance (microreactor with chemical hydride delivering hydrogen on hydrolysis). The repeatability of the system performance showed no degradation on long term

measurements. This approach significantly reduces the complexity of the system also not compromising its performance.

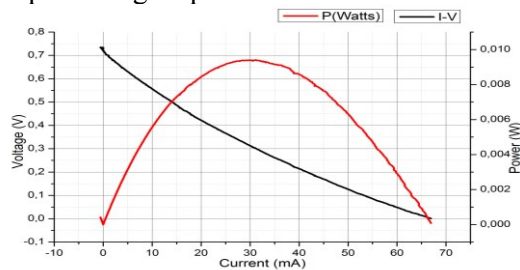


Figure 6 (a). Polarization characterization of fuel cell with pure hydrogen flow, with PMMA cathode plate design 1. Maximum power output in the range of approximately 0,009 Watts

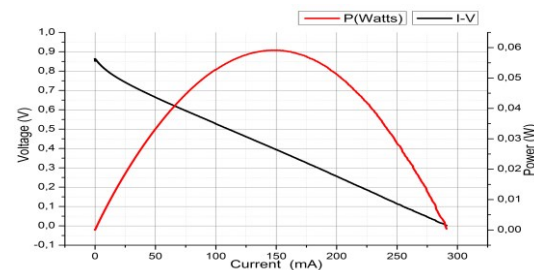


Figure 6 (b). Polarization characterization of fuel cell with pure hydrogen flow, with PMMA cathode plate design 2. Maximum power output in the range of approximately 0,06 Watts

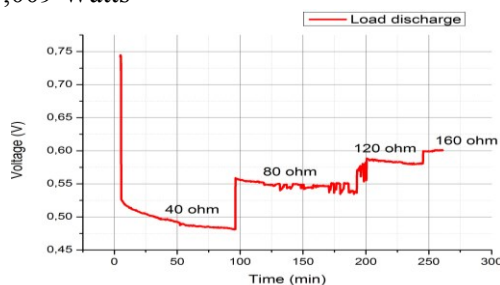


Figure 7 (a). System 1 (PMMA plat design 1) response for constant load

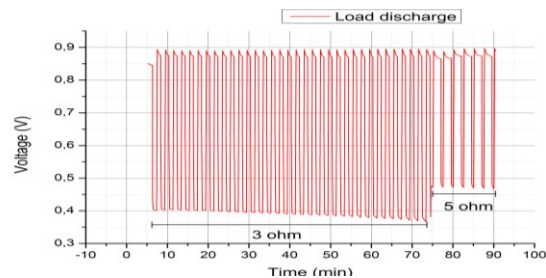


Figure 7 (b). System 2 (PMMA plat design 2) response for switching load.

This work provides an evident knowledge about the presented approach which can be scaled up or scaled down depending on the application demand. The next level is to implement the presented device concept on silicon substrate (shown in figure 8) fabricated by MEMS technology. This sets the stage for creating a new generation of Chip Integrated micro PEM Fuel Cell System (CI μ -PFCS) for realizing the future of energy sufficient autonomous microsystems which are long term stable.

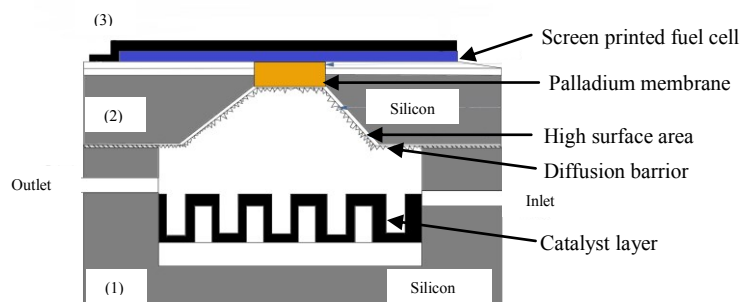


Figure 8. Schematic view of the system concept with silicon substrate, (1) base reactor (reactant inlet/outlet, micro pours catalyst), (2) high surface area palladium hydrogen transport layer, (3) screen printed fuel cell.

5. Reference

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