Design, Fabrication and Prototype testing of a Chip Integrated Micro PEM Fuel Cell Accumulator combined On-Board Range Extender

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Abstract. In this work we present the design, fabrication and prototype testing of Chip Integrated Micro PEM Fuel Cell Accumulator (CIµ-PFCA) combined On-Board Range Extender (O-BRE). CIµ-PFCA is silicon based micro-PEM fuel cell system with an integrated hydrogen storage feature (palladium metal hydride), the run time of CIµ-PFCA is dependent on the stored hydrogen, and in order to extend its run time an O-BRE is realized (catalytic hydrolysis of chemical hydride, NaBH₄). Combining the CIµ-PFCA and O-BRE on a system level have few important design requirements to be considered; hydrogen regulation, gas-liquid separator between the CIµ-PFCA and the O-RE. The usage of traditional techniques to regulate hydrogen (tubes), gas-liquid phase membranes (porous membrane separators) are less desirable in the micro domain, due to its space constraint. Our approach is to use a passive hydrogen regulation and gas-liquid phase separation concept; to use palladium membrane. Palladium regulates hydrogen by concentration diffusion, and its property to selectively adsorb only hydrogen is used as a passive gas-liquid phase separator. Proof of concept is shown by realizing a prototype system. The system is an assembly of CIµ-PFCA, palladium membrane and the O-BRE. The CIµ-PFCA consist of 2 individually processed silicon chips, copper supported palladium membrane realized by electroplating followed by high temperature annealing process under inter atmosphere and the O-BRE is realized out of a polymer substrate by micromilling process with platinum coated structures, which functions as a catalyst for the hydrolysis of NaBH₄. The functionality of the assembled prototype system is demonstrated by measuring a unit cell (area 1 mm²) when driven by the catalytic hydrolysis of chemical hydride (NaBH₄) and the prototype system shows run time more than 15 hours.

1. Introduction
The driving force for research in the field of micro power sources is due to the tremendous growth in portable electronics applications, for example cell phones, laptops, cameras and global positioning systems (GPS) [1]. But the biggest limiting factor for these portable electronics applications are the capacity and size of batteries utilized in them [2]. This ultimately leads to the developing new micro power sources with high energy density and reasonable power delivery. Miniaturized hydrogen driven fuel cell systems has been considered to be a good candidate for such requirements due to its high energy density and eco friendliness. Two major kinds of low temperature fuel cell which are under focus are alkaline fuel cell and acidic fuel cell. µ-PEMFC systems (type of acidic fuel cell) have been deeply
investigated in the recent decades owing to its advantages over other fuel cell types, but there are also few technical drawbacks in terms of on board hydrogen storage. In large scale fuel cell systems hydrogen is stored either in gaseous form (high pressure required) or liquefied form (very low temperatures required). Whereas in micro scale systems they are stored in the form of hydrides, hydrides are further classified into metal hydrides and chemical hydride. Metal hydrides store hydrogen in their atomic lattice and their hydrogenation and dehydrogenation are reversible under specific operating conditions. Chemical hydrides have chemically bonded hydrogen molecules under normal conditions and release the hydrogen when it undergoes a catalytic hydrolysis reaction. Some major advantages of chemical hydride over metal hydride are that they have the ability to release hydrogen under ambient conditions and they are easy to handle and doesn’t require sophisticated handling systems. A novel concept of fuel cell integrated metal hydride (palladium on-board hydrogen storage) system on a silicon substrate was presented by Edler et al. [3], Chip Integrated Micro PEM Fuel Cell Accumulator (CIµ-PFCA). In this concept, the PEM fuel cell was directly screen printed on the metal hydride storage and the fuel cell has a self-breathing cathode, the capacity of the system was dependent on the thickness of the metal hydride layer. One important feature of the system is that it has CMOS electronics in built, shown in figure 1. The hydrogen storage capacity of these systems were increased by replacing bulk palladium by palladium-polymer composite mixture, an increase in capacity and an increase in the run time of the system was demonstrated [4].

The storage capacity of the above mentioned system can be further increased by combining it with an On-Board Range Extender (O-BRE). O-BRE is a hydrogen production unit, where the hydrogen is produced from the catalytic hydrolysis of chemical hydride (sodium borohydride, NaBH₄). In this presented work NaBH₄ has been utilized due to its advantages of high gravimetric density, easy handling, non-toxic nature, longer shelf life and ambient operating conditions. The hydrolysis of NaBH₄ generates gaseous hydrogen, sodium borate and heat as reaction products (equation (1)) [5]. One mole of NaBH₄ reacts with two moles of water to delivers four moles of hydrogen under ideal conditions. The by-product NaBO₂ is non-toxic and can be regenerated into NaBH₄ by suitable processing techniques.

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\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2 + (-300 \text{ KJ/mol}) \quad (1)
\]

The self-hydrolysis of NaBH₄ is controlled by increasing the pH of the solution and then using an active catalyst to reinitiate the hydrolysis reaction.

1.1 System concept

In this work we present the design, fabrication and prototype testing of Chip Integrated Micro PEM Fuel Cell Accumulator (CIµ-PFCA) combined an On-Board Range Extender (O-BRE), but replacing the external hydrogen transport tubing and external gas-liquid phase separators by a palladium membrane, the schematic view of the system is shown in figure 2. There are 3 major parts that are marked (1) CIµ-PFCA, (2) palladium and palladium-alloy membrane, (3) O-BRE. Combining
CIµ-PFCA and O-BRE have few important design requirements to be considered; hydrogen regulation, gas-liquid separator between the CIµ-PFCA and the O-BRE. Traditional techniques to regulate hydrogen (tubes), separators (bulk porous hydrophobic modules) are less desirable in the micro domain. So in this work we present, our approach of using palladium membranes eliminating the use of above mentioned components. The property of palladium to selectively absorb and transport hydrogen (concentration diffusion) is used as passive regulator and gas-liquid phase separator. The concept of using palladium and palladium-alloys to selectively filter, absorb and transport hydrogen is a well-established technique used in small & large scale hydrocarbon reforming system (high temperature of operation > 350 °C) [6]. But in micro scale and meso scale system integration, using high temperatures is a drawback for the complete system in terms of system handling and external power requirement. So in this presented work the membrane is operated at ambient conditions. Some of the major advantages of such a system are; the system has high degree of freedom in terms of design (user defined) and the chemical hydride is used and this could be transformed into an energy harvesting device with few design changes.

**Figure 2.** Schematic view of the complete system; (1) CIµ-PFCA: Screen printed fuel cell & hydrogen storage chip, (2) palladium and palladium-alloy membrane: for hydrogen regulation, (3) On-board range extender (O-RE): catalytic hydrolysis of NaBH₄ for on-board hydrogen production.

2. Experimental

The prototype system realization was done in 4 steps; (i) fabrication of CIµ-PFCA (ii) fabrication of palladium membrane (iii) fabrication of O-BRE and (iv) system assembly. Detailed description is presented in the following section.

2.1 Fabrication

Fabrication of CIµ-PFCA: this is performed as a two silicon chip assembly (chip 1&2). Chip 1 consists of screen printed cathode layer, PEM layer & sputtered anode current collector, palladium-polymer composite casted in the wet etched groove of the silicon chip from the back side. Chip 2 consists of a µ-tunnel for the hydrogen transport which is realized by a combination of wet and dry etching of bulk silicon. The schematic view of CIµ-PFCA is shown in figure 3 (cross section). The complete fabrication process chain is described elsewhere [4]. The assembly of the 2 individually processed silicon chips is performed by room temperature polymeric bonding process. The size of the chip is 1 cm² consisting of 42 unit cells each has a size of 1 mm².

**Figure 3.** Cross section schematic view of CIµ-PFCA; (1) screen Printed PEM fuel cell, (2) silicon base chip with wet etch groove and sputtered anode current collector, (3) palladium-polymer composite (hydrogen storage), (4) low temperature polymeric bonding, (5) silicon chip with µ-tunnel for hydrogen transport.
Fabrication of palladium membrane: an electroplated sandwich stack consisting of 15 µm copper, 5 µm palladium, and 15 µm copper was performed. Copper act as mechanical support structures for the 5 µm palladium. The electroplated stack was selectively etched for copper only at the centre (diameter of ~ 5 mm) by protecting the other regions with photoresist. The fabricated palladium membrane with copper support structures was annealed at 500 °C for 20 min under argon atmosphere; to improve the mechanical stability of the membrane structures, for detailed electroplating parameters please refer [7].

Fabrication or O-BRE: the O-BRE was fabricated out of polymeric substrate. The miniaturization of O-BRE at step one would be a hurdle for us to study the system for better understanding. The O-BRE was fabricated with (Poly(Methyl MethAcrylate)-PMMA) substrate by micro milling process. Some of the reasons for using PMMA substrates are: low cost, fast to fabrication, alkaline stability and transparent. All these reasons give us an upper hand studying the system and are easily adaptability. The O-BRE has a total chamber volume of 28 cm³ (frustum shaped) it consists of catalyst (platinum) for the hydrolysis of chemical hydride, reactant inlet and outlet, nitrogen flush inlet and a temperature sensor.

The complete prototype system assembly was performed by fixing the CIµ-PFCA to a PCB board and wire bonded to larger contact pads for measurement convenience (figure 5 (a)), then the system is stacked as per the figure 2 and mechanically screwed together with O-Ring sealing’s which are chemically stable. The completely assembled prototype system is shown in figure 5 (b).

![Figure 5](image-url)

**Figure 5.** (a) CIµ-PFCA located on a PCB board and wire bonded to larger bond pads for measurement convenience, (b) completely assembled system: CIµ-PFCA, copper supported Pd membrane and O-BRE.

### 2.2 Performance measurement

The prototype system is tested for its performance using an experimental measurement platform consisting of syringe to insert the reactant and a computer controlled potentiostat to measure the system voltage. The prototype system is tested with pure hydrogen flow for measuring the I-V polarization characteristics of the CIµ-PFCA. A stock solution was prepared by dissolving NaBH₄ in 6M 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 platinum catalyst surface ultimately reducing the by-product clogging effect on the active sites. Before inserting the chemical hydride to the prototype system, it was constantly flushed with nitrogen gas, and then 5 ml of the chemical hydride stock solution was mixed with 15 ml of water and then inserted into the reactor. Open Circuit Voltage (OCV) and the voltage response for a constant electrical load of the unit cell which has total area 1 mm² and was measured under constant ambient conditions.

### 3. Result & discussion

The prototype system was tested for its functionality when driven by the hydrogen produced form the O-BRE. The chemical hydride was inserted and the open circuit voltage was measured till the unit cell reached a stable OCV value and then an electrical load of 10 MΩ was inserted and the voltage response of the unit cell was measured, the measurement results are shown in figure 6. From the figure one can observe that system reaches a stable OCV value of 600 mV about 250 min after the chemical hydride was inserted. The reason for this can be attributed to the time delay in the permeation and
diffusion of hydrogen through the palladium bulk membrane (rate limiting factor). A similar effect was reported by [8] as “time lag”, lower pressure difference causes increased time lag until a steady state permeation is achieved across the membrane. The time lag could be reduced by using thinner layers of palladium membrane. When the unit cell was subjected to a constant electrical load (10 MΩ) discharge for about 7 hours there is a drop in the voltage, depicted in figure 6. After the electrical load discharge the OCV of the system was measured till the system was completely depleted. The testing of the prototype system shows the feasibility of combining Clµ-PFCA and an O-BRE with a palladium membrane in-between.

4. Conclusion & outlook

Design, fabrication and prototype system testing of Clµ-PFCA combined O-BRE are presented. The concept of using palladium membrane instead of tubes and gas-liquid phase separators is proved to be functional. The prototype system functionality is demonstrated by measuring the Clµ-PFCA (unit cell) performance when driven by the hydrogen produced from the O-BRE. Future works are to focus on; (i) in-situ measurement of the prototype system (ii) fabricating the palladium membrane on chip level with the Clµ-PFCA assembly, and (ii) to design a self-controlled hydrogen production mechanism form O-BRE (catalyst actuation mechanism). This work sets the platform to develop a system level adaptable Clµ-PFCA (ready to connect to any hydrogen source (shown in figure 7)). This paves the way for a considerable grown in the field of energy sufficient autonomous microsystem for various small scale sensing applications.

5. Reference

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