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# Electrooxidation study of $NaBH_4$ in a membraneless microfluidic fuel cell with air breathing cathode for portable power application

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A microfluidic fuel cell (MFC) is constructed at laboratory for $NaBH_4$ electrooxidation using varying operating conditions. The temperatures of anode and cathode were varied from 40 °C to 70 °C, and the pressure was maintained at 1 bar. The anode and cathode electrocatalyst used was Pt (40 wt. %)/High Surface Area Carbon (CHSA) with loading in the range of 0.5 mg/cm$^2$ to 2 mg/cm$^2$. The oxidant at cathode was atmospheric oxygen (21 mol % $O_2$). The commercial gas diffusion layer (GDL) was used as substrate at anode and air breathing cathode side. The cell voltage and current density were measured for different fuel ($NaBH_4$) concentration, electrolyte (KOH) concentration, temperature and electrocatalyst loading at anode and cathode, respectively. The maximum open circuit voltage (OCV) of 1.079 V and power density of 24.09 mW/cm$^2$ at a current density of 54.97 mA/cm$^2$ were obtained for anode (Pt/$C_{HSA}$) and cathode (Pt/$C_{HSA}$) loading of 1 mg/cm$^2$ using 0.1 M $NaBH_4$ as fuel mixed with 1 M KOH as electrolyte at a temperature of 70 °C. Whereas the maximum power density of 8.47 mW/cm$^2$ at a current density of 34.04 mA/cm$^2$ was obtained at the temperature of 40 °C. Although similar cell conditions were used, the cell performance in terms of power density is significantly enhanced (about 65%) due to increase in temperature from 40 °C to 70 °C. These results were validated using cyclic voltammetry at single electrodes under similar conditions to those of the single microfluidic fuel cell.



## Introduction

The energy demand is generally met by primarily sources of energy like, fossil fuels such as natural gas, petroleum oil, and coal and to a lesser extent, nuclear by fission of radioactive elements, solar in direct heating and photovoltaic cells, hydroelectricity, wind, geothermal and biomass. However, about 75% of the today's energy demand is fulfilled by fossil fuels. Fossil fuels generate energy by combustion and produce pollutants e.g., oxides of sulfur, nitrogen, carbon and unburned hydrocarbons, which are introduced into the atmosphere resulting in large number of problems to the environment [1,2]. The environmental issues, depletion of fossil fuels and cost of fossil fuel coupled with low production rate compared to the demand are the reason to design and develop eco-friendly, compact and modular power generator, which is economically viable. Currently, fuel cells are found to be very

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promising energy generating devices for the stationary and mobile applications with significant environmental advantages [3–5]. Fuel cells generally use hydrogen or hydrogen rich molecules e.g., methanol, ethanol, acetic acid and formic acid etc [6–8] as fuel for power generation. Among all fuels, hydrogen is considered as a clean energy carrier because, the fuel cell system and combustion process both produce energy and by-product water only. Moreover, hydrogen gas has a high energy density (39.4 kWh $kg^{-1}$) than hydrocarbons and other fuels. However, the hydrogen gas has many disadvantages e.g., economical production of pure hydrogen gas and on board storage, safety issues related to the hydrogen gas as it is highly explosive and low power output per unit weight of fuel cell and processor together [9,10].

These drawbacks of hydrogen gas have propelled the researchers to work on alternate fuel e.g., $NH_3$, $N_2H_4$ and $NaBH_4$ for direct feeding in the fuel cell in place of pure hydrogen gas [11,12]. Among all these fuels, sodium borohydride ($NaBH_4$) has attracted much attention as potential hydrogen storage media due to high hydrogen capacity (10.6 wt %) [13]. It can be stored in liquid phase, and also it is a stable nonflammable alkaline solution. $NaBH_4$ is also renewable and environmentally friendly fuel. In addition, the use of hydrogen rich compound $NaBH_4$ in fuel cell could eliminate the storage and transportation problem. The production rate of hydrogen is easily controlled and pure hydrogen can be obtained by hydrolysis of $NaBH_4$ as shown below (Eq. 1) [14].

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad (1)$$

It is seen in Eq. (1) that hydrogen is the only gaseous product of the reaction. The hydrogen gas can be obtained from the above reaction after separating the borate, which can be recycled into sodium borohydride again. Hydrolysis of sodium borohydride is an exothermic reaction so this reaction does not requires any additional heat supply and can take place at room temperature [13].

Till date, only a few researches have been reported using $NaBH_4$ as fuel and liquid $H_2O_2$ as oxidant with traditional PEM-based design [15]. The use of liquid oxidant is associated with a reduced system energy density and must be improved in terms of fuel cell performance. The $NaBH_4$ solution has also been tested in alkaline fuel cell (AFC) using KOH solution as electrolyte in spite of their many disadvantages e.g., liquid alkali is corrosive and leakage problem with deterioration of life [16]. Moreover, $NaBH_4$ as fuel in solid alkaline membrane based fuel cell could provide high ohmic resistance with high cost of membranes and also results in stability problem at high temperature operation.

Recently, microfluidic fuel cells (MFCs) have attracted the attention of researchers across the globe due to their low manufacturing cost, miniaturized structure and promising potential in powering portable electronic devices like mobile phones, laptop computers, glucose sensors, pacemakers, health care diagnostics and DNA analysis devices etc [17]. The microfluidic fuel cell (MFC) converts stored chemical energy of a supplied fuel into electrical energy without the use of ion conducting membrane. In MFCs, two non-mixing laminar flow streams are fed into parallel micro-channel where the interface between the two flows works as a proton/ion conductor. The interface allows proton/ion transfer through it and eliminates the need of costly membranes [7,18]. The several other advantages of microfluidic fuel cells as compared to traditional proton exchange membrane (PEM)-based fuel cells are (i) fuel and oxidant streams may be combined in a single micro channel (ii) fuel and/or oxidant crossover can be minimized by adjusting the flow rate of the co-laminar streams (iii) no ion exchange membrane is required (iv) less requirement of sealing, manifolding, and fluid delivery infrastructure (v) hydration and water management issues of membranes are eliminated [17]. Nevertheless, microfluidic fuel cell has drawn much attention as a micro-power source to portable applications because of its high energy density compared to batteries [19,20]. All those factors advocate the use of $NaBH_4$ in microfluidic fuel cell as useful source for power generation. The overall conversion of $NaBH_4$ at room temperature by the self-hydrolysis reaction is about 7–8% [21,22].

Schlesinger et al. [14] investigated acid catalysis and metal-catalysis processes to improve the rates and yield of the hydrolysis of the reaction to generate $H_2$ from the $NaBH_4$ solution. Noble metals such as ruthenium and platinum or their alloys [23–25], Pd [26] catalyst, zeolite-confined ruthenium (0) nanoclusters [27], Pt–Ru supported on metal oxide [24], and Au/Ni bimetallic nanoparticles [28] show high activity in sodium borohydride hydrolysis reaction. However, they are very expensive and not available in plenty amount in nature [23]. It is found that non-noble metal electrocatalyst like cobalt and nickel based electrocatalyst shows favorable behavior and recyclability for catalytic hydrolysis of $NaBH_4$ in alkaline solution. Cobalt and nickel borides (Co– and Ni–B) have been studied as an alternative to noble catalysts and they are inexpensive and abundant in nature [29–31]. Fernandes et al. [29] reported that Co–P–B shows higher efficiency as electrocatalyst for hydrogen production than Co–B and Co–P. Lee and Kim [13] investigated on a micro PEM fuel cell system with $NaBH_4$ generator. It was a catalytic microreactor comprised of hydrogen separator, micropump, and a $NaBH_4$ solution cartridge. The microreactor generated a hydrogen flow rate of 16.1 ml/min. The maximum power output was 174.6 mW for a current of 0.45 A.

Elumalai et al. [32] studied on the effect of acid and alkaline media on membraneless fuel cell using sodium borohydride as fuel and sodium perborate as oxidant. Unsupported Pt black nanoparticles of 2 $mg/cm^2$ were used as anode and cathode electrocatalyst, respectively. The maximum power density of 27.75 $mW/cm^2$ was obtained with 0.15 M $NaBH_4$ in 3 M NaOH solution as fuel and 0.15 M perborate in 1.5 M $H_2SO_4$ as oxidant. Brushett et al. [33] investigated on laminar flow-based fuel cells (LFFCs) using different fuels (formic acid, methanol, ethanol, hydrazine and sodium borohydride) at anode. Very high loading (10 $mg/cm^2$) of noble electrocatalyst Pt black at anode and 2 $mg/cm^2$ of Pt black at cathode were used for each fuel. LFFCs operated with hydrazine and sodium borohydride exhibited power densities of 80 and 101 $mW/cm^2$, respectively.

To the best of our knowledge only a few research work on $NaBH_4$ electrooxidation in microfluidic fuel cell has been