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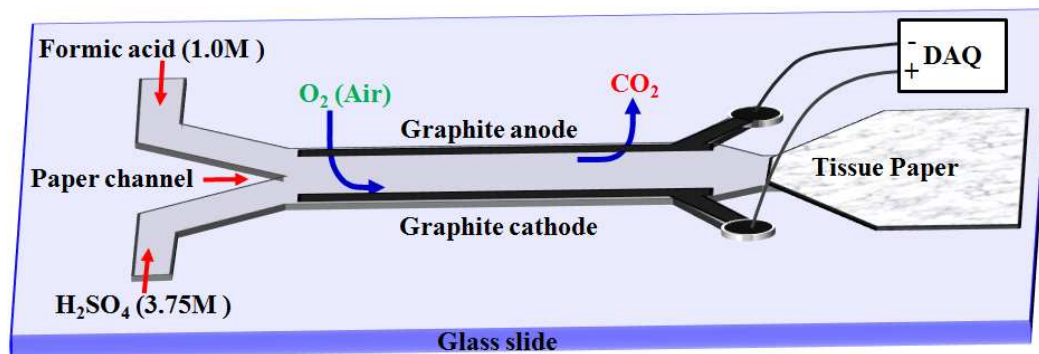
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We present a pencil stroked paper fuel cell to generate energy ($32 \text{ mW}\cdot\text{cm}^{-2}$) over prolonged duration (>1000 minutes) with low consumption of fuel ($\sim 1 \text{ mL}$)

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ARTICLE TYPE

Paper based self-pumping and self-breathing fuel cell using pencil stroked graphite electrodes

Ravi Kumar Arun,^aSaurav Halder,^aNripen Chanda,^aand Suman Chakraborty^{b*}

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We develop a paper based fuel cell in which fluids flow through capillary transport mechanism. The pencil stroked graphite electrodes take oxygen from quiescent air. This simple and efficient paper fuel cell can generate energy in the

10 **tune of 32 mW-cm⁻² over prolonged duration of around 1000 minutes, with the consumption of very low volume of formic acid as fuel (~1 mL).**

The microfluidics based laminar flow fuel cells have been under constant research endeavour for the development of miniature

15 power source for cell phones, laptops and space systems.¹ Significant efforts have been directed to make micro fuel cells low-cost, portable and efficient.² One such endeavour is to use membrane-less design which eliminates the need of a membrane.³ Though this approach has made the device significantly simple

20 and compact, external pumps and outlet systems are still required to maintain the fuel concentration and by-product removal respectively, thus indirectly increasing the overall dimension of the device.^{4,5} As an alternative to the external pumping system, a self-pumping or passive pumping method is thought to be a good

25 option to deliver the fluids in a micro-fuel cell. In this context, electrochemical reaction generated CO₂ bubble driven micro-fuel cells has been introduced to push the fluids which flow in either separate streams or single stream.⁶ The reported methods are still complicated by electrode fabrication for gas diffusion and limited

30 availability of fuels for longstanding performance in terms of power output.

With the idea of self-pumping mechanism, paper based micro fuel cells may be much more attractive than the traditional one.

35 Paper based microfluidics has been extensively investigated by researchers for various applications (such as disease diagnostics), in which transport may be sustained due to capillary action of fluids through fibers and pores in the paper.^{7,8} The fluid flow rates have been found to be very low (2-3 μl/min), so that a given

40 small volume of fluid can be delivered for long period of time in contrast to the syringe pump based arrangement.⁹ Thus, with the use of paper, the power generating capacity of the micro fuel cell may be enhanced significantly due to constant laminar flow of fluids for long time at low volume consumption. Another

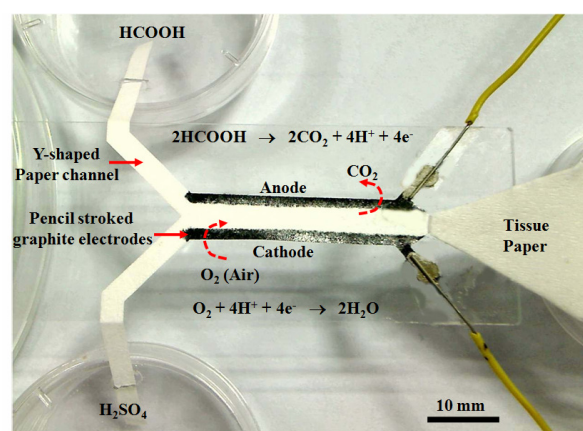
45 important factor that can practically reduce the cost and volume of the micro fuel cell is the nature of electrodes. To integrate air

breathing mechanism with the fluid self-pumping, researchers have modified the electrodes with in-built nanoporous structures or with nanomaterials coated on the surface. However, the

50 fabrication involves multi-step processes and costly chemicals such as Pt or Pd-black.¹⁰ Wu et al. used enzyme-MWCNT modified paper electrodes to enhance the performance of biofuel cells.¹¹ Recently, paper based batteries have been reported to develop variety of fuel cells, but no method has been suggested to

55 ensure the continuous supply of fluids to run the fuel cell for a long period of time.^{12,13} Of late, researchers have developed pencil-sketched inexpensive electrodes on paper based microfluidic devices.¹⁴ However, no study has been reported yet concerning the fabrication of micro-fuel cells with simultaneous

60 considerations of cost-effective fabrication and easy electrode preparation.



65 **Fig.1** Snapshot of paper-based channel with Hb-pencil stroked graphite electrodes to demonstrate a self-pumping and air-breathing fuel cell.

In this work, we present a novel and simple paper-based

70 membraneless formic acid fuel cell that operates on self-pumping and air-breathing mode by incorporating Hb-pencil stroked graphite as porous electrodes on paper to generate power for longer time (Fig.1). Wattman filter paper was used for the preparation of 'Y' shaped fuel cell channel by micro-machining

75 method carried out by CO₂ laser engraving system (VLS 2.30, Universal Laser Inc., USA) at 3 Watt. The engraved channel

parameters were as follows: length (l) = 25 mm, width (w) = 6 mm and height (h) = 0.1 mm. The filter paper channel was then soaked in warm De-Ionized water for 30 minutes to remove the impurities, if any. The Hb-pencil was stroked onto the dried filter paper channel to create graphite electrodes inspired by the method adopted by Mandal et al.¹⁴ The wires were connected at the electrode ends with silver conductive adhesive paste (Alfa Aesar). The SEM images (Hitachi S-3000N) of the paper, taken before and after repeated HB-pencil strokes to fabricate graphite electrodes, are shown in Fig S1. It can be depicted from the Fig. S1b that repeated strokes of the Hb-pencil allow the paper fibres to adsorb graphite for continuous flat shaped electrodes.

Formic acid (HCOOH) (1M) and Sulfuric acid (H₂SO₄) (3.75 M) were used as the fuel and oxidant, respectively.¹⁵ Both the fluids were kept in two 3 m L petri-dishes, in which the extended arms of the Y-channel were dipped as shown in Fig. 1. The two wires, already joined with graphite electrodes, were then connected with NI-data acquisition system (NI-PXI -1042) and LabView 8.5 to record the open circuit potential. The fluid flow started when the two arms are touched into the respective solutions.

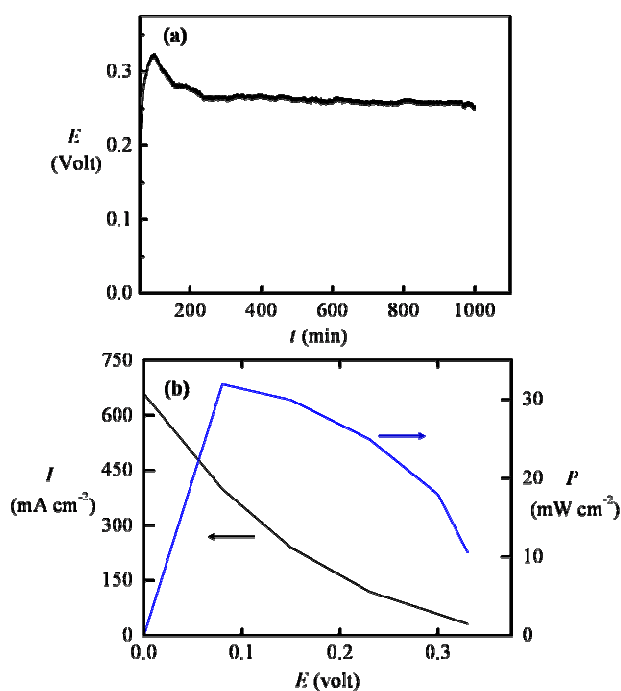


Fig. 2 Performance of paper-pencil based fuel cell. (a) The open circuit potential (E) is measured with respect to time for $t = 1000$ minutes at the consumption of ~ 1 ml fuel. (b) Polarization and power curves of single paper fuel cell.

The simple design of the paper fuel cell with pencil-graphite electrodes has been used to demonstrate the capillary action mediated pumping of the fuel-electrolyte solutions for facile power generation. The self flowing fuel and electrolyte solutions in the Y-shaped paper channel generated a constant open circuit potential for up to 1000 minutes as shown in Fig. 2a. The maximum open circuit was observed at 0.33 V which dropped to a constant value of 0.27 V after some time, which may be

attributed to the difference in porosity between the filter paper and tissue paper. The cell potential attained a stable value once the paper got wet completely by the capillary action. If the channel was first primed and then experiment was started, the potential became stable in short period of time. The current-potential and power-potential curves of the paper fuel cell are shown in Fig. 2b. The maximum power density was 32 mW-cm⁻², which is higher than the PDMS based fuel cells running on formic acid as fuel along with air-breathing electrodes.¹⁶ The maximum current density under such experimental conditions was 660 mA-cm⁻², which depends on the cathode performance.

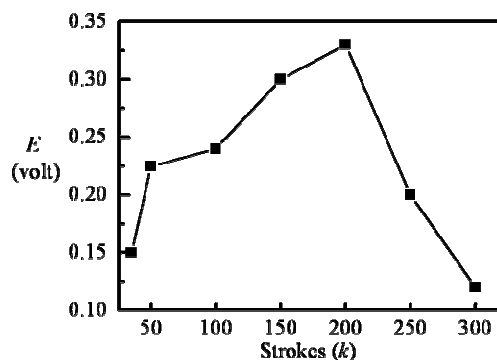


Fig.3 The open circuit potential (E) measured at different strokes (k) of the Hb-pencil. The resistance of the electrodes decreases with the increase in number of pencil strokes and consequently increases the observed potential. The potential starts decreasing after $k = 200$ as electrodes continuity starts interrupted.

Since the hand-held multiple strokes of Hb-pencil were used for the fabrication of graphite electrodes, the effect of such strokes on the paper has been studied to determine the performance of the fuel cell. The number of times Hb pencil is rubbed on paper may be named as number of strokes (k). A single stroke is the one that strikes straight from the inlet to the outlet of the channel in one direction not in the random way. The minimum number of strokes at which continuity of the electrode was visible was found to be $k = 35$. We have varied the number of strokes from $k = 35$ to 300 to investigate the performance of the paper fuel cell. Fig. 3 shows the graph of open circuit potential (E) vs. Number of strokes (k) of the paper fuel cell. At $k = 200$ strokes, the cell potential increased to maximum value of 0.33V where we measured all the cell performances (Fig. 2). The potential started decreasing after $k = 200$ that may be attributed to the increase in resistance of the electrode due to the loss in its continuity.

The current design of paper fuel cell easily overcomes the fuel-electrolyte pumping and oxygen delivery issues that practically hinder the miniaturization of microfluidic fuel cells. Here, the paper based pumping provides stable flow rates with small volume of fluids to run the fuel cell. In addition, the continuous laminar flow of fluids is ensured by attaching another piece of paper as reservoir at the outlet of the main channel. The paper based reservoir efficiently drives the fuel and electrolyte from inlets and ensures constant flow of the fluids. This synergistic action of the paper based channel and reservoir can flow relatively small volume of the fuel and electrolyte (~ 1 mL) for a

substantial duration of time (~ 1000 min) without refilling. Similar approach has been adopted where filter paper was used to drive protein solution in polymer-based microchannel.¹⁷ Moreover, papers with different porosities may be kept at the outlet, in an effort to vary the percentage of fluids that one wants to remove from the device. Regarding the supply of oxygen into the fuel cell from quiescent air, we have introduced Hb-pencil made porous graphite electrodes which act as the gas-diffusion system to trap oxygen directly from the air, thus avoiding the need to bubble the electrolyte with oxygen gas prior to start the fuel cell. In addition, this open paper fuel cell facilitates the venting of CO₂ gas formed at the anode to the atmosphere rather than its accumulation. The efficient removal of CO₂ gas as bubbles has been observed as spherical patches under the microscope (Fig S2).

To observe the fuel and electrolyte diffusive mixing and the proton movement towards the cathode, we have mixed methyl orange pH indicator in the formic acid solution (develops pink colour) keeping the sulphuric acid electrolyte unaffected (colourless). Fig.S3 shows the development of the interface between the two fluids and the proton concentration gradient in terms of pink colour dispersion from anode to cathode on the paper. This clearly indicates that the non-ordered complex paper fibre network allows the protons transfer towards cathode side without posing any resistance. Nevertheless, the deposited graphite makes the paper-electrode area hydrophobic in nature, thereby helping the fuel to wick very slowly near the electrode region and hence allowing the protons to pass through efficiently. The proton transfer through the cellulose fibre network is a unique phenomenon characterizing the fuel cells fabricated here as compared to conventional fuel cells, which can be further explored theoretically and experimentally

The membraneless architecture on thin paper (100 μm) used in this study also minimizes the fuel crossover to achieve stable potential over a reasonable period of time. The fuel consumption for 1000 min run for this fuel cell is found to be ~1 mL that would be comparable to 10 minutes run with 1 mL fuel in microfluidic environment if the flow rate is fixed at 100 μL·min⁻¹. This small consumption of fuel is beneficial for the development of fuel cartridges and further miniaturization of the fuel cell system. We have also found that if the outlet paper reservoir is replaced with fresh one, the paper fuel cell can generate power for more than two days without any drop in its performance (Fig. S4).

In summary, we have demonstrated for the first time a simple paper-based fuel cell using pencil stroked graphite electrodes that operates on self-pumping and air-breathing mode to eliminate the requirements of external pumping of the fuel and the oxygen saturated electrolyte or oxygen gas chamber or air blower. The maximum power density and current density were observed at 32 mW·cm⁻² and 650 mA·cm⁻² respectively, at the expense of low fluid volume, showing a new direction for a durable self-standing power source device. The present study helps in developing a completely miniaturized fuel cell by removing many challenges

we normally encounter with the existing state-of-the-art microfluidic fuel cell technology. At the same time, the present technology proves its potentiality for scalable design and manufacturing that may be comparable to regular power generation.

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Notes

^aMicro System Technology Laboratory, CSIR-Central Mechanical Engineering Research Institute, MG Avenue, Durgapur, India.
^bDepartment of Mechanical Engineering, Indian Institute of Technology Kharagpur, Kharagpur 721302, India
*Corresponding author, Email: suman@mech.iitkgp.ernet.in

† Electronic Supplementary Information (ESI) available: Details of SEM images of graphite–paper electrode, microscopic image of CO₂ venting and interfacial proton transfer, and a graph of an open circuit potential measured for long time ($t = 3500$ minutes) are available as supporting information. See DOI: 10.1039/b000000x/

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