Automated pencil electrode formation platform to realize uniform and reproducible graphite electrodes on paper for microfluidic fuel cells

Lanka Tata Rao1, Prakash Rewatkar2, Satish Kumar Dubey2, Arshad Javed1 & Sanket Goel2*

Graphite pencil stroked electrodes for paper-based Microfluidic devices are gaining immense attention due to their electrochemical properties, cost efficiency, and ease-of-use. However, their widespread use has been hindered by the challenges associated with their manual fabrication such as non-uniformity in graphite deposition, applied pressure, etc. This work presents the design and development of an automated graphite pencil stroking device for graphite electrode fabrication with high efficiency through a compact, inexpensive and automatic process, with reduced fabrication time and human intervention leading to more uniformity. The motion platform of Graphtec plotter was used to create multiple strokes with the help of the proposed device. Such inexpensive graphite electrodes (less than the US $1) have been observed to be porous in nature, acting as diffusion agents. The automated graphite electrodes were used to study the performance of microfluidic paper fuel cells (MPFCs) with formic acid, oxygen, and sulphuric acid acting as fuel, oxidising agent and electrolyte respectively. From this configuration, the maximum current density and power density were measured to be 1,305.5 µA cm⁻² and 135.5 µW cm⁻², respectively at 0.3 V stable OCP at 100 strokes. Overall, the study enumerates the development of an automated pencil stroke device for fabricating graphite electrodes, which can potentially be harnessed in numerous miniaturized paper based applications.

Microfluidic devices with integrated electrodes, or electromicrofluidic devices, have attained essential roles in diverse areas, including energy harvesting for portable applications and sensing devices1,2. Paper–pencil based microfluidic fuel cell is one of the most recent vital advancements to develop point of the source (POS) and point of care (POC) devices owing to the well-proven benefits of microfluidic environment and graphite electrodes3,4. In recent years, graphite pencils are being used as electrodes and have shown encouraging outcomes and promising features of MPFCs when compared with the existing approaches. Initially approaches on graphite electrodes, Aoki et al. demonstrated the first use for of graphite material (pencil lead), as electrodes6. Bandapati et al. investigated the performance of membraneless glucose biofuel cell with various grades of graphite pencils act as electrodes7,8. Rewatkar et al. examined 3D printed enzymatic biofuel cell performance with graphite pencil as an electrodes9.

In spite of the numerous benefits of such devices, they come with an inherent setback of the physically fabricated electrodes with non-uniform deposition of graphite due to the subjective nature of the applied pressure and manual counting of the number of strokes. Most of the recent researches in the field of paper–pencil based microfuel cells employ manual deposition of graphite on the paper for fabricating the electrode. Arun et al. reported formic acid microfluidic fuel cell with manual graphite pencil electrodes with diverse grades of pencils10,11. Veerubhola and Ye et al. studied performance with graphite pencil stroke electrodes on paper based microbial fuel cells12,13. Lal et al. showed a paper based microfluidic fuel cell using different filter papers, whereby graphite sheets acted an electrode, and formic acid and potassium permanganate acted as a fuel and an oxidant.

1Department of Mechanical Engineering, Birla Institute of Technology and Science (BITS) Pilani, Hyderabad Campus, Hyderabad 500078, India. 2MEMS, Microfluidics and Nanoelectronics Lab, Department of Electrical and Electronics Engineering, Birla Institute of Technology and Science (BITS) Pilani, Hyderabad Campus, Hyderabad 500078, India. 3email: sgoel@hyderabad.bits-pilani.ac.in
300 strokes with an average force of 2.1 N. was calculated with 'n' performed experiments (n = 3) showing excellent consistency in the force up to more than various graphite pencil strokes with an error bar is shown in Fig. 2, whereby the standard deviation (± 0.05 N) trodes. The step-by-step force-sensing operation of the FSR sensor is mentioned in Fig. S1. The value of force for time video of graphite electrodes formation is presented supplementary video S1.

be used to realize microchannel and electrodes of microfluidic paper fuel cell (MPFC) showing excellent power efficiency, and can be fabricated inexpensively. Moreover, the quantity of force can also be identified at the time graphite electrode fabrication time by force sensing resistor (FSR) sensor. The platform has been harnessed to be used to realize microchannel and electrodes of microfluidic paper fuel cell (MPFC) showing excellent power output. Overall, the platform is an accurate, fully-automated device for graphite electrode formation in an automated manner.

Automated graphite electrodes characterization. The surface morphology of automated and manual graphite pencil stroke electrodes, fabricated on porous nature Gr1 Whatman cellulose filter paper with graphite pencils (HB, 8B), at 50 strokes, were captured by scanning electron microscopy (SEM) and compared. As can be seen in Fig. 3, the enhancement, in terms of uniformity and repeatability, of graphite particle deposition with automated pencil stroke electrodes is more than the manual stroke electrodes. Figure 3 presents the microstruc-
ture (morphology) analysis of Gr 1 Whatman filter paper for automated graphite electrodes and manual stroke electrodes at different magnifications (500, 50 µm). Here, the primary aim of the SEM analysis was to identify the microstructure (pore size) of graphite electrodes in comparison with the plain filter paper (without graphite content).

In Fig. 3, automated (a-1, 2), and manual (b-1, 2) pencil strokes have been compared with the plain filter paper (c-1, 2). It can be observed that the effects of manual and automated strokes are different on the filter paper. The graphite scales formed through the automated process produce air breathable pores which utilise capillary transport and thus yield highly efficient electrodes as compared to the manual one. It can be observed that the deposition of graphite on the filter paper retains the porous property of the filter paper. The distorted graphite scale formation in the filter paper provides better air breathing capability to the electrode and thus leads to better performance.

Further, surface elemental characterization was performed by EDX analysis (energy dispersive X-ray). The difference between automated and manual composed graphite electrodes was observed, and surface elemental composition was evaluated with standard deviation. As shown in Table 1, the elemental composition of automated and manual composed graphite electrodes with 8B graphite pencil at 50 strokes was analysed. After an in-depth analysis of standard deviation, automated graphite pencil electrodes showed high uniformity, accuracy, and repeatability than manual pencil strokes, which can be interpreted from Table 1.
Application of an automated pencil stroke device fabricated electrodes. After successful graphite electrode fabrication using the proposed platform, such electrodes were utilized in a microfluidic paper fuel cell (MPFCs) with formic acid (1 M) acting as fuel, sulphuric acid (3.75 M) as an electrolyte, and oxygen as oxidant. Here, two different automated graphite electrodes (HB, 8B) were prepared with 30, 50, and 100 strokes with equal force and uniformity. From the literature, the graphite content present in graphite pencils were 68% in HB and 91% in 8B. The force (N) was measured at the time of electrodes fabrication, and an explanation is given in “Automated pencil stroke device setup with plotter” and Fig. 7. The fabrication, assembly, and characterization of the microfluidic paper fuel cells (MPFCs) were similar to our previous work. The complete experimentation setup with various automated graphite electrodes (HB, 8B) is shown in Fig. S2.

Initially, an Open Circuit Voltage (OCP) was observed in a MPFC with automated graphite electrodes. Subsequently, the polarization performance of MPFC was investigated by using the chronoamperometry technique with stable OCP of 300 mV. The microfluidic fuel cell polarization curves with various automated pencil strokes (i.e., 30, 50, and 100) are shown in Fig. 4.

The electrochemical characterization of MPFCs was carried out with several automated pencil electrodes with a varying number of strokes. These characterizations were carried out based on energy density (i.e., current density and power density) with the measured open circuit potential (V). In such configuration, the maximum current and power densities were observed to be 1,305.6 µA/cm² and 135.504 µW/cm², respectively, with 100 automated pencil strokes.

The aforementioned automated graphite pencil stroke device with plotter has shown excellent compatibility, robustness, and reproducibility. The fabrication process of the uniform electrodes is simple and inexpensive compared to the manual graphite stroke electrodes. It is clear that automated graphite pencil stroke device has a strong potential to enable various low-power applications, flexible electronic application, and sensing applications.

Conclusions
This paper presents the design and development of an automated pencil stroke formation device for electrode fabrication. Following are the main conclusions and the prominent features of the proposed device:

- The device has a promising potential for large scale fabrication of automated electrodes with uniform deposition and constant force at the time of electrode fabrication. Such fabricated electrodes can be utilized for energy harvesting, flexible electronics, and sensing applications.
- Different grades of graphite pencils such as HB, 8B, and a varying number of strokes can be used to obtain electrodes with varying properties and efficiency on porous Whatman filter paper as per the requirement with the help of automated pencil stroke device with graphtec plotter.

Table 1. Detail summary of EDX characterization for automated and manual pencil strokes on porous nature Whatman filter paper (Gr 1) with standard deviation (n = 3).

| S. no. | Elements (K) | Automated pencil strokes | Manual pencil strokes |
|--------|--------------|--------------------------|----------------------|
|        |              | Average value            | Standard deviation   | Standard error |
|        |              |                          |                      |               |
| 1      | C            | 72.087                   | 0.148                | 0.086         | 68.22        | 3.36         | 1.94         |
| 2      | O            | 17.157                   | 0.408                | 0.236         | 26.813       | 1.992        | 1.15         |
| 3      | Si           | 5.39                     | 0.384                | 0.222         | 2.953        | 0.531        | 0.306        |
| 4      | Fe           | 2.157                    | 0.097                | 0.056         | 1.15         | 0.087        | 0.05         |
| 5      | Al           | 1.497                    | 0.441                | 0.255         | 1.08         | 0.165        | 0.095        |

Figure 4. Polarization performance of microfluidic fuel cell with automated pencil electrodes at 30, 50, and 100 strokes with standard deviation (n = 3).
After rigorous experimentation, characterization, and analysis, MPFC with automated graphite pencil electrodes show the optimum performance with power and current densities of 1,305.6 µA/cm² and 135.504 µW/cm² respectively at 0.3 V stable OCP at 100 automated pencil strokes.

The proposed device also ensures uniform application of force at the time of electrode fabrication. The fabricated automated electrode device is very inexpensive (less than the US $1) and electrodes fabricated with this device can be used in a wide variety of applications.

Table 2. Detail description of an automated pencil holder device components.

| S. no. | Component/software | Technical feature | Function/role |
|--------|-------------------|-------------------|---------------|
| 1      | SolidWorks 2013 x 64 version | 3D Modelling Software | To create 3D models for printing |
| 2      | AutoCAD 2020      | 2D Drawing Software | To create an electrode configuration for making |
| 3      | Flash print       | Convert .stl file to a 3D Printer compatible format | Used to assign the type of filament used for parts design, their melting point |
| 4      | Flash Forge Creator Pro 3D Printer | Dual extruder printer with 1.75 mm filament compatibility | To print the designs based on the fed file |
| 5      | Unique Laser System (VLS Series) | CO₂ Laser capable of cutting and engraving | To cut the paper with precision |
| 6      | Microcontroller/Arduino Uno | Easily programmable and compact | Acts as the control unit, integrates all electronic components |
| 7      | Graphtec Cutting Plotter (CE6000-60 series) | Liner movement | For electrode making |
| 8      | FSR Sensor (402 series) | Force detector | To identifying the force on electrodes |
| 9      | Graphite pencils (different grades) | Carbon nature pencils | For graphite electrodes materials |
| 10     | Whatman cellulose filter paper | Porous nature filter paper | To create graphite electrodes on cellulose filter papers |

Figure 5. Detailed step-by-step fabrication procedure and a prototype model of automated pencil stroke device with FSR sensor.
The proposed device provides a platform to develop standardized electrodes, which can be used for various applications where the electrical output is needed. These applications include microfluidic fuel cells, electrochemical and amperometric sensors for toxic and nontoxic biochemical etc.

Standardized electrodes on paper substrates can be further used to carry out various processes of electrically sensitive organic molecules and analytes in miniaturized settings.

The utility of the proposed device can also be extended to develop standardized electrodes with wax, correction pens or other similar materials for diverse point-of-care applications.

**Methods and materials**

**Chemicals and material.** All chemicals were purchased from Alfa Aesar, India. Different pore sizes of Whatman filter paper Grades such as Gr 1, 6 were purchased from Sigma Aldrich, India. Multiple grades (HB, 8B) of Graphite pencils (Apsara brands) were purchased from a local stationery store. Graphite pencils (HB, 8B) were used for electrodes fabrication by automated pencil stroke device with uniformity, and constant force on porous nature filter paper. A PLA (polylactic acid) filament (FibReel, 1.75 mm, Rever Ind. procured from Sigma Aldrich, India) was used to fabricate the automatic pencil stroke device and its components by FDM based dual extruder 3D printer (Creator Pro, USA). The Force Sensing Resistor (FSR) sensor was used to identify the force (N) at the time of graphite electrode fabrication. The FSR sensor (Interlink 402 model, 0.5” sensing diameter) was procured from Interlink Electronics, India. Graphtec CE 6000-60 cutting plotter (X–Y motion) was used to

---

**Figure 6.** Complete graphite electrodes fabrication setup of an automated pencil stroke device with a plotter.

**Figure 7.** A complete representation of automated graphite pencil holder orientation (motion) with graphtec plotter.
fabricate graphite electrodes. Graphtec CE6000-60 cutting plotter was purchased from Graphtec America Inc. CE 6000 series, US.

**Automated pencil stroke device fabrication/assembly.** Prior to the automated pencil stroke device fabrication, FDM based 3D printer was used to fabricate an automated pencil stroke device and its components with selected dimensions. In the beginning, virtual design of an automated pencil stroke device, with various components, was created with the help of SolidWorks 2013 modeling software. Detailed step-by-step fabrication procedure and prototype of an automated pencil stroke device is mentioned in Fig. 5. The device assembly and disassembly videos are available in the supplementary as Video S2 and S3, respectively. Further, Table 2 shows a thorough description of the components of the automated pencil stroke device and their technical features with functions. Exhaustive dimensions of the automated pencil stroke device and assembly are given in Fig. S3. An FSR sensor was used to observe the force (N) at the time of graphite electrode fabrication on porous cellulose paper (Whatman filter paper). The schematic illustration and circuit diagram of the FSR sensor are shown in Fig. S1.

As can be seen, a spiral spring, with bolt and nut mechanism, was used to adjust the force on the FSR sensor and graphite electrodes fabrication time to maintain constant force and uniformity of graphite particles deposition on the porous cellulose paper (Whatman Gr 1 filter paper).

**Automated pencil stroke device setup with plotter.** Graphtec plotter was used to hold the pencil stroke device for electrodes fabrication with varies multiple strokes and to draw the pencil strokes on a porous paper based substrate. The complete experimentation setup of an automated pencil stroke device with plotter is illustrated in Fig. 6.

The complete schematic representation of graphite pencil holder with the motions (XYZ orientations) mechanism of the plotter is depicted in Fig. 7. Here, porous cellulose paper revolves around Y-axis (CW and CCW direction) for creating pencil graphite zones (as electrodes) on it. Moreover, the graphite pencil holder device moves around X-axis (left to right) for multiple strokes, and the automated device moves in Z-axis (top and bottom) for sensing the force magnitude at the time to realize the pencil graphite zones.

Here, two technical supporting softwares were employed for drawing graphite pencil strokes: Graphtec studio (GS) for operating the Graphtec plotter and AutoCAD to design the electrodes configuration. After designing the geometry of the electrodes, it has been converted into .dxf file and imported into Graphtec studio (GS) for automated pencil strokes. The complete outline representation of graphite electrodes fabrication with graphtec plotter motions (X, Y), graphite electrodes design procedure is mentioned in Fig. 8. Here, prior to the designing of the electrodes by AutoCAD software, that file was saved in .dxf format and convert into G-codes for X, Y motions (graphtec plotter) by graphtec studio software. All technical functions of automated pencil holder with graphtec plotter are summarized in Table 2. Moreover, the number of strokes can also be varied by the Graphtec plotter.

Evidently, most of the electrodes, on a paper microfluidic device, are fabricated manually and therefore are without uniformity in the quantity of force applied on electrodes. To overcome this, an FSR passive sensor was used for identifying the amount of force applied on electrodes at a particular fabrication time. For the FSR sensor, a microcontroller was used to operate a sensor for identifying the applied force on electrodes through MATLAB coding. This microcontroller was connected to the PC to communicate the force data. Afterwards, the Arduino Uno app was used to execute a Matlab program for capture, analyse, and tune the Force data.

---

**Figure 8.** The outline representation of graphite electrodes fabrication with graphtec plotter motions.

---

![Diagram](https://via.placeholder.com/150)
Received: 25 March 2020; Accepted: 8 June 2020
Published online: 15 July 2020

References
1. Goel, S. From waste to watts in micro-devices: review on development of membraned and membraneless microfluidic microbial fuel cell. Appl. Mater. Today 11, 270–279 (2018).
2. Kjeang, E., Djilali, N. & Sinton, D. Microfluidic fuel cells: a review. J. Power Sources 186, 353–369 (2009).
3. Wang, Z. L. & Wu, W. Nanotechnology-enabled energy harvesting for self-powered micro-/nanosystems. Angew. Chem. Int. Ed. 51(47), 11700–11721 (2012).
4. Annu, P., Sharma, S., Jain, R. & Raja, A. N. Review—pencil graphite electrode: an emerging sensing material. J. Electrochem. Soc. 163(3), 0375001 (2020).
5. David, I. G., Popa, D. E. & Buleandra, M. Pencil graphite electrodes: a versatile tool in electroanalysis. J. Anal. Methods Chem. https://doi.org/10.1155/2017/1905968 (2017).
6. Aoki, K., Okamoto, T., Kaneko, H., Nozaki, K. & Negishi, A. Applicability of graphite reinforcement carbon used as the lead of a mechanical pencil to voltammetric electrodes. J. Electroanal. Chem. 263(2), 323–331 (1989).
7. Bandapati, M., Krishnamurthy, B. & Goel, S. Fully assembled membraneless glucose biofuel cell with MWCNT modified pencil graphite leads as novel bioelectrodes. IEEE Trans. Nanobioscience 18(2), 170–175 (2019).
8. Bandapati, M., Rewatkar, P., Krishnamurthy, B. & Goel, S. Functionalized and enhanced HB pencil graphite as bioanode for glucose-O2 biofuel cell. IEEE Sens. J. 19(3), 802–813 (2019).
9. Rewatkar, P., Bandapati, M. & Goel, S. Miniaturized additively manufactured co-laminar microfluidic glucose biofuel cell with optimized grade pencil bioelectrodes. Int. J. Hydrogen Energy 44(59), 31434–31444 (2019).
10. Arun, R. K., Gupta, V., Singh, P., Biwas, G. & Chanda, N. Selection of graphite pencil grades for the design of suitable electrodes for stacking multiple single-inlet paper-pencil fuel cells. ChemSelect 4(1), 152–159 (2019).
11. Arun, R. K., Halder, S., Chanda, N. & Chakraborty, S. A paper based self-pumping and self-breathing fuel cell using pencil stroked graphite electrodes. Lab Chip. 14(10), 1661–1664 (2014).
12. Veerabhotla, R., Bandsadhpayy, A., Das, D. & Chakraborty, S. Instant power generation from an air-breathing paper and pencil based bacterial bio-fuel cell. Lab Chip. 15(12), 2580–2583 (2015).
13. Ye, D. et al. Performance of a microfluidic microbial fuel cell based on graphite electrodes. Int. J. Hydrogen Energy 38, 15710–15715 (2013).
14. Lal, S., Janardhanan, V. M., Deepa, M., Sagar, A. & Sahu, K. C. Low cost environmentally benign porous paper based fuel cells for micro-nano systems. J. Electrochem. Soc. 162(14), F1402–F1407 (2015).
15. Shen, L. L., Zhang, G. R., Venter, T., Biesalski, M. & Etzold, B. J. M. Towards best practices for improving paper-based microfluidic fuel cells. Electrochim. Acta 298, 389–399 (2019).
16. Eikerling, M., Kornyshev, A. A., Kuznetsov, A. M., Ulstrup, J. & Walbran, S. Mechanisms of proton conductance in polymer electrolyte membranes. J. Phys. Chem. B. 105(17), 3646–3662 (2002).
17. Rao, L. T., Dubey, S. K., Javed, A. & Goel, S. Statistical performance analysis and robust design of paper microfluidic membraneless fuel cell with pencil graphite electrodes. J. Electrochem. Energy Convers. Storage 17(3), 031015–031029 (2020).
18. Rao, L. T., Rewatkar, P., Dubey, S. K., Javed, A. & Goel, S. Performance optimization of microfluidic paper fuel-cell with varying cellulose fiber papers as absorbent pad. Int. J. Energy Res. 44, 3899–3904 (2020).
19. Jung, D. G. & Ahn, Y. Microfabricated paper-based vanadium co-laminar flow fuel cell. J. Power Sources 451, 227801 (2020).
20. Heumann, M., Eisengräber-Pabst, J., Öhse, J. & Moghiseh, A. Characterization of the formation of filter paper using the Bartlett spectrum of the fiber structure. Image Anal. Stereol. 32(2), 77–87 (2013).
21. Sousa, M. C. & Buchanan, J. W. Observational models of graphite pencil materials. Comput. Graph. Forum 19, 27–49 (2000).
22. The Interlink FSR 402 sensor datasheet and technical specification, web source https://www.trossenrobotics.com/productdoc/s/2010-10-26-DataSheet-FSR402-Layout2.pdf.

Acknowledgements
The authors would like to thank the Central Analytical Lab (CAL) and Clean Room facility at BITS-Pilani, Hyderabad Campus, Hyderabad, India, where SEM and EDX based characterizations and fabrications were performed.

Author contributions
L.T.R.: methodology, software, validation, investigation, analysis, data curation, writing, visualization; P.R.: validation, investigation, analysis; S.K.D.: conceptualization, methodology, analysis, resources, writing, supervision, funding acquisition; A.J.: conceptualization, methodology, analysis, resources, writing, supervision, funding acquisition; S.G.: methodology, resources, writing, supervision, project administration, funding acquisition.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41598-020-68579-x.

Correspondence and requests for materials should be addressed to S.G.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.
