A Needle-type Complementary Metal Oxide Semiconductor-compatible Glucose Fuel Cell Fabricated by Carbon Nanohorns for Biomedical Applications

Md. Zahidul ISLAM,^{a,b,*} Naofumi MATSUYAMA,^b Guowei CHEN,^b Atsuki KOBAYASHI,^b
Yuichi MOMOI,^c and Kiichi NIITSU^{b,d,*}

^a Institute of Materials and Systems for Sustainability (IMaSS), Nagoya University, Furo-Cho, Chikusa-Ku, Nagoya 464-8603, Japan

^b Department of Electronics, Graduate School of Engineering, Nagoya University, Furo-Cho, Chikusa-Ku, Nagoya 464-8603, Japan

^c Toyo Co., Ltd., 13-4, Kamitanabecho, Takatsuki, Osaka 569-0805, Japan

^d PRESTO, JST, Kawaguchi, Saitama 332-0012, Japan

* Corresponding authors: islam.md.zahidul@e.mbox.nagoya-u.ac.jp, niitsu@nuee.nagoya-u.ac.jp

ABSTRACT

This study details the development of a solid-state complementary metal-oxide semi-conductor (CMOS)-compatible glucose fuel cell, consisting of various amounts (% wt.) carbon nanohorns (CNHs). It was fabricated on an anode area using one-dimensional (1D) structural CNHs, which express an open-circuit voltage (OCV) of 375 mV, the power density of 8.64 $\mu\text{W}/\text{cm}^2$ and current density 23.05 $\mu\text{A}/\text{cm}^2$ in 30 mM glucose solution. The cell can be manufactured via a CMOS fabrication process, using materials biocompatible with the human body. The CNHs enhanced the fuel cell due to their high electrocatalytic ability. Here, CNHs were used to fabricate a 17.5 mm $\times$ 0.7 mm solid-state CMOS-compatible glucose fuel cell with 375 mV of OCV - the highest reported value for such a cell with an anode area of 16.2 mm $\times$ 0.3 mm. The highest power is 0.42 μW . Power generation is the main challenge for developing glucose fuel cells to make the implantable devices that can be used for biomedical applications.

© The Author(s) 2020. Published by ECSJ. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, <http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted reuse of the work in any medium provided the original work is properly cited. [DOI: 10.5796/electrochemistry.20-00044]. Uploading "PDF file created by publishers" to institutional repositories or public websites is not permitted by the copyright license agreement.

Keywords : Carbon Nanohorns, CMOS-compatible Glucose Fuel Cell, Open Circuit Voltage, Biomedical Applications

1. Introduction

CMOS-compatible products offer high-performance in terms of low-power computing, sensing, and communications to IoT-based healthcare systems. To satisfy these demands, several CMOS biosensor LSIs have been developed.^{1–3} CMOS technology can also improve the energy efficiency of IoT-based healthcare systems. However, energy-autonomous operations that use energy harvesting techniques have proved to be difficult to establish.

The main components in the design of glucose fuel cells are CNHs.⁴ 1D structural single-walled CNHs are a newly-developed carbon material.⁵ They are similar to single-walled carbon nano tubes (SWCNTs).^{6–8} CNHs have possible future applications across a wide range of materials fields. D-Glucose fuel cells are valuable power sources in biomedical areas, and for human homeostasis.^{9–11} These fuel cells are mainly generated by the electrochemical reaction between glucose and oxygen that occurs at electrodes. Glucose and oxygen are available in bodily fluids, such as blood, and interstitial fluid allows for the continuous production of electricity. These are the main advantages of the human body. The advantages of using CNHs as catalysts include that they exhibit less specificity and lower reaction rates compared with SWCNTs.

In recent years, glucose fuel cells have increasingly been used in solid-state CMOS bioelectronics devices, due to rapid improvements in their energy efficiency and function.^{12–21} Solid-state CMOS-compatible glucose fuel cells were developed for integration with CMOS circuitries and small systems.²²

However, these small systems showed low invasiveness in the limited power generation capacity of their fuel cells, which is required for their circuitries to be energy efficient. In spite of these advantages, their applications are limited because of their low output power.^{23–25} The energy sources for emerging next-generation

internet of things (IoT)-based healthcare systems have since been applied. In 2012, a CMOS-compatible glucose sensor was proposed and developed.²⁶

This work presents a proposal and for a new structure for improving the OCV. The performance of the fuel cell was enhanced by improving the electrocatalytic ability of the anode. An OCV of 375 mV was achieved, which is the highest value ever reported. This achievement will contribute to the developments of next-generation IoT-based healthcare technology.

2. Experimental Methods

2.1 Measurement methods

The systematic illustration of the CMOS-compatible glucose fuel cell are shown in Fig. 1. However, Raney platinum, which is used as a reagent, is a porous platinum.^{25,27} The main chemical reactions of Raney platinum are as follows:

As shown above, the oxidation of glucose and the reduction of oxygen occur at the anode and the cathode, respectively. The theoretical electromotive force generated due to the partial reaction is 1.30 V.^{28,29}

The fabrication process of the CMOS-compatible glucose fuel cell is shown in Fig. 2. Firstly, a 6-in silicon wafer, with a 1 μm thermal oxide, was prepared with a wafer thickness of 625 μm . The fabricated area was 17.5 mm $\times$ 0.7 mm for each side and the anode surface area was 16.2 mm $\times$ 0.3 mm. The cathode surface morphology was too rough after fabrication using CNHs, however. Secondly, the footprint and anode area were patterned with a wet

Figure 1. Systematic illustration of the CMOS-compatible glucose fuel cell.

Figure 2. Systemic image of the development procedure.

process. Titanium and platinum of 2 nm and 100 nm thickness, respectively, were deposited. Titanium was used as an adhesive layer. Thirdly, a 100-nm-thick aluminium layer was deposited on the platinum in the anode area. This was annealed, and a Pt/Al alloy was formed in the anode area. After annealing, the Al was etched from the Pt/Al alloy, so that only the porous Pt remained. The anode area occupied $16.2\text{ mm} \times 0.3\text{ mm}$. The ratio of Pt/Al was 1:1, due to their 100 nm layers on the wafer. Fourth, Nafion solution was prepared via a 1:5 dilution in 2-propanol (IPA) from Nafion liquid dispersion [Nafion® perfluorinated resin solution (5 wt.%) in a mixture of lower aliphatic alcohols and water, containing 45% water (Sigma-Aldrich)]. The Nafion solution was spin-coated at 400 rpm then heated at 60°C and 120°C , for 30 min at each temperature. This coating and heating process was repeated to form a thick Nafion layer. After the second coating and heating procedure, the formed Nafion layer was patterned using photolithography. Finally, single-walled CNHs (1–7 wt.%) were dispersed in 0.83% Nafion solution with ethanol ($\text{C}_2\text{H}_5\text{OH}$) to form a CNHs dispersed solution. CNHs from the NEC Corporation Japan were used. The CNHs solution was spin-coated once, before being heated at 80°C for three hours in an oven. The CNHs-based layer was then patterned onto the wafer as Fig. S1.

2.2 Measurement setup

Firstly, the manual prober and a DC multi-contact probe were used to establish electrical contact with the developed cells. Electrical measurements were verified with a tester (UI225A,

Figure 3. Measured CNHs wt.% dependent on the current and voltage results.

Agilent Technologies) and a source measure unit (SMU; GS610, Yokogawa). The measurements were performed after dropping a phosphate-buffered saline (PBS)-based glucose solution onto the cathode area. The load depends on the SMU; in the case of this study, both the supply current and the measured voltage, or the supply voltage and current, were observed. The glucose solution was prepared with D (+)-Glucose (Wako) and PBS 10X (Irvine Scientific). 30 mM glucose solution was used in these experiments.

3. Results and Discussion

3.1 Results

Figure 3 shows the voltage and current dependence on the power of the CNHs (1, 3, 5, and 7% respectively) regarding the measurement of the OCV in 30 mM glucose solution. The CNHs (1, 3, 5, and 7 wt.%), voltage (355, 375, 310, and 291 mV), current (1.10, 1.12, 1.06, and 1.01 μA), and power density (8.02, 8.64, 6.76, and 6.17 μW/cm^2) are shown. For the 3 wt.% CNHs, the highest OCV that was obtained is 375 mV, and the peak power density is 8.64 μW/mm^2 when the current density is 23.05 μA/cm^2 . It is assumed that this output is an important for the fuel cell performance. Figure S2 shows the CMOS-compatible glucose fuel cell images for (a) CNHs 1 wt.%, (b) CNHs 3 wt.%, (d) CNHs 5 wt.%, and (d) CNHs 7 wt.%. The power density, compared with CNHs wt.%, is shown in Fig. S3.

3.2 Discussion

Figure S3 shows that the results of the 3 wt.% CNHs on wafer-scale CMOS compatible glucose fuel cells achieved the highest OCV value. Various amounts (wt.%) of CNHs can be used to develop CMOS-compatible fuel cells with different OCVs and electrical conductivities for biomedical applications. The fuel cell was diffused on the anode surface. The anode reaction rate depends on the fuel concentration on its surface, meaning that current density is affected by the amount of CNHs (wt.%) due to their less specificity and lower reaction rates.^{30,31} When the CNHs wt.% is increased, the voltage and current decreased from 3 wt.%. After the glucose fuel cell was dropped on the CNHs surface, the OCV increased. The voltage decreased in the low current range. This is called activation polarization, and it is a common phenomenon in fuel cells. To obtain further power, it is necessary to minimize activation polarization through methods such as employing another catalyst.^{32,33}

The CNHs' resistances were lower when the amounts of CNHs at 3 wt.% were increased, due to their 1D structural carbon properties. Besides, the developed fuel cell (CNHs, 3 wt.%) was also fabricated by the various amount of glucose concentrations (5, 10, 20 and 30) mM. When the glucose concentrations (5, 10, 20 and 30) mM were

increased, the power density (2.9, 4.1, 6.5 and 8.64) $\mu\text{W}/\text{cm}^2$ also increased. So, the glucose concentration is an important issue for power generation.^{34,35} To conclude, the CMOS compatible glucose fuel cell with its anode side coated by 3 wt.% CNHs showed the highest performance. This corresponded with an OCV of 375 mV; the power was 0.41 μW , corresponding to a power density of 8.64 $\mu\text{W}/\text{cm}^2$. These values are promising for biomedical applications.

4. Conclusions

Here, a 17.5 mm $\times$ 0.7 mm solid-state CMOS-compatible glucose fuel cell was fabricated using CNHs in 30 mM glucose solution. The highest OCV (375 mV) was achieved at 3 wt.% of CNHs. The CMOS-compatible glucose fuel cell can deliver electric power to two connecting cells at room temperature. To conclude, this work exhibited different amounts of CNHs (1–7 wt.%) are performed on CMOS-compatible glucose fuel cells. This approach successfully enhanced the cell's OCV, and their electrical power could be applied to IoT technology into the healthcare industry.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.20-00044>.

Acknowledgments

This research was financially supported by JST, PRESTO (No. JPMJPR15D5); by JST, A-STEP (No. AS272S001b); by a Grant-in-Aid for Scientific Research (S) (Nos. 20226009, 25220906, 26220801); and by Grants-in-Aid for Young Scientists (A) (No. 16H06088) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. It was also supported by the Strategic Information and Communications R&D Promotion Programme (Nos. 121806006, 152106004) of the Ministry of Internal Affairs and Communications, Japan; by TOYOTA RIKEN; by the Hibi Science Foundation; and by The Nitto Foundation. Finally, Toyo Co., Ltd., (13-4, Kamitanabecho, Takatsuki, Osaka 569-0805, Japan) was supported by the materials of this work.

References

1. K. Niitsu, S. Ota, K. Gamo, H. Kondo, M. Hori, and K. Nakazato, *IEEE Trans. Biomed. Circuits Syst.*, **9**, 607 (2015).
2. K. Niitsu, T. Kuno, M. Takihi, and K. Nakazato, *IEICE Trans. Electron.*, **E99-C**, 663 (2016).
3. K. Niitsu, K. Yoshida, and K. Nakazato, *Jpn. J. Appl. Phys.*, **55**, 03DF13 (2016).
4. S. Zhu and G. Xu, *Nanoscale*, **2**, 2538 (2010).
5. S. Iijima, M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai, and K. Takahashi, *Chem. Phys. Lett.*, **309**, 165 (1999).
6. S. Arata, K. Hayashi, Y. Nishio, A. Kobayashi, K. Nakazato, and K. Niitsu, *Jpn. J. Appl. Phys.*, **57**, 04FM04 (2018).
7. S. Arata, K. Hayashi, X. Ge, S. Murakami, C. D. Bui, A. Kobayashi, and K. Niitsu, *Jpn. J. Appl. Phys.*, **58**, SBBG11 (2019).
8. K. Niitsu, T. Ando, A. Kobayshi, and K. Nakazato, *Jpn. J. Appl. Phys.*, **56**, 01AH04 (2017).
9. L. B. Wingard, Jr., C. H. Shaw, and J. F. Castner, *Enzyme Microb. Technol.*, **4**, 137 (1982).
10. H. Sakai, T. Nakagawa, Y. Tokita, T. Hatazawa, T. Ikeda, S. Tsujimura, and K. Kano, *Energy Environ. Sci.*, **2**, 133 (2009).
11. A. Kobayashi, K. Ikeda, Y. Ogawa, H. Kai, M. Nishizawa, K. Nakazato, and K. Niitsu, *IEEE Trans. Biomed. Circuits Syst.*, **11**, 1313 (2017).
12. K. Niitsu, S. Ota, K. Gamo, H. Kondo, M. Hori, and K. Nakazato, *IEEE Trans. Biomed. Circuits Syst.*, **9**, 607 (2015).
13. K. Niitsu, T. Kuno, M. Takihi, and K. Nakazato, *IEICE Trans. Electron.*, **E99-C**, 663 (2016).
14. K. Niitsu, K. Yoshida, and K. Nakazato, *Jpn. J. Appl. Phys.*, **55**, 03DF13 (2016).
15. Y.-T. Liao, H. Yao, A. Lingley, B. Parviz, and B. P. Otis, *IEEE J. Solid-State Circuits*, **47**, 335 (2012).
16. F. Zhang and Y. Lian, *IEEE Trans. Biomed. Circuits Syst.*, **3**, 220 (2009).
17. M. Khayatzaadeh, X. Zhang, J. Tan, W.-S. Liew, and Y. Lian, *IEEE Trans. Biomed. Circuits Syst.*, **7**, 583 (2013).
18. J. M. Song, J. Mobley, and T. Vo-Dinh, *J. Chromatogr. B*, **783**, 501 (2003).
19. T. Kuno, K. Niitsu, and K. Nakazato, *Jpn. J. Appl. Phys.*, **53**, 04EL01 (2014).
20. K. Niitsu, M. Sakurai, N. Harigai, T. J. Yamaguchi, and H. Kobayashi, *IEEE J. Solid-State Circuits*, **47**, 2701 (2012).
21. Y.-T. Liao, H. Yao, A. Lingley, B. Parviz, and B. P. Otis, *IEEE J. Solid-State Circuits*, **47**, 335 (2012).
22. X. Liu, L. Li, and A. J. Mason, *IEEE Trans. Biomed. Circuits Syst.*, **8**, 25 (2014).
23. R. Cabrera, I. Weaver, A. Banerjee, R. Sarpeshkar, and T. Thorsen, *ECS Trans.*, **72(3)**, 31 (2016).
24. K. Niitsu, T. Ando, A. Kobayshi, and K. Nakazato, *Jpn. J. Appl. Phys.*, **56**, 01AH04 (2017).
25. J. Tan, W.-S. Liew, C.-H. Heng, and Y. Lian, *IEEE Trans. Biomed. Circuits Syst.*, **8**, 497 (2014).
26. B. I. Rapoport, J. T. Kedzierski, and R. Sarpeshkar, *PLoS One*, **7**, e38436 (2012).
27. S. Kerzenmacher, M. Schroeder, R. Brämer, R. Zengerle, and F. von Stetten, *J. Power Sources*, **195**, 6516 (2010).
28. K. Niitsu, T. Ando, A. Kobayshi, and K. Nakazato, *Jpn. J. Appl. Phys.*, **56**, 01AH04 (2017).
29. S. Kerzenmacher, J. Ducreé, R. Zengerle, and F. von Stetten, *J. Power Sources*, **182**, 1 (2008).
30. G. Wu and B. Q. Xu, *J. Power Sources*, **174**, 148 (2007).
31. M. A. Masadeh, K. Kuruvinschetti, M. Shahparni, P. Pillay, and M. Packirisamy, *IEEE Trans. Ind. Electron.*, **64**, 1561 (2017).
32. S. Kerzenmacher, J. Ducreé, R. Zengerle, and F. von Stetten, *J. Power Sources*, **182**, 1 (2008).
33. S. Prilutsky, P. Schechner, E. Bubis, V. Makarov, E. Zussman, and Y. Cohen, *Electrochim. Acta*, **55**, 3694 (2010).
34. M. Z. Islam, S. Arata, K. Hayashi, A. Kobayashi, and K. Niitsu, *Nanosci. Nanotechnol. Lett.*, accepted (2019).
35. M. Z. Islam, S. Arata, K. Hayashi, A. Kobayashi, and K. Niitsu, *Sens. Mater.*, accepted (2020).