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A novel flexible conductive sponge-like electrode capable of generating electrical energy from the direct oxidation of aqueous glucose

D Desmaële^{1*}, F La Malfa^{1,2*}, F Rizzi¹, A Qualtieri¹, M Di Lorenzo³ and M De Vittorio^{1,2}

¹Istituto Italiano di Tecnologia (IIT), Center for Biomolecular Nanotechnologies, Via Barsanti, 73010, Arnesano, Italy

²Dipartimento di Ingegneria dell'Innovazione, Università del Salento, 73100, Lecce, Italy

³Department of Chemical Engineering, University of Bath, Bath BA2 7AY, United Kingdom

* These authors equally contributed to this work

E-mail: denis.desmaele@iit.it, M.di.Lorenzo@bath.ac.uk, massimo.devittorio@iit.it

Abstract. This paper presents a new sponge-like electrode (SLE) material structured with porous gold (PG). The fabrication process is simple and no specific equipment is required. Notably, the use of liquid metal particles enables the direct growth of PG into the pores of a flexible conductive support matrix. With a SLE sample 13 mm long, 6 mm wide and 1.5 mm thick immersed in a 10 mM glucose solution, we demonstrate that a volumetric power density of $2.4 \text{ mW} \cdot \text{cm}^{-3}$ at $\approx 5 \text{ mA} \cdot \text{cm}^{-3}$ and 0.48 V can be reached without using any enzymes. Because the process presented is versatile and scalable, we envision SLEs with long-term stability that could meet the power budget of various wearable/bioelectronic devices.

1. Introduction

Considering the ever increasing demand for thin, lightweight and compliant electronic systems, recent research efforts have been made to develop correspondingly miniature power sources [1]. For healthcare and/or biomedical related applications, bioelectrochemical energy sources are an attractive option. Efforts in this field, however, have predominantly focused on the development of enzyme-based configurations. Enzymes can for instance be efficiently employed to generate useful amount of electricity from lactate [1] or glucose [2] at concentrations that can be found in body fluids (e.g., sweat or blood). Nonetheless, it is well recognized that the limited stability of enzymes poses great challenges for applications targeting long periods of operations (e.g., cardiac pacemakers). Alternatively, porous gold (PG) appears as a promising option for developing new electrodes featuring longer term stability. PG can indeed directly convert the chemical energy of glucose into electricity without using enzymes [3]. The hydrogen assisted electrodeposition technique (HAET) is one of the fastest and most affordable methods recently discussed to fabricate PG electrodes [4]. Most works that discussed the HAET, however, reported PG predominantly grown on rather thick/solid underlying substrates (e.g., gold disk electrodes). Here, we report an alternative facile, fast and low-cost fabrication technique that can be used to grow PG of flexible porous conductive matrices in order to obtain a sponge-like electrode (SLE) material that can catalyze glucose oxidation.



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2. Experiments

Unless otherwise stated, all chemicals were obtained from Sigma-Aldrich and used as received.

2.1. Preparation of the sponge-like electrode (SLE)

2.1.1. Fabrication of the porous conductive support matrix: As a first step, a porous conductive support matrix made of polydimethylsiloxane and carbon nanofibers (PDMS-CNFs) was prepared by adapting a protocol reported elsewhere [5]. Briefly, CNFs (250 mg) were dispersed in 10 mL of isopropyl alcohol (IPA) using a probe sonicator (Labsonic P, Sartorius) operating at a power of 160 W (operating frequency=24 kHz, duty cycle=1, time=15 min). In parallel, a liquid mixture of PDMS (Sylgard 184, Dow Corning) was prepared in a 1:10 ratio of curing agent and PDMS monomer. The CNFs solution was then mixed with 2030 mg of PDMS (12 wt% of CNFs) under constant stirring at 60 °C for 30 min. After the IPA in excess completely evaporated, 5 g of sugar particles (average diameter estimated \approx 760 μ m, n=9) were poured into the PDMS-CNFs. The mixture was stirred and then placed in a thermostatic oven (G-therm, Fratelli Galli) and heated at 85 °C during 45 min in order to completely solidify the PDMS. The resulting solidified slab encompassing PDMS, CNFs and sugar was placed in a beaker containing 500 mL of water. The beaker was positioned onto a hot plate (C-MAG HS7, IKA) set to 120 °C. After 2 h, the temperature of the hot plate was decreased to 85 °C. Heating and continuous stirring were maintained overnight to ensure the complete removal of the entrapped sugar grains.

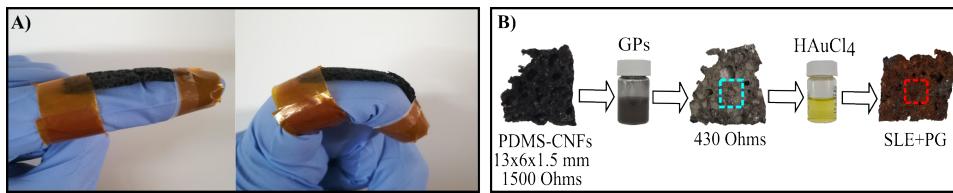


Figure 1. A) Images illustrating the body-conforming capabilities of the conductive PDMS-CNFs used as a support matrix. B) The three main subsequent steps of the process to obtain the SLE with PG.

2.1.2. Incorporation of the PG: The subsequent steps of the fabrication process to obtain the SLE are summarized in figure 1B. At this stage a small piece (denoted SP hereafter) was cut from the slab of PDMS-CNFs prepared. The SP was 13 mm long, 6 mm wide and 1.5 mm thick. The key concept to grow gold nanostructures here is to exploit the liquid metal Galistian as a substrate [6]. To that end, Galistian particles (GPs) were synthesized based on a protocol published elsewhere [7]. Here, 1 g of Galistian (62% Gallium, 22% Indium and 9% Tin by weight, Smart-elements) was added into a 5 mL screw-capped glass vial filled with 2.25 mL of ethanol. The vial was then placed in a larger screw-capped laboratory glass bottle. The vial was turned on its side and half immersed in water. The bottle was placed in an ultrasonic bath (Labsonic LBS1, FALC Instruments) for 2 hours. After sonication, the solution appeared opaque and gray (figure 1B). To increase its hydrophilicity, the PDMS-CNFs SP was exposed to an oxygen plasma (Diener Nano, Diener Electronic GmbH) operating at a power of 50 W during 1.5 min. Immediately after plasma treatment, the SP was dipped in \approx 0.2 mL of the solution of GPs. The SP was then dried overnight at room temperature. It was subsequently placed in a custom made PDMS reservoir containing 2 mL of a 10 mM solution of gold (III) chloride trihydrate (HAuCl₄). Noteworthily, we used here a concentration of HAuCl₄ ten times lower when compared to other works (e.g., [3]). A thin black colored layer appeared onto the SP covered with the GPs after a few minutes it entered in contact with the HAuCl₄ solution. During the reaction, the later

turned progressively from yellow to transparent. After ≈ 3 hours, a faintly reddish-brown color started to appear and the SP was removed from the reservoirs. The final SP obtained was again dried overnight at room temperature prior further tests.

2.2. Microstructure characterization and instrumentation

The morphology of the SLE created was analyzed using a scanning electron microscope (SEM, Helios NanoLab 600i, FEI). Measures of electrical resistance were performed using a RCL meter (e4980AL, Keysight). For the electrochemical measurements, a stock solution of glucose (10 mM, a concentration that can be found in the human body) was prepared in a neutral phosphate buffer and allowed to mutarotate overnight before use. The SLE was used to catalyze glucose oxidation. It was immersed with a platinum (Pt) cathode (10x25 mm) in a beaker filled with the glucose solution (see inset figure 2).

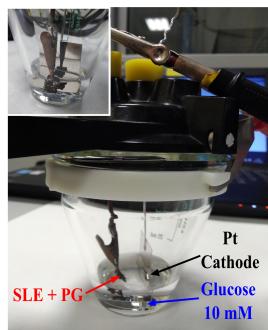


Figure 2. Experimental setup used for evaluating the performance of the SLE with PG.

Pt was selected because it exhibits one of the highest oxygen reduction potential in phosphate buffer pH 7 [8, 9]. Polarization curve measurements were performed at room temperature ($\approx 20^\circ\text{C}$) using a potentiostat (Autolab, Eco chemie).

3. Results

Figure 1A demonstrates that large flexible slabs of PDMS-CNFs with good body-conforming capabilities could be manufactured. The porosity of such slabs is estimated to be $\approx 60\%$. When considering the initial cut SP (black colored PDMS-CNFs), its electrical resistance was $\approx 1.5\text{ k}\Omega$. The measure was repeated later with the gray SP covered with the GPs. Interestingly, the electrical resistance dropped to $430\text{ }\Omega$. This confirms that the layer of GPs can notably enhance the initial conductivity of the PDMS-CNFs. The GPs were then inspected in more details using the SEM (figure 3A). A good affinity is observed: the GPs penetrate and cover well the inner walls of the SP's pores. Because no specific filtration step was utilized during the synthesis of the GPs, their size range from hundred of nanometers up to $\approx 7\text{ }\mu\text{m}$. Although numerous GPs have a spherical shape, irregular shapes can also be noticed. Having GPs with inhomogeneous shapes and sizes, however, does not appear a critical issue for the application targeted here. Figure 3B confirms the growth of gold nanostructures onto the GPs. The resulting structure is a rough surface with complex shapes whose dimensions range from a few micrometers down to tens of nanometers.

The performance of SLE was then evaluated. Figures 4A and 4B show the polarization curve and the power curve obtained, respectively. With no current flowing through an external load, the open circuit voltage is 0.9 V. Surface current and power densities shown in figure 4 are normalized with respect to the electrode projected surface area (PSA), namely only the rectangular base footprint of the SLE is considered [10, 11]. As can be seen, the highest surface peak power density reached is $\approx 360\text{ }\mu\text{W}\cdot\text{cm}^{-2}$ at $\approx 745\text{ }\mu\text{A}\cdot\text{cm}^{-2}$ and 0.49 V. If considering

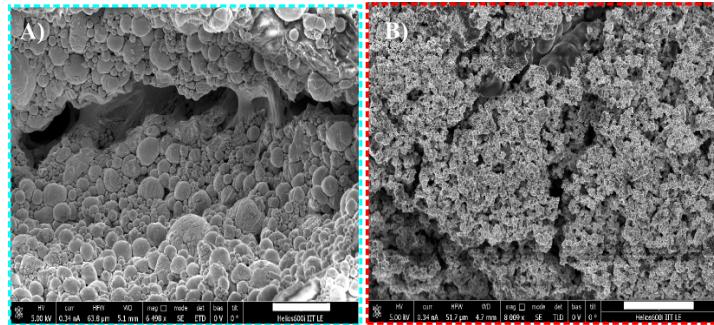


Figure 3. SEM micrographs: A) GPs covering the PDMS-CNFs (see blue dashed line in figure 1). Scale bar is 10 μm . B) PG obtained after immersion of the PDMS-CNFs+GPs in the HAuCl₄ solution (see red dashed line in figure 1). Scale bar is 10 μm .

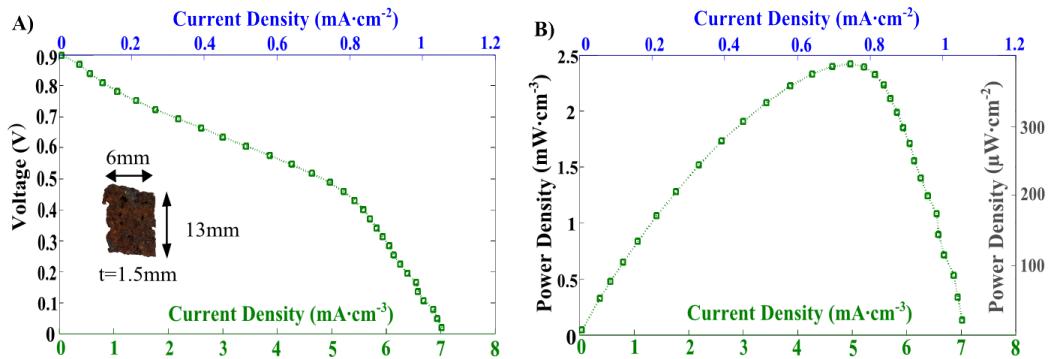


Figure 4. Performance measured for the SLE with PG fabricated. A) Polarization curve. B) Power curve.

the geometrical area accounting for both sides of the SLE (data not shown in figure 4), the surface peak power density drops to $\approx 180 \mu\text{W}\cdot\text{cm}^{-2}$ at $\approx 372 \mu\text{A}\cdot\text{cm}^{-2}$. In both cases, however, performance evaluations based on the PSA or the geometrical area can be untrue (see discussion in [10]). For the SLE, they indeed appear of limited significance because they completely neglect its porosity. Likewise, they do not provide enough information with regard to its true three dimensional nature (including its thickness). Like in [10], we believe it is here more representative to rather consider the performance of the SLE in terms of volumetric densities. In this case, the power density achieved is $\approx 2.4 \text{ mW}\cdot\text{cm}^{-3}$ at $\approx 5 \text{ mA}\cdot\text{cm}^{-3}$ and 0.48 V. Importantly, and independently of the normalized values favored, the net electrical power generated by the SLE is almost 300 μW at 0.48 V. It was previously demonstrated that a net power of 105 μW generated at 0.35 V can already be exploited to drive a cardiac pacemaker [12]. We therefore envision that SLEs of various dimensions might be able to supply power to various wearable/implantable/bioelectronic systems in the future.

4. Conclusions

A distinctive feature of the new fabrication method presented in this paper is that porous gold (PG) can be grown onto flexible porous support matrices. To the best of our knowledge, such a possibility has not been reported with the more established hydrogen assisted electrodeposition

technique (HAET). Specifically, we demonstrate that the method can be utilized to easily grow PG structures into the pores of a sponge-like electrode (SLE) made of conductive PDMS. When immersed in a 10 mM glucose solution, the small SLE can directly generate almost 300 μ W at 0.48 V without using enzymes (the corresponding volumetric peak power density is almost 2.5 $\text{mW}\cdot\text{cm}^{-3}$ at \approx 5 $\text{mA}\cdot\text{cm}^{-3}$). Further research is now required to investigate the repeatability of the fabrication process. With the long-term goal of developing novel compliant miniature power sources, we also plan to study the stability of the PG with respect to bending and/or stretching.

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