Using Galistan to fabricate porous gold electrodes: toward non-enzymatic glucose fuel cells with enhanced performance for driving wearable/bioelectronic devices

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Abstract. This paper presents a new facile route for the fabrication of enzyme-free porous
gold electrodes (PGEs) which can directly convert the chemical energy of glucose into electricity.
The method is low-cost and does not require any special equipment: porous gold is simply
grown on carbon paper containing liquid metal particles. As a first proof-of-concept, we report
on the fabrication of circular PGEs having a diameter of 12.5 mm. When immersed in a
10 mM glucose solution, such PGEs can produce up to 25 µW (maximum power density
10 µW·cm⁻² at 45 µA·cm⁻²). Because the process presented is versatile and scalable, we envision PGEs with long-term stability that could be stacked to meet the power budget of various wearable/bioelectronic devices.

1. Introduction
PGEs appear particularly attractive for supplying power to biosensors and biodevices requiring
long periods of operation (e.g., cardiac pacemakers). Because PGEs can directly convert
the chemical energy of glucose into electricity without using enzymes [1], they might indeed
bring solutions to the well recognized limited stability of conventional enzyme-based electrodes.
Despite this promise, a major hindrance to the practical deployment of PGEs might be related
to their fabrication. The hydrogen assisted electrodeposition technique (HAET) is one of the
fastest and most affordable methods recently discussed [2]. Most works that discussed the
HAET, however, reported PGEs with rather small geometrical dimensions [1, 3]. To the best of
our knowledge, the possibility to upscale the HAET to fabricate enzyme-free PGEs that could
meet the power budget of real electronic devices remains to be demonstrated. As an alternative
to the HAET, we here introduce a novel fabrication process to straightforwardly produce PGEs
of various dimensions. Compared to the HAET, our novel fabrication process offers distinctive
features: i) no specific equipment (e.g., potentiostat) is required; ii) the amount of gold used
can be an order of magnitude lower.
2. Experiments

Unless otherwise stated, all chemicals were obtained from Sigma-Aldrich and used as received. Toray carbon paper (TCP) was used as the support material for all electrodes. TCP sheets purchased were 110 μm thick (TCP-H-030, Toray). They were not coated for wet proofing.

Three TCP disks (TCP-Ds) having a diameter of 12.5 mm were cut by xurography using a cutting plotter (CE 6000-40, Graphtec [4]). To increase the hydrophilicity of the TCP, all disks were exposed to an oxygen plasma (Diener Nano, Diener Electronic GmbH) operating at a power of 50 W during 1.5 min.

2.1. Preparation of the electrocatalytic electrodes

Two PGEs (hereafter referred as PGE₁ and PGE₂) were used as anodes to catalyze glucose oxidation. The fabrication process involves solely three simple steps (figure 1). The key concept is to exploit the liquid metal Galistan as a substrate to grow gold nanostructures [5]. Galistan particles (GPs) were synthesized based on a protocol published elsewhere [6]. Here, 1 g of Galistan (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 an ultrasonic bath (Labsonic LBS1, FALC Instruments) for 2 hours. After sonication, the solution appeared opaque and gray (figure 1). Prior to be used, the solution was vigorously shaken for a few seconds with a laboratory vortex and transferred in a 1 mL plastic needleless syringe. Immediately after plasma treatment, ≈0.1 mL of the solution of GPs was directly drop-casted onto both sides of each TCP-D. The two TCP-Ds were then dried overnight at room temperature. They were subsequently placed in custom made polydimethylsiloxane cylindrical reservoirs containing 2 mL of a 10 mM solution of gold (III) chloride trihydrate (HAuCl₄). A thin black colored layer appeared onto the TCP-Ds after a few minutes they entered in contact with the HAuCl₄ solution. During the reaction, the later turned progressively from yellow to transparent. After ≈2-3 hours, a faintly reddish-brown color appeared and the TCP-Ds were removed from the reservoirs. The two PGEs obtained were finally dried overnight at room temperature prior further tests.

For the cathode, platinum was selected for oxygen reduction because it exhibits one of the highest oxygen reduction potential in phosphate buffer pH 7 [7, 8]. Immediately after plasma treatment, a liquid paint containing a precursor of platinum (Plastisol T, Solaronix) was drop-casted with a pipette onto both sides of the disk until the TCP appeared visually saturated with liquid. The wet TCP-D was then immediately fired in an muffle furnace (B180, Nabertherm) at 460 °C for 15 min.

2.2. Characterization and electrochemical measurements

The morphology of the PGEs created was analyzed using a scanning electron microscope (SEM, Helios NanoLab 600i, FEI). For the electrochemical measurements, a stock solution of glucose
(10 mM) was prepared in a neutral phosphate buffer and allowed to mutarotate overnight before use. PGE$_1$ and PGE$_2$ were immersed one after the other with the cathode in a 5 mL beaker filled with the glucose solution (see inset figure 3A). The distance between PGE$_{1,2}$ and the Pt cathode was 1 cm. Polarization curve measurements were performed at room temperature ($\approx 20^\circ$C) using a potentiostat (Autolab, Eco chemie).

3. Results
First, the GPs injected into the TCP-Ds were visually inspected with the SEM. As can be viewed from figure 2A, the GPs penetrate relatively well into the fibrous electrode structure (see comparison to bare TCP shown in inset). They tend to fill the voids between the fibres. Because no specific filtration step was utilized during the synthesis of the GPs, their size range from hundred of nanometers up to $\approx 7 \mu$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 2B confirms the growth of gold nanostructures onto the GPs. The resulting structure is a rough surface with complex, highly branched, shapes. Interestingly, we observed leaf-like structures similar to the feather-like structures obtained via the HAET even though we used a concentration of HAuCl$_4$ ten times lower [1]. A large number of such sharp edges can drastically enhance catalytic activities [9].

The performance of PGE$_{1,2}$ was then evaluated. Figures 3A and 3B show the polarization curves and the power curves obtained, respectively. With no current flowing through an external load, the open circuit voltage is 0.42 V for PGE$_1$ (red dotted line) and 0.47 V for PGE$_2$ (dashed blue line).

![Figure 2. SEM micrographs: A) GPs entrapped into the TCP fibers (inset shows bare TCP for comparison). B) PGE obtained after immersion of the TCP+GPs in the HAuCl$_4$ solution (inset: the leaf-like gold structure is $\approx 1.4 \mu$m long).](image)

![Figure 3. Performance measured for two different PGEs when immersed in a 10 mM glucose solution with a platinum cathode: (A) Polarization curves and (B) Power curves.](image)
Normalized values shown were estimated accounting for the geometrical areas for both sides of the electrodes, but not taking into account the internal surface of the porous TCP-Ds. The highest peak power density reached is 10.3 µW·cm$^{-2}$ at 45 µA·cm$^{-2}$ (PGE$_2$). This power density compares favorably with some previous works. For instance, a previous enzyme-free glucose fuel cell generated 2 µW·cm$^{-2}$ at 15 µA·cm$^{-2}$ (glucose concentration 5 mM) [10]. Noteworthily, unlike in [10], our fabrication method does not require advanced or costly microfabrication techniques. Comparatively the maximum power density reached by PGE$_1$ is $\approx 19\%$ less (8.4 µW·cm$^{-2}$). We currently assume that such performance discrepancies between the two PGEs are likely due to an inhomogeneous penetration of the GP solution through the TCP. If the underlying layer of GPs is different from sample to sample, it stands to reason that it leads to PGEs with different amounts of branched gold structures. Further research is required to investigate the repeatability of the fabrication process of figure 1. Nonetheless, the net electrical power delivered by PGE$_1$ and PGE$_2$ is $\approx 20 \mu W$ and $\approx 25 \mu W$, respectively. In [11], it was demonstrated that a net power of 12.5 µW can already be sufficient to drive a wireless temperature sensor. We therefore envision that even smaller PGEs might be able to supply power to various wearable/bioelectronic systems, as illustrated in figure 4.

![Figure 4](image)

4. Conclusions

The fabrication of porous gold electrodes (PGEs) via the new method presented here appears as an interesting alternative to the hydrogen assisted electrodeposition technique (HAET). Although the HAET is faster, the dimensions of the PGEs obtained are often rather limited because of the setup required. Comparatively, we here show that circular PGEs having a diameter of 12.5 mm can be straightforwardly produced without any specific equipment. Such PGEs are capable of generating up to 25 µW in a 10 mM glucose solution without using enzymes. In the near future, our efforts will be focused on enhancing the reproducibility of the fabrication method presented. Additionally, we will investigate the long-term stability of the PGEs fabricated.

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