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Printing biocathodes: construction and characterization of an air breathing platform

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Short abstract

As a virtuous technology, printed biofuel cells are emerging as a promising way to supply low-power devices in the context of Internet of Things or healthcare, while addressing the environmental challenges of our century. The aim of this study is to produce a functional biosurface for an effective oxygen reduction as a fuel cell biocathode. The challenge of this technology is to neutralize the environmental impact of current power sources by introducing bio-based materials to a functional ink formulation for a printed biocathode. In this concept, cathodic enzymes need to be localized near the electroactive sites to optimize the Direct Electron Transfer (DET) thanks to an optimized percolation network. Another function of this novel biosurface is the increase of O_2 levels in the microenvironment of biocathode to improve the electrochemical activity. Hence, different parameters of the ink formulation were also studied: hydrophobicity/hydrophilicity control of printed biocathode surfaces via contact angle measurements, surface structure via microscopy after printing, total solid content, particle size, pH and rheological properties. Finally, a new environmentally friendly formulation has been developed, by using only bio-based components and water as solvent. After optimization, stable catalytic current above 1 mA/cm^2 has been achieved. In full cell configuration, maximum power reached is 75 µW/cm^2. This printable cathode ink is therefore promising for sustainable applications.

Keywords: biocathode, functional printing, enzymatic biofuel cell, biosensors

1. Introduction and background

The rise of connected and miniaturized devices has increased the need for flexible low power apparatus. These devices have a short life span, and they currently use batteries which contain toxic ingredients for the environment. Among them, lithium-ion batteries, known as one of the most used types for those connected devices, always end up in landfill or are incinerated. Moreover, incorrect disposal of this type of battery does not only contaminate the environment but also cause fire incidents (Mrozik, et al., 2021). Hence, the demand of alternative options for those batteries has increased and oriented to study biodegradable components as an alternative for the toxic ingredients in currently used batteries.

Fuel cells can be an alternative way to power connected devices. But they currently raise some issues due to the use of synthetic materials. For instance, to overcome the problem of oxygen accessibility and cathode flooding, fuel cell cathodes are using hydrophobic components made from fluorine chemistry. Indeed, Chi, et al. (2018) demonstrated that adjusting the ratio between hydrophobicity and hydrophilicity improved the performances. In fact, by adding polytetrafluoroethylene (PTFE) or Nafion™, they generate a balance between cathode flooding and system hydration for proton flow. In addition, fuel cells such as H_2-O_2, use metal catalysts such as platinum, an expensive and non-recyclable metal which is difficult to industrialize because of its chemical reactivity. Therefore, the drawback of this technology has been the presence of non-disposable components such as fluorinated binders or metallic catalysts.

Compared to standard fuel cell cathode, biocathode can work with natural catalyst such as enzymes to enable the O_2 reduction. Equation [1] represents the half-reaction that occurs at the cathode. To operate as a complete cell, a bioanode and a separator are required. For glucose-O_2 biofuel cell, glucose oxidation occurs at the bioanode side (Equation [2]).

$$\frac{1}{2}O_2 + 2e^- + 2H^+ \rightarrow H_2O \quad [1]$$

$$\text{Glucose} \rightarrow \text{Gluconolactone} + 2e^- + 2H^+ \quad [2]$$

Enzymes used for O_2 biocathode are usually multicopper oxidases. They can perform with Direct Electron Transfer (DET) approach, so they do not need any mediator or promoter to do the electron transfer. Several types of enzyme immobilization can be used on the electrode surface: adsorption, covalent bonding, cross-linking or encapsulation (Abreu, 2018). The selection of the enzymes and the way to immobilize it on the electrode surface have a significant impact on the biofuel cell performances in terms of power and/or current. Electrical transfer properties are also studied to improve performances by introducing highly conductive materials such as Carbon Nanotubes (CNTs), carbon nanodots or graphene oxide (Huang, et al., 2019). These enzymatic biocathodes are well known at lab scale with optimized enzyme immobilization. However, their industrialization is complicated to consider. Therefore, the use of printing technologies is investigated in this study to unlock scale up production.

Thus, the objective of this work is to formulate an ink for a biocathode which can be printable with screen printing or coating. Particle size measurements, rheological characterization and printing trials were carried out to demonstrate the printability of this ink. Moreover, characterization tests of the biocathode were performed in terms of ionic, electronic conductivity, enzyme activity and hydrophobic behavior. The new ink was also largely made up of biobased components and is likely to be biodegradable within a few weeks. Some of these components and specific process are confidential for the moment for reasons of intellectual property. They will not be mentioned in this extended abstract.

2. Materials and methods

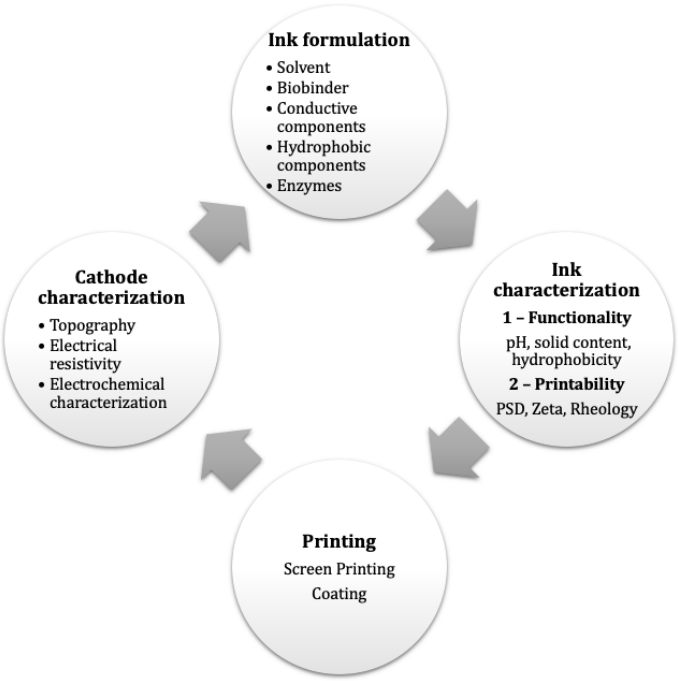


Figure 1: Development process of the cathode ink formulation and its printing

Figure 1 shows the process of ink formulation and printing implementation with associated characterizations. The material selection was done in coordination with the different characterizations. The ink formulation consists of a combination of bio-binders, conductive components, hydrophobic components and enzymes. The solvent used is MiliQ water. The ink samples were characterized by different methods.

The first objective is to allow biocathode functionality by choosing certain components:

- The pH has to be adjusted to allow the best enzyme activity and to allow a stable state of charged particles and polymers. It was measured with pH-meter from Mettler Toledo.
- Solid content is measured to estimate residual amount deposited on the substrate after printing. This measurement allows to calculate the deposited volumes by coupling this with thickness and topography measurements. Finally, layers density and microstructure can be estimated. It was measured with thermobalance HC103 from Mettler Toledo.
- Hydrophobic components have been developed to avoid cathode flooding and allow O_2 diffusion. They were characterized with Ossila's contact goniometer and its related software. It has been done for the biobinder blends, which is a mix between hydrophobic and hydrophilic components. Different ratios have been prepared. The polymer blend solutions were coated on glass and dried. A 10 µL droplet of distilled water was used to perform the contact angle measurement. Measured contact angle represents the angle between the solid interface and water. If this angle is superior to 90°, the solid is considered as hydrophobic.

The second objective of ink characterizations is to make the ink printable by adjusting the appropriate components and processes:

- The particle size distribution can affect the ink rheological behavior and the layer architectural nano and microstructure. Furthermore, D90 parameters is directly connected to mesh opening selection. It was measured with electroacoustic spectroscopy DT1202 from Dispersion Technology because of carbon suspensions opacity which excluded light scattering techniques.
- The residual charges of polymers and particles in inks play a role in suspension stability. The zeta potential is used to stabilize inks with adjusting the pH, double layer charge state and ionic forces. It was measured with electroacoustic spectroscopy DT1202 from Dispersion Technology.
- Rheological measurements are also essential to understand the behavior of the ink under shear rate induced by printing process. By modeling those printing steps, it is possible to adjust the formulation thanks to screen printing or coating requirements. They were performed with a rheometer (HR20 – TA Instrument) thanks to a parallel plate geometry with a diameter of 40 mm and a gap of 1 mm at 20 °C. Solvent cage was used to avoid sample evaporation. Flow curve was plotted to determine the rheological behavior of the inks. Oscillation tests were also conducted to determine the viscoelastic behavior of the ink (G' and G'' moduli).

After several iterations of formulation and characterization, suitable inks have been produced and printed. As a starting point, inks have been coated with a traditional coating table. Metal templates with 200 mm thickness were used on the substrate material as Gas Diffusion Layer (GDL). This substrate was chosen as a conductive, hydrophobic, and porous surface that allows oxygen diffusion (so called air breathing) and avoids cathode flooding. Additionally, it plays a current collector role since it is electrically conductive. Figure 2 represents the printed biocathodes on GDL.

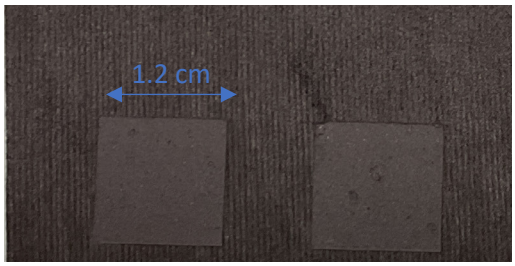


Figure 2: Coated cathodes on GDL

Finally, some characterizations were conducted on this cathode electrode:

- Surface reconstruction in 3D had been performed to study the topography of the printed layer. Microscopic surface characterization was carried out with an Axioscope 7 from Optic Concept Zeiss, with its associated software DeltaPix Insight.
- Electrical resistivity was measured with 4 points probe DAQ973A from Keysight. This ink was first coated on glass prior to measurement in order to remove substrate conductivity contribution.
- Electrochemical characterizations were finally performed to assess catalytic activity. Measurements were performed on a MPG2, Biologic™ potentiostat. Bioelectrodes were tested in a half-cell configuration with a 3-electrode setup including an Ag/AgCl reference electrode and a Pt counter electrode within GDL/Ink/Enzyme as working electrode. Open circuit voltage (OCV), which represents the potential reached without any applied current, and cyclic voltammetry (CV) were performed from 0.7 V to 0 V with a 1 mV/s scan rate. These electrochemical characterizations were repeated 10 times.
- For the characterization of full cell, a reference enzymatic bioanode was added but it will not be described in this study. Polarization tests were conducted with different current discharges from 0 µm to 500 mA.

3. Results and discussion

3.1 Ink characterization

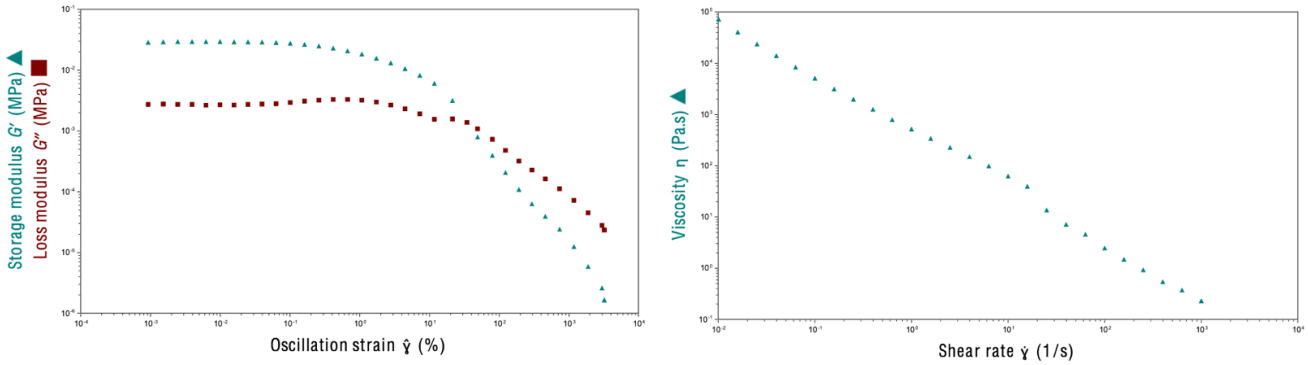
Different characterization and optimization loops were performed for the biocathode to adjust the ink performances and printability:

- Conductive components ratio has been adjusted to control the ink rheological behavior and ink solid content (20 %, w/w).
- The polymer matrices have been made compatible by modifying the ratio of the dispersion polymers and the binder polymer, which have opposite charges.
- An optimal pH has been determined within the range 5 and 6 in regards of maximum enzyme catalytic activity and zeta potential stability. In the carbon dispersion, zeta potential is −14.32 ±0.13 mV, means that the global charge of carbon particle induces repulsive interactions that stabilizes the system. Steric stability given by the binder polymer also enhances overall dispersion stability (Tadros, 1991; Bajpai, et al., 2007).
- Particle size distribution shows a maximum particle size in the carbon dispersion at 36.40 ±0.12 nm. Thus, the opening diameter of the screen-printing mesh should not be less than three times this value.

3.1.1 Rheological characterization

Figure 3a represents the variation of G’ and G’’ moduli as a function of oscillation strain. Under strain of 40 %, G’ > G’’, meaning that the elastic behavior is preponderant, and the ink behaves as an elastic solid. Over 40 % of oscillation, the ink behaves as a viscous liquid.

Figure 3b shows the variation of viscosity as a function of shear rate. Ink viscosity decreases when the shear rate increases, and power law index is 0.35 which demonstrates the shear-thinning behavior of this ink.



a) *b)*

Figure 3: (a) Elastic and viscous modulus and (b) flow curve of the ink

Screen printing process usually requires a high viscosity at low shear rate and a shear-thinning behavior, associated to pronounced thixotropy. In the first step, the ink is applied onto the screen. At this stage, the ink shouldn't spread and should stay under flow threshold. Secondly a high shear rate is applied to force the ink pass through the mesh screen: at 100 s^{-1}, the ink reaches low viscosity around 1 Pa·s. Ink should recover its solid behavior rapidly after screen unmold and material reconstruction properties are mandatory to reach homogenous layers. The viscoelastic behavior of the ink shows that ink can be reconstructed after printing. These rheological properties are compatible with the screen-printing process and are sufficient conditions for the ink to be printable. However, process parameters such as squeegee pressure and speed, and off-contact conditions will also have an influence (Kuscer, 2021).

3.1.2 Hydrophobic biobinder – O_2 accessibility

As Chi, et al. (2018) shown, balance between hydrophilic and hydrophobic components is an important parameter to avoid cathode flooding while promoting ionic conductivity. For this ink, hydrophobic microstructures have been developed to enhance O_2 diffusion near catalytic centers.

Contact angle measurements of the hydrophobic bio-binder have been carried out to select the best ratio of hydrophobic component in the bio-binder. Table 1 represents the results of contact angle measurements.

Biobinder A, with the lower amount of hydrophobic compound reaches an apparent contact angle of 71°. As this value is under 90°, it shows that it has a dominant hydrophilic behavior. Biobinders B, C and D which contain more hydrophobic compounds have reached an apparent contact angle higher than 90°, that confirms their macroscopic hydrophobic behavior. As expected, the higher the hydrophobic content, the higher the contact angle.

Table 1: Contact angle for different hydrophobic ratios

Biobinder name	Ratio of hydrophobic component	Contact angle (°)
A	-	71 ± 5
B	+	90 ± 2
C	++	98 ± 3
D	+++	100 ± 3

Biobinders B, C and D were incorporated in the ink formulation, printed and tested in full cell with an enzymatic anode reference. A control ink with PTFE was also printed and tested with the reference enzymatic anode. Polarization tests were done for each printed fuel cell. Table 2 presents the open circuit voltage (OCV) prior to polarization sequences. The higher the ratio of hydrophobic component in the hydrophobic biobinder, the higher the OCVs. As expected, the control PTFE ink reached the maximum OCV because the structure cannot be flooded by water at all. The maximum power achieved by the biofuel cells is impacted by the ratio of hydrophobic components in the biobinder. Indeed, the maximum power reached for ink with ratio D is much higher than for ratio B and C. Maximum power can be reached thanks to an optimized O_2 accessibility and a high ionic conductivity. The biobinder blend based on ratio D enhances oxygen diffusion and preserves ionic conductivity on the cathodic enzyme side allowing the printed biofuel cell to reach higher maximum power. In this study, a new natural biobinder component was developed, offering advantageous alternative compared to fluorinated binders such as PTFE.

Table 2: Polarization tests results for different printed fuel cells

Hydrophobic compounds	OCV (mV)	Maximum Power (µW)
B	654 ± 3	29 ± 5
C	672 ± 3	35 ± 5
D	684 ± 13	107 ± 14
PTFE	695 ± 8	95 ± 4

3.2 Biocathode characterization

3.2.1 Surface characterization

A 3D reconstruction of the cathode printed on Gas Diffusion Layer (GDL) allowed to evaluate the surface roughness of the electrode and the material organization on its surface. Therefore, the thickness is estimated as approximately 91 ± 3 µm.

3.2.2 Electrical resistivity

This electrical resistivity must be as low as possible to optimize the electron transfer. GDL substrate shows resistivity of about $3{\cdot}10^{-5}$ Wm, which is suitable for biocathode current collector applications. Conductive network has been optimized in the biocathode formulation by adjusting particle aspect ratio and particle size distribution. The optimal resistivity obtained is about $3{\cdot}10^{-3}$ Wm.

3.2.3 Electrochemical characterization

3 series of half-cells have been tested electrochemically: the bare substrate (GDL), the ink without enzyme printed on the substrate (GDL/Ink) and the ink with enzymes printed on the substrate (GDL/Ink/Enzymes).

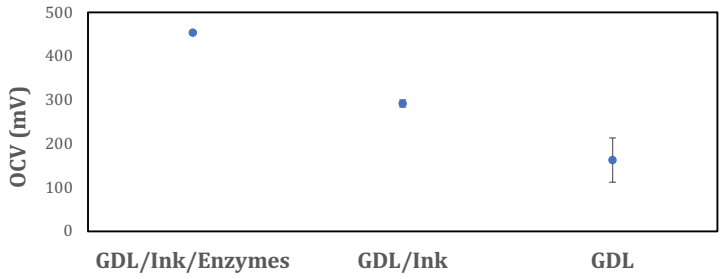


Figure 4: OCV results for printed inks and bare substrate

Figure 4 represents the Open Circuit Voltage (OCV) values measured by the potentiostat. For the bare substrate, the value is completely dispersed and means that there is no spontaneous dioxygen reduction possible in this surface. The OCV about 300 mV reached by the printed ink without enzymes shows that a moderate spontaneous dioxygen reduction can take place in the surface. Then, the OCV around 450 mV for the printed ink with enzymes shows typical OCV value observed for the type of enzymes used. It means that the O_2 catalytic reduction occurs on the surface of the electrode.

Figure 5 shows cyclic voltametric results. A scan from 0.7 V to 0 V is realized and a drop is observed around 0 V for the printed electrode with enzymes. It can be assigned to O_2 reduction, and the catalytic current reached is about 1 mA/cm^2. No signal apart from the capacitive envelope is observed for the printed layer without enzyme and the bare substrate. This result shows that the printed biocathode with enzymes can be used in a full cell configuration with an optimized power.

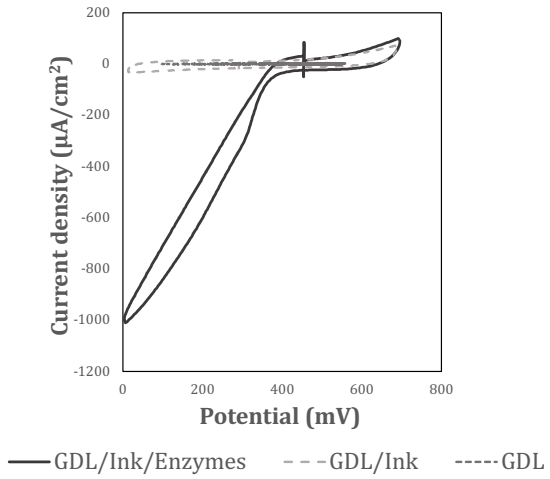


Figure 5: Comparison of the different surfaces via cyclic voltammetry; measurements were performed at a scan rate of 1 mV/s and ambient temperature

4. Conclusions

This study shows the development, characterization and optimization of a printed enzymatic biocathode. The ink components have been specifically studied for their biosourced and biodegradable properties. The new biocathode tackles the well-known challenges toward oxygen diffusion and cathode flooding in full cell technology. An optimized biobinder blend have been developed to manage the balance between hydrophobic region and ionic conductivity. Moreover, electrical conductivity and enzyme activity have been improved. Finally, the biocathode inks are suitable with screen printing process and are expected to have a low environmental impact due to their composition. Properties of cohesion, adhesion to the substrate and thermal drying impact should be studied to go forward a full industrialization.

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