A microfluidic device for electrochemical detection based on thick film and LTCC technologies

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Abstract

A Low Temperature Cofired Ceramics (LTCC) microfluidic device with an integrated thick film electrochemical detector was designed, manufactured and tested. Standard solutions of $Fe(CN)_6^{3-/4-}$ and H_2O_2 were used in the electrochemical measurements. The constructed structure is found to be a useful and inexpensive device for electrochemical analysis.

Keywords: LTCC; Electrochemical Detection; Microfluidics

1. Introduction

Low temperature co-fired ceramic (LTCC) technology has been used for the last 25 years in high reliability applications in military, avionics, automotive as well as in multi-chip modules (MCM) for communications [1]. This technology offers a wide and powerful tool for fabricating 3D structures using multiple layers. Properly combined with thick film (TF) technology provides the possibility of integration of fluidic channels, heaters, sensors, electronics and package in one LTCC module. On-line monitoring devices for chemical analysis have been developed taking advantage of LTCC and integrated with optical devices [2].

Thick film (TF) technology can be followed back to the 1950s. One of the key factors which distinguishes a TF device is the method of film deposition, namely screen printing, that comprises layers of special inks (or pastes) deposited onto an insulating substrate [3].

In this work we present two microfluidic systems which include microchannels, reservoirs and electrodes made of LTCC and TF technologies, for the electrochemical determination of hexacianno-ferrate ions and hydrogen peroxide in quiescent and flow systems.

2. Experimental

2.1 Thick film electrodes

The sensor design was based on a previous study carried on Pt electrodes on Si and glass substrates [4]. A commercial Pt organometallic paste (Heraeus RP 10003) diluted in a proper solvent

(Heraeus RV-372) and 96 % α-Al_2O_3 substrates were employed.

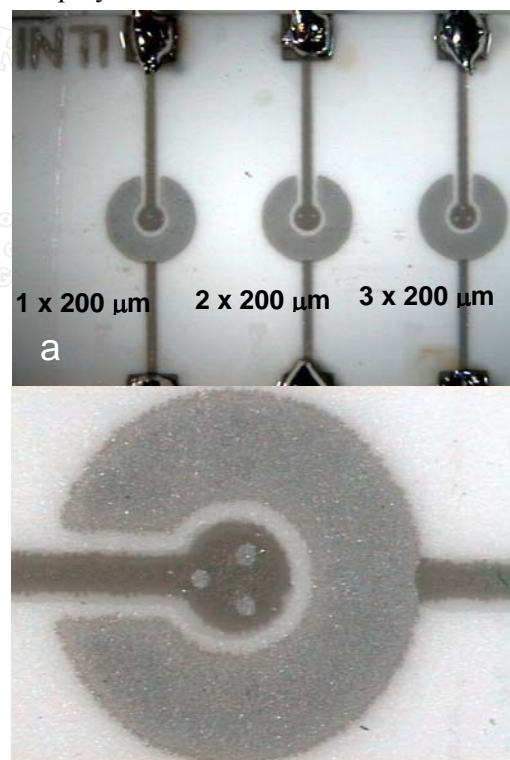*Figure 1. Photograph of different thick film electrodes: a) electrode n x 200 μm shows n active circular areas with a diameter of 200 μm diameter for the working electrode; b) detail of a 3 x 200 μm electrode.*

The electrodes were printed by conventional TF technology. The two-electrode layout was transferred by means of photolithography to a stainless steel mesh (400 wires per inch) with a photosensitive film (Ulano CDF-2). Pt ink printing was carried with an EKRA Microtronic-II Printer

and dried at 125ºC during 15 min. The resulting electrodes are shown in Figure 1.

2.2 LTCC structures

Two types of microfluidic systems were developed using LTCC a TF technology: static and dynamic. The first type, static system, was conceived to dispense a fixed volume of 15µl, while the dynamic system have reservoirs (4.5mm diameter and 300µm height) connected to flow channels (500µm x 300µm).

Cell cavities (shown in Figure 2) were made of low temperature cofired ceramic (DuPont 951-AT). Six layers of Dupont 951 foil were used to make the cells with a resulting thickness of 1.37 mm by heating at 80ºC during 150 s under an applied load of 50 kg cm^{-2}. Glass paste (4026-A ESL) was used as an adhesive between the LTCC structure and the alumina substrate. Ag/Pd conducting paste (Hereaus C1218) was used to cover the contacts. The structures were cofired in an oven at 600ºC (Lindberg). Tubes for the microfludics measurements were manually adhered with a commercial two-component epoxy.

Figure 2. Thick film electrode in a LTCC cell.

2.3 Electrochemical measurements

The electrochemical measurements were carried out with a EG&G PAR 273A potentiostat using two-electrode cells. Test solutions of x mM $K_3Fe(CN)_6$ + x mM $K_4Fe(CN)_6$ + 0.1 M KCl and x mM H_2O_2 + 0.138 M NaCl in a KH_2PO_4/K_2HPO_4 67 mM buffer of pH 7.2 (x = 2.5, 5, 10, 15, 20, 30, 40) were made from analytical grade reagents and doubly distilled water. In the potentiostatic step measurements, a potential difference of +0.400 V was applied in the $Fe(CN)_6^{3-/4-}$ solutions and +0.800 V in the H_2O_2 solutions; current transients were collected up to 200 s. In the voltammetric measurements, potential was scanned at a scan rate of 20 mV/s between -0.650 V and +0.650 V,

starting from the cathodic limit. In the microfluidics measurements, solutions were introduced into the microcells by means of a homemade syringe-based pump.

3. Results and discussion

3.1 Electrochemical response in quiescent solutions

A cyclic voltammogram obtained in a solution of 2.5 mM $K_3Fe(CN)_6$ + 2.5 mM $K_4Fe(CN)_6$ + 0.1 M KCl for an electrode with a diameter of 1000 µm is shown in Figure 3. The main features of this voltammogram are two unsymmetrical peaks, centered a 0 V, with a peak potential difference of about 80 mV; additionally, the anodic current seems to approach to a limit value of about 2 A m^{-2} at the positive potential limit (in the negative potential limit, an additional cathodic process overlaps with the $Fe(CN)_6^{3-}$ reduction at about -0.4 V, probably oxygen reduction, as the measurement were carried out in air saturated solutions).
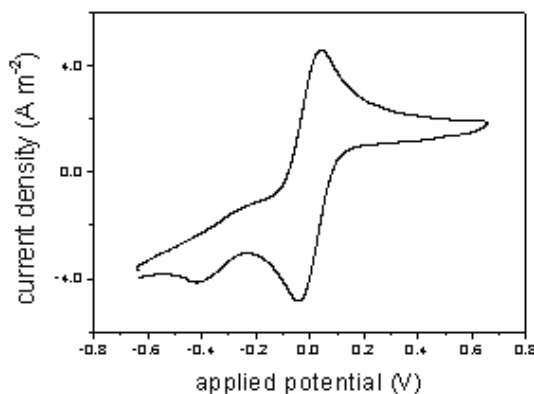

Figure 3. Cyclic voltammograms obtained in a solution of 2.5 mM K3Fe(CN)6 + 2.5 mM K4Fe(CN)6 + 0.1 M KCl for electrodes of 1000 µm diameter

Figure 4a shows a typical current versus time curve obtained after applying an overpotential potential of +0.4 V. It can be seen that the current attains a constant value for a time long enough. From the limit current values obtained at several concentration solutions, calibration curves can be constructed as shown in Figure 4b. The slope of these curves yields the sensitivity, which is shown for various electrodes configurations in Figure 4c. The occurrence of limiting currents is a quite surprising result and deserves some further discussion. Steady state currents are found in microelectrodes (diameter < 25 µm) in quiescent conditions. In the present case, however, the electrodes must be considered as macroelectrodes.
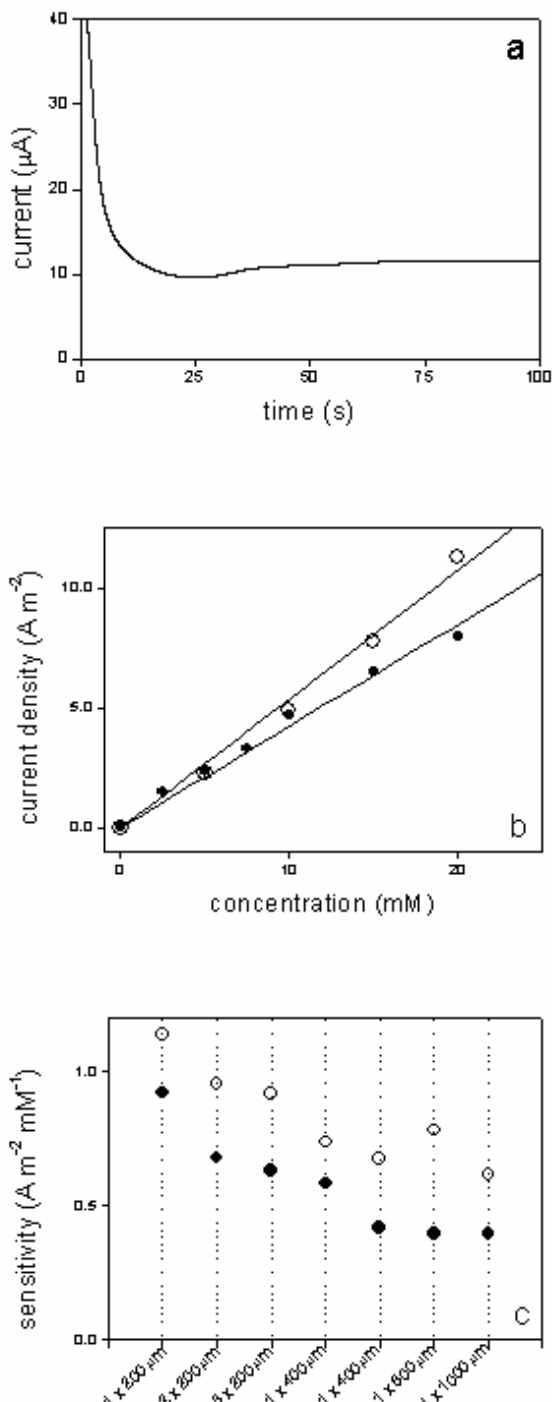
O, occurs and an anodic current is generated. In turn, as the electroneutrality must be maintained, a cathodic current due to the reduction reaction O → R will be produced in the counter-electrode, so that the cathodic current equals the anodic current. In a conventional, three electrodes cell the counterelectrode is far apart from the working electrode and the products do not interfere each other. In the cells used in the present work, the electrodes are separated by a gap of ~200 μm and the reactions products remain confined in a very small volume (~ 15 μl). In these conditions, the diffusion fields of anode and cathode overlap and the cell behaves as a generator-collector system [5] as is schematically shown in Figure 5.
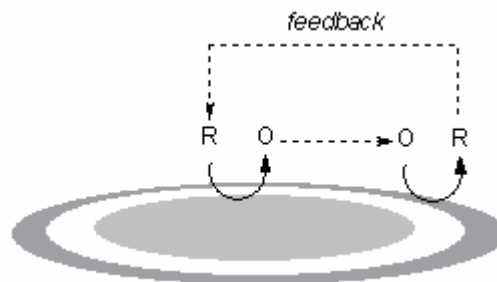

Figure 5. Schematic representation of two concentric electrodes operating in the generator-collector mode.

In this system, the collector will convert part of R in O. Then part of O will feed back towards the generator given rise to a current proportional to the concentration of O in the generator coming from the collector. Thus, the total current in the generator (working electrode) will have two components: one due to R coming from the bulk that will tend to zero at long times, and the feed back current that will attain an steady state value. This second component will present a delay due to the time that initially takes R to diffuse from the ring toward the disk. The induction time is given approximately by $d^2/\pi D$, where d is the gap between the electrodes and D is the diffusion coefficient of the reactant. For d = 200 μm and D = 5.10^{-6} cm^2 s^{-1} , a value of about 25 s is obtained.

3.2 Electrochemical measurements in microfluidic device

Figure 6a shows cyclic voltammograms obtained in in solutions of $K_3Fe(CN)_6/K_4Fe(CN)_6$ x mM (2.5 < x < 20) + 0.1 M KCl, in an electrochemical cell where the solution was flowing at a volumetric flow of 0.24 ml s^{-1}. It can be noted that the electrochemical response is quite different from obtained in quiescent solutions, such as Figure 3, where a peak can be observed. In quiescent solutions, current reaches a maximum value and then decreases as a consequence of the reactant consumption. On the other hand, a constant supply of reactant is provided in the microfluidic device

Figure 4. Potentiostatic step measurements: a) current transient obtained in 20 mM K3Fe(CN)6,+ 20 mM K4Fe(CN)6 en 0.1 M KCl; b) limit current vs. concentration of Fe(CN)63-/4- (o) (slope = 0.537 A m-2 mM-1 ±0.016 μA m-2 mM-1) and H2O2 (•) (slope = 0.423 A m-2 mM-1 ±0.012 μA m-2 mM-1) for 1 x 200 μm electrode; b) sensitivity for various electrodes.

In this case, the Cottrell equation for planar semi-infinite diffusion applies [5] and the current should tend to zero at long times, which clearly is not the case (Fig. 4a). This can be explained taking into account the geometry of the ring-disk configuration. Consider a generic redox couple, R/O. When a positive overpotential is applied to the working electrode, the oxidation reaction, R →

and the cyclic voltammogram has a sigmoidean shape rather than a peak. As the reactant concentration is increased, higher limit current values are obtained, and the voltammogram is distorted as a consequence of an uncompensated ohmic potential drop present in two-electrode configurations.
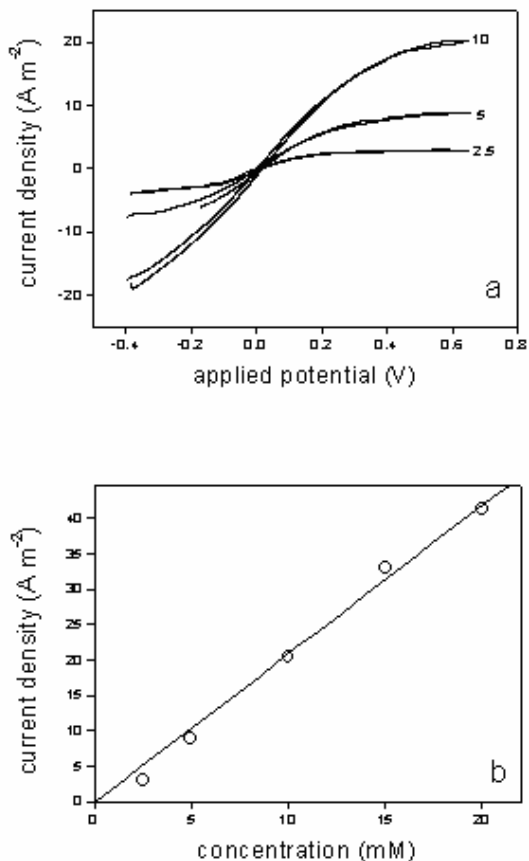

Figure 6. a) Cyclic voltammograms for 1 x 1000 μm electrode obtained at microfluidic (volumetric flow: 0.24 ml s⁻¹) device in solutions of x mM K₃Fe(CN)₆ + x mM K₄Fe(CN)₆ + 0.1 M KCl at 20 mV s⁻¹ with x = 2.5, 5, 10, 15, 20; b) anodic limit current density vs. concentration, with linear regression slope of 2.08 A m⁻² mM⁻¹ ± 0.06 A m⁻² mM⁻¹.

As shown in Figure 6b, a linear relation between limit current and analyte concentration is obtained, which yields a sensitivity of 2.08 A m^{-2} mM^{-1} ±

0.06 A m^{-2} mM^{-1}; this result is between twice and five times the sensitivity obtained in quiescent solutions.

4. Conclusions

Electrochemical microcells were constructed by combining LTCC and TF technologies. The electrochemical response of these microcells was studied by potentiostatic and potentiodynamic methods, in solutions containing $Fe(CN)_6^{3-/4-}$ and H_2O_2, in quiescent and flow conditions. Linear relations were found between limit current and concentration in the 2-25 mM range. From these plots, sensitivity values can be obtained in both quiescent and flow systems. Therefore, reliable microfluidic cells can be obtained by the combination of LTCC and TF technology, which are suitable for the electrochemical determination of redox species.

Acknowledgements

References

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