

Application Notes

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ELECTROCHEMISTRY: INTERDIGITATED ARRAY
MICROELECTRODES APPROACH

>> INTRODUCTION

Electrochemical detection is coming into widespread use for the trace determination of easily oxidizable and reducible organic and inorganic compounds, because it provides a rather easy procedure for direct and selective detection.

Likewise, miniaturization is a growing trend in the field of analytical chemistry. Thus, **microelectrodes** are very small-size electrodes with at least one dimension not greater than 25 μm .

Microelectrodes provide unique electrochemical properties such as small capacitive-charging currents, reduced ohmic (iR) drop, and steady-state diffusion currents. Moreover, the small size of the microelectrodes permits measurements on very limited solution volumes.

Microelectrodes also enable the use of different materials, geometric shapes and configurations. In this sense, **interdigitated array (IDA) microelectrodes** have demonstrated to be a very useful tool in electroanalytical applications.

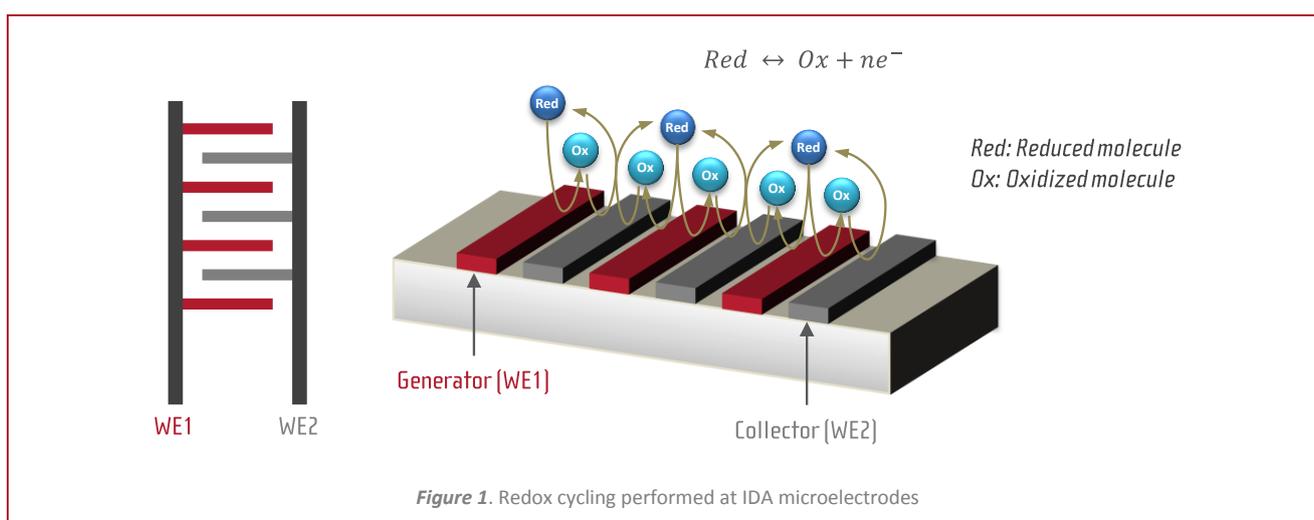
IDA electrodes consist of a pair of array microelectrodes that mesh with each other. Each set of microelectrodes can be potentiostated individually in order to carry out **redox cycling** as it is shown in **Figure 1**. Interactions between the individual

electrodes in the microelectrode arrays enable the regeneration of the electroactive substance through redox cycling.

In this way, a redox species, which is transformed (oxidized or reduced) at one electrode (**generator**), can diffuse across a small gap and be regenerated (reduced or oxidized) at an adjacent electrode (**collector**), and the regenerated species diffuses back to the original electrode. Thus, the particular analytical performance of interdigitated array microelectrodes lead to the improvement of the signal-to-noise ratio, enhancing the detection sensitivity for reversible or quasi reversible charge transfer reactions.

Microelectrodes can be useful in **applications** such as the study of electrochemical reaction mechanisms and kinetics, trace electrochemical analysis, electrochemical reactions in solutions of very high resistance, *in-vivo* measurements on biological objects, multichannel (bio)sensors as well as detection in flowing liquids (FIA, HPLC, CE...).

Therefore, IDA-based approaches can become a powerful, simple, rapid and cost-effective analytical tool for environmental, food and clinical analysis compared to available conventional electrodes.



>> EXPERIMENTAL

Samples: Standard solutions of benchmark redox species.

Sample volume: 5 μL .

Electrodes: Platinum & Gold thin-film IDA microelectrodes. (Ref. ED-IDA1-Pt and ED-IDA1-Au)

Pre-cleaning: Generator (WE1) potential cycled from -1.5 to +1.5 V at 100 mV/s (10 cycles) in the BGE. Collector (WE2) at open-circuit.

>> RESULTS & DISCUSSION

Interdigitated array (IDA) microelectrodes enable two different configurations: “single-mode” and “dual-mode”.

In “single-mode” just one of the working electrodes (WE1) is connected to potentiostat (open-circuit mode, one of the paired electrodes in the IDA, WE2, is disconnected), working in similar way than single-electrode approach.

In “dual-mode”, both working electrodes (WE1 and WE2) are connected. Thus, redox cycling (R_c) can be performed in the microelectrode arrays, enhancing the analytical signals (**Figure 1**). In this configuration, the potential of WE1 (*generator*) is cycled, meanwhile the potential of WE2 (*collector*) is fixed.

Typical electroactive species such as dopamine (DA), *p*-aminophenol (*p*AP) and hydroquinone (HQ) have been evaluated with the thin-film Pt electrodes using different background electrolytes (BGE):

- 0.1 M KCl
- 0.1 M HCl
- 0.1 M H_2SO_4
- 0.02 M MES, pH = 6
- 0.1 M PBS, pH = 7

The electrochemical reaction depends on the BGE and electrode material. Thus, reversible, quasi-reversible or irreversible redox process can be achieved on the electrode surface.

*p*AP shows a **reversible** redox process in all the evaluated BGE's. However, the best analytical signals were recorded at PBS buffer. In *dual-mode*, the analytical signals are enhanced showing a R_c (ratio between limiting current in *dual-mode* and anodic current in single-mode) of 2.1 with an efficiency of 75%. **Figure 2** shows the cyclic voltammograms for *p*AP in *single-* and *dual-mode*.

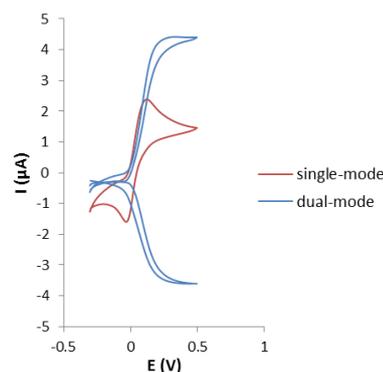


Figure 2. Cyclic voltammograms for 1 mM *p*AP using a thin-film Pt IDA electrode in *single-* and *dual-mode*. Conditions: BGE: PBS pH = 7, $\nu = 50$ mV/s, WE2: -0.3V (*dual-mode*).

DA has shown a **quasi-reversible** redox process using KCl as background electrolyte. In this BGE, the enhancement of the analytical signal is also observed using *dual-mode*, with a R_c of 2.6 and an efficiency of 75%. **Figure 3** depicts the cyclic voltammograms in *single-* and *dual-mode* for DA using KCl as BGE.

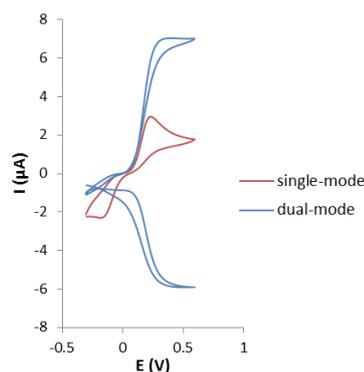
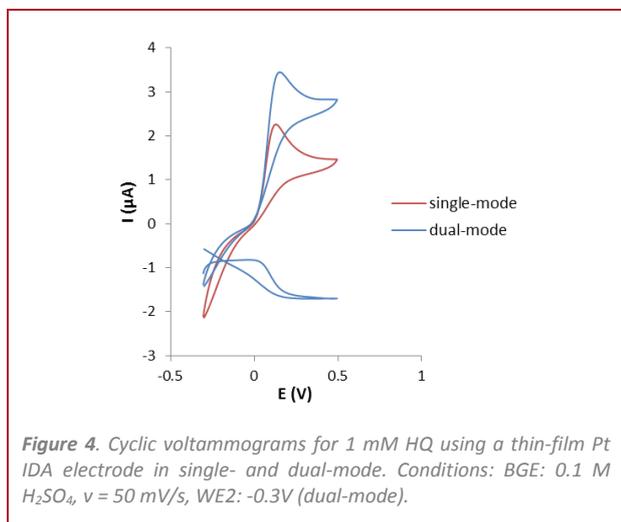


Figure 3. Cyclic voltammograms for 1 mM DA using a thin-film Pt IDA electrode in *single-* and *dual-mode*. Conditions: BGE: 0.1 M KCl, $\nu = 50$ mV/s, WE2: -0.3V (*dual-mode*).

In the other BGE's, the redox process was irreversible and the microelectrode behavior was not completely enabled in *dual-mode*.

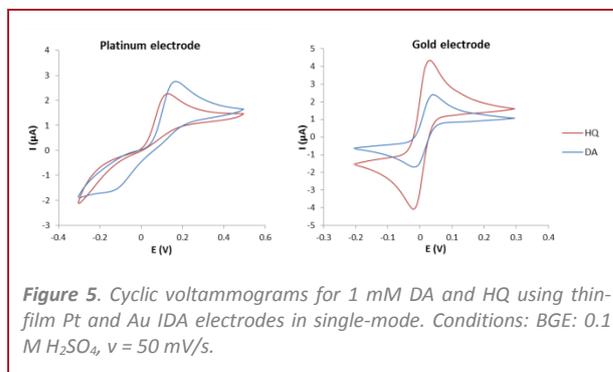
Finally, HQ has shown an **irreversible** redox process in most of the evaluated BGE's. Therefore, the typical steady-state of the microelectrodes was not reached using the *dual-mode*, and the analytical signals were not enhanced. **Figure 4** presents the cyclic voltammograms in *single-* and *dual-mode* for HQ using H_2SO_4 as BGE.



Clearly, the performance of IDA electrodes will be affected by the nature of the redox process. Thus, the best performance is achieved for reversible or quasi-reversible redox reactions. In these cases, the steady-state is reached using the *dual-mode* taking advantage of the microelectrode behavior and enhancing the analytical signals.

In the same way, the electrochemical reaction is also affected by the electrode material. Thus, the use of a gold surface instead of a platinum electrode can improve the electrochemical process keeping the other conditions.

It is demonstrated with the electrochemical reaction of DA and HQ that becomes **reversible** on a gold surface using H_2SO_4 as background electrolyte (other BGE's containing chlorides; KCl, HCl or PBS, cannot be used with gold electrodes). **Figure 5** depicts the cyclic voltammograms for DA and HQ in single-mode at Pt and Au IDA electrodes.



Therefore, the selection of the background electrolyte as well as the electrode material will be extremely important in order to achieve the best performance of the IDA microelectrodes for every analyte to be determined.

IDA-based microelectrodes enable the enhancement of the analytical signals through redox cycling. Moreover, the absence of a capacitive charging current at the collector electrode (it has a fixed potential) improves the signal-to-noise ratio. In single-mode cyclic voltammetry, the charging current is proportional to the potential sweep rate. Thus, a higher sweep rate provides a lower signal-to-noise ratio. However, the charging current in the collector electrode will not be affected by the scan rate.

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