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The Effects of Electrode Design to The Electrochemical Biosensor Performance

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INTRODUCTION

The overall design of an electrochemical sensor involves many parameters to be carefully considered and studied such as electrode design, surface chemistry, recognition element immobilisation on surface, assay conditions and enzyme / mediator selection. The aim of the study has been to come up with a new electrode array design that is not only easy to fabricate, having arrays with smaller imprint and hence simple, smaller sensor designs with cheaper electrodes, but also performs best in terms of electrochemical detection. As well as the size of the electrodes, two parameters have been considered when designing new arrays, one was the **use of Au as quasi-reference electrode** instead of conventional Ag/AgCl electrodes, the other was the use of **shared reference and counter electrodes**. All of these 3 parameters have been investigated to find out best array geometry for electrochemical detection.

Methodology and Results

3 different electrode arrays were designed and later fabricated by the evaporation of Ti / Au (20 nm / 200 nm) layer on glass slides using Fine Metal Masks.

- Design 1 consists of 8 Au electrodes of different sizes (diameter sizes: 1.5, 2, 3, 4 mm) that each has its own Au counter and quasi-reference electrode.
- Design 2 consists of 8 Au electrodes of different sizes (diameter sizes: 1.5, 2, 3, 4 mm) that all share the same Au counter and quasi-reference electrodes.
- Design 3 consist of 8 Au electrodes of 1.5 mm diameter that all share the same Au counter and quasi-reference electrodes. A flow cell was designed and fabricated using PMMA for the assays.

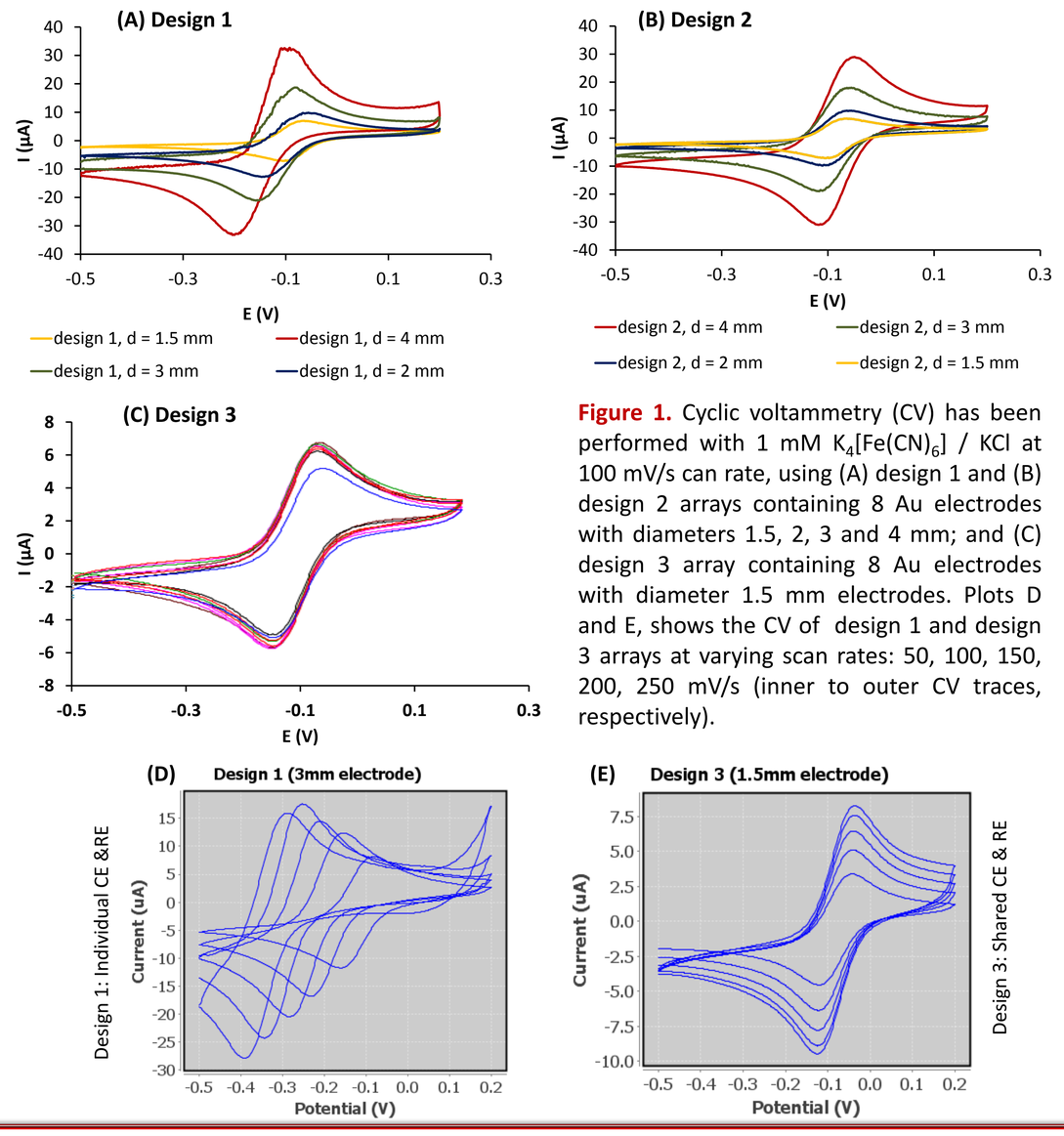
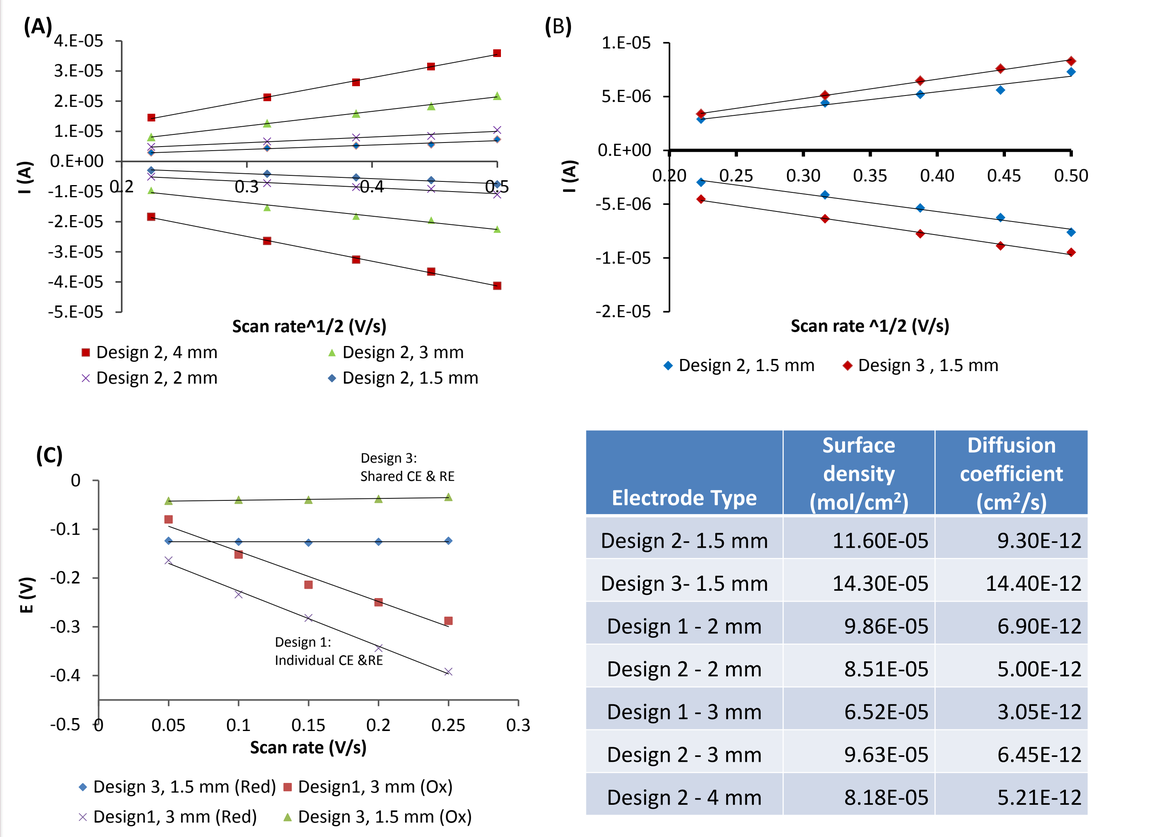


Figure 1. Cyclic voltammetry (CV) has been performed with 1 mM $K_4[Fe(CN)_6]$ / KCl at 100 mV/s can rate, using (A) design 1 and (B) design 2 arrays containing 8 Au electrodes with diameters 1.5, 2, 3 and 4 mm; and (C) design 3 array containing 8 Au electrodes with diameter 1.5 mm electrodes. Plots D and E, shows the CV of design 1 and design 3 arrays at varying scan rates: 50, 100, 150, 200, 250 mV/s (inner to outer CV traces, respectively).



Electrode Type	Surface density (mol/cm²)	Diffusion coefficient (cm²/s)
Design 2- 1.5 mm	11.60E-05	9.30E-12
Design 3- 1.5 mm	14.30E-05	14.40E-12
Design 1 - 2 mm	9.86E-05	6.90E-12
Design 2 - 2 mm	8.51E-05	5.00E-12
Design 1 - 3 mm	6.52E-05	3.05E-12
Design 2 - 3 mm	9.63E-05	6.45E-12
Design 2 - 4 mm	8.18E-05	5.21E-12

Figure 2. The results of cyclic voltammograms at varying scan rates have been used to obtain scan rate vs. oxidation/reduction current (A and B), and scan rate vs. oxidation/reduction potential. In terms of reaction reversibility, the design 1 showed quasi-reversible properties, whereas design 2 and 3 show full reversibility. From this result we may judge that, when Au is used as quasi-reference electrode, the arrays with shared reference and counter electrodes (design 2 and 3) results in faster electron transfer kinetics.

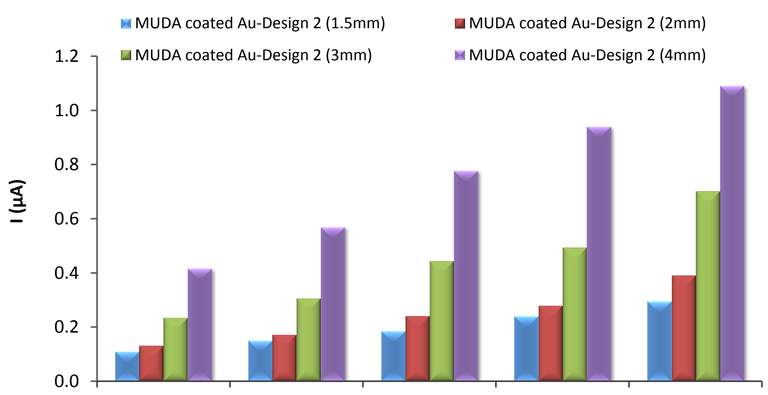


Figure 3. Enzyme assays were performed by mixing horse radish peroxidase (HRP) and TMB + H_20_2 solution, then adding to the MUDA coated electrodes in a flow cell for chronoamperometry test. The current measurements were taken after 60 s of of the reaction at 100 mV potential.

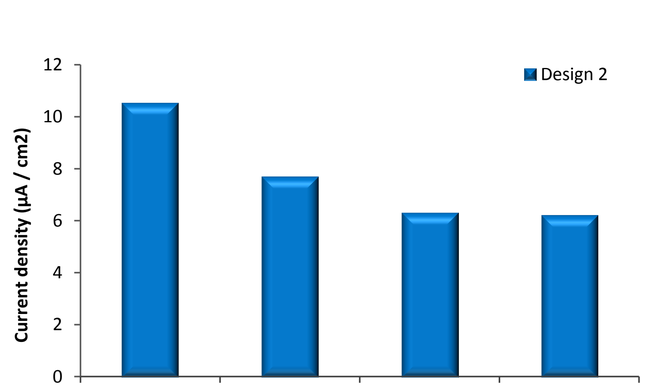


Figure 4. The current response obtained from the chronoamperotry results after the addition of 200 ng/ml HRP (and TMB + H_20_2 mixture) were used to assess the current density on different sized electrodes

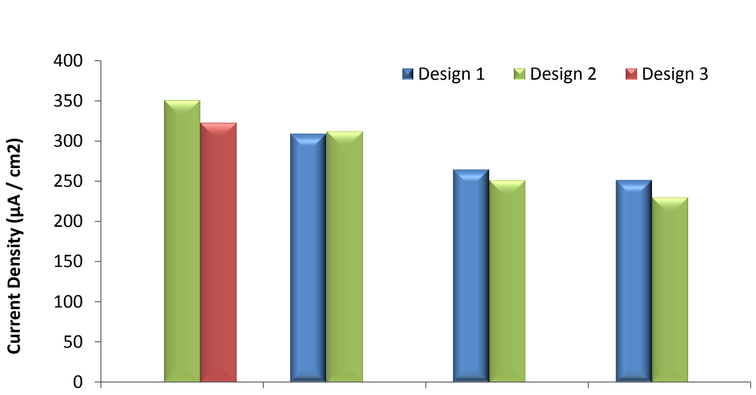


Figure 5. The current density of the Au electrode arrays have been calculated using the oxidation peak current obtained from the cyclic voltammetry (1 mM K4[Fe(CN)6]/KCl) at scan rate 100 mV/s.

CONCLUSION

As expected, the results of the experiments show that diffusion coefficient and surface density is higher when smaller electrodes have been used. Here the significance is that different designs (individual [design 1] and shared electrode design [design 2]) behaved similarly in terms of surface density and diffusion coefficient. However in terms of reaction reversibility, the design 1 showed quasi-reversible properties, whereas design 2 show full reversibility. From this result we may judge that, when Au is used as quasi-reference electrode, the arrays with shared reference and counter electrodes (design 2) results in faster electron transfer kinetics and hence could be preferred with respect to design 1 to be used as electrochemical sensors. Within design 2, electrodes with 1.5 mm diameter has shown highest current density, surface density and diffusion coefficient. In addition, it provides a smaller sensor chip imprint that especially would be useful when a flow cell is designed for the sensing. While 1.5 mm diameter electrodes is small enough for an efficient electrochemical sensing, it is also large enough to be fabricated by means of a Fine Metal Mask rather than a more expensive and time consuming photolithography process. Therefore, a new sensor array has been designed (design 3) that has 8 working electrodes with 1.5 diameter and shared quasi-reference and counter electrodes , both CV and HRP assays have been successfully repeated using this new sensor to investigate the performance of all 8 sensors with respect to each other. In conclusion, design 3 has been selected as the best performing sensor array within the arrays tested for electrochemical assays. Studies will continue to investigate possible applications for this new electrode array design.

Reference: Uludag, Y.; Olcer, Z.; Sagiroglu, M. S., Design and Characterisation of a Thin-film Electrode Array with Shared Reference/Counter Electrodes for Electrochemical Detection. Biosensors and Bioelectronics 2014, DOI:10.1016/j.bios.2014.01.048.

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