

# Electrochemistry Experiments to Develop Novel Sensors for Real-World Applications

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## ABSTRACT

These novel STEM (Science Technology Engineering and Mathematics) Electrochemistry experiments have been designed to increase the integrated science content, pedagogical, and technological knowledge for real-world applications. This study has focused on (1) the fundamental understanding on the relationship of metal oxide films and polymers to electrochemical sensors, and (2) the development of new materials which have great application of electrode materials.

Following the inquiry based learning strategy the research students learn to develop and study the electrode surfaces to meet the needs of stability and low detection limits.

Recently, new advances in environmental health are revealing the anthropogenic or naturally occurring harmful organic chemicals in sources of water supply expose a great health threat to human and aquatic life. Due to their well-known carcinogenic and lethal properties, the presence of human produced toxic chemicals such as phenol and its derivatives poses a critical threat to human health and aquatic life in such water resources. In order to achieve effective assessment and monitoring of these toxic chemicals there is a need to develop in-situ (electrochemical sensors) methods to detect rapidly. Electrochemical sensors have attracted more attention to analytical chemist and electrochemistry engineers due to its simplicity, rapidness and high sensitivity. However, there will be real challenges of achieving successful analysis of chemicals (phenol) in the presence of common interferences in water resources, which will be discussed regarding the students challenging learning experiences in developing an electrochemical sensor. The electrochemical sensor developed (TiO<sub>2</sub>, ZrO<sub>2</sub> or sol-gel mixture TiO<sub>2</sub>/ZrO<sub>2</sub>) will be illustrated and the successes will be shown by cyclic voltammetry data in detection of 1,2-dihydroxybenzenes (catechol, dopamine and phenol).

**Keywords:** Hands-on/Inquiry-based learning, Professional development. Electrochemistry and Informing via Research.

## INTRODUCTION

The goal of the experiments was to provide an application to study the oxidation and reduction reactions of 1,2-dihydroxybenzenes and their derivatives. The use of novel metal oxide films and polymers as electrochemical sensors are of great interest to neuroscientists and environmental scientist. Utilizing modified electrodes such as TiO<sub>2</sub>, ZrO<sub>2</sub> or sol-gel mixture TiO<sub>2</sub>/ZrO<sub>2</sub> to detect 1,2-dihydroxybenzenes and their derivatives such as phenol can be detected by cyclic voltammetry, CV. CV is a potentiodynamic electrochemical measurement utilized to detect the 1,2-dihydroxybenzenes with the TiO<sub>2</sub>, ZrO<sub>2</sub> or sol-gel mixture TiO<sub>2</sub>/ZrO<sub>2</sub> [1-4]. The cycle of the oxidation and reduction reactions in CV involves the current at the working electrode plotted versus the potential. The solution of 1,2-dihydroxybenzenes being analyzed is oxidized and reduced and the CV graph should be reversible for optimum detection. However, phenol will be irreversible in detection by CV. However, the CV graph may have three prospective shapes which are the following: reversible, irreversible and quasi-reversible. If the analyte of interest remains at equilibrium throughout the potential scan then the redox process would be reversible following the Nernst equation. The potential is related to the concentration as expressed in the Nernst equation below:  $E = E^0 - (0.0592/n) \log Q$ ; where "n" is the number of exchanged electrons, E<sup>0</sup> relates to the average of E<sub>pa</sub> (potential of the anode) and E<sub>pc</sub> (potential of the cathode). The peak potential separation is expressed as  $\Delta E = E_{pc} - E_{pa}$ ; and Q is the reaction quotient. A reversible reaction such as the 1,2-dihydroxybenzenes (catechol, L-DOPA and dopamine) would have  $\Delta E$  independent of the scan rate as equivalent to 59/n mV at all scan rates at 25°C. In a reversible process current ratio (i<sub>pa</sub>/i<sub>pc</sub>) would equal 1. When the current ratio differs from 1, this is indicative of a much less reversible response [1-4]. This lab is ideal since students will obtain reversible and irreversible responses for the different compounds such as dopamine (reversible) and phenol (irreversible).

## EXPERIMENTAL

### Reagents

Pyrocatechol (Sigma-Aldrich), Dopamine (3, Hydroxytyramine HCl) (United States Biochemical Corporation) were dissolved in 0.1 M Sulfuric Acid to prepare 5 mM solution. Phenol solution, 5 mM, was prepared in phosphate buffer (pH ~ 7), and 0.1 M NaOH solution was used to adjust pH level.

### Safety/Hazards

All solution preparations and synthesis were carried out under a fume hood. Protective garment and gloves were worn at all times.

### Apparatus

All CV measurements were performed on Bioanalytical Systems (BAS) Instrumentation in a three-electrode compartment cell (auxiliary Platinum electrode, Ag/AgCl reference electrode).

### Synthesis of $ZrO_2$ , $TiO_2$ and Sol-Gel Mixture ( $TiO_2/ZrO_2$ )

Titanium (IV) isopropoxide (97%, Sigma-Aldrich), zirconium (IV) propoxide (70 wt% in 1-propanol, Sigma-Aldrich), de-ionized water, acetylacetone (Sigma-Aldrich) and ethanol (99.5%, Sigma-Aldrich) were used. The molar ratio of zirconium (IV) propoxide (and/or titanium (IV) isopropoxide): water: acetylacetone: ethanol was 2:4:1:62. All chemicals were used as received.

### Construction of Bare Electrode

A 0.5 mm O.D., 12.5 cm long copper wire was inserted into a capillary tube (Sutter Instrument, 0.69 mm I.D., 1.2 mm O.D., 10 cm long, borosilicate glass both ends open) as the wire was exposed by 2.5 cm only on one end of the tube; the wire functioned as an electrical contact component. 0.7g of graphite powder (Alfa Aesar, 99.0%, 7-10  $\mu$ m) was added 0.3g of silicon oil (Xiameter PMX-200 Silicon fluid 100cs, Sigma-Aldrich) with magnetic chip in a vial. This carbon paste mixture was placed on stir pan for 5 minutes in order to homogenize the carbon paste. Previously made capillary tube with copper wire core was dipped firmly into the graphite packing. The electrode was smoothed on a piece of transparent paper to obtain a uniform surface prior to each use.

### Construction of Sol-gel Modified Electrodes

Solutions of  $ZrO_2$ ,  $TiO_2$ , and sol-gel mixture ( $TiO_2/ZrO_2$ ), prepared at molar ratio mentioned previously, were stirred vigorously. The bare carbon electrodes (described above) were dipped into sol-gel solutions ( $ZrO_2$ , or  $TiO_2$ , or  $TiO_2/ZrO_2$ ) coating for 3 seconds. After 5 minutes of drying time, the coating process was repeated four more times. Then the electrode was heated at 230°C for 20 minutes and cooled down naturally under room temperature conditions.

## RESULTS / DISCUSSION

In this work,  $ZrO_2$ ,  $TiO_2$ , and sol-gel mixture ( $TiO_2/ZrO_2$ ) were used to modify the carbon paste electrode surface to study the electron transfer of catechol and dopamine (phenol derivatives) and phenol in order to establish a new type of electrochemical sensor.

### Detection of phenol derivatives (dopamine and catechol)

Figure 1 depicted the cyclic voltammograms of dopamine (5 mM) obtained with four different working electrodes, bare

carbon paste electrode,  $TiO_2$  sol-gel modified carbon paste electrode,  $ZrO_2$  sol-gel modified carbon paste electrode, and  $TiO_2/ZrO_2$  mixture sol-gel modified carbon paste electrode. From these CVs, a significant enhancement in sensitivity toward dopamine was observed for the modified electrodes compared to that of the bare electrode. The cathodic peaks current obtained with the  $TiO_2$  sol-gel and  $ZrO_2$  sol-gel modified carbon paste electrode were almost three folds higher than that of the bare electrode; four folds enhancements in sensitivity was observed with the  $TiO_2/ZrO_2$  mixture sol-gel modified carbon paste electrode. In addition, the anodic branch also exhibited similar sensitivity improvement (except for the  $TiO_2$  sol-gel modified carbon paste electrode as the anodic branch was not well-defined for this particular electrode). Furthermore, redox process of dopamine appeared to be more reversible when the  $ZrO_2$  sol-gel and  $TiO_2/ZrO_2$  mixture sol-gel modified carbon paste electrodes were used as the potential separations decreased significantly. Overall, when comparing the performances of the four working electrodes, it was observed that the  $TiO_2/ZrO_2$  mixture sol-gel modified carbon paste electrode gave the best response for dopamine detection, in term of both redox couple reversibility and electro-analytical sensitivity.

In addition to cyclic voltammetric analysis of dopamine individually, simultaneous detection of dopamine and catechol utilizing the four working electrodes was also investigated. Figure 2 illustrated the cyclic voltammograms of dopamine and catechol (both at 5 mM) simultaneous detection using the four working electrodes. It is observed that, with respect to anodic peak current magnitude, the sensitivity toward dopamine was enhanced by two folds when utilizing the  $TiO_2$  sol-gel and  $ZrO_2$  sol-gel modified carbon paste electrodes, and four and one-half folds when the  $TiO_2/ZrO_2$  mixture sol-gel modified carbon paste electrode was used, compared to that of the bare electrode. Similar sensitivity enhancement pattern was also observed for the cathodic branch. In addition, when the  $ZrO_2$  sol-gel and  $TiO_2/ZrO_2$  mixture sol-gel modified carbon paste electrodes were used, oxidation and reduction peaks for catechol were also observed, which were not seen when the bare or  $TiO_2$  sol-gel electrodes were utilized. This illustrated the potential for simultaneous detection of catechol and dopamine using the  $ZrO_2$  sol-gel and  $TiO_2/ZrO_2$  mixture sol-gel modified carbon paste electrode, without prior separation of 1,2-dihydroxybenzenes. Overall, in term of electro-analytical sensitivity, the  $TiO_2/ZrO_2$  mixture sol-gel modified carbon paste electrode offered the best response for dopamine and catechol detection.

### Detection of phenol

In the past, cyclic voltammetric analysis has shown that phenol redox was an irreversible process [4]. The CV data obtained for phenol in our study supported this previous finding as only the anodic peak was observed. Cyclic voltammograms of phenol (5 mM) obtained with the four different working electrodes were illustrated in Figure 3. It was observed that phenol was undetectable using the bare electrode, while the anodic peak, indicating the oxidation of phenol, was well-defined when the sol-gel modified electrodes were used. Overall, the  $TiO_2$  sol-gel and  $ZrO_2$  sol-gel modified carbon paste electrodes gave similar response in term of phenol sensitivity, while the  $TiO_2/ZrO_2$  mixture sol-gel modified carbon paste electrode provided the best response toward phenol, almost seven times better than that of the  $TiO_2$  sol-gel modified carbon paste electrodes.

## CONCLUSION

In this study, students demonstrated the successful development of a new class of sol-gel sensor in detection of phenol and its derivatives. Of the three different sol-gel modified electrodes investigated, the  $\text{TiO}_2/\text{ZrO}_2$  sol-gel modified carbon paste electrode gave the best analytical response toward phenol and its derivatives (catechol and dopamine). Future studies will involve estimating detection limits and linear detection range for phenol and its derivatives utilizing the  $\text{TiO}_2/\text{ZrO}_2$  sol-gel modified carbon paste electrode, as well as determination of electro-kinetic parameters via CV analysis for the upper level electrochemistry students.

This lab has provided valuable hands-on skills for students to build a novel electrode for the detection of 1,2-dihydroxybenzenes and its derivatives. This lab is an extension of previous polymer modified electrodes to detect 1,2-dihydroxybenzenes. This lab has allowed students' interdisciplinary skills with chemistry and engineering in one lab experiment (STEM) focused.

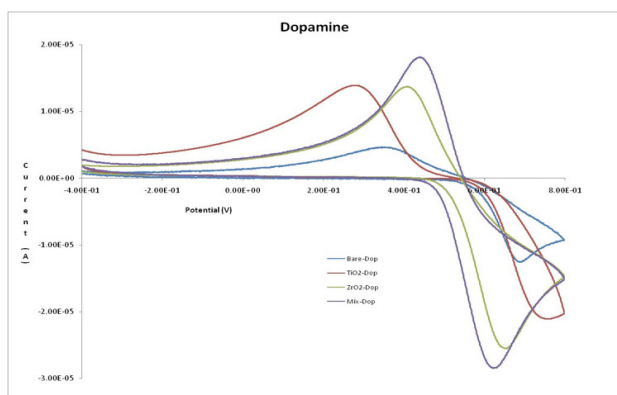


Figure 1. CV analysis of 5mM dopamine in 0.1 M Sulfuric acid utilizing: Bare,  $\text{TiO}_2$  sol-gel,  $\text{ZrO}_2$  sol-gel,  $\text{TiO}_2/\text{ZrO}_2$  sol-gel modified carbon paste electrodes

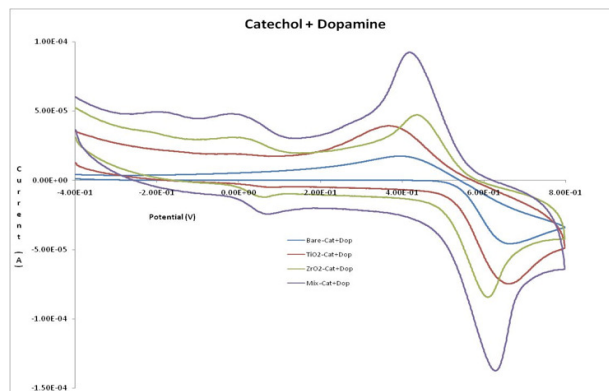


Figure 2. Simultaneous CV analysis of 5 mM dopamine and 5 mM catechol in 0.1 M Sulfuric acid utilizing: Bare,  $\text{TiO}_2$  sol-gel,  $\text{ZrO}_2$  sol-gel,  $\text{TiO}_2/\text{ZrO}_2$  sol-gel modified carbon paste electrodes

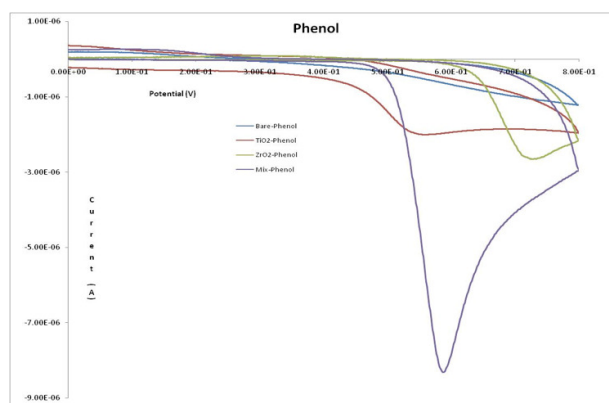


Figure 3. CV analysis of 5 mM phenol in 0.1 M phosphate buffer (pH ~ 7) utilizing: Bare,  $\text{TiO}_2$  sol-gel,  $\text{ZrO}_2$  sol-gel,  $\text{TiO}_2/\text{ZrO}_2$  sol-gel modified carbon paste electrodes

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