

Electrochemical Detection of Phenol Utilizing a Synthesized Sonogel-Carbon Zirconium Oxide (ZrO_2)

Suzanne K. Lunsford, Amber Yeary, PhuongKhanh Quoc Nguyen, and Rachel Kingdom

Department of Chemistry, Wright State University, 3640 Colonel Glenn Hwy., Dayton, OH 45435, USA

Corresponding author: Suzanne K. Lunsford

Abstract: The experiment described is part of an Inorganic Chemistry course for senior undergraduate students. It requires the synthesis of a sonogel-carbon electrode modified with a ZrO_2 sol-gel and heated at high temperatures. The electrochemical response of the ZrO_2 modified electrode was compared to that of an unmodified (bare) sonogel-carbon electrode to detect phenol. The students were required to determine if the modified electrode detects phenol with greater efficiency than bare electrode. The students gain electrochemical instrumentation skills and synthesis skills in the fabrication and testing of the modified electrode via the oxidation of phenol.

Introduction:

The detection of phenol and other phenolic related compounds in water samples is of great importance due to their toxicity and high solubility. These compounds are contaminants in environmental matrices, food, and medicine products that can easily be absorbed through humans and animals' skin or mucous membranes. This absorption affects vital organs and tissues (1 - 4). This lab focuses on the ability to enhance phenol detection by further modifying the surface of bare sonogel-carbon electrodes with ZrO_2 .

This research can be challenging for students since it requires the synthesis of a sonogel-carbon electrode modified with zirconium oxide and operation of a potentiostat. The analysis for

the laboratory exercise includes a comparison of a modified electrode's cyclic voltammogram with that of a bare sonogel-carbon electrode. Cyclic voltammetry is a widely used method in teaching electrochemistry. The current at the working electrode is plotted against the potential applied. When the potential is sufficiently "negative" or "positive", the component in solution being analyzed got reduced or oxidized at the electrode surface, respectively. A jump of current is observed when the component is electrolyzed (oxidized or reduced) corresponding to a peak on the graph. The most important parameters of a cyclic voltammogram are the magnitudes of the peak currents (anode and cathode) as well as the potentials at which the peaks occur. Reversibility is a vital concept in analyzing a cyclic voltammogram. For a reversible couple, the separation of peak potential is independent of the scan rate. However, an irreversible couple's peak separation depends on the scan rate (5). The graph of cyclic voltammogram can have one of three shapes: reversible, quasi-reversible, or irreversible. When the anode and cathode peak currents' height ratio is very close to 1, the process is reversible. Similarly, when the peak height ratio is less than or greater than 1, the process is quasi-reversible. In an irreversible process, only one peak (either oxidation or reduction) is observed. Both quasi-reversible and irreversible cyclic voltammogram exhibit an irreversible couple, because as the scan rate increases or decreases, a quasi-reversible plot will become irreversible. This experiment is designed to fit into two lab sessions, where each lab session is approximately five hours long. This lab has been created for Project REEL (Research Experiences to Enhance Learning). The project goal is to help undergraduate students develop problems solving and analyzing techniques by incorporating research-intensive programs. These research modules (programs) were introduced during into introductory chemistry courses and carried out through the senior level, which

encourages students to pursue further scientifically oriented training and increase graduation in science related fields. Further details can be found at

www.ohio-reel.osu.edu/project.php

Experimental:

Safety/Hazards

All solution preparations and syntheses were carried out under a fume hood. Phenol is harmful upon contact with tissue or ingested. Upon mixing the $ZrNO_3$ the following precautions should be followed during synthesis of the modified electrode: Protective garment and gloves were worn at all times. For preparation of the modified sonogel-carbon zirconium oxide, all steps were carried out under a hood and care was taken not to inhale the $ZrNO_3$ or graphite powder.

All MSDS information for chemicals involved can be found at

www.sigmaldrich.com

Construction of the unmodified (bare) electrodes

A 0.50 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 length, borosilicate glass both ends open) so as the wire was exposed by 2.5 cm only on one end of the tube; the wire functioned as an electrical contact component. 500 μ L MTMOS and 100 μ L 0.2 M HCl was added to a 40 mL borosilicate glass vial. 1.0 g of graphite powder (Alfa Aesar 99.9%, 2-15 micrometer) was added and homogenously dispersed via sonication in the same vial containing the MTMOS and HCl solution. The vial contained the mixture was ultrasonicated (2510R-DH, Branson) (with cap on) for 15 seconds. The sonicated graphite mixture was manually packed. Previously made

capillary tube with copper wire core was dipped firmly into the graphite packing so as about 0.5 cm of the dipping end of the tube was filled with the packing mixture.

Construction of the modified electrodes

The zirconium nitrate material was utilized to prepare the zirconium oxide coating solution as follows: 2.62 grams of Tween 80 (Aldrich) were dissolved in isopropanol (99%, Fisher), followed by the addition 0.68 mL of concentrated acetic acid (Aldrich) and 4.6 grams of zirconium nitrate under vigorous stirring. A bare electrode (as the one made above) was dipped into the zirconium oxide coating solution for 5 seconds. After coating, the electrode was heated at 500°C for 20 minutes, and cooled naturally.

Voltammetric Studies

All electrochemical measurements were carried out on a Bioanalytical System Epsilon, in a three electrodes set up (sonogel carbon zirconium oxide working electrode, Ag/AgCl /3 M NaCl reference electrode and platinum auxiliary electrode wire). The phenol was purchased from Sigma-Aldrich (99+% purity). All phenol solutions were made with a phosphate buffer (0.1 mol/L NaH₂PO₄ and 0.1 M NaCl, pH ~4) solvent. 0.1 M NaOH solution was used to adjust pH level. Cyclic voltammetry at a scan rate of 100mV/s was the electrochemical technique applied to study the oxidation behavior of phenol. The oxidation peak of the zirconium oxide modified electrode appeared at approximately 620 mV in a phenol concentration of 0.005 M. No reduction peak was observed. The sensitivity of this electrode is notable as Figure 3 shows the limit of phenol detection to be a at 10⁻⁵M. The optimum response pH of 7.5 was utilized to observe a phenol oxidation peak with this modified electrode. At the lower and the higher pH values of solutions with the same phenol concentrations, no peak was observed or detected. The

electrode without the zirconium oxide coating (bare carbon) did not produce an oxidation peak when a cyclic voltammogram in phenol solution was carried out.

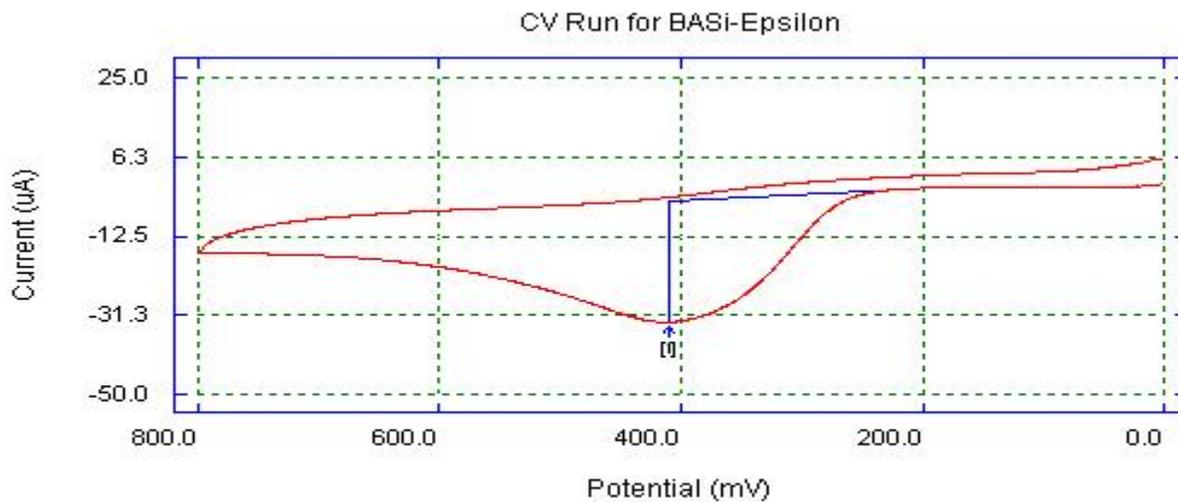


Figure 1: Cyclic Voltammogram of ZrO_2 electrode utilized to detect 0.005 M phenol in phosphate buffer (pH=7.5), (100mV/s) vs. Ag/AgCl/3M NaCl.

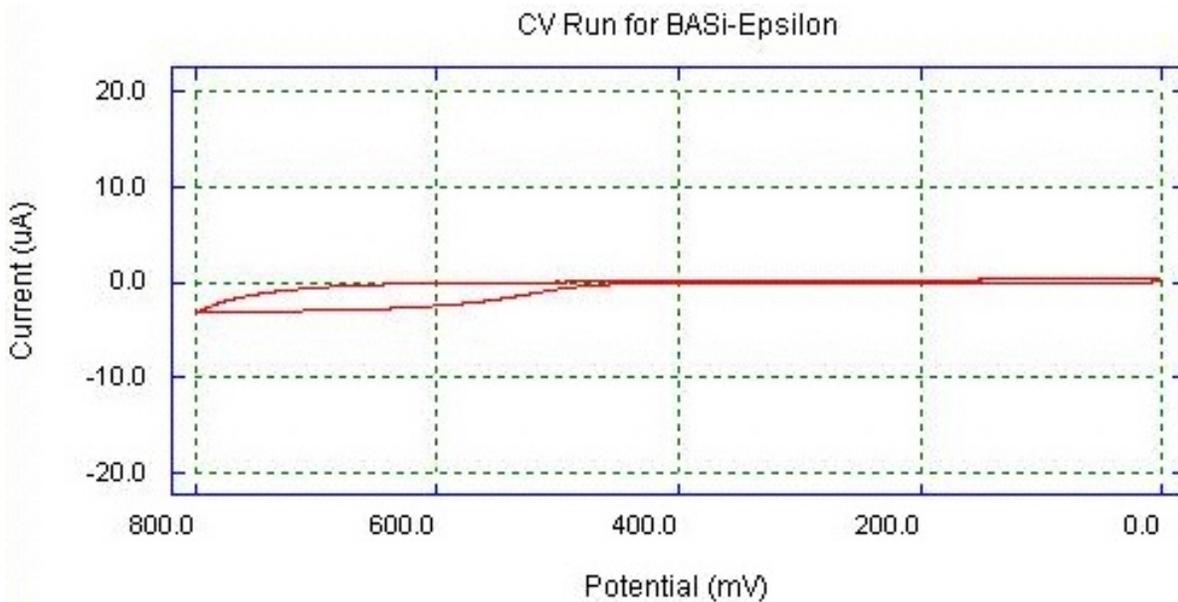


Figure 2: Cyclic voltammogram of bare carbon electrode to detect 0.005 M phenol in phosphate buffer (pH=7.5), (100 mV/s) versus Ag/AgCl/ 3M NaCl

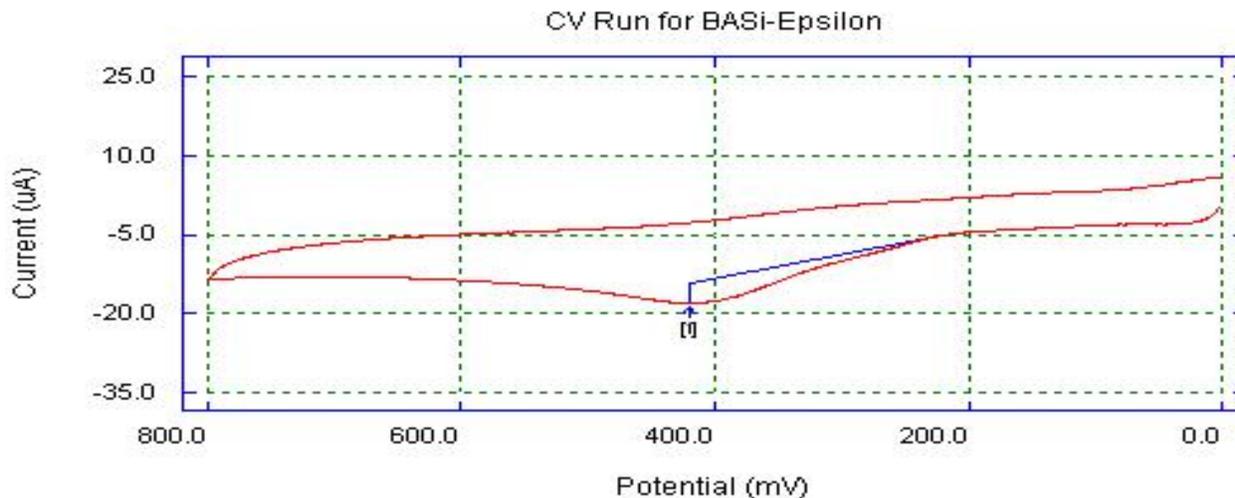


Figure 3: Cyclic voltammogram of ZrO_2 electrode to detect 5×10^{-5} M phenol in phosphate buffer (pH=7.5), (100mV/s) versus Ag/AgCl/3M NaCl.

Conclusion:

Cyclic voltammogram of phenol detection using zirconium modified sonogel-carbon electrode showed an irreversible response. Phenol in solution was only oxidized and not reduced. The fact that the modified electrode worked best at pH at 7.5 provided a great advantage to the real world application of the electrode since most contaminated water samples had a pH value near 7.5. Since only the modified electrode was able to detect the presence of phenol, this lead to a conclusion that zirconium oxide coating provided a suitable surface for electron transfer. Due to contamination of electrolyzed component on the electrode surface, it is highly discouraged to reuse the electrode. After a successful laboratory experiment, the students should be familiar with the operation of the potentiostat, how oxidation is represented in graphical form in a cyclic voltammogram, and construction of both bare and zirconium oxide coated sonogel-carbon electrodes. Emphasis on environmental applications of this sensor can be expounded upon as an in-class exercise.

References:

1. G.P., Jin, X.Q. Lin, and Y.F. Ding, *J. Solid State Electrochem.* **10** (2006) 987.
2. M. El Kaoutit, I. Naranjo-Rodriguez, K.R. Temsanani, and J.L. Hivalgo-Hidalgo, *Biosensors and Bioelectronics* **22** (2007) 2958.
3. M. Ferreira, H. Varela, R.M. Torresi, and G. Tremiliofi-Filho, *Electrochimica Acta* **52** (2006) 434.
4. P. I. Iotov, S.V. Kalcheva, *J. Electroanal. Chem.* **44** (1998) 219.
5. W. R. Heineman, P. T. Kissinger, *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Marcel Dekker, New York, 1996.