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# Molybdenum Coupled Electrochemical Sensing Systems

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***Abstract*—To improve the efficiency of crop production, widespread agricultural monitoring of important nutrients and environmental factors must be developed. Electrochemical sensors have the ability to be compact and composed of transient materials, making them a powerful tool for this purpose. This paper investigates the use of molybdenum as a phosphate sensor, by characterizing two modalities: amperometric with 3 electrodes and potentiometric with 2 electrodes. Mo was utilized as the working electrode in both instances, and tin and gold were used as counter and reference electrodes in the two- and three-electrode systems correspondingly. When open circuit potential (OCP) tests were run, there was no clear trend between voltage output and phosphate concentration, suggesting that this type of sensor will not be suitable. To test the possibility of an amperometric sensor, cyclic voltammetry (CV) and chronoamperometry tests were run, and both presented promising data. Furthermore, direct current values were correlated to varying phosphate concentrations, allowing a precedent to be set for the sensor. When the electrochemical cell was biased at 1.2 V, the sensitivity of current to phosphate concentration was found to be 0.8179 dec/dec over the range of 1E-1 M to 1E-4 M. Now that the feasibility of an environmentally benign phosphate sensor has been established, future work is necessary in the area of packaging and construction of the sensor, to ensure its biodegradability and compactness.**

***Index Terms*—Eutrophication, biodegradable, potentiometric, amperometric, orthophosphates.**

## I. INTRODUCTION

Phosphorus is an essential nutrient for plant life and is typically introduced to crops through fertilizers containing phosphate. However, if an excessive amount of fertilizer is applied, phosphate may enter local bodies of water through agricultural runoff. This leads to eutrophication which deteriorates water quality and harms marine life. Real-time phosphate concentration monitoring is needed to give farmers the knowledge of exactly how much fertilizer needs to be used.

Two important factors to consider when approaching this issue are biodegradability and latency. It is vital that data collection and communication be quick and easily accessed, and that the tools used can disappear after their functional lifetime while not causing harm to the surrounding environment. Electrochemical sensors and power sources can be portable, biodegradable, low-cost, and quick in collecting and communicating real-time data. Already, a multitude of chemical sensing systems exist to detect measurands, such as pH change, oxygen, sodium ($Na^+$), potassium ($K^+$), and glucose ($C_6H_{12}O_6$) in the human body [5]. However, there are vast differences between the environment of the human body and that of soil. In soil, much larger ranges of temperature, pH, humidity, and ion selectivity must be accounted for, whereas in the human body, physiological factors remain in narrow ranges.

In previous works, Mo has been used as a working electrode to sense one of the plant available phosphates ($HPO_4^{2-}$) [2]. It has also been incorporated into dissolvable electronics and occurs in soil with a concentration of about 40 to 60 ppm [1, 6]. However, previous literature uses a Ag/AgCl or saturated calomel electrode as a reference electrode. These materials are incompatible with our application due to the toxicity of their composition. To begin the search for a suitable reference electrode for use in degradable systems, transient materials will need to be identified and tested. In this paper, Mo was used as a working electrode, along with Sn and Au as counter and reference electrodes. A series of tests were conducted to determine if these more environmentally benign reference electrodes could be used to detect varying phosphate concentrations.

## II. BACKGROUND

While research surrounding molybdenum's ability to detect phosphate has been conducted, there are still many unknowns when considering the feasibility of its function in the scope of widespread agricultural monitoring. These uncertainties are mainly in concern with the biodegradability of materials selected. The following sections describe material selection and the experiments performed to verify their performance.

### *A. Material Selection*

Mo has been successfully used in a potentiometric oxygen sensor [1], as well as tested by multiple researchers on its sensitivity towards orthophosphates ($HPO_4^{2-}$ and $H_2PO_4^{2-}$), which are the plant available phosphates (PAPs) found in soil [2-3]. Mo has been shown to have near Nernst characteristics with a sensitivity of -26.9±0.5 mV/decade towards hydrogen phosphate ($HPO_4^{2-}$) in alkaline solutions (pH~8.5) with a limit of detection of 1e-6 M and high selectivity over other ions [2]. In these studies, Mo was used

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as the working electrode coupled with saturated calomel in a two-electrode system [2] as well as with platinum mesh as a counter electrode with a silver/silver chloride (Ag/AgCl) reference electrode in a three-electrode system [3].

Cobalt has also shown promising results in being able to detect orthophosphates, specifically dihydrogen phosphate ($H_2PO_4^{2-}$), however, similarly to Mo, it only gives accurate data while functioning in a narrow pH range, favoring acidic conditions (pH~6) [3]. The reason Mo and Co have this specificity concerning pH range is because they are each only responsive to a particular phosphate ion, and each ion dominants in a particular pH range. Because of these restraints, when considering agricultural applications, one must choose the working electrode to match the given field conditions. Ultimately, since Mo has shown repeated success in being able to detect orthophosphates with low limits of detection and high selectivity, as well as being used in an already functioning potentiometric sensor [1], it was chosen as the working electrode.

Ag/AgCl is a commonly chosen reference electrode and is known to give predictable and accurate data, however, Ag is toxic to marine life in large quantities [4], and therefore cannot be used for the scope of biodegradable agricultural monitoring. Similarly, saturated calomel must be taken out of consideration due to its composition of mercury, which would be dangerous to introduce into farmland. Other metals such as Sn and Au were tested as reference and counter electrodes as they are environmentally benign and believed to not have any adverse effects in small quantities once broken down.

### *B. Sensor Design*

In this work, two types of sensors were explored. The first option was a potentiometric sensor, which directly correlates voltage output to phosphate concentration. It has the ability to be a sensor and a power source, all driven by the electrochemical reactions occurring within the cell. The sensor can operate in two modes, one being the “battery” mode, and the other being “sensor” mode, allowing it to be self-powered. This technique was successful in detecting oxygen in solution [1], and it will be explored in the case of phosphate sensing.

Another option to consider is an amperometric sensor, which is biased at a certain voltage, and consequently creates a current that is directly correlated to local phosphate concentration. This would require an outside power source to supply the voltage to the sensor. We have evaluated the performance at a bias of 1.2 V because that value can be supplied by existing biodegradable Zn-Air batteries [7].

## III. Materials and Methods

A Gamry reference 600 and WaveDriver 10 were used to conduct open circuit potential, cyclic voltammetry, and chronoamperometry tests. The experimental set-up consisted of a ring stand, 50 mL beaker, and magnetic stir rod. A laser cutter was used to create a structure for the electrodes to fit through and attach to the leads, as shown in Figure 1. All three electrodes were cut using scissors, following a template that allowed about 1 $cm^2$ of electrode to be suspended in solution. Before every test, the Mo electrode was sanded, then cleaned with isopropyl alcohol and deionized water. Phosphate buffer solution (PBS) was mixed to a concentration of 1e-1 M using phosphate buffer powder from Sigma Aldrich, and deionized water. A pH meter was used to record the pH of PBS before every experimental run.

**Figure 1:** Experimental set-up

## IV. Experimental Results

### *A. Potentiometric Approach*

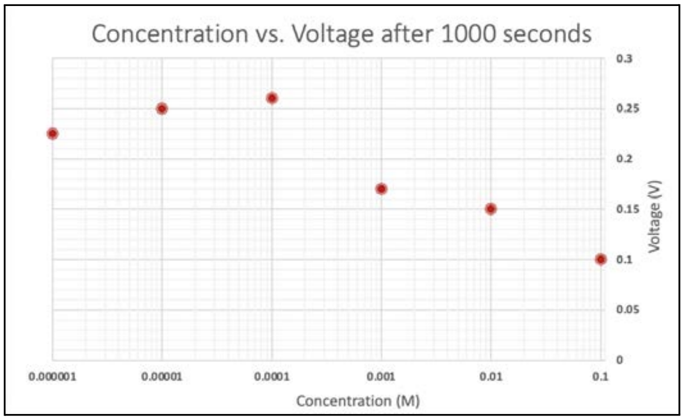

**Figure 2:** Open circuit potential between Mo and Sn measured 1000 s after submersion at varying phosphate concentration

The open circuit potential between Mo and Sn was measured in varying phosphate concentrations. The voltage was recorded after the system had settled for 1000 s.

## *A. Amperometric Approach*

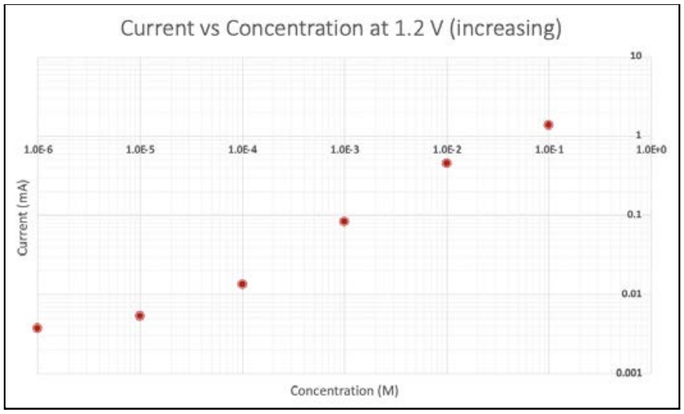

**Figure 3:** CV results at voltage of 1.2 V

Cyclic voltammetry was used to sweep the electrochemical cell from a voltage of 0.5 V to 1.5 V in 1e-2 M phosphate buffer solution, and the current at 1.2 V was extrapolated and graphed above.

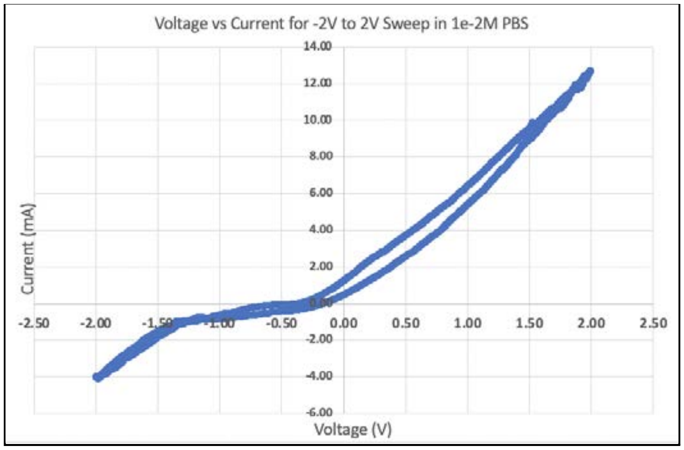

**Figure 4:** CV results with 3-electrode system

In the attempt to see if the current would reach a peak, the electrochemical cell was sweeped from -2 V to 2 V in 1e-2 M phosphate buffer solution. A three-electrode system was used, Mo as the working electrode and Au as the counter and reference electrodes.

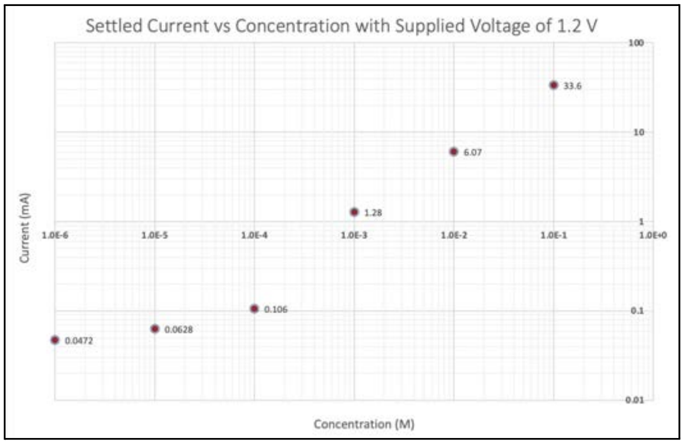

**Figure 5:** Chronoamperometry results

*Table 1:* Time for current to settle at 1.2 V

| Concentration (M) | Time (s) | Time (min) |
|---|---|---|
| 1e-1 M | 300 | 5 |
| 1e-2 M | 2500 | 41.67 |
| 1e-3 M | 500 | 8.33 |
| 1e-4 M | 500 | 8.33 |
| 1e-5 M | 800 | 13.33 |
| 1e-6 M | 400 | 6.67 |

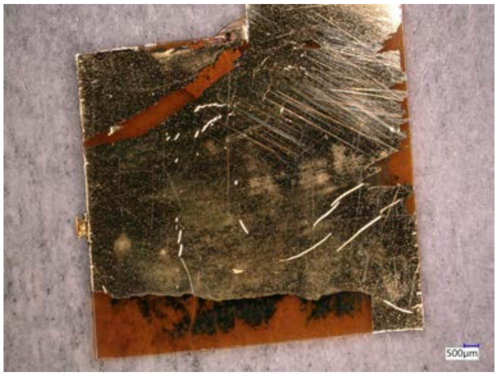

**Figure 6:** Au electrode in 1e-1 M PBS after 1.2 V

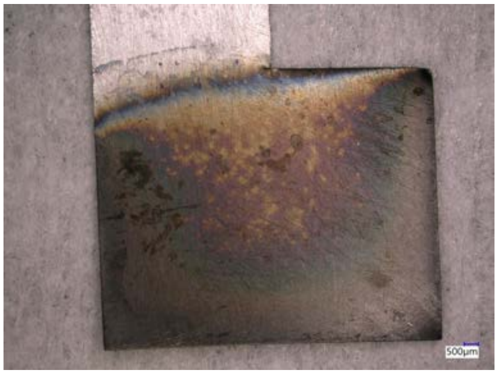

**Figure 7:** Mo electrode after submersion in 1e-1 M PBS and applied voltage of 1.2 V

Finally, chronoamperometry was used to directly correlate current values to specific phosphate concentrations. The electrochemical cell was biased at 1.2 V and both the final settled current value and the time it took for the current to settle were recorded. This was done in the three-electrode, Mo and Au set-up.

## V. Discussion and Conclusion

The results in Figure 2 show that a potentiometric approach may not be suitable for this sensor. There is not a clear trend between open circuit potential and change in phosphate concentration. We concluded that since Sn has not been widely used as a reference electrode in the literature, its relative stability is still unknown. This could have resulted in the shifting OCP values that were recorded.

To test the feasibility of an amperometric sensor, cyclic voltammetry was used to sweep a voltage over the electrochemical cell and measure the current. In Figure 3, it is apparent that there is an increase in current with increasing phosphate concentration. To further verify our results and understand the behavior of Mo as the working electrode, this measurement was repeated with a three-electrode system, and Au was used as the counter and reference electrodes.

Under this new set-up, cyclic voltammetry and chronoamperometry were used to measure the change in current with the change in phosphate concentration. First, we wanted to see if we could determine a peak current, however, as shown in Figure 4, no maximum value was concluded. This could possibly be due to other competing reactions in the solution. Finally, in order to have current values that directly correspond to local phosphate concentration, the electrochemical cell was biased at 1.2 V and the current was allowed to settle. This is because it is much more simple to make a circuit that biases the sensor to a set voltage, instead of sweeping the voltage, making it very complex. In Figure 5, there is still a clear trend, and a precedent can now be set for the sensor. From the graph, a sensitivity of 0.8179 dec/dec and a limit of detection of 1e-4 M can be concluded.

The feasibility of a phosphate sensor completely made of transient materials has been confirmed. In the future, research can be conducted in regard to the miniaturization of the sensor and the biodegradability of its packaging. There will also need to be a further exploration into the design of an interface circuit for this sensor.

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## References

[1] D. She, and M. G. Allen, “A Self-Powered, Biodegradable Dissolved Oxygen Microsensor,” *Journal of Microelectromechanical Systems*, vol. 29, no. 5, p. , Oct. 2020.

[2] Y. Li, T. Jiang, X. Yu, and H. Yang, “Phosphate Sensor Using Molybdenum,” *Journal of the Electrochemical Society*, vol. 163, no. 9, p. B479, Jun. 2016, doi: 10.1149/2.0161609jes.

[3] R. Zeitoun and A. Biswas, “Electrochemical Mechanisms in Potentiometric Phosphate Sensing Using Pure Cobalt, Molybdenum, and their Alloy for Environmental Applications,” *Electroanalysis*, vol. 33, no. 2, pp. 421-430, 2021, doi: 10.1002/elan.202060215

[4] “The Facts on Silver,” Dartmouth Toxic Metals (2021). Retrieved July 20, 2021, from https://sites.dartmouth.edu/toxmetal/more-metals/silver-metal-of-many-faces/the-facts-on-silver/

[5] G. S. Wilson and M. Amman, “*In vivo* biosensors,” *The FEBS Journal*, vol. 274, no. 21, doi: 10.1111/j.1742-4658.2007.06077.x

[6] “Molybdenum - Crop Nutrients,” *The Mosaic Company (*2021). Retrieved July 20, 2021, from cropnutrition.com/nutrient-knowledge/molybdenum

[7] J. Lee, S. T. Kim, R. Cao, N. Choi, M. Liu, K. T. Lee, and J. Cho, “Metal-Air Batteries with High Energy Density: Li-Air versus An-Air,” *Advanced Energy Materials*