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Embedded Electrochemistry with a Miniaturized, Drone-Based, Potentiostat System for Remote Detection Chemical Warfare Agents

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Abstract**—**The development of an embedded miniaturized drone-based system for remote detection of Chemical Warfare Agents (CWAs) is proposed. The paper focuses on the software/hardware system design of the electrochemical Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) signal processing for future deployment on drones. The paper summarizes the progress made towards hardware and electrochemical signal processing for signature detection of CWA. Also, the miniature potentiostat signal is validated by comparing it with the high-end lab potentiostat signal.

Keywords**—**Drone-based, remote detection chemical warfare agents, miniaturized, potentiostat.

I. Background

THERE is significant interest in the detection, decontamination, and quantification of CWAs and high explosives, particularly crucial in today's politically charged climate where the threat to a nation's security is imperative to the safety of one's country. There is a continuing endeavor to design remote sensing platforms. Whereby, the acquisition of information and data is either beamed back or collected and then brought back to a home base for further analysis. Therefore, any physical contact with the affected site is reduced. This application will have significant use in military, intelligence, forensic, commercial, economic, planning, and humanitarian applications.

The use of drones is a desirable method for making observations from a distance. One of the challenges is to place sensors that can selectively target CWAs or explosives on the drone that can transmit the data back to a home base. The combination of adding sensor arrays to drones offers promise for expanding sensing capabilities, beyond intrinsic related optical signs, for detecting and characterizing potential threats and targets of interest present in the operational environment (biological and chemical materials). This approach would be seen as advancing sensing capabilities for components that are identified and differentiated based on their electrochemical signatures.

Miniaturizing electrochemical potentiostat is an active research area; Hoilett et al. [1] proposed a coin-sized potentiostat for high-resolution electrochemical analysis. Cruzat et al. [2] proposed a low-cost miniaturized potentiostat for point-of-care diagnosis, which uses Texas Instruments microcontroller interfaced with three electrode system. Ning et al. [3] proposed a portable potentiostat based on a three-electrode electrochemical measurement system, which can be powered and communicated through the OTG interface of a smartphone. Adams et al. [4] proposed miniaturized potentiostat that uses Microchip Technology ATxmega32E5 microcontroller. Segura et al. [5] proposed a low-cost miniature systems of CV. All these miniaturized potentiostats have low voltage compliance range (around 2 volts), so, they are not suitable for the application of CWA detection, which requires high voltage compliance range of 8 volts. The design goal of miniature potentiostat for the CWA detection is the development of a platform for future deployment on drones.

II. Proposed Design

A. Electrochemistry

CWAs are very toxic chemicals, used in wars for the purpose of harming or to incapacitate the enemies, and are frequently used in terrorist attacks [6]. One of the important CWAs are nerve agents (classified as G and V series), which are organophosphate group containing compounds and can be synthesized easily [7]. Nerve agents are considered fatal because they increase the aggregation of acetylcholine in neuronal synapses inducing excess stimulation of nervous system [8]. Due to nerve agents being highly lethal, the mimicking agents (which show the similar properties, shape, size, but lesser toxicity than nerve agents) have been used in labs for sensor development to detect the CWAs. These mimicking agents are called simulants. Examples include Diisopropyl fluorophosphate (DFP), Dimethyl methyl phosphonate (DMMP), O,S-diethyl methyl phosphonothioate (DEMPT), etc. [9], [10]. Here, coumarin derivatives like CE2 has been synthesized to capture these simulants. Fig. 1 shows the chemical structure of two nerve agents, Tuban (GA), Soman (GD) and three simulants, DFP, DMMP, and DEMPT.

At first, the electrochemical reduction-oxidation (redox) properties of coumarin compound (CE2) were studied to detect the simulants. In the first stage, lab experiments using CHI

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Instrument of model number CHI 660A potentiostat was used for this study. As shown in Fig. 2, three oxidation peaks were observed with first, second and third oxidation potentials at 0.74 V, 1.16 V, 1.61 V, respectively, for DPV and 0.78 V, 1.17 V, 1.62 V, respectively for CV. The first oxidation peak was assigned to be from the oxidation of tertiary amine group (-N attached with propyl group), the second from oxime group (-N with OH attached) and the third oxidation group is still unclear.

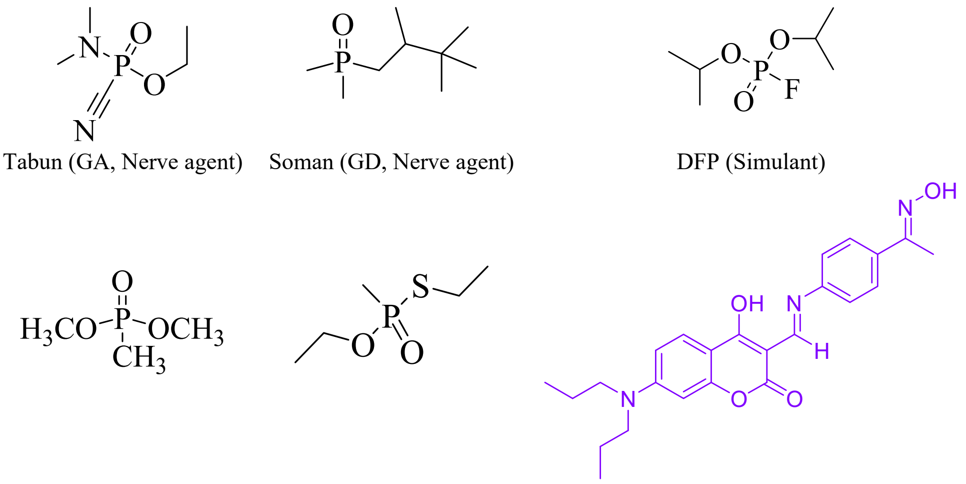

Fig. 1 Structures of G-series nerve agents - Tabun and Soman; Simulants – DFP, DMMP and DEMPT; Coumarin derivative compound - CE2

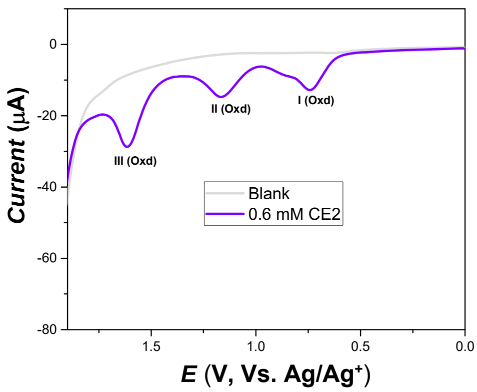

Fig. 2 (a) DPV study of 0.6 mM CE2

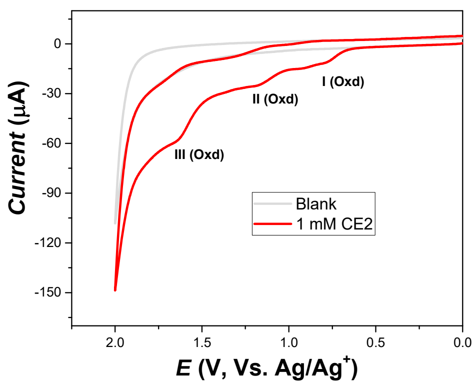

Fig. 2 (b) CV study of 1 mM CE2

The organic solvent system was a mixture of 20% nitrobenzene and 80% acetonitrile, with 0.1 M tetrabutylammonium perchlorate as electrolyte, glassy carbon electrode as working electrode and Ag/Ag^+ as reference electrode. For DPV, 0-1.8 V potential range was chosen. For CV, scan rate of 50 mV/s with 0-2 V as potential range were used

Based on the reaction of simulants like DFP with CE2 as shown in Fig. 3, it is expected to observe changes in the redox behavior of coumarin compound CE2. So, we plan on addition of different equivalences (for example 0, 0.5, 1, 2, 3) of simulants like DFP to the CE2 solution and run CV and DPV experiments.

For the electrochemical studies, a three-electrode cell system will be used, consisting of glassy carbon electrode (GCE) as working electrode, Ag/Ag^+ (10 mM $AgNO_3$ with 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile (MeCN)) as the reference electrode and platinum (Pt) wire as counter electrode. The solvent system preferred is 20% nitrobenzene, 80% MeCN with 0.1 M TBAP as the electrolyte.

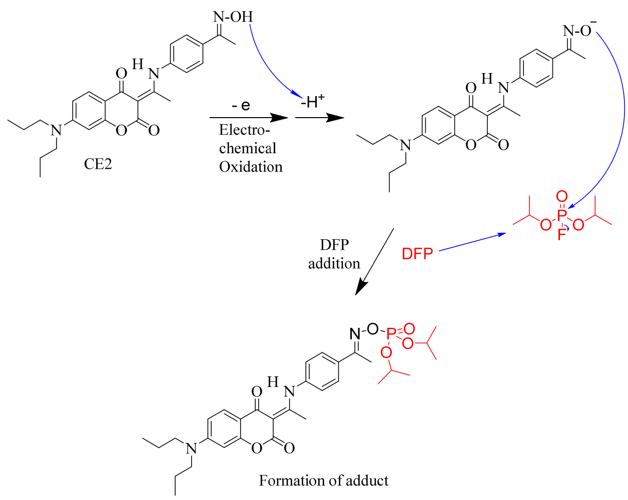

Fig. 3 Mechanism of reaction of CE2 after addition of DFP

B. Miniature Drone-Based Design

1. Hardware and Software

Palmsense Emstat4S is research-grade miniaturized potentiostat that will be used as a hardware platform to collect electrochemical CV and DPV signals. Emstat4S provides better voltage compliance range (8 volt) than all other systems summarized in the background section [1]-[5]. Table I summarizes the electronic characterization Emstat4S.

PSTrace for Windows provides simple user-interface support for all techniques and device functionalities. Also, Palmsense MATLAB Software Development Kit (SDK) library functions for system development. This includes establishing communication, loading parameters for CV and DPV, and analyzing measurements.

TABLE I
ELECTRONIC CHARACTERIZATION OF EMSTAT4

Voltage compliance range	± 8 volts
Applied potential resolution	183 µV
Current ranges	100 mA
Max. current	± 200 mA
frequency range	200 kHz

2. Validation of Emstat4 in Comparison with CHI Potentiostat 660A

To validate Emstat4 we compared its CV signal to the CV signal generated by chemistry lab CHI potentiostat 660A.

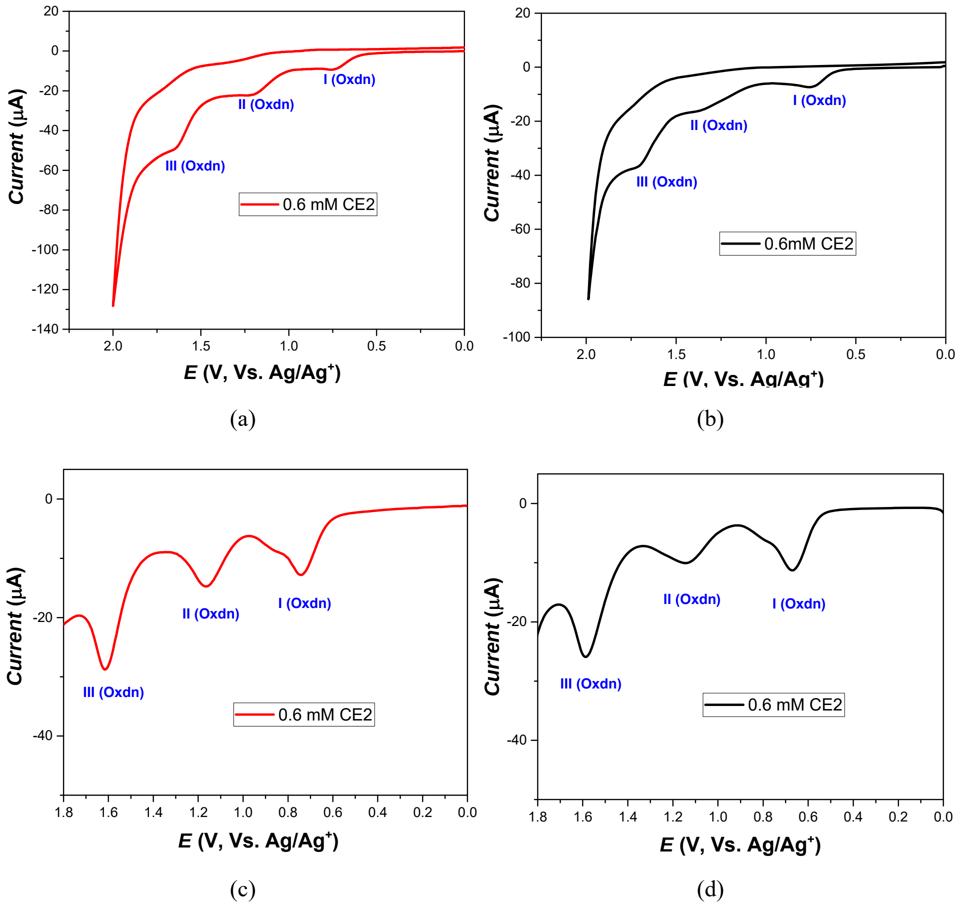

Fig. 4 Comparison of the electrochemical behavior (oxidation) of CE2 using DPV: CV studies of 0.6 mM CE2 in (A) CHI 660A potentiostat (B) Emstat 4s potentiostat; DPV studies of 0.6 mM CE2 in (C) CHI 660A potentiostat (D) Emstat 4s potentiostat

As shown in Fig. 4 (a) the red voltammogram was obtained with CHI 660A while (b) the black CV plot was with Emstat 4s potentiostat. Both plots showed indistinguishable oxidation behavior of CE2 i.e., they had three oxidation peaks. For CHI 660A, oxidation peaks were at potentials 0.75 V, 1.20 V, and 1.63 V as I (Oxdn), II (Oxdn), and III (Oxdn), respectively. Also, for Emstat 4s oxidation potentials were measured at 0.75 V, 1.36 V and 1.69 V as I, II, and III oxidation peaks, respectively. The oxidation potential values were found to be closer and favorable for further studies.

Figs. 4 (c) and (d) showed the DPV studies of 0.6 mM CE2 with potentiostats CHI 660A and Emstat 4s. Both showed identical electrochemical properties of the compound CE2. CE2 had three oxidation peaks. For the CHI 660A, the DPV measured the oxidation potentials at 0.74 V, 1.16 V, and 1.61 V, respectively. Likewise, the Emstat 4s also measured the first, second and third oxidation peaks at 0.67 V, 1.15 V and 1.59 V, respectively. These potentials from both the potentiostats were very similar (within 10% of current peak voltages).

Since, Emstat 4s potentiostat performance was observed to be similar as the research lab-based CHI 660A, therefore, it can be concluded that the Emstat 4s can also be utilized for the future electrochemical studies to detect CWA simulants.

III. Discussion and Conclusions

Future work includes feature extraction to recognize the pattern associated with presence of CWA. Also, other modules related to drone deployment will be handled at a later stage. The development of embedded miniaturized drone-based system for remote detection of CWA is proposed. The paper summarizes the progress made towards hardware and electrochemical signal processing for signature detection of CWA. Also, the miniature potentiostat signal is validated by comparing it with a high-end lab potentiostat signal.

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