Low Frequency Noise in Electrochemical Sensors for Water Quality Monitoring

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Abstract—**In the past several decades, water pollution has increased drastically due to rapid industrialization and population growth. Water contamination with pharmaceuticals are becoming an emerging problem as even a very low concentration may pose risks to human health and aquatic lifeforms. Since the safe limit of some chemicals such as painkillers and hormones in drinking water are in the range of ppm, the requirements for low-level detection of pharmaceuticals in water are demanding. Therefore, the development of new water quality monitoring sensors with improved limit-of-detection and sensitivity are critical. State-of-the-art water quality monitoring systems include sensors for pH, free chlorine and dissolved oxygen. As opposed to conventional techniques, many novel sensors are based on electrochemical redox reactions, which are described by the Nernst equation. However, one important practical problem in realizing a highly sensitive and wide dynamic range sensor is that few ppm changes of activity or concentration results in a signal of only several microvolts. This results in a poor signal-to-noise (SNR) ratio, making the signal indistinguishable from the low frequency noise (LFN). Therefore, characterization of the sensor performance is indispensable. In this paper, we present our approach to the fabrication and results on the noise and sensitivity of several sensors (acetaminophen and estrogen, pH, free chlorine and temperature) for water quality monitoring.**

Keywords—Low frequency noise, electrochemical sensors, water monitoring, pharmaceuticals sensor, pH, free chlorine, temperature

I. INTRODUCTION

The study of noise mechanisms in electrochemical sensors is critical for accurate in-vivo detection of analytes [1]. The detection efficiency of an electrochemical sensor depends on its ability to recognize small changes in the transduced signals that also brings uncertainty [2]. Therefore, an improved understanding of the sources of noise in an electrochemical sensor is crucial to accomplish high sensitivity and low limit-of-detection. Understanding of noise sources can help in developing new models and designs for the electrochemical sensors towards an improved system integration. For example, the noise behavior of an electrochemical sensor can provide insights into optimization of the sensor performance. The sensor performance is generally modified with different nanomaterials and functionalization methods. While noise phenomena are widely studied in solid-state electronic and photonic devices, noise in electrochemical sensing systems with solid-liquid interfaces are rarely investigated.

Noise fluctuations have been well-understood in common electronic components [3]–[5]. Based on their spectral densities, these fluctuations are generally classified in different types, such as thermal noise, shot noise and flicker noise [6]. The noise power spectral density (PSD) of the Johnson-Nyquist thermal voltage noise of a resistor is expressed as:

$$S_R = 4k_BTR \qquad (1)$$

where k_B is the Boltzmann's constant, T is the absolute temperature and R is the resistance of the resistor. Shot noise is an electronic noise that comes from the discrete nature of the electric charges while overcoming a potential barrier. Equation (1) shows that thermal noise is proportional to the temperature. On the other hand, shot noise does not depend on temperature, but on the current. The frequency independent behavior of the thermal and shot noise up to relatively high frequencies gave rise to their name white noise, in analogy with the spectrum of the white light. In contrast, the flicker noise PSD depends reciprocally on the frequency, so it is often called $1/f$ noise. Generally, $1/f$ noise is dominant at low frequencies.

Many experimental and theoretical studies on $1/f$ noise suggested that the $1/f$ noise is inversely proportional to the active area in electronic devices [7], and the electrode area of electrochemical devices [8]. Another study made some conclusions about the type of graphitic electrode material that can minimize flow-associated noise [9]. The major contribution to the understanding of noise in electrochemical systems originates from Faradaic interfacial processes, which were divided into two fundamental areas such as: (1) the method of creating perturbation of an equilibrium followed by measuring the induced current and the associated transfer function of the interface phenomena [10], [11], and (2) the noise that naturally occurs in the interfaces as homogeneous processes [12]–[19]. In both cases, a few fundamental insights into noise processes were found. Specifically, fundamental noise sources such as Johnson-Nyquist thermal noise and shot noise were neglected due to their very low magnitudes compared to $1/f$ noise.

In recent years, nanomaterials have attracted great attention in electrochemical sensing and biosensing applications due to their unique electronic, physical and chemical properties leading to highly sensitive and robust sensing/biosensing platforms [20]–[22]. In particular, carbon based nanomaterials such as carbon nanotubes were widely investigated as an efficient electrode modifier that enhanced the efficiency of electrochemical sensors/biosensors [23]. For example, modification of the sensing electrodes with multiwalled carbon

nanotubes (MWCNTs) with/without β-cyclodextrin (βCD) resulted in improved charge transfer efficiency and better sensing performance [24], [25]. However, the behavior of noise in electrochemical sensors that operate in the voltammetric modes with or without nanomaterial modifications is still not well studied and well understood.

In this work, we realize an experimental set up that mimics the voltammetric sensing operation, and then study the low frequency noise of the unmodified/modified Screen Printed Electrodes (SPE) under different conditions. The effect of the bias voltage and two types of electrolyte solutions (Phosphate Buffer Saline (PBS) and Potassium Ferricyanide ($K_3[Fe(CN)_6]$)) on the noise level is investigated. The effect of using sensing electrodes functionalized with MWCNTs and βCD on the electrochemical potential and noise level is investigated. We also study the noise of palladium/ palladium oxide (Pd/PdO) based pH sensor (in potentiometric configuration), amine-modified carbon electrode based free chlorine sensor (in voltammetric configuration), and PEDOT:PSS/silicon based thermistors. The experimental set up is described in section II, followed by results and discussions in section III.

II. Experimental Setup

A. Materials and reagents

Carbon based SPEs (Zensor), a glass based Ag/AgCl reference electrode and platinum counter electrode were purchased from CH Instruments. Potassium Ferricyanide ($K_3[Fe(CN)_6]$) in the form of powder and PBS tablets were purchased from Sigma. The $K_3[Fe(CN)_6]$ powder was dissolved into deionized (DI) water to get 5 mM concentration. Each PBS tablet was dissolved into 200 ml of DI water to get 0.01 M PBS buffer with pH 7.4.

B. Preparation of electrodes

Modifications of the SPEs were done with MWCNTs and β-cyclodextrin to get three types of modified SPEs such as: MWCNT/SPE, MWCNT-βCD(Phys)/SPE and MWCNT-βCD(SE)/SPE. The MWCNT/SPE electrode was modified with only pure MWCNT. The MWCNT-βCD(Phys)/SPE electrode was modified by MWCNT which was non-covalently (i.e., physically) functionalized with βCD. In MWCNT-βCD(SE)/SPE electrode, MWCNT modified by which was covalently (i.e., Steglich esterification) functionalized with βCD. The detailed MWCNT modification processes were described in previous paper [25].

C. Apparatus

The noise measurements of the electrochemical sensors were done in a three-electrode configuration similar to a potentiostat configuration that performs cyclic voltammetry or differential pulse voltammetry, as shown in Figure 1 and details in Table 1. A dynamic signal analyzer (SR785, Stanford Research Systems) was used to acquire and analyze the noise signal from the working electrode (Channel B of SR785) (i.e., bare SPE, MWCNT/SPE, MWCNT-βCD(Phys)/SPE and MWCNT-βCD(SE)/SPE electrodes). The reference and the counter electrodes were connected to a low-noise voltage amplifier (SR560, Stanford Research Systems) to its negative and positive input terminals, respectively. A low noise current amplifier (SR570) was used to amplify the output current of the working

electrode. A custom-made battery cell with potentiostat was used as the bias voltage source. Three multimeters were used to monitor the voltages at the biasing battery source, the reference electrode and the output of the current amplifier which corresponds to current from the working electrode by the factor of the amplifier gain ranging from 0.5 to 10 µA/V.
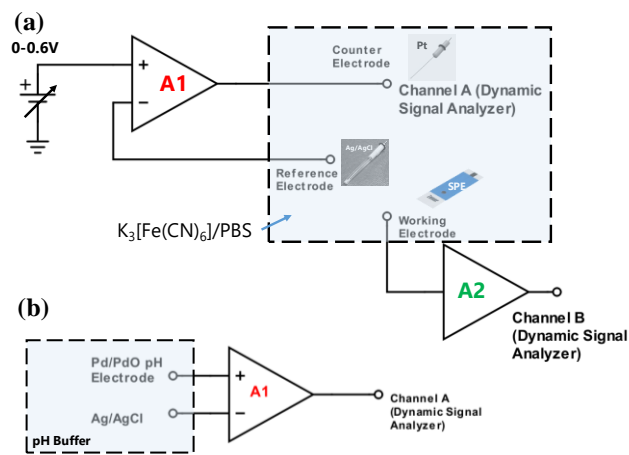

Fig. 1. The experimental setup for the noise measurement of (a) SPE electrodes modified with multi-walled carbon nanotubes and β-cyclodextrin, and amine modified carbon electrodes; (b) Pd/PdO based pH sensing electrode.

D. Noise data processing and analysis procedure

The noise data processing and analysis procedure requires several steps. In step 1, the raw data of noise signal from the Dynamic Signal Analyzer (SR785) is extracted to a personal computer in *.csv file format using VEE Pro 9.33 software developed by Keysight Technologies. The extracted noise spectra contained 60 Hz harmonics signal, which was due to interference from electrical power networks. In step 2, the 60 Hz harmonics from the signals were removed from the spectra using a 2nd order Butterworth notch filter implemented in MATLAB. In step 3, the filtered signals were then scaled with the gain of the current amplifier (SR570). Finally, in step 4, the current voltage (I-V) characteristics were obtained along with other noise related parameters.

III. Results and Discussions

The noise measurement setup for the electrochemical sensing electrodes was based on the potentiostat three-electrode configuration, since the actual electrochemical measurements also use the same. In this potentiostat configuration (Figure 1), we analyzed the current noise fluctuations at the working electrode. In electrochemical sensing measurements, the applied bias voltages are scanned between two voltages, which is usually in the range of few hundred millivolts. Therefore, we also used multiple bias voltages from 0 V to 0.6 V to analyze the effect of the bias voltages on the sensor noise (Table I). Figure 2 shows the power spectral density (PSD) spectra of the noise current when the electrodes were immersed into $K_3[Fe(CN)_6]$ (a-d) and PBS (e-h) solutions. In each type of electrode, the bias voltage applied between the reference and counter electrodes is set at 0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 V. The frequency range of the PSD spectra is from 2 Hz to 1.6 kHz and each spectrum is

obtained by averaging 64 acquisitions.

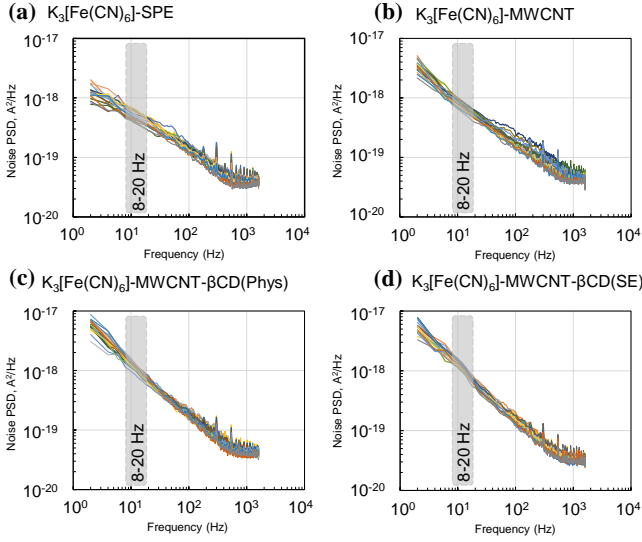| Type of Electrolyte	Type of Electrode	Bias Voltages
$K_3[Fe(CN)_6]$ (5mM)	SPE	0.0 V
	MWCNT-SPE	0.1 V
	MWCNT-βCD(Phys)/SPE	0.2 V
	MWCNT-βCD(SE)/SPE	0.3 V
PBS (pH 7.4, 0.01 M)	SPE	0.4 V
	MWCNT-SPE	0.5 V
	MWCNT-βCD(Phys)/SPE	0.6 V
	MWCNT-βCD(SE)/SPE	
pH Buffer	Pd/PdO based pH electrode	
PBS (pH 7.4, 0.01 M)	Amine modified carbon electrode	0.0 V 0.1 V
Tap Water	Si and PEDOT:PSS thermistors	

Fig. 2. The power spectral density (PSD) spectra of the noise current (at the working electrode) with $K_3[Fe(CN)_6]$ solution for (a) SPE, (b) MWCNT/SPE, (c) MWCNT-βCD(Phys)/SPE, and (d) MWCNT-βCD(SE)/SPE electrodes.

A. Noise in the pharmaceutical/heavy metal sensor

To investigate noise correlation between the working electrode and the reference/counter electrode, we performed correlation/coherence measurement with the Dynamic Signal Analyzer (SR785). First, we performed correlation between the voltages and currents of all electrode terminals. However, there was no significant correlation between them. This signifies that the noise originating from the electrode terminals were based on independent processes that only happens within the vicinity of the corresponding electrode and does not affect the other two electrodes. After that, we performed coherence measurement which showed coherence value of less than 30%, again signifying little coherence between the noise sources of all electrode terminals.

The effects of biases/materials/solutions on noise characteristics were studied. The current noise PSD spectra in Figure 2(a-d) and Figure 3(a-d) shows seven noise PSD spectra which were recorded with seven different applied bias voltages ranging from 0 V to 0.6 V. There is no specific pattern or

variation of the seven different noise PSD spectra showing very weak dependence on the applied bias. However, there is an increase in the noise PSD level from $\sim 10^{-18}$ A²/Hz to $\sim 10^{-17}$ A²/Hz in lower frequency range (2-10 Hz) when the bare SPE electrode is modified with MWCNT and MWCNT-βCD(Phys/SE), as shown in Figure 2(a-d) and Figure 3(a-d). The increase in the noise level with the addition of MWCNT on the SPE electrode may indicate that the noise behavior are due to the inherent materials properties of the electrodes. Also, the noise may be related to the concentrations of ions of the solutions going into the working electrode. However, when the electrodes are changed from $K_3[Fe(CN)_6]$ solution to PBS buffer solution, the noise level remains almost the same, which means that the noise does not depend on the type or concentration of ions that are present in the electrolyte solution. Thus, the noise behavior that are observed in Figure 2(a-d) and Figure 3(a-d) are simply due to characteristics of each electrode itself. The noise PSD spectra shown in Figure 2(a-d) for $K_3[Fe(CN)_6]$ solution shows $1/f$ noise characteristics since the level of the noise spectra decreases by approximately one decade per decade of frequency. The $1/f$ noise refers to the phenomenon of the spectral density, $S(f)$, of a stochastic process having the form [26]:

$$S(f) = \frac{K_F (I_{avg} \text{ or } V_{avg})^2}{f^\alpha}, \qquad (2)$$

where f is frequency, I_{avg} or V_{avg} are the average current/voltage of the sensor, K_F is the flicker noise coefficient, and the exponent α is in the range of $0.8 < \alpha < 1.2$, and is usually close to 1, and this noise is known as flicker noise. $1/f$ fluctuations are widely found in nature. The noise PSD spectra shown in Figure 3(a-d) for PBS solution are, however, not purely pink noise. In this case, the value of α is somewhere between 0.5 and 1. Moreover, the noise PSD spectra in Figure 3(a-d) also show very weak Lorentzian humps at around 100 Hz, which could be due to defect-assisted generation-recombination (GR) processes [27] or other bistable random fluctuation [28]. Figure 3(e-h) shows the noise PSD spectra multiplied with frequency to identify the level of $1/f$ noise and the frequency at which the Lorenztian humps are observed. The initial flat region of the curves in Figure 3(e-h) in the lower frequency range provides the level of $1/f$ noise. It is observed from Figure 3(e-h) that the $1/f$ noise increases by only few times when the electrodes are modified with MWCNT and βCD. Also, the Lorentzian humps are observed at around 100 Hz for all the electrodes.

The applied bias influenced the electrochemical potential and noise level. Figure 4(a) shows the "$V_{re}-V_{we}$" vs I_w, where V_{re} is the voltage in the reference electrode, V_{we} is the voltage at the working electrode, and I_w is the current in the working electrode. This current-voltage relationship of the working electrode with respect to the reference electrode (i.e., $V_{re}-V_{we}$) shows two different types of characteristic curves of the set of electrodes due to the two electrolyte solutions (i.e., $K_3[Fe(CN)_6]$ and PBS solutions, separated by a dashed gray line).

In case of PBS, the I_w ranges from ~ 0.1 μA to ~ 8 μA, whereas in case of $K_3[Fe(CN)_6]$, the current varies in a narrow range between ~ 9 μA to ~ 11 μA. If we extrapolate the I-V curves, their intercepts on the vertical axis will provide corresponding electrochemical potentials of the electrodes. The electrochemical potential of the SPE and modified SPE

electrodes in PBS solution can be estimated to be close to 0 mV. However, the electrochemical potential can be extrapolated to at least below −200 mV when $K_3[Fe(CN)_6]$ solution was used. It is also observed in Figure 4(a) that the electrochemical potential reduces with the functionalization of the SPE electrode with MWCNT and MWCNT-βCD(Phys/SE).

(a) PBS-SPE
(e) PBS-SPE
(b) PBS-MWCNT
(f) PBS-MWCNT
(c) PBS-MWCNT-βCD(Phys)
(g) PBS-MWCNT-βCD(Phys)
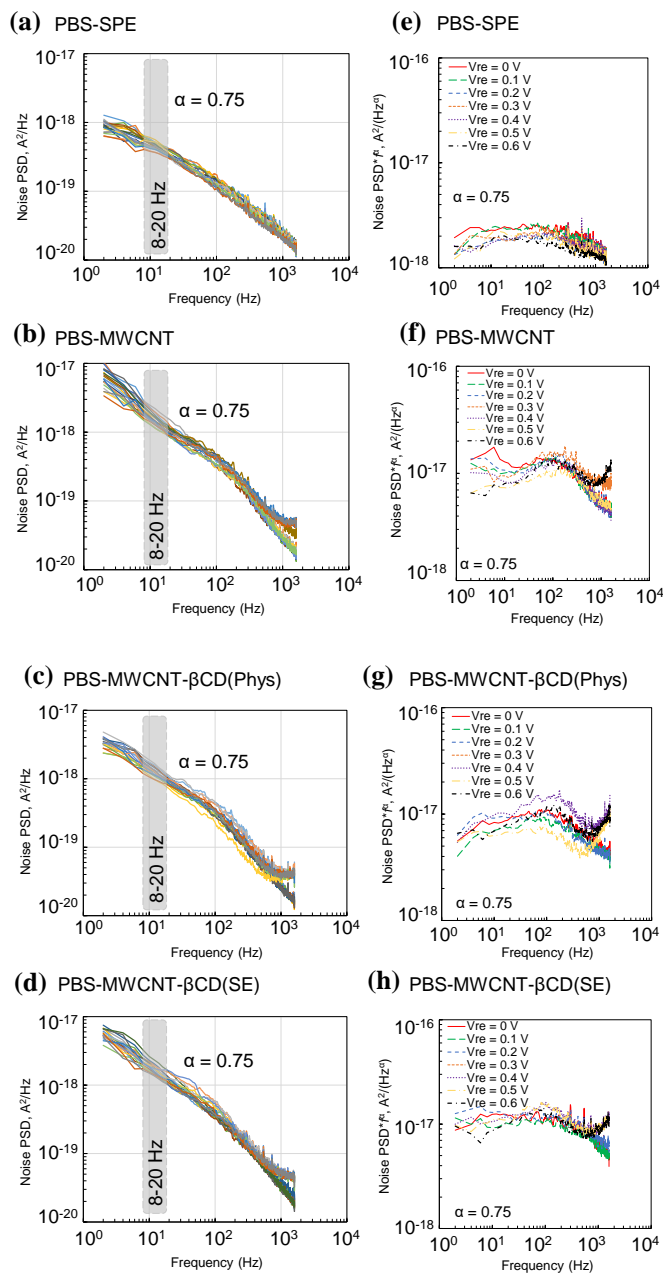**(d)** PBS-MWCNT-βCD(SE)
(h) PBS-MWCNT-βCD(SE)

Fig. 3. The power spectral density (PSD) spectra of the noise current (at the working electrode) with PBS solution for (a) SPE, (b) MWCNT/SPE, (c) MWCNT-βCD(Phys)/SPE, and (d) MWCNT-βCD(SE)/SPE electrodes. The noise PSD spectra multiplied with frequency for (e) SPE, (f) MWCNT/SPE, (g) MWCNT-βCD(Phys)/SPE, and (h) MWCNT-βCD(SE)/SPE electrodes.

Figure 4(b) shows the "Low Frequency Noise (LFN) between 8 and 20 Hz" vs I_w in the working electrode. These curves were derived from the normalized noise PSD spectra.

Similar to the case as shown in Figure 4(a), the I_w has a wider range when PBS solution is used as the electrolyte compared to that of $K_3[Fe(CN)_6]$ solution. However, the LFN noise in band 8-20 Hz remains almost constant at different current of the working electrode (I_w, which is proportional to the bias voltages), signifying negligible bias dependence of the LFN noise level. However, the level of LFN noise increases around three times when the SPE electrode is modified with MWCNT and MWCNT-βCD(Phys/SE).
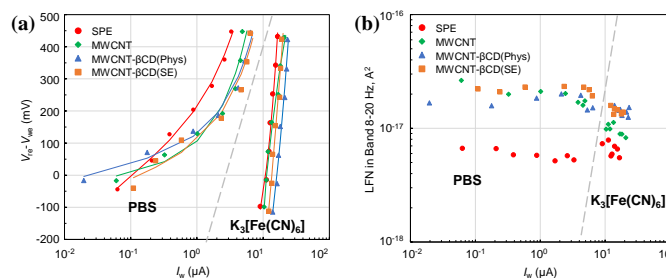
Fig. 4. (a) Current voltage characteristics of SPE and modified SPE working electrodes with PBS and $K_3[Fe(CN)_6]$ solutions measured in potentiostatic configuration, (b) Low frequency noise (LFN) of SPE and modified SPE working electrodes with PBS and $K_3[Fe(CN)_6]$ solutions in frequency band of 8-20 Hz with respect to the current at the working electrodes.

Based on the abovementioned observations, the noise level of the SPE and modified SPE electrodes have negligible bias dependence and a very small dependence on the electrode materials. In fact, the noise level only increases by ~3 times when MWCNT or MWCNT-βCD(Phys/SE) is attached to the SPE electrode. The increase of the noise level is not significant compared to the increase of the electrochemical sensing signals when MWCNT based modification are done. Moreover, since the noise level has a negligible bias dependence, the signal-to-noise ratio of the electrodes during actual sensing experiments will not depend much upon the range of the scanning potential. Therefore, these results signifies that the modification of SPE with MWCNT and functionalized MWCNT will not introduce any significant noise to the electrochemical sensing signals.

The influence of the analyte concentration on the noise of the pharmaceutical sensor was investigated by using three different concentrations of acetaminophen (APAP) with the MWCNT-βCD(Phys)/SPE electrode. The three concentrations of APAP were 1, 3 and 6 μM, which were prepared in PBS (7.4) buffer solution. The bias voltage used in the noise measurement was 0.3 V that is close to the APAP oxidation potential. Applying this bias voltage mimics the actual conditions during the sensing experiment so that the noise behavior can be estimated and related to the experimental conditions. The APAP concentration dependent noise spectra is shown in Figure 5(a).

It is observed that the low frequency noise PSD increases by around one to two orders of magnitude when the concentration of APAP is increased. However, the peak current at the oxidation potential is at least few orders of magnitude higher than the base-line current. Therefore, the increase in the noise due to higher APAP concentration does not significantly deteriorate the overall noise, as shown in Table II. Also, the increase of noise at very low concentration of APAP (<1μM) is

also insignificant compared to the noise at high APAP concentration (e.g., 6 µM). Another noise characteristic is the value of α corresponding to $1/f^\alpha$ noise parameter. In the case of blank PBS solution, the value of α is 0.7 which increases to 2 with high concentrations of APAP (i.e., 6 µM). Higher value of α corresponds to sharper decrease of slope of the noise PSD spectra.

B. Noise in the pH sensor

The noise in Pd/PdO based pH sensors was studied by using three different pH buffers (i.e., 4, 7 and 10). As the pH sensors are operated in potentiometric configurations, where the pH of the solution is transduced into corresponding output potential, the noise PSD of the pH sensor was measured by connecting the pH sensor and a reference electrode to the positive and negative terminals of a low-noise amplifier, respectively. As shown in Figure 5(b), the value of α in the noise PSD is 2 for all the pH buffers in the frequency range of 4-100 Hz. Also, the noise power increases by one order of magnitude in pH buffer 4 and 10 compared to that of pH 7 in lower frequency range. The increase in the noise power at pH 4 and 10 may be attributed to the higher concentrations of H_3O^+ and OH^- ions, respectively, compared to that of neutral pH 7. However, the noise power levels (i.e., nanovolts square) for different pH are significantly smaller than the signal of the pH sensors, which are in the range of few tens to hundreds millivolts. Thus, the noise power of the pH sensor does not introduce any significant experimental uncertainty during the pH measurement.

C. Noise in the free chlorine sensor

The noise in the amine-modified carbon electrode-based free chlorine sensor was studied by using the electrode in a three-electrode voltammetric configuration along with an Ag/AgCl reference electrode and a platinum counter electrode, as shown in Figure 5(c). The bias voltages used in the noise were 0 V and 0.1 V, since the free chlorine sensor was operated only in these two biasing conditions in chronoamperometry measurement. It is observed that the noise behavior does not change with the biasing voltages. Also, the value α in $1/f^\alpha$ parameter is 2 in both biasing conditions. Moreover, the noise power is in the range of less than few nanovolts square per Hz, whereas, the minimum current detected in the free chlorine sensing is in the range of few tens of nanovolts. Therefore, the noise behavior of the free chlorine sensor does not introduce additional degradation in the sensitivity and limit-of-detection of the sensing signal.
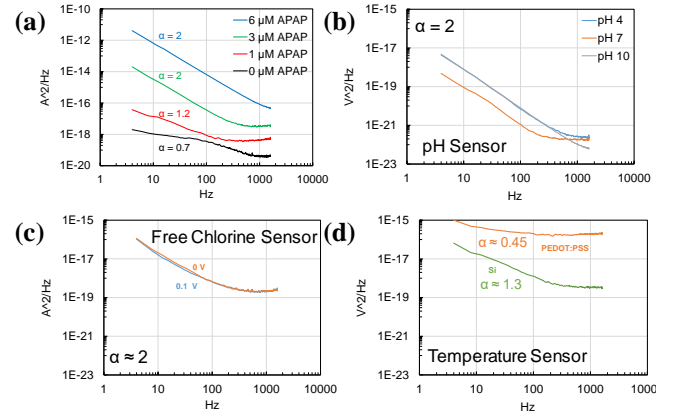

Fig. 5. (a) Noise with different APAP concentration using MWCNT-βCD(Phys)SPE electrode, (b) Noise with different pH buffer using Pd/PdO based pH sensing electrode, (c) Noise with different bias voltages using ammonium carbamate modified and carbon based free chlorine sensing electrode, and (d) Noise in the PEDT:PSS and silicon thermistors used for temperature sensing.

D. Noise in the temperature sensor

The temperature sensor used in the integrated water quality monitoring system was based on a Wheatstone-bridge based temperature sensor made of PEDOT:PSS and silicon (Si) thermistors. Therefore, the output signal of the temperature sensor provides a potential difference. The overall noise behavior of the temperature sensor depends on the individual PEDOT:PSS and Si thermistors. Thus, we studied the voltage noise of the individual thermistors, as shown in Figure 5(d). The noise power of the PEDOT:PSS thermistor was ~1 to 3 orders of magnitude higher than that of the Si thermistor. This could be due to polymeric nature of the PEDOT:PSS thermistor which possesses higher molecular irregularity/defects compared to that of silicon, where the atoms are arranged in an almost perfect crystalline structure. Also, the $1/f^\alpha$ parameters shows that the value of α were 0.45 and 1.3 for PEDOT:PSS and Si, respectively. This difference in the α value could be related to the transport mechanism of the two types of semiconductors. The noise power levels for both of the thermistors were in the range of few nanovolts square, which is much below the temperature induced voltage difference in the range of few hundreds of millivolts.

TABLE II. NOISE K_F AND LFN IN DIFFERENT SENSORS COMAPRED TO THE NOISES DURING ACTUAL MEASUREMENTS.

Sensor	Analyte	α	Signal (in actual measurement)	Noise K_F	Noise (in actual measurement)	LFN in band 8-20 Hz
MWCNT-βCD(Phys)	0 µM APAP	0.7	0.6 µA	1.56×10^{-5}	< 10 nA	3.64 nA
	1 µM APAP	1.2	~3 µA	1.16×10^{-5}	< 0.1 µA	9.14 nA
	3 µM APAP	2.0	~5 µA	2.26×10^{-3}	< 0.5 µA	0.11 µA
	6 µM APAP	2.0	~8 µA	1.77×10^{-1}	< 2 µA	1.55 µA
Pd/PdO	pH 4	2.0	~60 mV	2.08×10^{-14}	< 0.1 mV	2.12 nV
	pH 7	2.0	~200 mV	1.92×10^{-16}	< 0.1 mV	0.74 nV
	pH 10	2.0	~400 mV	4.7×10^{-16}	< 0.1 mV	2.14 nV
Free chlorine	PBS 7.4	2.0	~100 to 1500 nA	$< 1.84\times10^{-1}$	< 20 nA	11 nA
Temperature	Si	1.3	~100 to 800 mV	$< 3.97\times10^{-14}$	< 0.1 mV	10 nV
	PEDOT:PSS	0.45	~100 to 800 mV	$< 1.86\times10^{-14}$	< 0.1 mV	55 nV

IV. Conclusions

In this study on noise in electrochemical sensors, several experiments were reported in an effort to understand the dependence of noise level on the type of electrolyte solutions, bias voltages and electrode materials. This would allow us to identify possible effect of noise on electrochemical sensing performances. Analyte types and electrode modifications, as well as bias voltages dependent $1/f$ noise were studied in screen printed electrode (SPE) and MWCNT/MWCNT-βCD(Phys/SE) modified SPE. The experimental results showed that the noise level remains almost constant, independent on the type of electrolyte solutions or bias voltages. However, a slight increase of the noise level (about three times) was observed when SPE electrode was modified with MWCNT and MWCNT-βCD(Phys/SE). The PBS solution showed wider current range of the working electrode to that of $K_3[Fe(CN)_6]$ solution. Also, the electrochemical potential of the electrodes in PBS solution was close to 0 mV, whereas it was below −200 mV for $K_3[Fe(CN)_6]$ solution. The increase of the noise level due to MWCNT and MWCNT-βCD(Phys/SE) modifications has negligible impact on the signal-to-noise ratio in the electrochemical sensing measurements. In fact, SNR improves when surfaces are functionalized with MWCNT. The noise in pH, free chlorine and temperature sensors are also analyzed. From the noise measurements, it is shown that there was negligible influence on the sensing signal, and the noise is lower than the limit-of-detection reported in previous chapters.

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