




# Effects of Nitrogen Content on Square Wave Anodic Stripping Voltammetric Performance of Nitrogen-Doped Tetrahedral Amorphous Carbon Thin Films

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## Keywords:

*N-taC thin films*  
*N doping*  
*LSCV*  
*SWASV*  
*Pb<sup>2+</sup> and Cu<sup>2+</sup> ions*

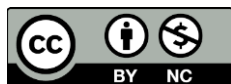
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## ABSTRACT

Nitrogen-doped tetrahedral amorphous carbon (N-taC) thin films were prepared on silicon (Si) substrates via filtered cathodic vacuum arc (FCVA) deposition by varying the N<sub>2</sub> flow rate from 10 to 60 sccm to get different N contents in the films. The electrochemical potential windows (EPWs) of the N-taC thin films were measured in potassium chloride (KCl) solution by applying a linear sweep cyclic voltammetric (LSCV) technique. The square wave anodic stripping voltammograms (SWASVs) of lead (Pb) and copper (Cu) on the film surfaces were acquired by varying deposition time and potential and metal ion concentration. The effects of N content on the EPWs and SWASV performance of the N-taC thin films were also investigated. The results clearly showed the apparent influences of deposition time and potential, metal ion concentration, and N content on the SWASVs of both Pb and Cu obtained by the N-taC thin films. It was found that the N-taC thin films were able to detect Pb<sup>2+</sup> and Cu<sup>2+</sup> ions in the KCl solution at the μM level.

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## 1. INTRODUCTION

The presence of heavy metals such as mercury (Hg), lead (Pb), copper (Cu), etc., released from anthropogenic sources, in the aquatic ecosystem implicates not only biota but also

human beings [1-3]. Water may be seen as clean and transparent as it is, but there are usually those heavy metals present in it that are not visible to the human eye. When water containing undetected heavy metals is consumed, they can have harmful and

detrimental effects on the human body since most of them are toxic [4]. An accumulation of heavy metals in the body can eventually lead to serious health problems over time.

Pb is one of the most toxic heavy metals with a wide range of applications, such as batteries, printing pipes, pigments, fuels, welding, and so on [1-3,5]. The Pb concentration of more than  $4 \times 10^{-6}$  M in drinking water is detrimental to fetuses and children with possible development of neurological problems [1-3,5]. For instance, an overdose of Pb results in poisoning, which can cause irreversible neurological damage, renal disease, cardiovascular effects, hypertension, and reproductive toxicity [1-3,5]. Although Cu has relatively low toxicity to human beings and its small concentrations are essential to life, prolonged consumption of excessive Cu of more than  $8 \times 10^{-5}$  M can result in some health complications with adverse chronic effects (e.g., liver failure) [1-3,6]. Cu can come from many sources, such as waste from metal cleaning and plating baths, the fertilizer industry, paperboard, paper, pulp, and so on [1-3,6]. The use of contaminated drinking water with heavy metals can cause their accumulation in the bodies of human beings and animals, leading to serious health problems [7]. Therefore, it is of paramount importance that the drinking water is free of heavy metals before consumption. One possible way to ensure that the water is clean and hygienic for domestic use is to detect the presence of any unwanted heavy metals in it at an early stage and remove them effectively [8]. Therefore, it becomes challenging for analysts to quickly detect and effectively determine heavy metals in aqueous solutions.

Hg and carbon (C) (glassy carbon, graphite, etc.)-based electrodes are widely used for electroanalytical purposes, but they have their own limited electrochemical performance [9-11]. Boron (B)-doped diamond thin films have been introduced for stripping analysis of various heavy metals such as Pb, Cu, cadmium (Cd), zinc (Zn), manganese (Mn), silver (Ag), etc. at  $\mu\text{M}$  level [12-14]. But they require high deposition temperatures, which demand high energy consumption and manufacturing costs [12-14]. Compared to B-doped diamond thin films, diamond-like carbon (DLC) thin films can be practically prepared at room temperature (RT) [9,15-18]. In addition, DLC thin films are well known for their exceptional properties, such as high hardness, low coefficient of friction, and excellent wear resistance [19,20].

Besides, the insulating property of DLC thin films causes them to be excellent in corrosion resistance in aggressive solutions but makes them impossible to be applied in electrochemical applications [19-21]. However, nitrogen (N) doping can make DLC thin films conductive to be suitable for electrochemical analysis [9,15-18]. Yoo et al. [15] first reported that N doping improved the electrical conductivity of DLC thin films and made them suitable for electrochemical applications. The N-DLC thin films had a wider electrochemical potential window (EPW) in an  $\text{HClO}_4$  solution than B-doped diamond thin films. Zeng et al. [22,23] introduced N-DLC thin films for stripping analysis of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  ions in an aqueous solution and measured their EPWs in various aqueous solutions. Lagrini et al. [24] studied the EPWs of N-DLC thin films in a  $\text{LiClO}_4$  solution with different  $\text{N}_2$  partial pressures. Khun et al. [16,25] further reported the EPWs of N-DLC thin films in various aqueous solutions and their electrochemical performance of detecting single and multiple elements in an aqueous solution. Based on the reported results in the literature, it is still necessary to further improve the sensitivity of N-DLC thin films to heavy metal ions by reducing their background currents for their successful application in electrochemical analysis.

The filtered cathodic vacuum arc (FCVA) deposition method is often chosen to produce taC thin films over other physical vapor deposition (PVD) methods for electrochemical applications because of several advantages, such as the high percentage of  $\text{sp}^3$  bonds, uniform thickness, good film quality, high deposition rate, and relatively low operating cost [26]. As a result, the taC thin films have higher hardness, Young's modulus, wear, and corrosion resistance compared to sputtered DLC thin films. It is therefore expected that taC thin films have high resistance to prompt anodic dissolution in electrolytes, which is essential for promising thin film electrodes, since the poor corrosion resistance of an electrode can negatively affect its electrochemical performance, such as sensitivity, accuracy, repeatability, robustness, stability, etc. [27].

Voltammetry is an analytical technique based on the measure of the current flowing through an electrode that is immersed in an electrolyte containing electrochemically active species while a potential scan is imposed on it [9]. The cyclic voltammetric (CV) technique is always used to first

access the electrochemical performance of new electrodes by measuring their EPWs in various aqueous solutions because of its high information content and simplicity [9]. An EPW is defined by a difference in potentials for hydrogen ( $H_2$ ) and oxygen ( $O_2$ ) gas evolution, within which metals are supposed to be detected, so that the wider EPW allows the detection of a greater variety of metals in aqueous solutions [9,23,25,28,29]. The stripping voltammetric (SV) technique offers a simple, fast, and cheap way of detecting heavy metals among many electroanalytical techniques [9]. Although there are several SV techniques, such as anodic, cathodic, and absorptive SV techniques, the anodic stripping voltammetric (ASV) technique is the most broadly used technique for heavy metal detection because of its remarkably high sensitivity to metal ions, very low detection limit, and ability to simultaneously detect multiple heavy metals by relatively inexpensive instrumentation [9,23,25,28,29]. The ASV technique consists of two main steps: a pre-concentration or accumulation step, in which analytes of interest are accumulated from the solution onto a suitable working electrode surface by applying a negative deposition potential, and a stripping step involving pre-concentrated analytes that are then stripped from the electrode surface into the solution by the application of a potential scan, with a resulting Faradaic current allowing direct quantification of the number of analytes present [9,23,25,28,29]. The stripping voltammograms of heavy metals are greatly influenced by their concentrations as well as electrochemical deposition parameters such as deposition time and potential [9,23,25,28,29]. It is therefore necessary to systematically investigate the effects of metal ion concentrations and deposition parameters on the ASV performance of N-taC thin films.

In this study, N-taC thin films were prepared on Si substrates via FCVA deposition by varying the  $N_2$  flow rate from 10 to 60 sccm. The effects of N content on their EPWs in an aqueous KCl solution were evaluated using the linear sweep cyclic voltammetric (LSCV) technique. Their detection performance of  $Pb^{2+}$  and  $Cu^{2+}$  ions was systematically investigated using the square wave anodic stripping voltammetric (SWASV) technique with respect to N content, deposition time and potential, and metal ion concentration, since the SWASV technique had excellent sensitivity, rejection of background current, and fast scanning speed [9].

## 2. EXPERIMENTAL DETAILS

### 2.1 Sample preparation

A FCVA deposition system (Nanofilms) was used to deposit N-taC thin films with an estimated thickness of 100 nm on Si substrates (100, n-type, 150 mm diameter, 0.7 mm thick, 0.001-0.0035  $\Omega$ cm). For the N dopant, the  $N_2$  gas was introduced into the deposition chamber via a mass flow controller at flow rates of 10, 20, 40, and 60 sccm, while a pure graphite target (99.995%) was used as the C source. All the depositions were carried out for 250 s at RT ( $\sim 22-24^\circ C$ ), with a fixed substrate pulsed bias of 800 V and a current of 30 A on the cathode. Prior to the film deposition, the Si substrates were cleaned with an  $N_2$  ionizing gun. It was found that the N contents of the N-taC thin films measured by X-ray photoelectron spectroscopy (XPS, Kratos) with monochromatic Al K $\alpha$  (1486.6 eV) X-ray radiation were 2.6, 2.8, 3.4, and 5.1 at.% for 10, 20, 40, and 60 sccm  $N_2$ , respectively.

### 2.2 Characterization

All the electrochemical measurements were carried out using a BioNano LK6200 electrochemical workstation. A K0235 flat cell kit with three electrodes was used. A platinum mesh was used as the counter electrode, while a standard silver/silver chloride (Ag/AgCl) electrode in a saturated KCl solution (0.197 V at  $25^\circ C$ ) was used as the reference electrode. The N-taC thin film-coated samples with 2 cm  $\times$  2 cm were used as the working electrodes, and their back sides were coated with a gold layer to make them have a good electrical connection. The testing areas of the working electrodes were a circle of 1 cm in diameter. The amount of different solutions used was 250 ml.

The EPWs of the N-taC thin films in a deaerated and unstirred 0.1 M KCl solution without adjusting its pH value were measured using the LSCV technique by scanning from -2 V to 3 V at a scan rate of 100 mV/s.

The ASV performance of the N-taC thin films in a deaerated and unstirred 0.1 M KCl solution was analyzed using the SWASV technique. Both the potential increase and amplitude were 0.15 V. The frequency was 10 Hz, and the quiet time was 10 s. These parameters were fixed to measure the

stripping currents of both Pb and Cu with respect to deposition time and potential and metal ion concentration. The deposition potential of -1.2 V was fixed to get the SWASVs of both Pb and Cu with different deposition times of 60 s to 240 s. The deposition time of 60 s was fixed for the SWASVs of both Pb and Cu with different deposition potentials of -0.8 to -1.2 V. The deposition potential of -1.2 V and the deposition time of 60 s were fixed for the SWASVs of both Pb and Cu with different metal ion concentrations of  $1 \times 10^{-6}$  M to  $1.5 \times 10^{-5}$  M.

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of N<sub>2</sub> flow rate on LSCVs of N-taC thin films

Figure 1 shows the LSCVs of the N-taC thin films with different N<sub>2</sub> flow rates measured in a 0.1 M KCl solution. In a CV, a potential difference between hydrogen ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\uparrow$ ) and oxygen ( $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 4\text{e}^- + \text{O}_2\uparrow$ ) gas evolution gives rise to an EPW where decomposition of water occurs ( $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ ) [9,23,25,28,29]. The wider EPW allows detection of a wider range of different elements in aqueous solutions for metal tracing analysis, since specific metal elements within the EPW can only be detected [9,23,25,28,29]. The N-taC thin film with a N<sub>2</sub> flow rate of 10 sccm has potentials of -1.5 V and 2.3 V for H<sub>2</sub> and O<sub>2</sub> gas evolution, respectively, on its surface, so it has a wide EPW of 3.8 V, as found in Figure 1 and Table 1. Increasing the N<sub>2</sub> flow rate to 60 sccm shifts the potentials for H<sub>2</sub> and O<sub>2</sub> gas evolution on the N-taC thin film surface to -1.1 V and 2 V, respectively, as well as decreases its EPW to 3.1 V. The increased N content of the N-taC thin film decreases its electrical resistivity because the extra electron of the doped N atom enhances its n-type semi-conductivity, while the N doping narrows its band gap via its graphitization [28,29]. The lower electrical resistivity of the N-taC thin film with a higher N<sub>2</sub> flow rate results in an earlier evolution of H<sub>2</sub> and O<sub>2</sub> gases via the higher kinetics of electron transfer through it, which is confirmed by the shifts of potentials for H<sub>2</sub> and O<sub>2</sub> gas evolution to less negative and positive potentials, respectively, as found in Table 1 [22,23,25]. The increased N content of the N-taC thin film, therefore,

decreases its EPW, which means that a range of different elements for metal tracing analysis is decreased as a result of an earlier occurrence of the obstacle associated with H<sub>2</sub> and O<sub>2</sub> gas evolution during electrochemical measurements.

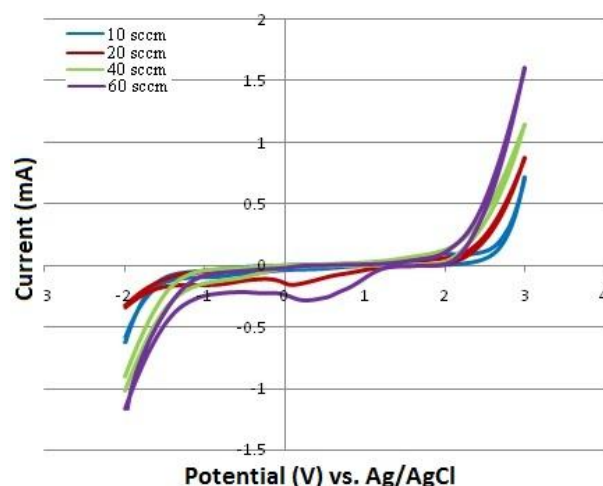


Fig. 1. LSCVs of N-taC thin films with different N<sub>2</sub> flow rates measured in a 0.1 M KCl solution at a scan rate of 100 mV/s.

Table 1. EPWs of N-taC thin films with different N<sub>2</sub> flow rates

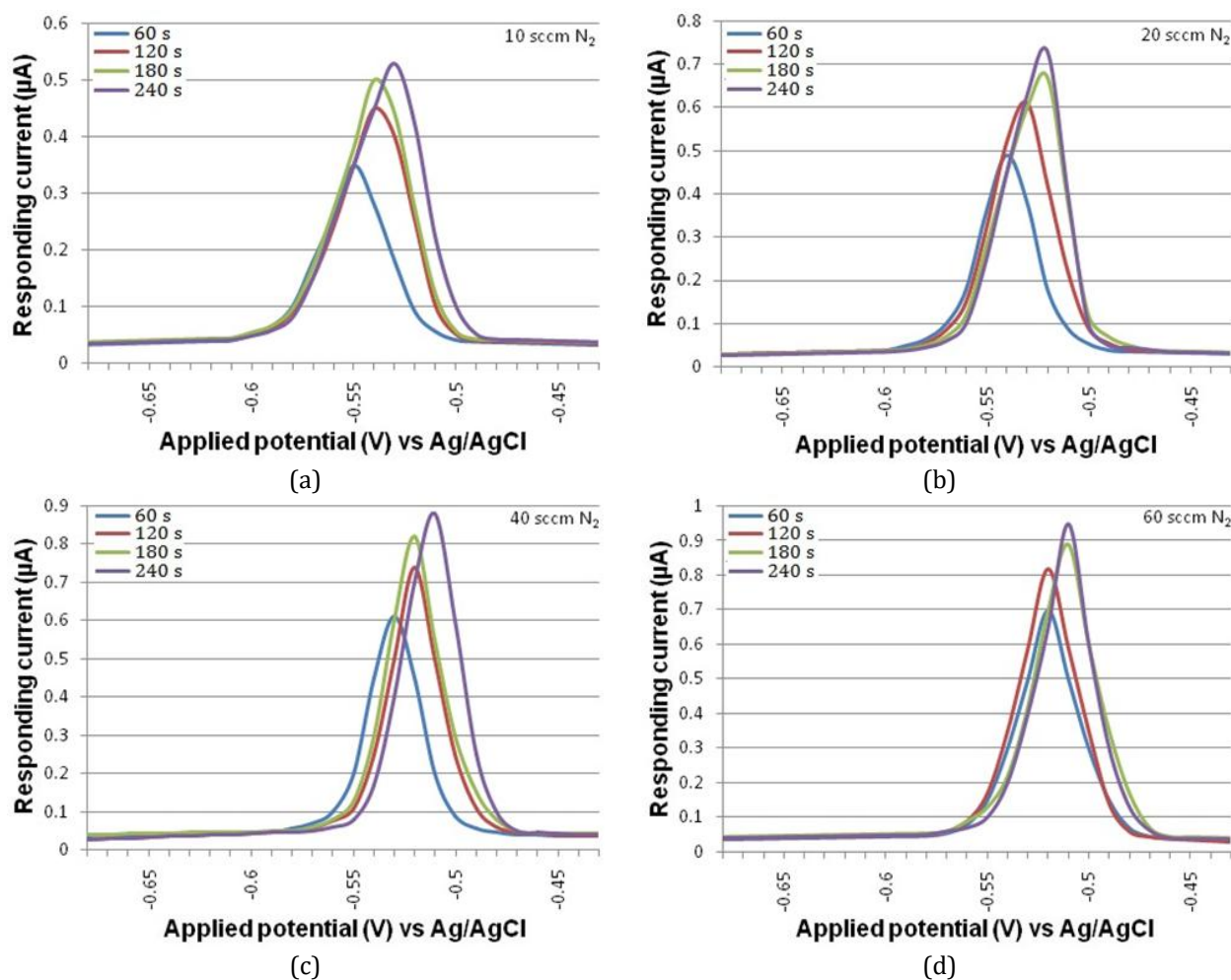
N <sub>2</sub> flow rate	H <sub>2</sub> ↑	O <sub>2</sub> ↑	EPW
10 sccm	-1.5 V	2.3 V	3.8 V
20 sccm	-1.4 V	2.2 V	3.6 V
40 sccm	-1.2 V	2.1 V	3.3 V
60 sccm	-1.1 V	2.0 V	3.1 V

The positive portions of the EPWs of the N-taC thin films are wider than their negative ones for all the N<sub>2</sub> flow rates, which implies that they can trace more elements with positive electrochemical potentials. Although the EPWs of the N-taC thin films decrease with increased N content, their positive portions are still wider than their negative ones, as reported in Table 1. The peak observed in the reduction half-cycle probably results from the catalytic activity for Cl<sub>2</sub>/Cl<sup>-</sup> [15,23,25]. No observation of any peak in the oxidation half-cycle indicates the durability of the N-taC thin film to high anodic potentials in the KCl solution [23]. The slight slope of current versus potential in the oxidation half-cycle is indicative of a contribution of background current, which may result from the increased anodic dissolution of surface oxides of the N-taC thin film, exposed to

air for some time after the deposition, with shifting the applied potential to more positive values [25]. Nevertheless, the contribution of background current to the LSCVs of the N-taC thin films is not very significant for all the N<sub>2</sub> flow rates, which is essential to their high signal-to-background ratios and high sensitivity to heavy metal ions [9,25].

### 3.2 Effect of deposition time on SWASVs of Pb and Cu

Figures 2a-d show the SWASVs of Pb obtained by the N-taC thin films with different N<sub>2</sub> flow rates, measured in a 1×10<sup>-6</sup> M Pb<sup>2+</sup> + 0.1 M KCl solution at a deposition potential of -1.2 V, as a function of deposition time.



**Fig. 2.** SWASVs of Pb obtained by N-taC thin films with N<sub>2</sub> flow rates of (a) 10 sccm, (b) 20 sccm, (c) 40 sccm, and (d) 60 sccm in a 1×10<sup>-6</sup> M Pb<sup>2+</sup> + 0.1 M KCl solution as a function of deposition time. The deposition potential was -1.2 V.

Generally, there are two main steps for the AS analysis of Pb: (1) pre-concentration of Pb<sup>2+</sup> ions and (2) stripping of reduced Pb atoms. In the pre-concentration step, Pb<sup>2+</sup> ions in the KCl solution are reduced into Pb atoms on the N-taC thin film surface via a reduction reaction of  $Pb^{2+} + 2e^- \rightarrow Pb$  at an applied negative potential. Then, in the stripping step, the reduced Pb atoms on the N-taC thin film surface are stripped into Pb<sup>2+</sup> ions into the solution through an oxidation reaction of  $Pb \rightarrow Pb^{2+} + 2e^-$  by shifting an applied potential to more positive values with the generation of a

Faradaic current [12,16]. Since the amount of reduced Pb atoms on the N-taC thin film surface depends on the deposition time, an increase in the deposition time results in an increase in the amount of reduced Pb atoms on the film surface in the pre-concentration step and, subsequently, a proportional increase in the amount of stripped Pb<sup>2+</sup> ions in the stripping step [12,16]. Therefore, the stripping peak intensities of Pb obtained by the N-taC thin films apparently increase with increased deposition time for all the N<sub>2</sub> flow rates, as shown in Figures 2a-d.

It has been known that the increased N content in the N-taC thin film decreases its electrical resistivity, which in turn increases the kinetics of electron transfer through it to the film/solution interface [16,28,29]. Therefore, the higher kinetics of electron transfer facilitates the reaction of the N-taC thin film to give rise to a larger amount of reduced Pb atoms on its surface within the same amount of deposition time, resulting in a proportionally larger amount of stripped  $Pb^{2+}$  ions [9,16-18]. Therefore, the promoted reaction of the N-taC thin film is responsible for an increase in the stripping peak intensity of Pb with an increased  $N_2$  flow rate for the same deposition time, as shown in Figures 2a-d.

In Figures 2a-d, the stripping potentials of Pb obtained by the N-taC thin films with different  $N_2$  flow rates shift to less negative values with longer deposition times. As reported above, the longer deposition time is responsible for the larger amount of stripped  $Pb^{2+}$  ions. According to the Nernst Equation [9,16]:

$$E = E^{\circ} + \frac{RT}{zF} \ln [Pb^{2+}] \quad (1)$$

where  $E$  = stripping potential,  $E^{\circ}$  = standard half-cell potential of Pb,  $R$  = universal gas constant,  $T$  = absolute temperature in Kelvin,  $z$  = number of electrons transferred in the half-reaction, and  $F$  = Faraday constant, it is found that the  $E$  value becomes less negative with a higher concentration of stripped  $Pb^{2+}$  ions. This causes the stripping potential ( $E$ ) of Pb to shift to a less negative value with a longer deposition time. The SWASVs of Pb obtained for different deposition times also shift to less negative values with higher  $N_2$  flow rates in Figures 2a-d. From the point of  $Pb^{2+}$  ion concentration, this can be explained by the less negative value of the  $E$  with the higher concentration of stripped  $Pb^{2+}$  ions associated with the promoted electrical conductivity of the N-taC thin film [9,16-18]. Figures 3a-d show the SWASVs of Cu obtained by the N-taC thin films with different  $N_2$  flow rates, measured in a  $1 \times 10^{-6}$  M  $Cu^{2+}$  + 0.1 M KCl solution at a deposition potential of -1.2 V, as a function of deposition time. The stripping peak intensities of Cu become higher with a longer deposition time for all the  $N_2$  flow

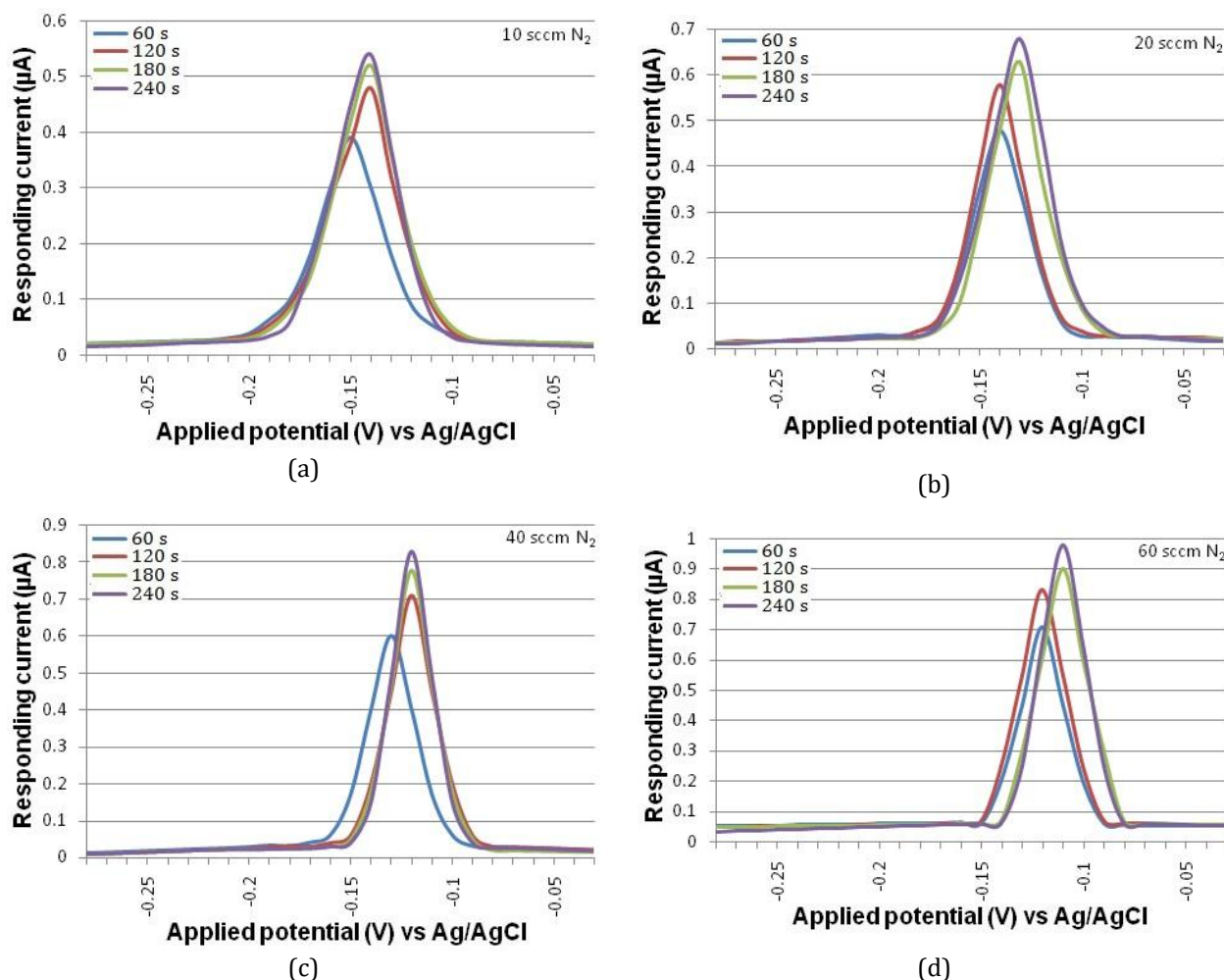
rates. It indicates that increasing the deposition time increases the amount of reduced Cu atoms on the film surface via a reduction reaction of  $Cu^{2+} + 2e^{-} \rightarrow Cu$  in the pre-concentration step and then results in a proportional increase in the amount of stripped  $Cu^{2+}$  ions via an oxidation reaction of  $Cu \rightarrow Cu^{2+} + 2e^{-}$  in the stripping step [9,30,31]. It is consistently found that the stripping peak intensities of Cu obtained for different deposition times are higher for the higher  $N_2$  flow rates as a result of the promoted electrical conductivity of the N-taC thin film.

In Figures 2a-d and 3a-d, the well-defined stripping peaks of both Pb and Cu are obtained by the N-taC thin film with the lowest  $N_2$  flow rate of 10 sccm for the shortest deposition time of 60 s in the KCl solution with  $1 \times 10^{-6}$  M  $Pb^{2+}$ . It indicates that the N-taC thin film, even with the lowest N content of 2.7 at.%, can effectively trace  $Pb^{2+}$  and  $Cu^{2+}$  ions at  $\mu M$  level.

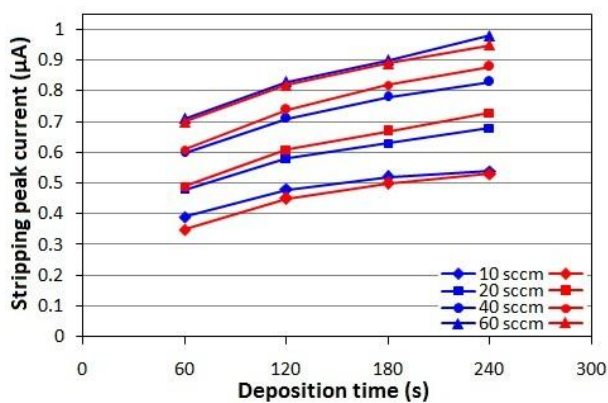
In Figures 3a-d, the stripping potentials of Cu shift to less negative values with longer deposition times for all the  $N_2$  flow rates, which can be related to the larger amount of stripped  $Cu^{2+}$  ions according to the Nernst Equation [9,16]. Besides, the stripping potentials of Cu obtained by the N-taC thin films with higher  $N_2$  flow rates exist at less negative values compared to those obtained by the ones with lower  $N_2$  flow rates as a result of the larger amount of stripped  $Cu^{2+}$  ions [9,16,18].

It is clear that the stripping potentials of both Pb and Cu are influenced by the deposition time and the  $N_2$  flow rate. In addition, the stripping potentials of Cu exist at less negative values than those of Pb, as shown by the comparison of Figures 2a-d and 3a-d, and such a difference in their stripping potentials is due to their different redox potentials [16].

Figure 4 shows the replotted stripping peak currents of Pb and Cu as a function of deposition time. The stripping peak currents of both Pb and Cu become higher with longer deposition times for all the  $N_2$  flow rates, confirming that the longer deposition time gives rise to more reduction of both  $Pb^{2+}$  and  $Cu^{2+}$  ions on the N-taC thin film surface.



**Fig. 3.** SWASVs of Cu obtained by N-taC thin films with N<sub>2</sub> flow rates of (a) 10 sccm, (b) 20 sccm, (c) 40 sccm, and (d) 60 sccm in a  $1 \times 10^{-6}$  M Cu<sup>2+</sup> + 0.1 M KCl solution as a function of deposition time. The deposition potential was -1.2 V.



**Fig. 4.** Stripping peak currents of (red) Pb and (blue) Cu, replotted from SWASVs of Pb and Cu in Figures 2 and 3, respectively, as a function of deposition time.

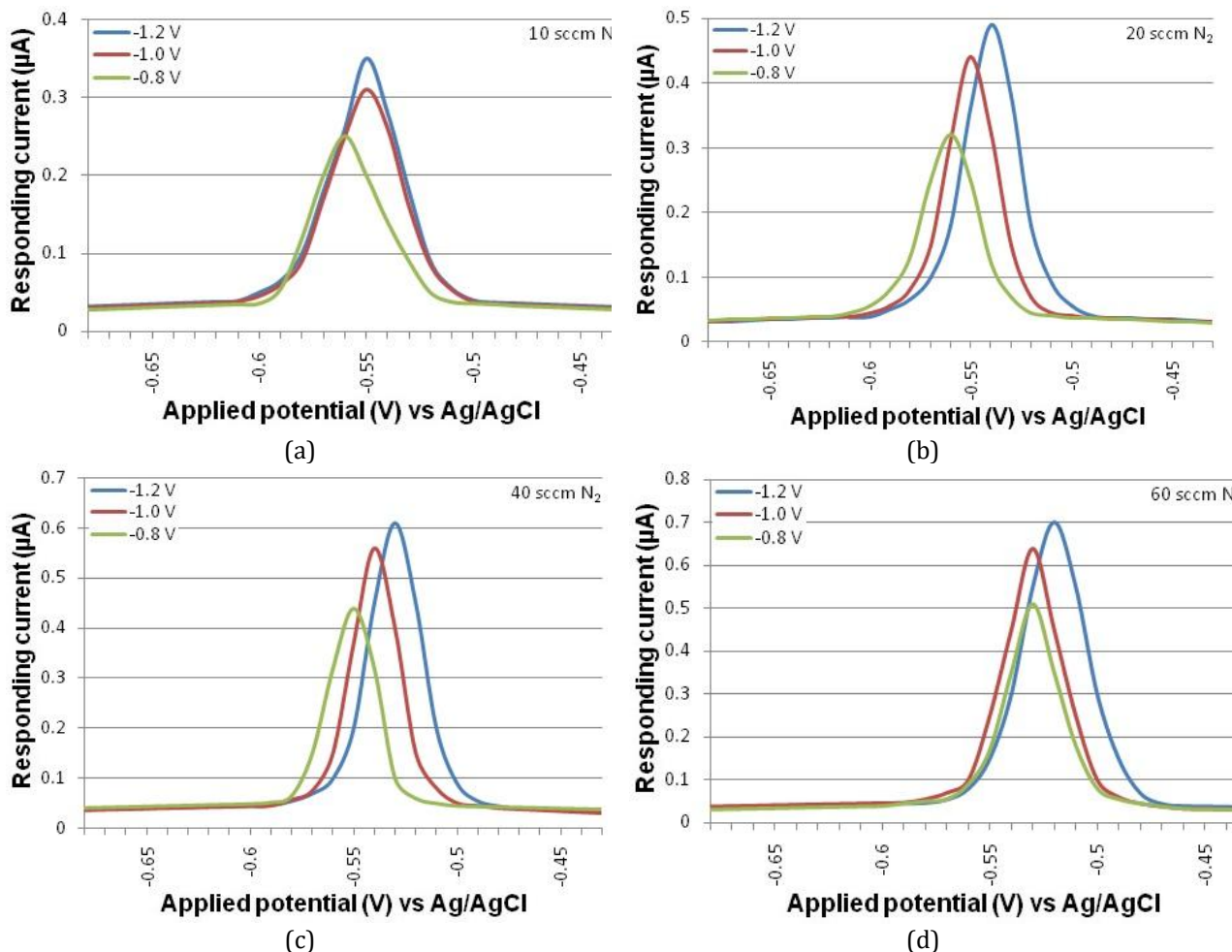
For both Pb and Cu, the trends of stripping peak current versus deposition time are higher for higher N<sub>2</sub> flow rates, which is indicative of the promoted sensitivity of the N-taC thin film to Pb<sup>2+</sup> and Cu<sup>2+</sup> ions in the KCl solution with its increased N content.

### 3.3 Effect of deposition potential on SWASVs of Pb and Cu

Figures 5a-d show the SWASVs of Pb obtained by the N-taC thin films with different N<sub>2</sub> flow rates, measured in a  $1 \times 10^{-6}$  M Pb<sup>2+</sup> + 0.1 M KCl solution for 60 s, as a function of deposition potential. Shifting the deposition potential to more negative values increases the reduction of Pb<sup>2+</sup> ions on the N-taC thin film surface by accelerating the mobility of Pb<sup>2+</sup> ions in the pre-concentration step and then gives rise to a proportional increase in the amount of stripped Pb<sup>2+</sup> ions in the stripping step, resulting in the higher stripping peak intensity of Pb with more negative deposition potential [16,17]. As expected, the stripping peak intensities of Pb deposited at different deposition potentials become higher with higher N<sub>2</sub> flow rates. In Figures 5a-d, the stripping potential of Pb shifts to less negative values by shifting the

deposition potential to more negative values. This can be explained by the higher concentration of stripped  $Pb^{2+}$  ions associated with shifting the deposition potential to a more negative value according to the Nernst

Equation [9,16-18,31,32]. Herein, the stripping potentials of Pb deposited at different deposition potentials shift to less negative values with higher  $N_2$  flow rates due to the higher concentration of stripped  $Pb^{2+}$  ions.



**Fig. 5.** SWASVs of Pb obtained by N-taC thin films with  $N_2$  flow rates of (a) 10 sccm, (b) 20 sccm, (c) 40 sccm, and (d) 60 sccm in a  $1 \times 10^{-6}$  M  $Pb^{2+}$  + 0.1 M KCl solution as a function of deposition potential. The deposition time was 60 s.

Figures 6a-d show the SWASVs of Cu obtained by the N-taC thin films with different  $N_2$  flow rates, measured in a  $1 \times 10^{-6}$  M  $Cu^{2+}$  + 0.1 M KCl solution for 60 s, as a function of deposition potential. It is consistently found that the more negative deposition potentials result in the higher stripping peak intensities of Cu for all the  $N_2$  flow rates via the faster mobility of  $Cu^{2+}$  ions during accumulation [9,16,18].

The promoted electrical conductivity of the N-taC thin film with an increased  $N_2$  flow rate is responsible for the increased stripping peak intensities of Cu for all the deposition potentials [9,16,18]. In Figures 6a-d, the

stripping potentials of Cu consistently shift to less negative values with more negative deposition potentials, as the stripping potentials of Cu obtained at different deposition potentials shift to less negative values with higher  $N_2$  flow rates as a result of the higher concentration of stripped  $Cu^{2+}$  ions.

Figures 7a-d show the replotted stripping peak currents of Pb and Cu obtained by the N-taC thin films with different  $N_2$  flow rates as a function of deposition potential. The increased stripping peak currents of both Pb and Cu, with shifting the deposition potential to more negative values are found for all the  $N_2$  flow rates.

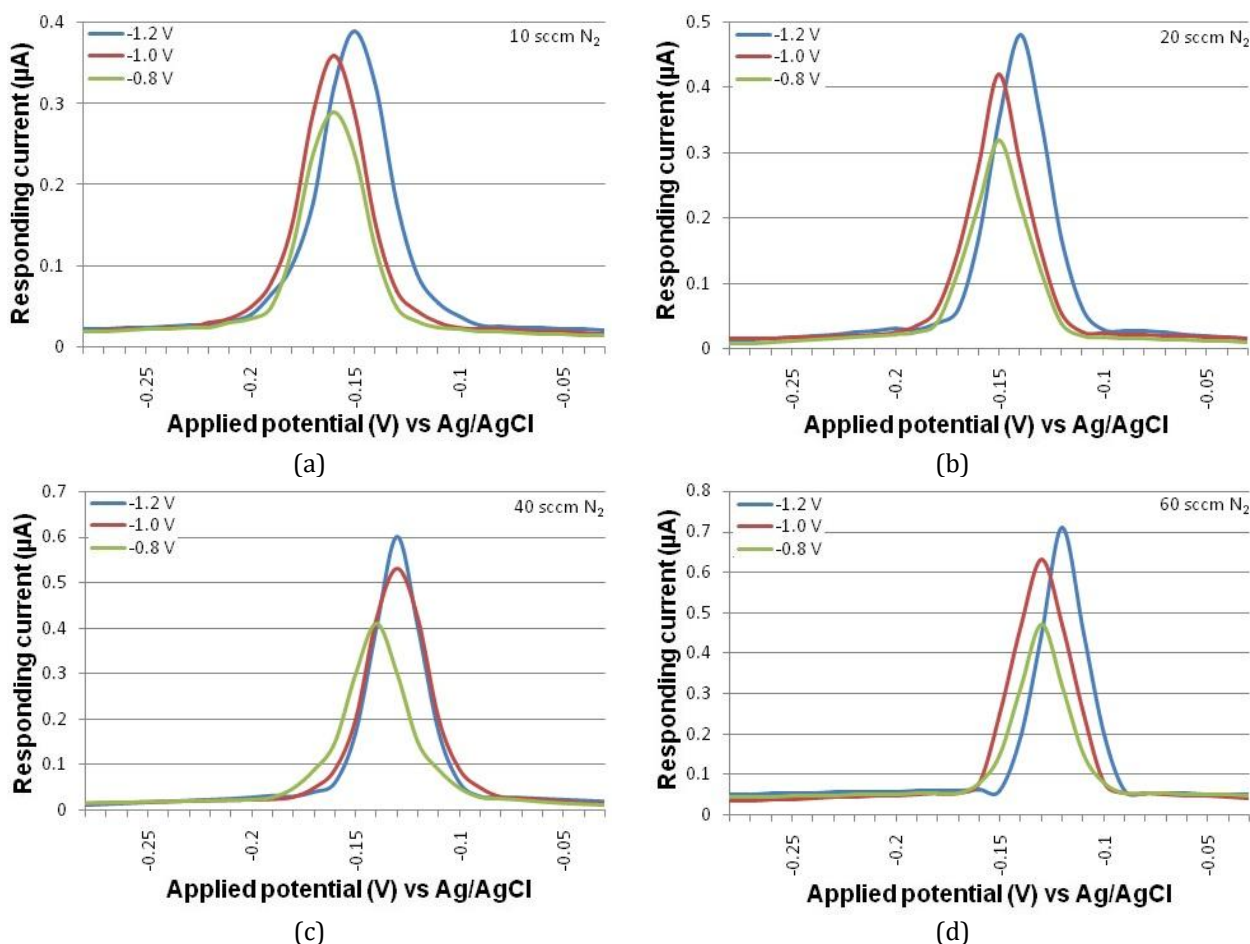


Fig. 6. SWASVs of Cu obtained by N-taC thin films with N<sub>2</sub> flow rates of (a) 10 sccm, (b) 20 sccm, (c) 40 sccm, and (d) 60 sccm in a  $1 \times 10^{-6}$  M Cu<sup>2+</sup> + 0.1 M KCl solution as a function of deposition potential. The deposition time was 60 s.

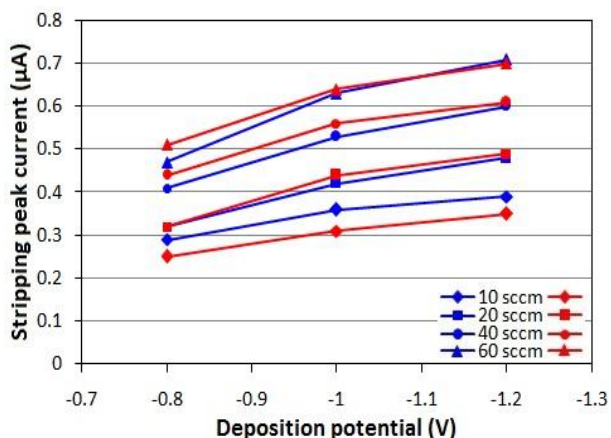
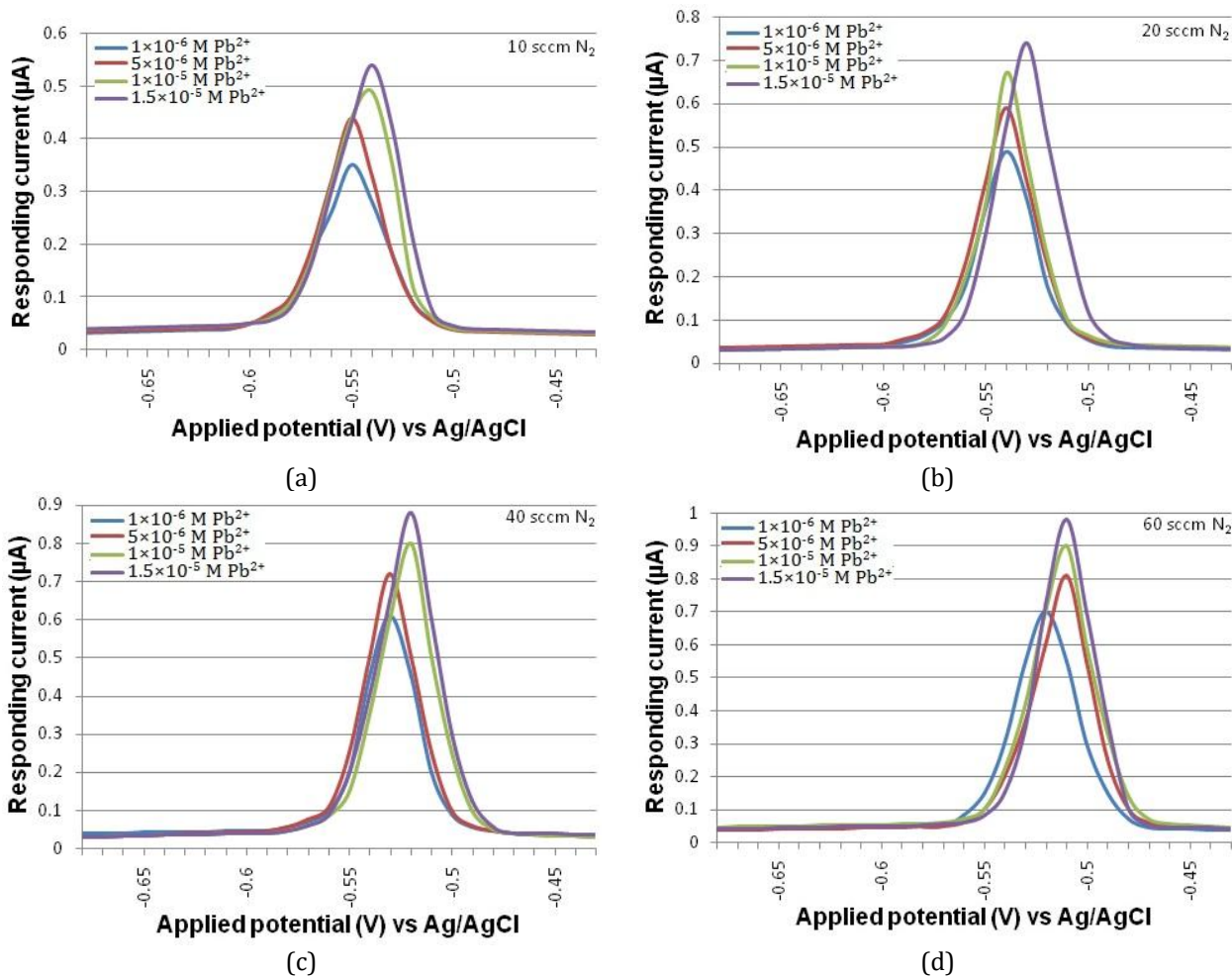


Fig. 7. Stripping peak currents of (red) Pb and (blue) Cu, replotted from SWASVs of Pb and Cu in Figures 5 and 6, as a function of deposition potential, respectively.

The promoted electrical conductivity of the N-taC thin film with a higher N<sub>2</sub> flow rate is responsible for the higher trends of stripping peak current versus deposition potential of both Pb and Cu [9,16,18].

### 3.4 Effect of metal ion concentration on SWASVs of Pb and Cu

Figures 8a-d show the SWASVs of Pb obtained by the N-taC thin films with different N<sub>2</sub> flow rates, measured in a 0.1 M KCl solution at a deposition potential of -1.2 V for 60 s, as a function of Pb<sup>2+</sup> ion concentration. It is found that the stripping peak intensities of Pb obtained by the N-taC thin films with different N<sub>2</sub> flow rates become higher with higher Pb<sup>2+</sup> ion concentrations. Since a high concentration of Pb<sup>2+</sup> ions in the bulk solution can continuously supply them to the interface by causing and maintaining their great concentration gradient between the surrounding solution and the interface, the higher concentration of Pb<sup>2+</sup> ions allows for their more reduction on the film surface via their faster transport in the pre-concentration step and thereby their more oxidation in the stripping step for the higher stripping peak intensity of Pb [9,16,18].

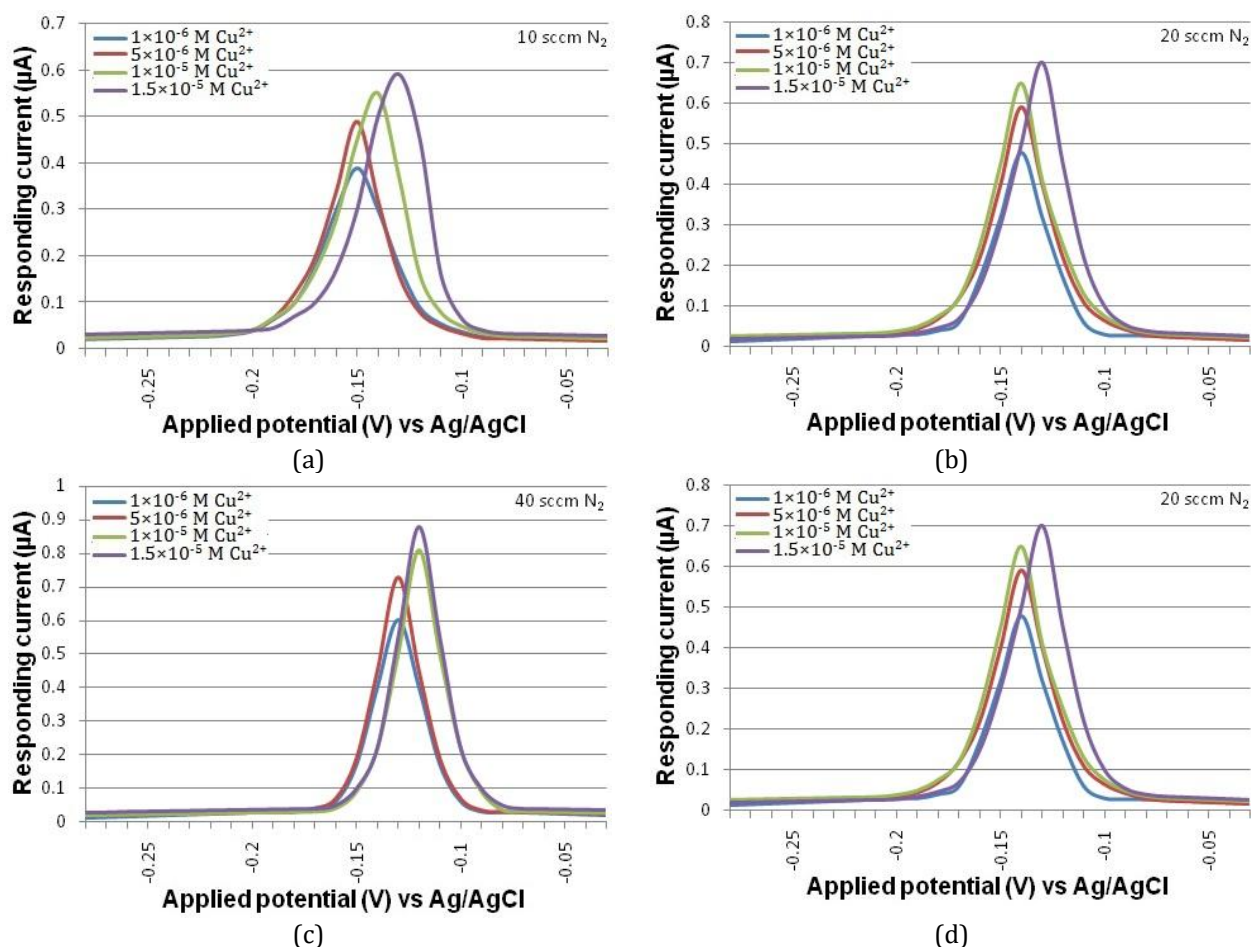


**Fig. 8.** SWASVs of Pb obtained by N-taC thin films with N<sub>2</sub> flow rates of (a) 10 sccm, (b) 20 sccm, (c) 40 sccm, and (d) 60 sccm in a 0.1 M KCl solution as a function of Pb<sup>2+</sup> ion concentration. The deposition potential and time were -1.2 V and 60 s, respectively.

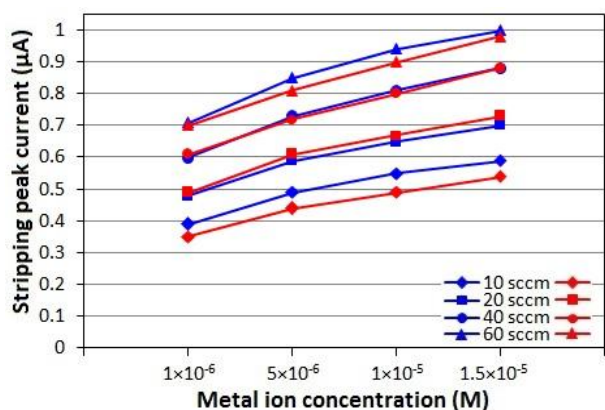
For all the Pb<sup>2+</sup> ion concentrations, the stripping peak intensities of Pb become higher with higher N<sub>2</sub> flow rates due to the promoted electrical conductivity of the N-taC thin film [9,16,18]. As shown in Figures 8a-d, the stripping potentials of Pb shift to less negative values with higher Pb<sup>2+</sup> ion concentrations or higher N<sub>2</sub> flow rates, which can be correlated to the higher concentration of stripped Pb<sup>2+</sup> ions according to the Nernst Equation [9,16]. Figures 9a-d show the SWASVs of Cu obtained by the N-taC thin films with different N<sub>2</sub> flow rates, measured in a 0.1 M KCl solution at a deposition potential of -1.2 V for 60 s, as a function of Cu<sup>2+</sup> ion concentration. As expected, the stripping peak intensities of Cu increase with increased Cu<sup>2+</sup> ion concentrations or increased N<sub>2</sub> flow rates. A shift of the stripping potentials of Cu to less negative values with higher Cu<sup>2+</sup> ion concentrations or higher N<sub>2</sub> flow rates is also noticed. This can be explained by applying the Nernst equation since

the less negative value of the E associated with the higher concentration of stripped Cu<sup>2+</sup> ions is responsible for the less negative value of the stripping potential of Cu [9,16].

Figure 10 shows the replotted stripping peak currents of Pb and Cu obtained by the N-taC thin films with different N<sub>2</sub> flow rates as a function of Pb<sup>2+</sup> and Cu<sup>2+</sup> ion concentrations, respectively. The N-taC thin films have an increase in the stripping peak currents of Pb and Cu with increased Pb<sup>2+</sup> and Cu<sup>2+</sup> ion concentrations, respectively, for all the N<sub>2</sub> flow rates. Increasing the concentration of metal ions in the bulk solution sufficiently supplies them to the interface region as much as they are reduced on the film surface, resulting in a proportional increase in the stripping peak current. The trends of stripping peak current versus metal ion concentration of both Pb and Cu are higher for the higher N<sub>2</sub> flow rates [9,16,18].



**Fig. 9.** SWASVs of Cu obtained by N-taC thin films with N<sub>2</sub> flow rates of (a) 10 sccm, (b) 20 sccm, (c) 40 sccm, and (d) 60 sccm in a 0.1 M KCl solution as a function of Cu<sup>2+</sup> ion concentration. The deposition potential and time were -1.2 V and 60 s, respectively.



**Fig. 10.** Stripping peak currents of (red) Pb and (blue) Cu, replotted from SWASVs of Pb and Cu in Figures 8 and 9, as a function of Pb<sup>2+</sup> and Cu<sup>2+</sup> ion concentrations, respectively.

#### 4. CONCLUSION

The EPWs of the N-taC thin films with different N<sub>2</sub> flow rates were measured in a 0.1 M KCl solution using the LSCV technique. Then, their SWASV

performance was investigated by tracing Pb<sup>2+</sup> and Cu<sup>2+</sup> ions in the same solution with respect to deposition time and potential, metal ion concentration, and N<sub>2</sub> flow rate. The following conclusions were drawn.

- The EPW of the N-taC thin film measured in the KCl solution was relatively wide but had an 18.4% decrease from 3.8 V to 3.1 V with an increased N<sub>2</sub> flow rate from 10 to 60 sccm because its lower electrical resistivity associated with its higher N content resulted in the higher kinetics of electron transfer through it and thereby its narrower EPW by causing earlier evolution of H<sub>2</sub> and O<sub>2</sub> gases.
- The stripping peak currents of both Pb and Cu obtained by the N-taC thin films with different N<sub>2</sub> flow rates increased with increased deposition time since the longer deposition time allowed the larger amounts of reduced Pb and Cu atoms on the film

surfaces in the pre-concentration step and, subsequently, the larger amounts of stripped  $Pb^{2+}$  and  $Cu^{2+}$  ions in the stripping step.

- The stripping peak currents of both Pb and Cu obtained by the N-taC thin films with different  $N_2$  flow rates were higher with more negative deposition potentials because the more negative deposition potential gave rise to the higher mobility of  $Pb^{2+}$  and  $Cu^{2+}$  ions from the surrounding solution to the interface to reduce them on the film surfaces in the pre-concentration step and thereby the larger amounts of stripped  $Pb^{2+}$  and  $Cu^{2+}$  ions in the stripping step.
- The stripping peak currents of both Pb and Cu obtained by the N-taC thin films with different  $N_2$  flow rates were higher for the higher concentrations of  $Pb^{2+}$  and  $Cu^{2+}$  ions because the higher concentrations of  $Pb^{2+}$  and  $Cu^{2+}$  ions resulted in the larger amounts of reduced Pb and Cu atoms on the film surfaces by causing their greater concentration gradients between the surrounding solution and the interface and hence the larger amounts of stripped  $Pb^{2+}$  and  $Cu^{2+}$  ions.
- The stripping peak currents of both Pb and Cu increased with increased  $N_2$  flow rate as a result of the promoted electrical conductivity of the N-taC thin film.
- The well-defined SWASVs of Pb and Cu at the  $\mu M$  level clearly indicated that the N-taC thin film had relatively high sensitivity to both  $Pb^{2+}$  and  $Cu^{2+}$  ions in the aqueous solution.
- It could be concluded that the electrochemical performance of the N-taC thin films was apparently influenced by the deposition time and potential, metal ion concentration, and N content.

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