



# A Comparative Study of Electrochemical Behaviors of Acrylamide on Glassy Carbon, Platinum and Gold Electrode Surfaces by Cyclic Voltammetry

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## ABSTRACT

In this research, electrochemical and spectroelectrochemical behaviors of acrylamide (AA) have been studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Cyclic voltammetric studies of AA in acetonitrile (CH<sub>3</sub>CN) containing 100 mM tetrabutylammonium tetrafluoroborate (NBu<sub>4</sub>BF<sub>4</sub>) on glassy carbon (GC) electrode was performed between 0.0 mV and +2600 mV potential range, on platinum (Pt) electrode was performed between 0.0 mV and +1500 mV potential range and gold (Au) electrode was performed between +600 mV and +2200 mV potential range at 100 mV s<sup>-1</sup> scan rate with 10 cycles. The surface characterization process was carried out using CV and EIS technique in both aqueous and non-aqueous media.

**Keywords:** acrylamide, modified electrode, glassy carbon electrode, platinum electrode, gold electrode

## INTRODUCTION

Acrylamide (AA) is a commercially produced substance which can be naturally composed in foods rich in starch at high temperatures. The first report was announced by Swedish scientists from Stockholm University in 2002 [1]. AA is a low-molecular-weight hydrophilic compound known for its use as a monomer in the production of polyacrylamide, which in turn is used in plastics and as an electrophoresis medium [2]. High levels of AA have been found in potato chips, French fries, biscuits, and several other common foods [1, 3]. AA formation ensues during the browning process by Maillard reaction of reducing sugars with asparagine at

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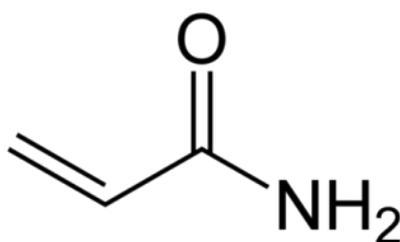
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temperatures greater than 120°C. The major reactants leading to the release of AA are sugars and asparagine [4, 5].

The International Agency for the Research on Cancer (IARC) has categorised acrylamide in Group 2A (probable carcinogen to humans). It has been verified that AA causes cancer in rats and mice, which is a multi-organ carcinogen, causing tumors of lungs, uterus, mammary gland etc. [6] Usually analysis of AA in food products focuses on chromatographic methods such as GC-MS [7], LC-MS/MS [8], HPLC-MS [9], and LC-DAD [10], all of which are time-consuming and expensive.

Electrochemical methods are commonly used in the environmental assessment. They are widely used for the determination of inorganic ions and molecules (heavy metals, noble metals) [11]. Modified electrodes are being used mostly in the voltammetric determination of organic compounds because of their selectivity and efficiency, which can be obtained by varying the modifier [12, 13]. The advantages of the electrochemical determinations are the low cost of materials and equipment. The other advantages are unquestionably the relatively short measuring time including the sample preparation [14, 15].

Different voltammetric techniques are used for determination of AA. The amounts of acrylamide in potato chips were measured by square-wave voltammetry (SWV) [2]. Adsorption stripping voltammetry was used for the determination and quantification of AA content in food samples [16]. A carbon-paste electrode modified with hemoglobin was used for direct electrochemical determination of acrylamide by CV and osteryoung square wave voltammetry (OSWV) [17].



**Figure 1.** Chemical structure of acrylamide

The aim of this study, AA was covalently modified on GC, Pt and Au electrode surfaces by electrochemical oxidation in non-aqueous media. Electrochemical and spectroelectrochemical behaviors of AA were investigated by CV and electrochemical impedance spectroscopy (EIS).

## EXPERIMENTAL

### Chemicals

AA,  $\text{NBu}_4\text{BF}_4$ , KCl,  $\text{CH}_3\text{CN}$  (HPLC grade) and other chemicals were obtained from Sigma-Aldrich (Buchs SG, Switzerland) or Riedel de Haën (Seelze, Germany), chemical companies and so no further purification was performed. Ultrapure quality of water with a resistance of  $18.2 \text{ M}\Omega \text{ cm}$  (Millipore Milli-Q purification system, Millipore Corp. Bedford, MA, USA) was used in preparations of aqueous solutions, cleaning of the glassware and polishing the electrodes. The electrodes were kept in  $\text{CH}_3\text{CN}$  in all experiments when they were not in use. AA solution was prepared at 1 mM concentration. Prior to the electrochemical experiments, solutions were thoroughly deoxygenated by purging with purified argon gas (99.99%) for 10 min.

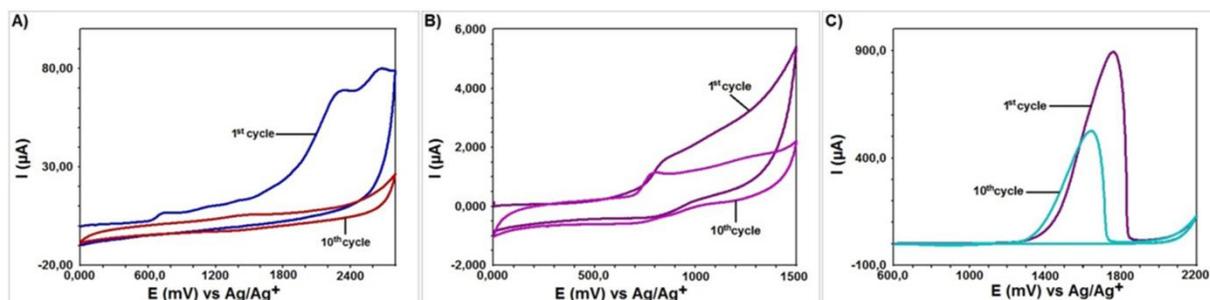
### Electrochemical equipment and apparatus

Electrochemical measurements were carried out with GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA from GAMRY Instruments (PA, USA), using a standard cell with three electrodes. The CV technique was performed with PHE200 Physical Electrochemistry software, EIS was applied with EIS300 Electrochemical Impedance Spectroscopy software. The working electrodes were a GC electrode BAS (Bioanalytical Systems, West Lafayette, IN, USA) model MF-2012 (3.0 mm dia.), a Pt electrode BAS model MF-2013 (1.6 mm dia.) and an Au electrode BAS model MF-2013 (1.6 mm dia.). Pt wire (BAS Model MW-1032) was used as counter electrode. The reference electrodes an Ag/Ag<sup>+</sup> (10 mM  $\text{AgNO}_3$ ) (BAS Model MF-2042) for non-aqueous media and a Ag/AgCl/3 M KCl (BAS Model MF-2063) for aqueous media were used.

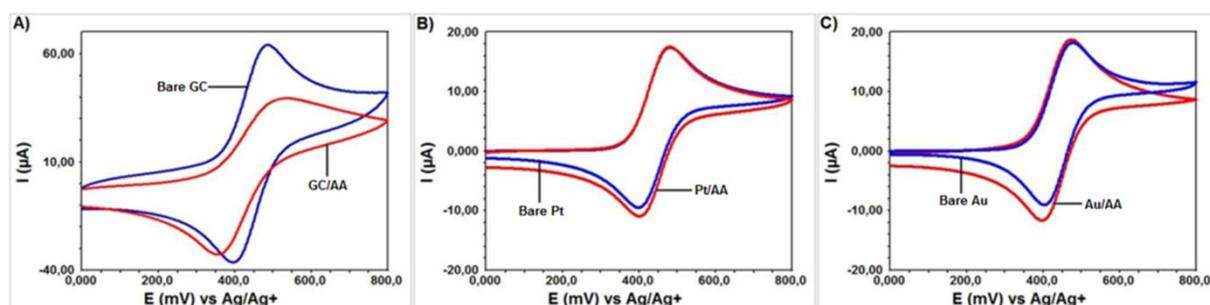
### Cleaning and Polishing of GC, Pt and Au Electrodes

The GC electrode, geometric area of the former was  $0.071 \text{ cm}^2$  and O-ring delimited area of the latter was 3.0 mm dia., surfaces were prepared for the experiments by polishing to gain a mirror-like appearance, first with fine wet emery papers (grain size 4000) and then with  $1.0 \mu\text{m}$  and  $0.3 \mu\text{m}$  alumina slurry on micro cloth pads (Buehler, USA). After the initial polishing, the GC electrodes were resurfaced with  $0.05 \mu\text{m}$  alumina slurry. First, in the following order, the GC electrodes were sonicated both in an ultrasonic water bath (Bandelin RK 100, Germany), and then in 1:1 (v/v) isopropyl alcohol (IPA) and  $\text{CH}_3\text{CN}$  (IPA +  $\text{CH}_3\text{CN}$ ) mixture for 5 min [18]. The electrodes were kept in  $\text{CH}_3\text{CN}$  when they were not in use, in all experiments. Electrode surfaces were sonicated with  $\text{CH}_3\text{CN}$  before and after each treatment.

The size of Pt working electrode was 1.6 mm dia. Prior to the surface modification, the Pt electrode was shined on a polishing cloth with wet alumina powders, starting with  $0.3 \mu\text{m}$  particle size and then with finer grades down to  $0.05 \mu\text{m}$ . The Pt electrode was then rinsed with ultrapure water and sonicated for 5 min [19].



**Figure 2.** Cyclic voltammograms of 1 mM AA in CH<sub>3</sub>CN containing 100 mM NBu<sub>4</sub>BF<sub>4</sub> vs. Ag/Ag<sup>+</sup>/(10 mM AgNO<sub>3</sub>) onto the GC (**A**), Pt (**B**) and Au (**C**) working electrodes. Potential range from 0.0 mV to +2600 mV onto the GC, 0.0 mV to +1500 mV onto the Pt and +600 mV to +2200 mV onto the Au electrode, scan rate is 100 mV s<sup>-1</sup>



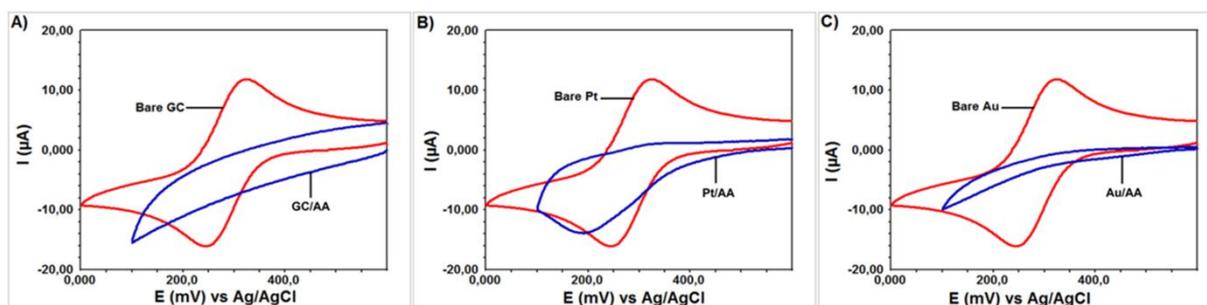
**Figure 3.** Overlaying cyclic voltammograms for 1 mM ferrocene redox probe solution vs. Ag/Ag<sup>+</sup> (10 mM AgNO<sub>3</sub>) in CH<sub>3</sub>CN containing 100 mM NBu<sub>4</sub>BF<sub>4</sub> at 100 mV s<sup>-1</sup> scan rate (**A**, GC; **B**, Pt; **C**, Au working electrodes)

The Au electrode was polished to a mirror finish with 0.3 micron alumina on a smooth polishing cloth. Then the Au electrode was rinsed with methanol and millipore water prior to each electrochemical measurement. All the measurements were performed at room temperature [20].

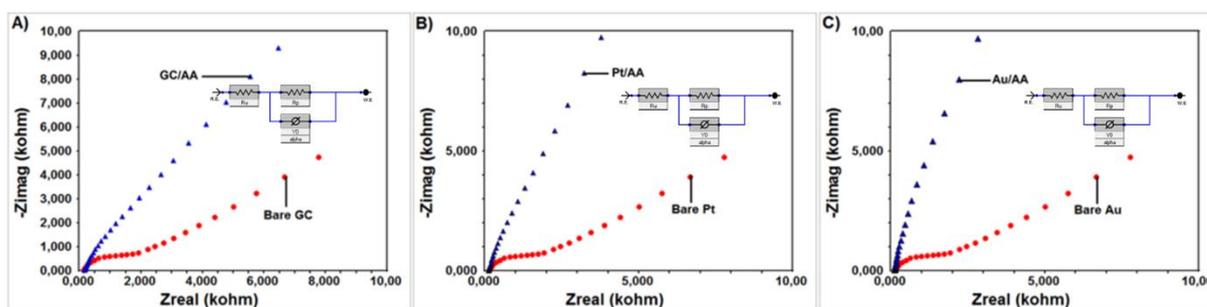
## RESULTS AND DISCUSSION

### Modification of GC, Pt and Au electrode surfaces with AA

Cyclic voltammetric experiments were carried out using 1 mM AA solution in CH<sub>3</sub>CN containing 100 mM NBu<sub>4</sub>BF<sub>4</sub> in the range from 0.0 mV to +2600 mV potential range on GC electrode, 0.0 mV and +1500 mV potential range on Pt electrode, +600 mV and +2200 mV potential range Au electrode at 100 mV s<sup>-1</sup> scan rate with 10 cycles in non-aqueous media vs. Ag/Ag<sup>+</sup>/(10 mM AgNO<sub>3</sub>). As it is clear from the **Figure 2**, AA was modified onto GC electrode surface, but AA was not modified on Pt and Au electrode surface (**Figure 2-A, 2-B, 2-C**). Although two cycles is enough for the modification of AA molecule on GC electrode, ten cycles has been employed for filling the pin holes completely.



**Figure 4.** Overlapping cyclic voltammograms for 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  redox probe solution vs. Ag/AgCl/3 M KCl reference electrode in BR buffer solution, pH= 2, at  $100 \text{ mV s}^{-1}$  scan rate (A, GC; B, Pt; C, Au working electrodes)



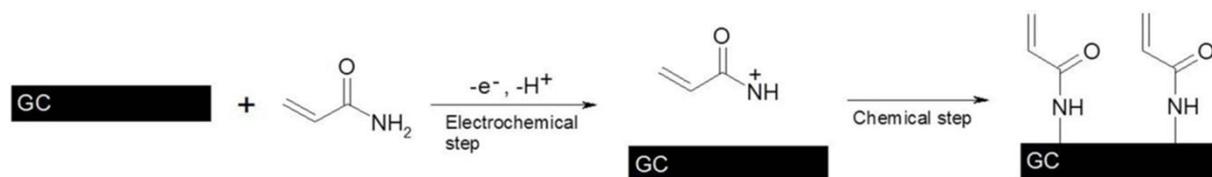
**Figure 5.** Nyquist plots for electrochemical impedance spectra of 1 mM  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  redox couple solution in 100 mM KCl at the frequency range of 100.000–0.05 Hz at 10 mV wave amplitude, on GC (A), Pt (B) and Au (C) working electrodes

### Characterization of AA/GC, AA/Pt and AA/Au electrode surfaces by CV and EIS

Surface characterizations after the modification process were carried out by CV and EIS. In the characterizations with CV, 1 mM ferrocene solution in 100 mM  $\text{NBu}_4\text{BF}_4$  was carried out the potential range from 0.0 mV to +800 mV in non-aqueous media. Figure 3-A, 3-B, 3-C exhibits the voltammograms ferrocene, respectively. When the voltammogram obtained in ferrocene is overlaid with the voltammogram obtained for bare GC, bare Pt and bare Au electrode, it is clear that the modified surfaces are allow electron transfer.

In the second step of CV characterization process, hexacyanoferrate (III),  $\text{Fe}(\text{CN})_6^{3-}$ , redox probe test was performed in aqueous medium. 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  in Britton-Robinson (BR) buffer solution, pH 2, was performed the potential range from +600 mV to 0.0 mV in aqueous media at scan rate of  $100 \text{ mV s}^{-1}$ . The cyclic voltammograms of modified and bare GC electrodes, modified and bare Pt electrodes, modified and bare Au electrodes were compared for  $\text{Fe}(\text{CN})_6^{3-}$  redox probe, it is clear that the modified surfaces are not allow electron transfer in aqueous media.

EIS is a precious method to monitor the impedance changes of the electrode surface during the modification process. Impedance measurements were carried out in 1 mM



**Scheme 1.** Modification mechanism of AA at GC electrode surface (in  $CH_3CN$  containing 100 mM  $NBu_4BF_4$ )

$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$  mixture in 100 mM KCl in the range from 100.000 Hz to 0.05 Hz frequency by EIS and the Nyquist plots were recorded. The semicircle diameter of Nyquist plot reflects the  $R_{ct}$ , which is from the electron transfer of the redox probe  $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$  solution. The Nyquist plot of the modified electrodes was compared with the EIS data of bare electrodes. The surfaces obtained after characterization processes were evaluated and then it was presupposed that the surface obtained after the modification in non-aqueous medium was more suitable for the application. This case was supported by the results of the EIS obtained by using 10 mV potential and a mixture of 1 mM  $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$  at 100.000 Hz and 0.05 Hz. The EIS graphs obtained after modifications in both aqueous and non-aqueous media are given in [Figure 5-A, 5-B, 5-C](#).

### Electrografting AA onto the GC electrode surface

After the oxidation of  $-NH_2$  group in solution (E mechanism), GC electrode surface was found to be electroactive from the chemically grafting process (C mechanism) is given in Scheme 1 (EC mechanism).

### CONCLUSION

By the use of AA for the modification of GC electrode surface, an electroactive surface was obtained in this study. Modification process has been performed using CV, electrochemical and spectroelectrochemical surface characterization processes have been done using CV and EIS. The following step of this research will be focused for the quantitative determination of AA in different media by using square wave voltammetry (SWV) and differential pulse voltammetry (DPV).

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