

Electrochemical Study of Redox Reaction of Various Gold III Chloride Concentrations in Acidic Solution

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Abstract

The redox reaction of gold III chloride in acid solutions has been electrochemically investigated using a cyclic voltammetry technique. This paper emphasizes the current and potential sites at which gold III chloride is reduced in hydrochloric acid that is vital to electrochemical evaluation of gold recovery. The solutions were prepared by reacting HCl with AuCl₃ in various concentrations thus 30 and 60 mg/L AuCl₃ in 0.1 and 0.5 M HCl, respectively. Solutions of 0.1 and 0.5 M HCl containing 0, 30 and 60 mg/L AuCl₃, respectively were tested for possible reduction and oxidation reactions by cyclic voltamogram experiment using a glassy carbon, a saturated calomel and a platinum wire mesh as working, reference and counter electrodes, respectively. The results showed no peak in the case of the absence of AuCl₃ in the solutions, but appreciable cathodic and anodic peaks for the reduction and oxidation of various concentrations of AuCl₃ in acid solutions. The reaction between AuCl₃ and HCl was found to be reversible because the ratio of oxidation peak current and reduction peak current was 1. The concentration of AuCl₄⁻ on the surface of the working electrode at the reduction site for each AuCl₃ concentration using Nernst equation was 1.22×10^9 ppm and 2.44×10^9 ppm. The reduction potentials were independent of concentration, while the current was highly dependent of concentration.

Keywords

Redox Reaction, Cyclic Voltammetry, Nernst Equation, Gold, Chloride

1. Introduction

The demand for gold in the global market has jolted researchers into gold re-

covery methods from either a lean ore or waste products of consumer electronics (urban mining). Sometimes, synthetic solutions are used to study the extraction of gold in a preliminary laboratory experiment. Gold III chloride is the auric salts commonly used to achieve this purpose [1]. Hydrochloric acid has been the popular leachant for precious metals from secondary sources [2]. Hence, in this study, solutions of gold III chloride in HCl were prepared to investigate reversible and redox reactions using a cyclic voltammetry technique.

Few studies have been carried out on the electrochemical reduction to metal, such as the electrochemical reduction of silver from iodide solutions [3]. Fourcade and Tzedakis [3] used a potentiostat as the electrochemical apparatus with a silver disk working electrode, a saturated calomel reference electrode and a platinum counter electrode to measure all the electrode potentials during the adsorption experiments. Tao *et al.* [4] reported scanning tunneling microscopy (STM) and electrochemical study of the interplay between redox properties, adsorption, and self-assembly processes of porphins on Au surfaces.

The cyclic voltammetry technique is generally used to study the electrochemical properties of an analyte in solution [5] [6] [7]. The theory of voltammetric methods is based on the solution of the Nernst Equation (1). Voltammetry is a method in which information about an analyte is obtained by measuring the current generated as the applied potential to the working electrode is varied. Potential is measured between the working electrode and the reference electrode, while current is measured between the working and the counter electrode [8] [9]. The Nernst Equation is expressed in terms of potential at the working electrode.

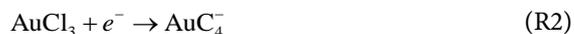
$$E = E^0 - \frac{RT}{nF} \ln Q \quad (1)$$

where, E = measured potential, E^0 = standard electrode potential, R = gas constant, T = temperature (°K), Q = reaction quotient, n = number of electrons exchanged, and F = Faraday's constant.

The redox reaction and half-cell reaction of gold III chloride in HCl are represented in reactions R1 and R2 respectively thus,



For half-cell reaction,



The result from the experiment showed no reasonable cathodic or anodic peak for hydrochloric acid solution without the presence of gold III chloride, while peaks were observed during the measurement of various concentrations of the gold III chloride in hydrochloric acid solution. It could be deduced from the experiment the reaction of gold III chloride with HCl is a redox and reversible reaction.

The objective of this work was to investigate the reaction processes in gold III chloride acid solution using cyclic voltammetry.

2. Experimental

2.1. Materials and Instrumentations

Glassware, analytical grade hydrochloric acid, gold (III) chloride, and de-ionized water were used for the preparation of the solutions. The electrochemical equipment consisted of a PAR 283 Potentiostat/Galvanostat (PS/GS) and a Solartron 1260 Frequency response analyzer, Glassy carbon electrode was used as working electrode (WE), a platinum mesh served as counter electrode (CE), while a saturated calomel electrode (SCE) was the reference electrode (RE).

2.2. Experimental Procedure

2.2.1. Preparation of Solution

Solutions of 30 ppm and 60 ppm of AuCl_3 in 200 mL of 0.1 and 0.5 M HCl were prepared. The reaction between AuCl_3 and HCl is a redox as shown in R1. AuCl_3 was reduced to AuCl_4^- and HCl was oxidized to H^+ . This redox reaction was electrochemically measured by subjecting the gold chloride solution to cyclic voltammogram experiment, in which the cathodic and anodic current peaks were determined relative to applied potentials. This was achieved with a core driven software PAR 283 Potentiostat/Galvanostat (PG/GS) and a Z-plot driven solartron instrument [3]. Cleaning of the electrodes was done prior to the experiment, for the purpose of revealing the surface of the electrodes which might have been covered by impurities, and conditioned them for the experiment as reported by Feng *et al.*, [10]. The 0.5 M HCl was prepared, and the electrodes were immersed in the diluted solution. The electrodes were then connected to the Potentiostat which was set at cyclic voltammogram experiment mode for cleaning. The vertex potential 1 and 2 were set at -0.25 and 1.25 V respectively at a scan rate of 5.0 mV/s. The cleaning was done for 1 h.

Subsequently, about 100 mL of 30 ppm AuCl_3 (in 0.1 M HCl) was poured into a 250 mL beaker. The electrodes were immersed into the solution and connected with connecting cables to the Instrument accordingly.

2.2.2. Cyclic Voltammetry Measurement

The cyclic voltammogram experiment was performed with a PAR potentiostat/galvanostat. The schematic of the setup is as shown in **Figure 1**. The applied potential was set between -0.25 V and 1.25 V. The scan rate was set at 5 mV/s, and the No. of cycles was maintained at 1 mV/point. During the measurement, the scanning of the potential was from -0.25 to 1.25 , and then back to -0.25 at a rate of 5 mV/s for 1 cycle. This procedure was performed on all the prepared solutions and the measurement of peaks was recorded via the plot of current density as a function of the potential. The experiment was carried out at a room temperature of 25°C .

3. Results and Discussion

The experimental results are depicted in **Figures 1-6**. The system moved through the various dynamic regime (start-finish), and the oxidation and reduction

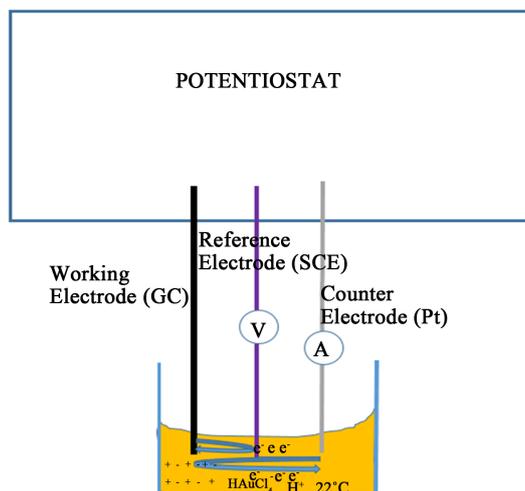


Figure 1. Cyclic voltammetry measurement of 30 ppm AuCl_3 in 0.1 M HCl at room temperature (25°C).

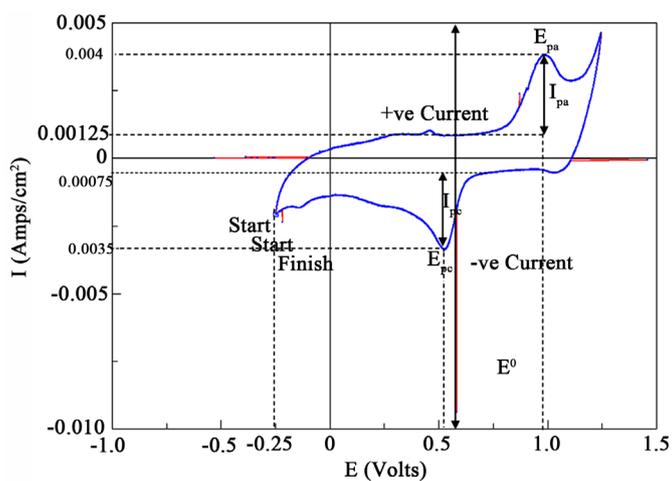


Figure 2. Cyclic voltammetry measurement of 60 ppm AuCl_3 in 0.1 M HCl solution at room temperature (25°C).

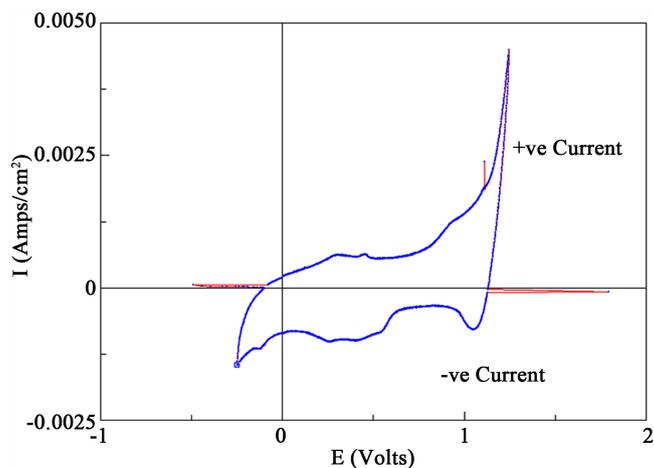


Figure 3. Cyclic voltammetry measurement of 0 ppm AuCl_3 in 0.1 M HCl solution at room temperature (25°C).

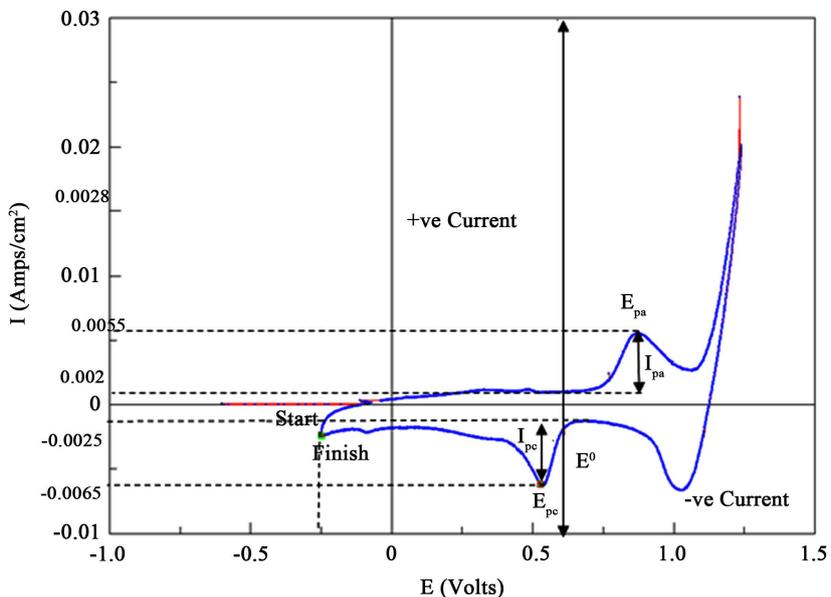


Figure 4. Cyclic voltammery measurement of 30 ppm AuCl_3 in 0.5 M HCl solution at room temperature (25°C).

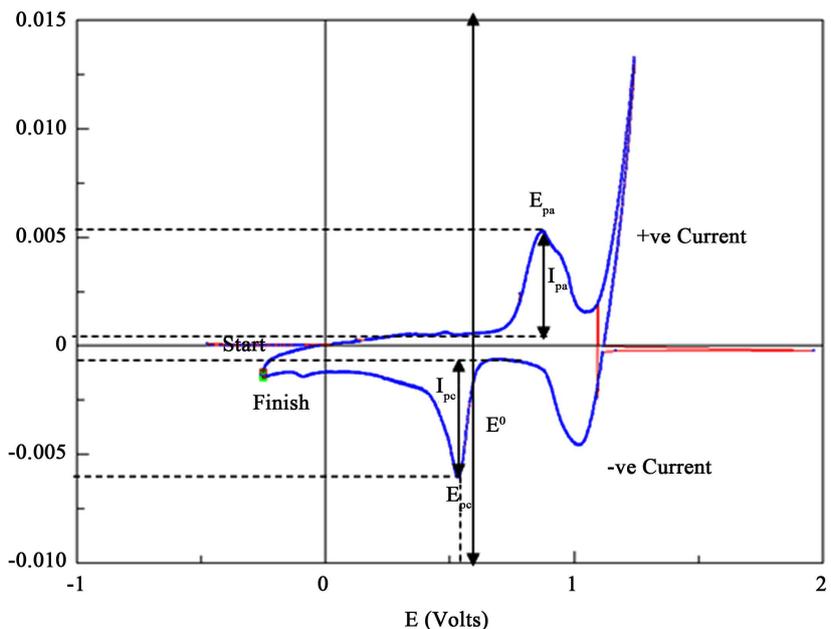


Figure 5. Cyclic voltammery measurement of 60 ppm AuCl_3 in 0.5 M HCl solution at room temperature (25°C).

peaks could be observed through the voltammogram. The figures represent the current generated by applied cyclic potentials on 30 ppm, 60 ppm, 0 ppm AuCl_3 in 0.1 and 0.5 M HCl, respectively. Where, E_{pa} and E_{pc} were oxidation and reduction potential peaks, respectively, and I_{pa} and I_{pc} were the corresponding current at the peak of oxidation and reduction in that order. There are reports on the formation of these asymmetry peaks during voltammetric measurements [3] [4] [11].

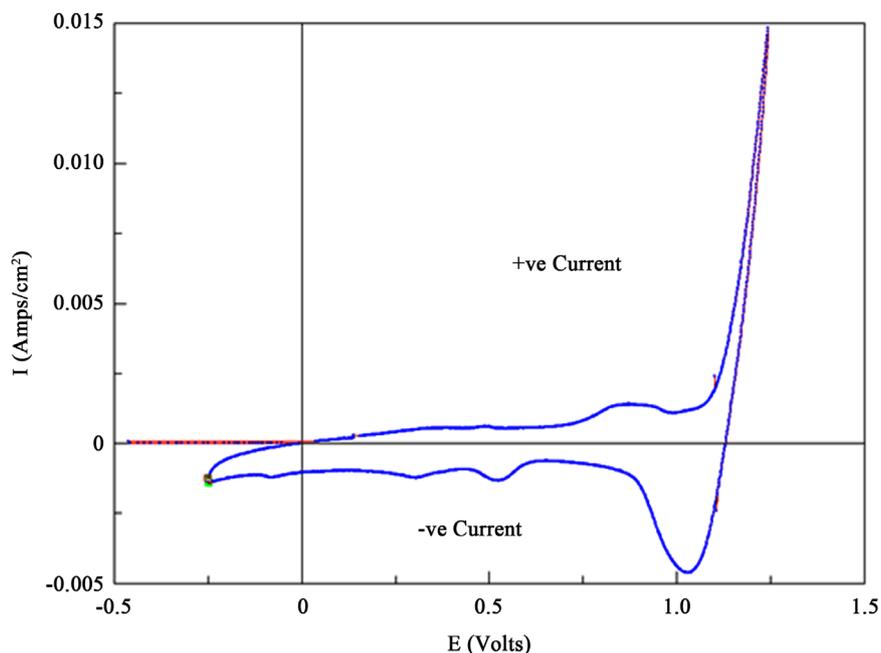


Figure 6. Cyclic voltammetry measurement of 0 ppm AuCl_3 in 0.5 M HCl solution at room temperature (25°C).

In **Figure 1**, oxidation peak was reached at about 1 V (E_{pa}), and 0.0028 A/cm^2 current density (I_{pa}) was generated. At this point the HCl was oxidized completely to H^+ . On the other hand, the complete reduction of AuCl_3 to AuCl_4^- was achieved at a potential E_{pc} and current I_{pc} of 0.55 V and 0.0028 A/cm^2 , respectively. Khunathai *et al.* reported the standard reduction potential E^0 of AuCl_4^- to be 1.0 V [11]. The Nernst equation (1) was employed to determine the concentration of reduced auric chloride ion (AuCl_4^-) at the surface of the working electrode in 30 ppm solution, thus:

$$E = E^0 - \frac{RT}{nF} \ln Q$$

From the half-reaction depicted in reaction R2,

$$\begin{aligned} \ln Q &= \ln \frac{\text{concentration of } \text{AuCl}_4^-}{\text{concentration of } \text{AuCl}_3} = (E^0 - E) \frac{nF}{RT} \\ &= (1 - 0.55) \times \frac{1 \times 96500}{8.314 \times (273 + 25)} = 17.52 \end{aligned}$$

$$\text{Concentration of } \text{AuCl}_4^- = 30 \times e^{17.52} = 1.22 \times 10^9 \text{ ppm}$$

For a reversible reaction [6],

$$I_{pc} : I_{pa} = 1 \quad (2)$$

In **Figure 1**, $I_{pc} = 0.0035 - 0.00075 = 0.00275$

$$I_{pa} = 0.004 - 0.00125 = 0.00275 .$$

Hence, $I_{pc} : I_{pa} = 0.00275 : 0.00275 = 1$.

From this experiment, 30 ppm of AuCl_3 would be reduced to AuCl_4^- at the reduction peak on the surface of the working electrode at a concentration of 1.22×10^9 ppm. The reaction was also a reversible reaction, considering the ratio of I_{pc} to I_{pa} which was found to be 1 [6].

Figure 2 shows voltammetry measurement of 60 ppm AuCl_3 in 0.1 M HCl solution, with the E_{pc} and E_{pa} obtained at 0.55 V and 1.23 V, respectively. The corresponding cathodic and anodic peak current density (I_{pc} and I_{pa}) were 0.0022 and 0.0024 A/cm². From Equations (1) and (2) respectively, the concentration of the AuCl_4^- at reduction peak on the surface of the electrode was 2.44×10^9 ppm, and the ratio of I_{pc} to I_{pa} was 1. Hence, the reaction was also a reversible one.

Figure 3 depicts the voltammetry measurement of 0.1 M HCl without AuCl_3 (0 ppm AuCl_3), no peak was feasible either at the oxidation zone or reduction zone. This confirmed electrochemically, that the reaction between HCl and water was not a redox reaction but a dissociation

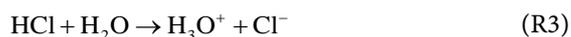


Figure 4 and **Figure 5** represented the higher concentration of AuCl_3 and HCl, however the values of E_{pc} was the same as that of **Figure 1** and **Figure 2** (0.55 V), indicating evidence that the standard potential and reduction potential peaks did not change with concentration. The reduction peak current varied with concentration as shown in **Figure 1** and **Figure 4** was -0.0035 and -0.0065 A/cm², respectively. **Figure 6**, just like **Figure 3**, had no peak because it was not a redox reaction.

Summary of Cyclic Voltammetry (CV) Curves for Various Concentrations

The form of CV curves as depicted in **Figure 7** are like those published in various literature under similar experimental conditions [11] [12] [13] [14] [15].

4. Conclusion

The redox reaction of AuCl_3 in HCl solution of various concentrations has been electrochemically studied using a cyclic voltammetry technique. The concentration of the reduced AuCl_4^- ion was determined using the Nernst equation. The results showed that anodic and cathodic peaks were present in the solution containing AuCl_3 of various concentrations, while no peaks were generated in HCl solution in the absence of AuCl_3 . The measured E_{pc} in the tested solutions was the same showing evidence that the reduction potentials were independent of the concentration. However, the reduction current varied with the concentration of solution, affirming the dependency of current on concentration. This study has interesting implication to determine the electrochemical parameters of gold reduction during leaching and adsorption processes with more accurate results obtained for specific process.

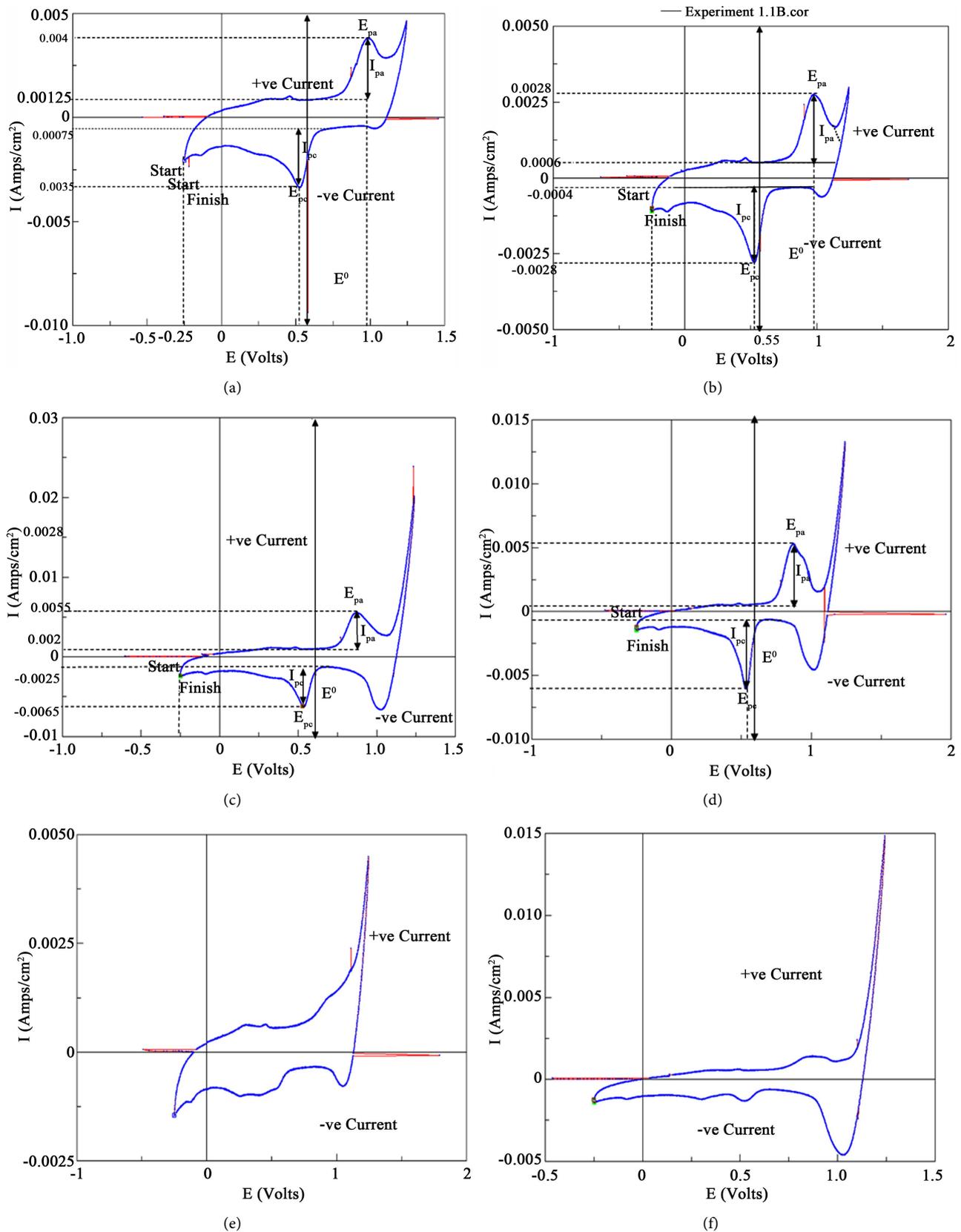


Figure 7. Cyclic voltammograms of (a) 30 ppm AuCl₃ in 0.1 M HCl; (b) 60 ppm AuCl₃ in 0.1 M HCl; (c) 30 ppm AuCl₃ in 0.5 M HCl; (d) 60 ppm AuCl₃ in 0.5 M HCl; (e) 0 ppm AuCl₃ in 0.1 M HCl and (f) 0 ppm AuCl₃ in 0.5 M HCl at room temperature.

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