Figure 1a shows the cyclic voltammetry measurements and the frequency variation using the EQCM-CV procedure. These curves correspond to the deposition of Au^{3+} ions on a gold-coated quartz crystal electrode, in 100 mg·L^{-1} HAuCl$_4$ during a potential scan between 0 and 0.95 V at a scan rate of 5 mV·s^{-1}. Scanning starts from + 0.8 V to the cathode region. All frequency changes were measured with respect to the zero ΔFrequency which was set using the Reset EQCM ΔFrequency command while the working electrode was kept at 0.95 V vs Ag/AgCl (3 M KCl).

As the potential is scanned in the positive direction, the mass deposition of Au^{3+} ions onto gold-electrode starts at around +0.65 V. This is followed by a sharp increase of cathodic current at around +0.5 V, which is detected by a sharp decrease in EQCM ΔFrequency. The frequency continues to decrease after the lower vertex potential is reached until the current passes through 0 and becomes

(a)

(b)

Fig. 1. (a) – Cyclic voltammetry and ΔFrequency vs. potential plots recorded with gold electrode in 100 mg·L^{-1} HAuCl$_4$ solution at 5 mV·s^{-1}, (b) – Frequency plots for a gold electrode at various scan rates: 5, 10, 20, 40 and 50 mV·s^{-1}.

positive again. This triggers an increase of the frequency and the ΔFrequency value finally returns to roughly 0 Hz at the positive end of the scan as the deposited gold is removed from the surface.

Figure 1b illustrates the changes in the mass of the electrode during the discharge-ionization process of a gold electrode on a piezoelectric element within the cell filled with a gold-containing acidic solution. The figure shows the minima of the change in the frequency of the oscillation of the piezoelectric quartz. If we take the absolute values then the maxima are seen. The change in the value of the oscillation frequency is given with a negative sign because during the electrodeposition of gold, an increase in the mass of the element occurs, thus leading to a decrease in the oscillation frequency. Prior to the start of voltammetric measurements, a calibration was carried out to take into account the influence of the solution mass on the change in frequency of the oscillation of the piezoelectric quartz, while the point zero (start of measurement) corresponds to the open circuit potential E$_{ocp}$.

A further decrease in the oscillation frequency from a potential of -0.8 to 0 V can be divided into two sections. The first section to -0.4 V, which is nonlinear, corresponds to the formation of the effective thickness of the diffusion layer and is characterized by a peak on the curve of the voltammogram. The second section has a linear shape during which the electroreduction of gold at a limiting diffusion current is observed at -0.4 ... 0 V ... -0.6 V (the diffusion layer has an effective thickness). The observed minima of the oscillation frequency of the piezoelectric crystal characterize the mass of electrodeposited gold, in particular, at a potential scan rate of 5 mV·s^{-1}, the minimum oscillation frequency is 645.82 Hz.

By integrating the I – t curve of the measured voltammograms, the amount of electricity (Q) spent on the reduction of gold was calculated and presented in Table 1. From the value of Δf, the practical mass (m_{pr}) of gold after its electrodeposition was calculated according to Eq. 1.

Since the practical mass was known, then according to Faraday's law it was possible to calculate the number of electrons participating in the reaction. As shown in Table 1, the calculated values of the number of electrons are equal to three; this allows us to represent the electroreduction of gold according to the following reaction:
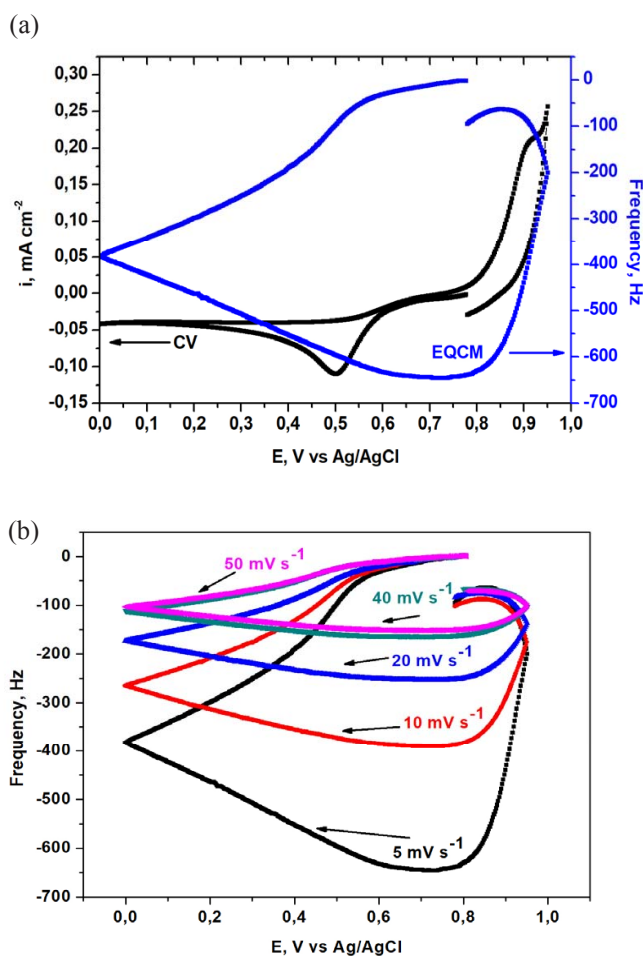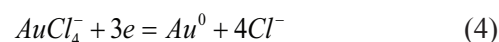
$$AuCl_4^- + 3e = Au^0 + 4Cl^- \qquad (4)$$