ELECTROCHEMICAL BEHAVIOR OF THIN PALLADIUM LAYER

M. Łukaszewski [a] , A. Czerwiński [a, b]

[a] *Warsaw University, Department of Chemistry, Pasteura 1, 02-093 Warsaw, Poland*
[b] *Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*

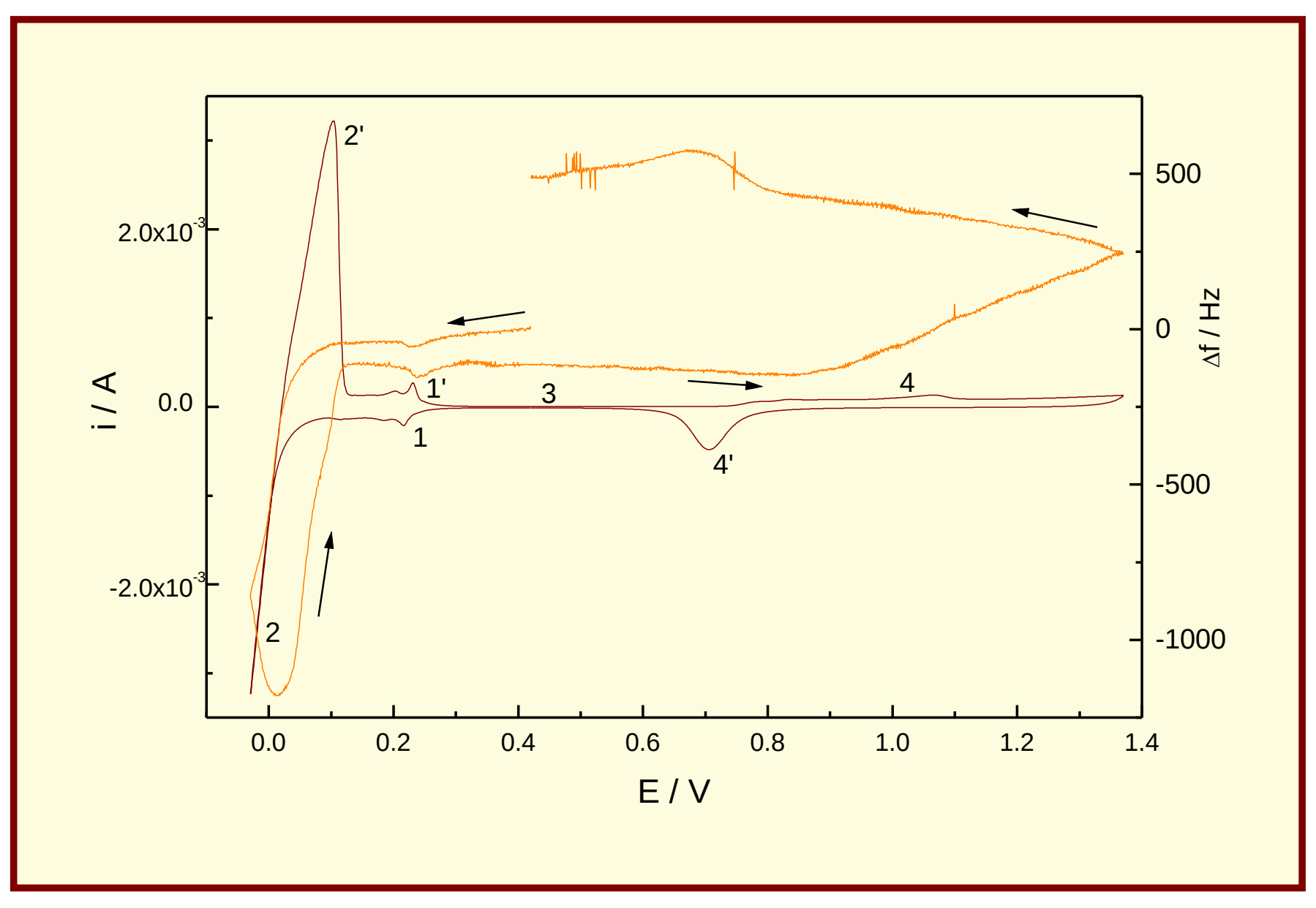

Fig. 1. Cyclic voltammogram and frequency-potential curve for Pd; scan rate 0.01 V/s.

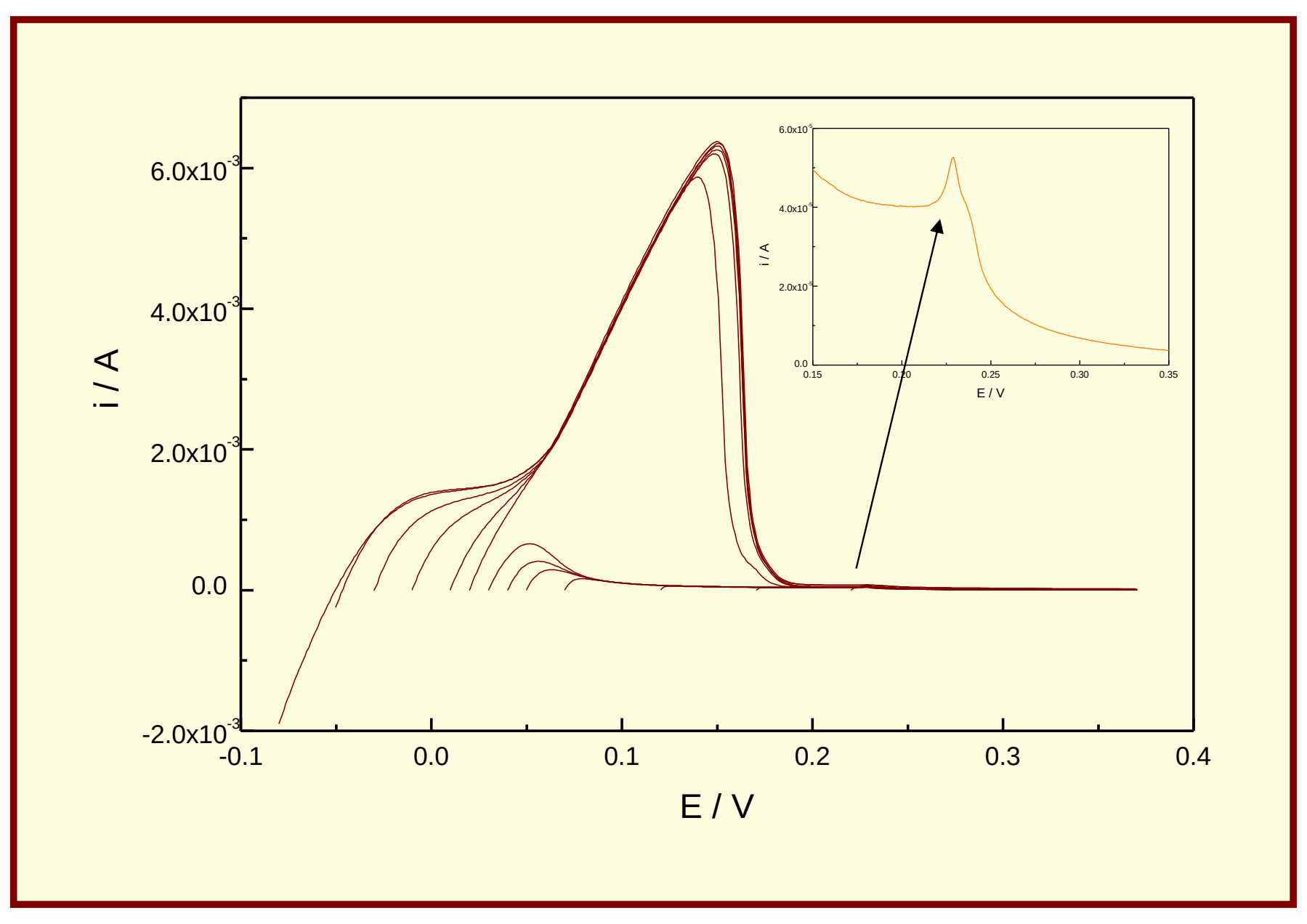

Fig. 2. Hydrogen oxidation currents after hydrogen electrosorption in Pd at various potentials; scan rate 0.01 V/s.

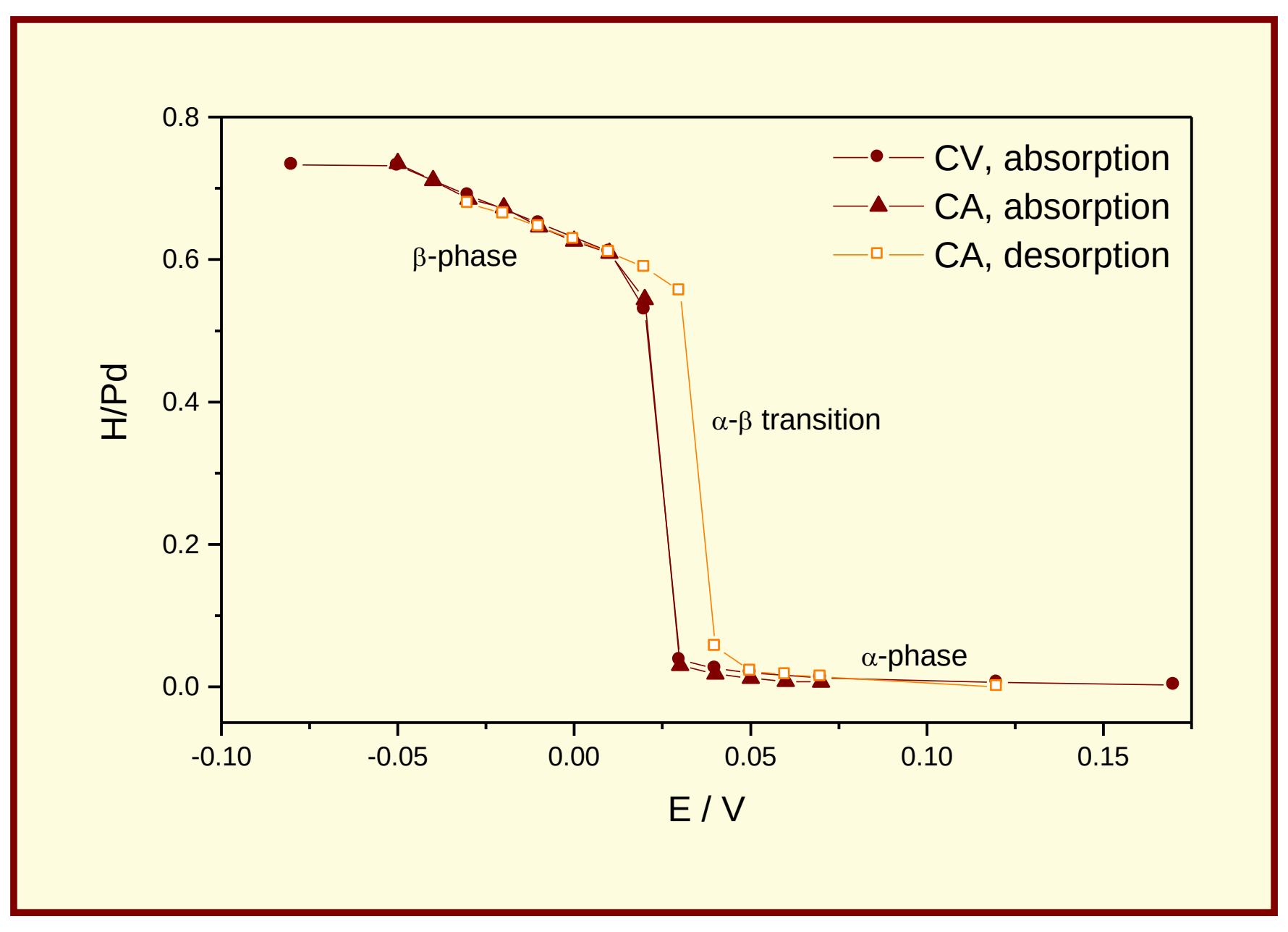

Fig. 3. Hydrogen absorption capacities versus potential for absorption and desorption obtained in cyclic voltammetric and chronoamperometric experiments.

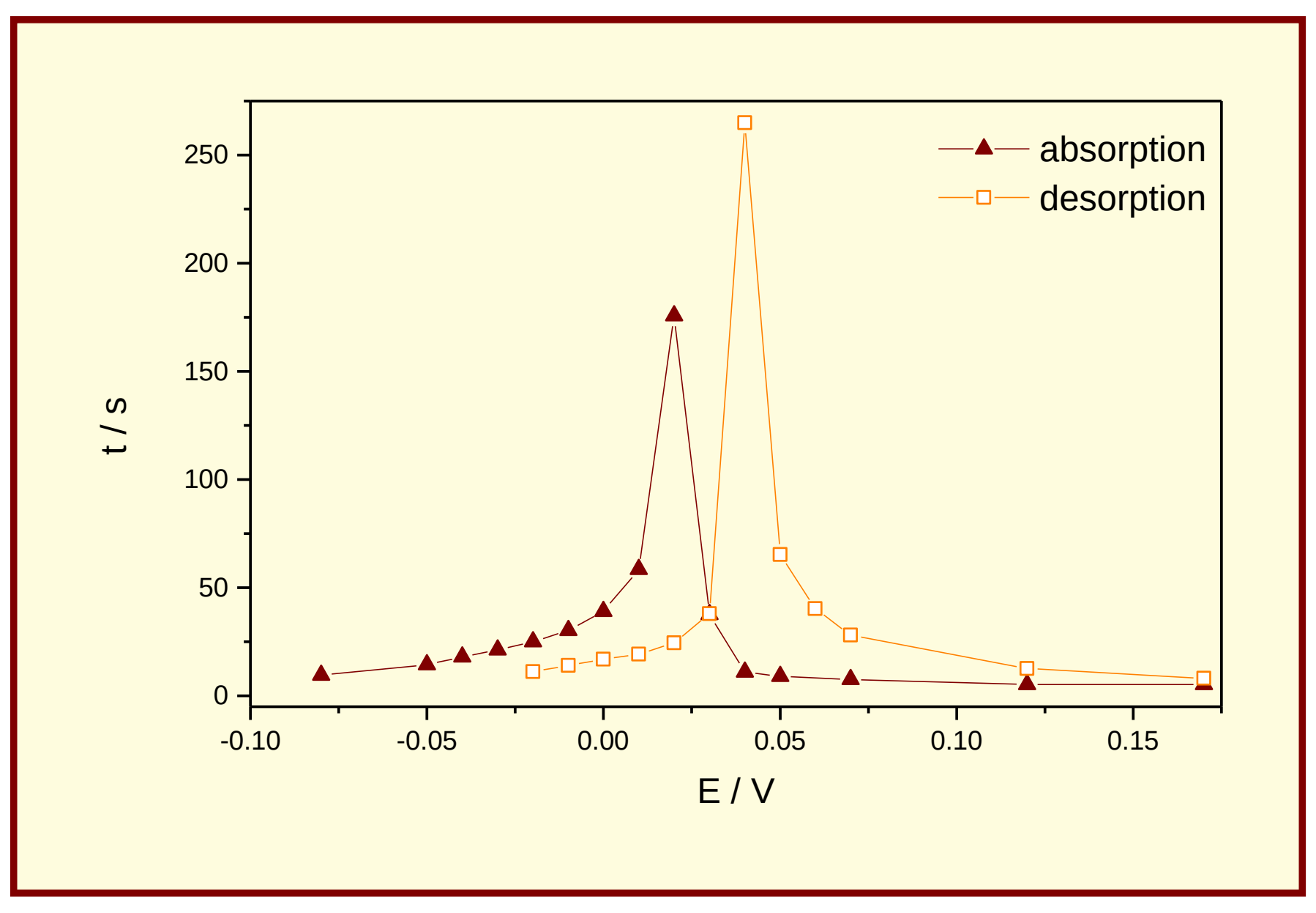

Fig. 4. Time needed for a steady-state electrode saturation with hydrogen and time needed for the oxidation of hydrogen electrosorbed at -0.03 V versus potential of absorption and desorption, respectively.

Hydrogen-metal systems have been investigated for 140 years. Among the system capable of hydrogen absorption is Pd – historically the first metal known to absorb hydrogen. It rapidly absorbs large amounts of hydrogen from the gas phase as well as from the electrolytes. Although great atomic mass and high cost are the main reasons for the limited practical application of the Pd-H system, it remains important as a model system to study fundamental properties of hydrogen absorbing materials. The knowledge of electrochemical behavior of Pd allows us to understand better hydrogen absorption/desorption processes occurring on the electrodes of this type. However, despite numerous studies on hydrogen absorption in Pd certain electrochemical aspects of this process are still not well known.

In this work the electrochemical behavior of thin Pd layers (0.3 μm) was examined using cyclic voltammetry (CV), chronoamperometry (CA) and quartz crystal microbalance (EQCM). 10 MHz AT-cut Pt-plated crystals were used in the EQCM experiments. The calibration constant (C) determined by Ag and Pd deposition was 1.2 ng Hz^{-1}, very close to the theoretical value based on Sauerbrey equation. All experiments were performed at room temperature in 0.5 M H_2SO_4 solutions deoxygenated using an Ar stream. All potentials are recalculated with respect to the SHE.

On a CV curve for Pd electrode (Fig. 1) one can distinguish currents due to hydrogen electrosorption (hydrogen region), i.e. signals connected with adsorption and absorption in the α-phase (1), followed by large signals originating mainly form hydrogen absorption in the β-phase (2) (see Fig. 2). After reversing polarization currents are observed due to oxidation of respective forms of electrosorbed hydrogen (1’, 2’). Then there is a potential region free of faradaic currents (double layer region, 3), while at more positive potentials signals originating from surface oxide formation (4) and reduction (4’) are visible (oxygen region). The characteristic feature of the frequency-potential curve is that it is not closed and a resultant frequency increase occurs, which suggests that electrochemical dissolution of the electrode material takes place, reflected also in the rapid frequency rise in the oxygen region. On the other hand, a significant frequency decrease in the hydrogen region results not only from mass increase due to hydrogen absorption but also from stresses in metal lattice induced by this process.

The amount of hydrogen absorbed in Pd increases with a decrease in electrode potential. On H/Pd vs. potential plot (Fig. 3) there are regions of α- and β-phase existence as well as the α-β transition region. The α-β transition during absorption occurs at a lower potential than the reverse β-α transition during desorption, which is reflected in a hysteresis on H/Pd vs. potential plots obtained in chronoamperometric experiments. The relationship between time needed for hydrogen absorption/desorption and electrode potential (Fig. 4) exhibits a maximum placed in the phase transition region. It suggests that the slow process of α-β transition controls the overall rate of hydrogen absorption and desorption into/from thin Pd layers.

Due to the influence of stress on the EQCM signal this method can be utilized as a valuable tool for studies of stress effects accompanying hydrogen absorption. The existence of stresses results in the values of apparent molar mass of absorbed hydrogen distinctly higher than unity (Fig. 5). Moreover, the the stress-related frequency shift depends on the amount of absorbed hydrogen and is different for absorption and desorption (Fig. 6). It reflects the differences in the magnitude and distribution of stresses in the crystal lattice during these processes.

Fig. 7 shows a series of chronoamperometric potential steps from the potential of the α-phase existence through the α-β phase transition region to the potentials of the β-phase existence (absorption steps) and then in the opposite direction (desorption steps). It should be noted that for the potential corresponding to the phase transition region (0.03 V) there are substantial differences between the stress-related frequency shift during absorption and desorption runs. It is the potential value for which the hysteresis on H/Pd vs. potential plot is observed. On the other hand, such differences are not visible when potential jumps are performed within the region corresponding to pure β-phase existence, i.e. for potential values where the hysteresis does not occur. Therefore, these results seem to confirm the important role of stresses in the phenomenon of absorption/desorption hysteresis.

The EQCM method is a useful tool for studying the metal dissolution process. In order to explore this phenomenon the electrode was polarized to various upper potential limits and the mass of dissolved metal was calculated (using Sauerbrey equation) from the difference in frequency between two consecutive anodic scans measured at anodic vertex potential. The amount of dissolved Pd increases with an increase in upper potential limit and a decrease in scan rate applied in a cyclic voltammetric experiment (Fig. 8).

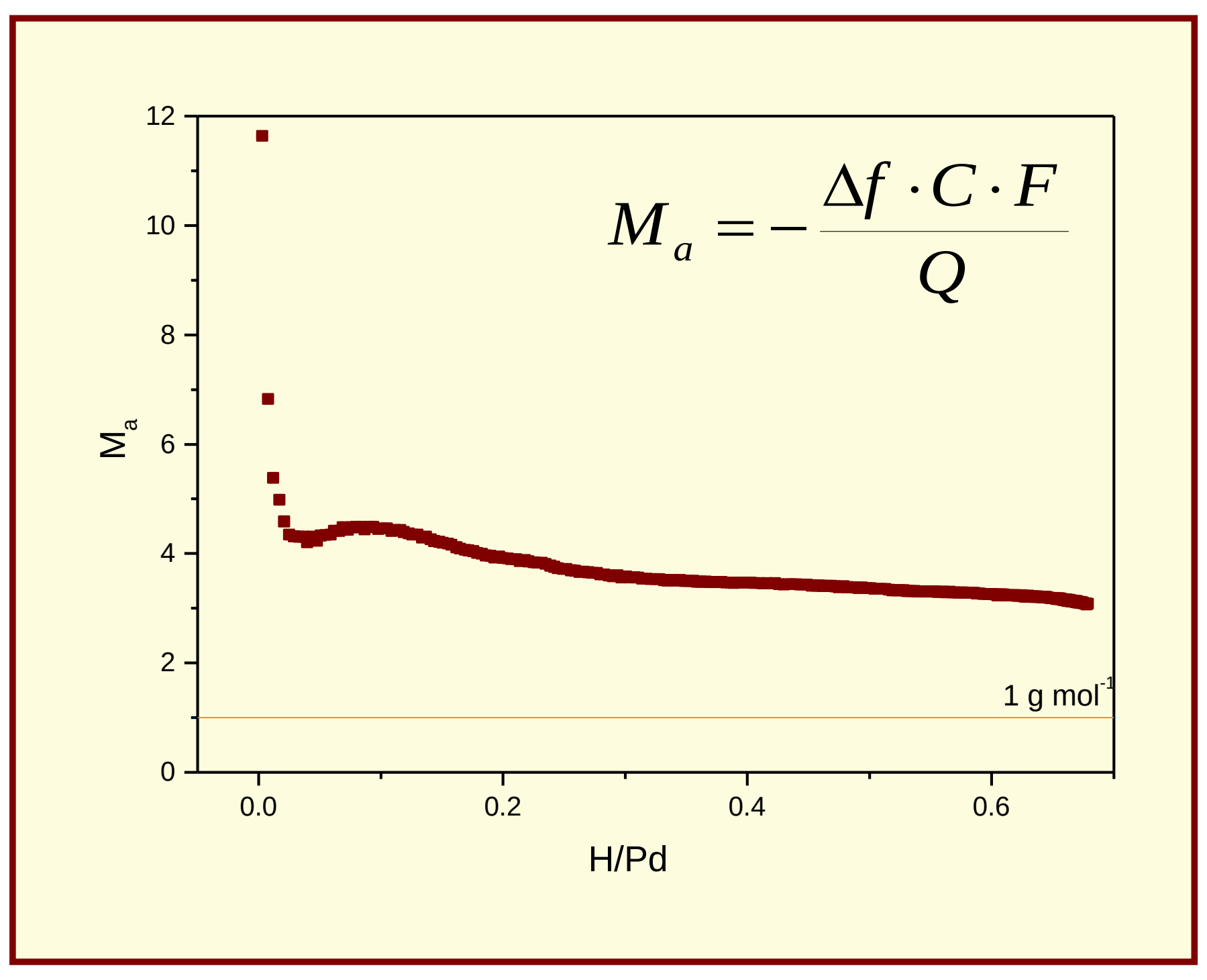

Fig. 5. Apparent molar mass of electrosorbed hydrogen as a function of its amount in Pd during chronoamperometric absorption (potential step from 0.37 to -0.03 V).

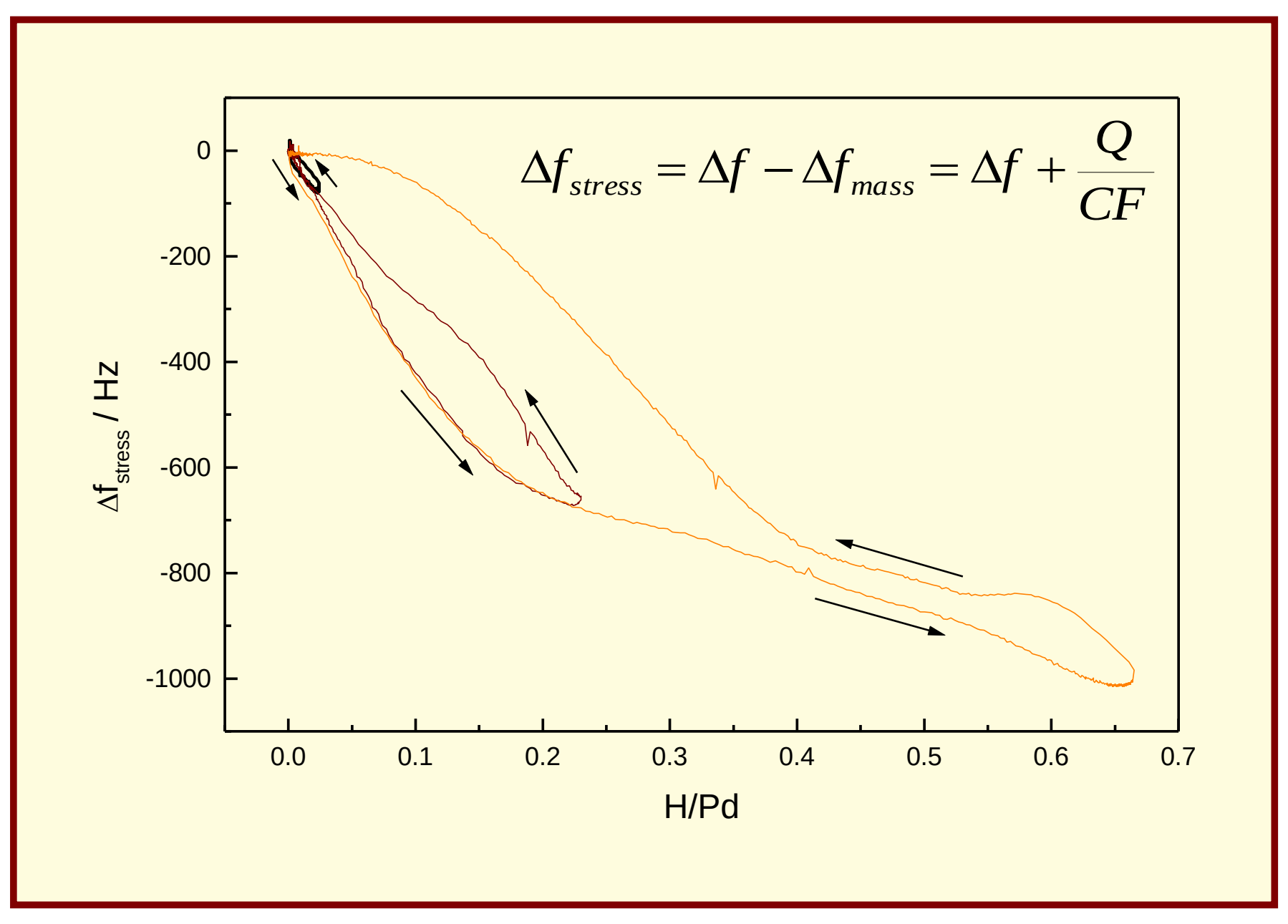

Fig. 6. Dependence of the stress-related frequency shift on the amount of hydrogen electrosorbed in Pd during absorption and desorption.

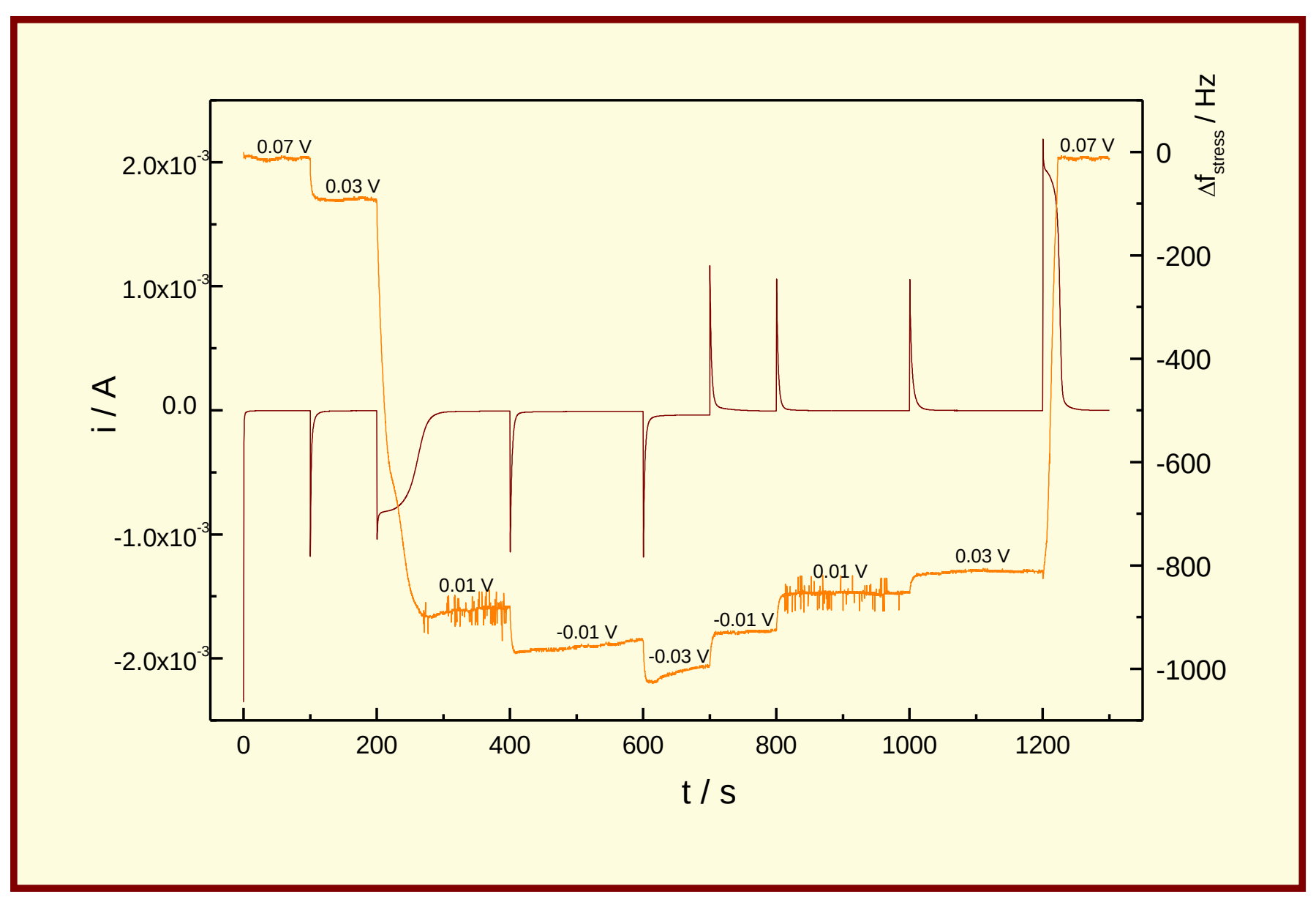

Fig. 7. Chronoamperograms and the stress-related frequency shift for potential steps within the phase transition and the β-phase existence region.

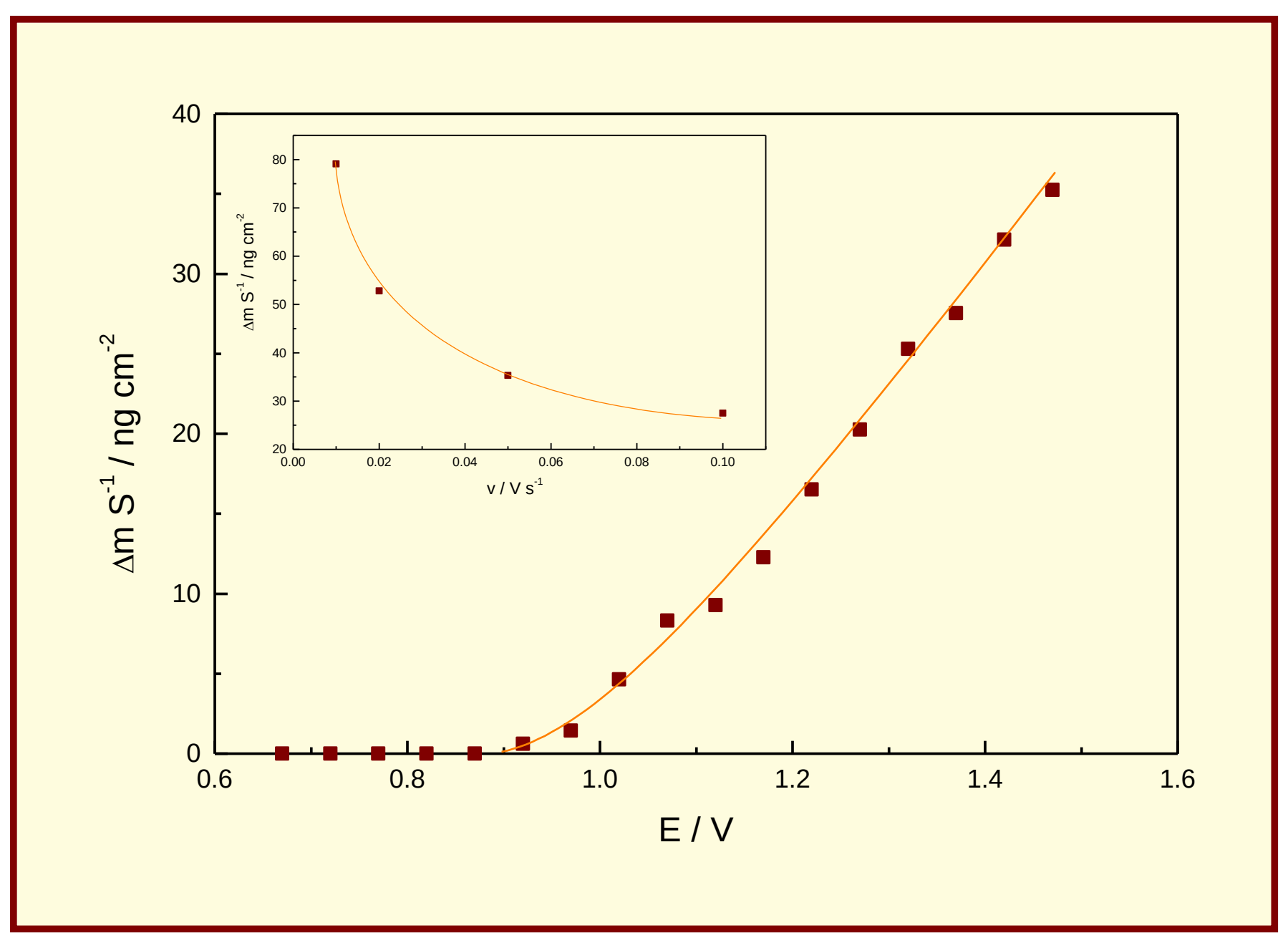

Fig. 8. Dependence of the loss in Pd electrode mass per the unit of real surface area (calculated from surface oxide reduction charge) on upper potential limit in a cyclic voltammetric experiment; scan rate 0.1 V/s. Insert: influence of scan rate on electrochemical dissolution of Pd.