# Совершенно поляризуемые электроды - соадсорбция

Underpotential deposition (upd) – образование адатомов при потенциалах положительнее равновесного

Металлы группы платины

потенциал максимальной адсорбции анионов

H upd

O upd: $H_2O - 2e = 2H^+ + O_{ад}$

«двойнослойная» область

E (RHE), V

Cu upd: $Cu^{2+} + 2e = Cu_{ад}$

0

1.23
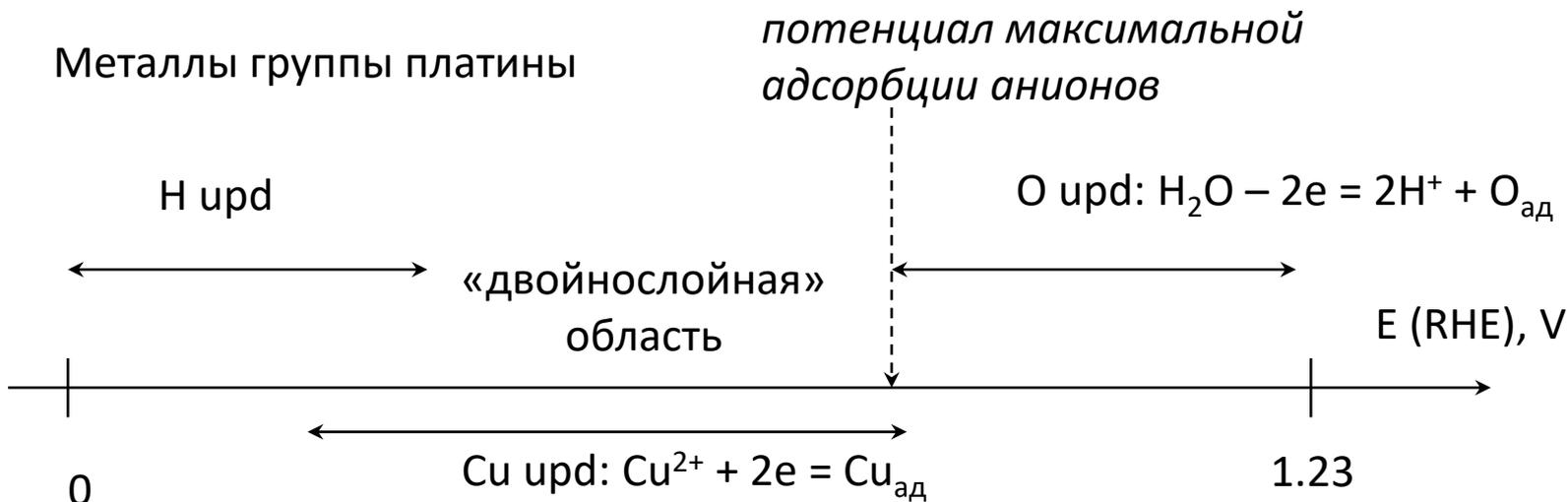
RHE – reversible hydrogen electrode (обратимый водородный электрод в том же растворе, SHE - 0.059pH)

40
30
20
10
0
-10
-20
-30
-40

i (µA)

(110)

(100)

HClO$_4$ (pH=0.2)
Acetate buffer (pH=5.2)
Phosphate buffer (pH=6.7)
(bi)carbonate buffer (pH=10.7)
KOH (pH=12.8)

0.0 0.2 0.4 0.6 0.8 1.0 1.2

$E_{iR\text{-}free}$ (V versus RHE)
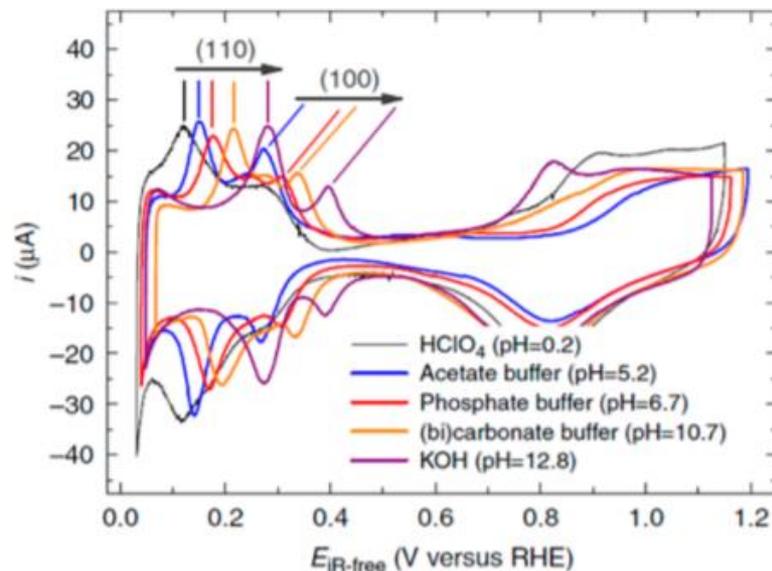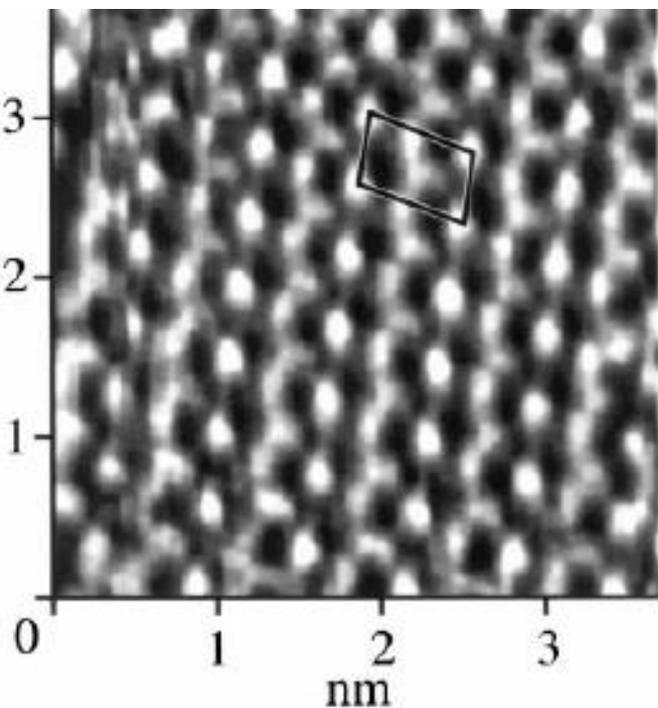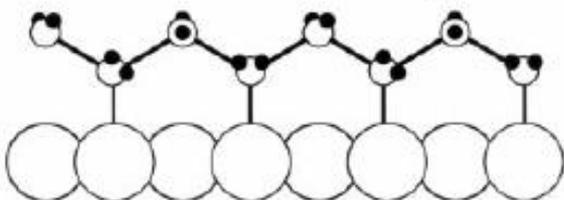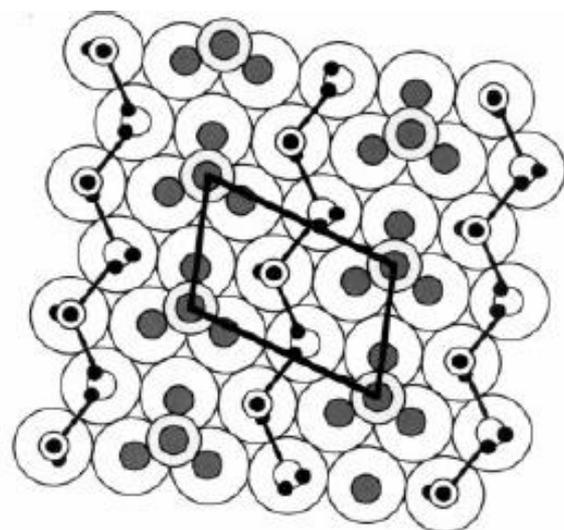
Pd(111)

Cu - полислой

water chain (side view)

Pd SO_4^{2-} H_2O (1st layer) H_2O (2nd layer)

Commensurated adlayer

Cu/Pd(111) - монослой

Phys Chem Chem Phys
3 (2001) 3297-3302
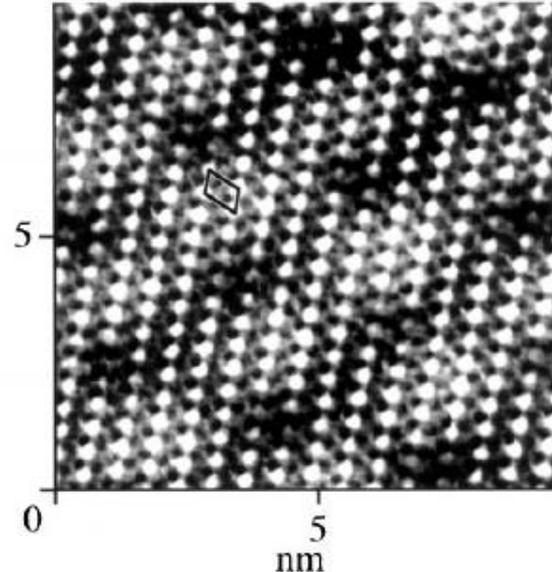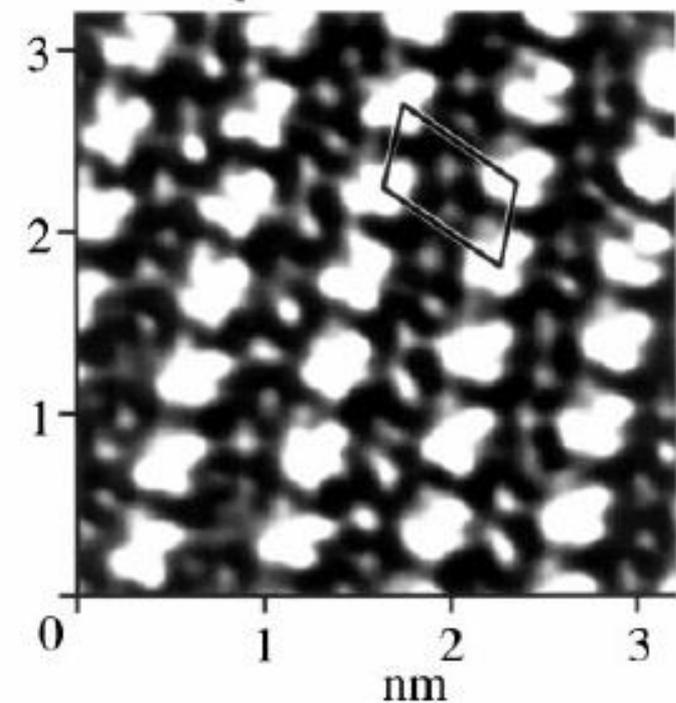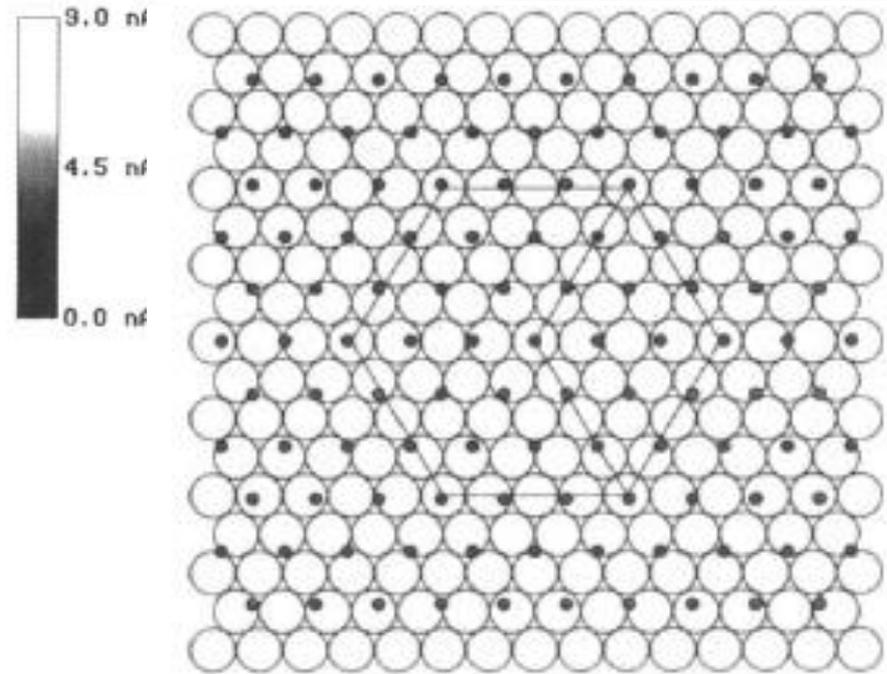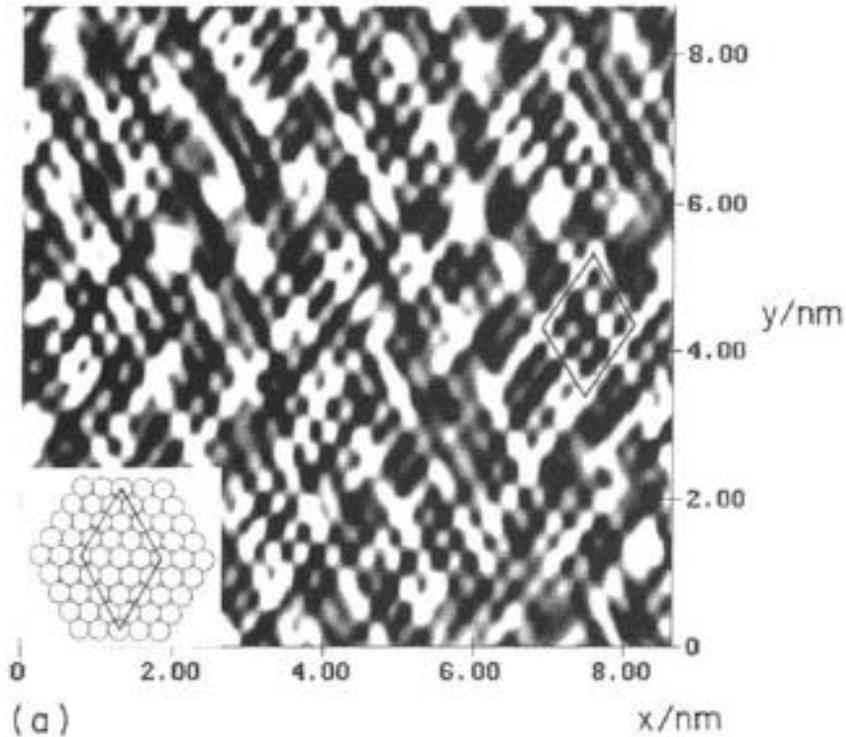
Phase [a]	Tl–Tl separation/Å		Rotation angle/deg		Tl coverage	
	STM	SXS	STM	SXS	STM	SXS
Rotated hexagonal	3.4	3.33	6	5.1	0.74	0.73
Aligned hexagonal	3.8	3.92	0	0	0.56	0.55
Low coverage hexagonal	–	3.92	0	1.5	–	0.5

J Electroanal Chem 376 (1994) 41-47

+ HCl

I / μA cm⁻² — vertical axis, values 40, 30, 20, 10, 0, -10, -20, -30

U_{SCE} / V — horizontal axis, values 0.0, 0.1, 0.2, 0.3, 0.4, 0.5

Cl
Cu
Au

Pt (111)

1mM Cu^{2+}

— 0.1 M H_2SO_4

– – – 0.1 M $HClO_4$

······ 0.3 M HF

10μA

E/V — horizontal axis, values 0, 0.4, 0.8, 1.2
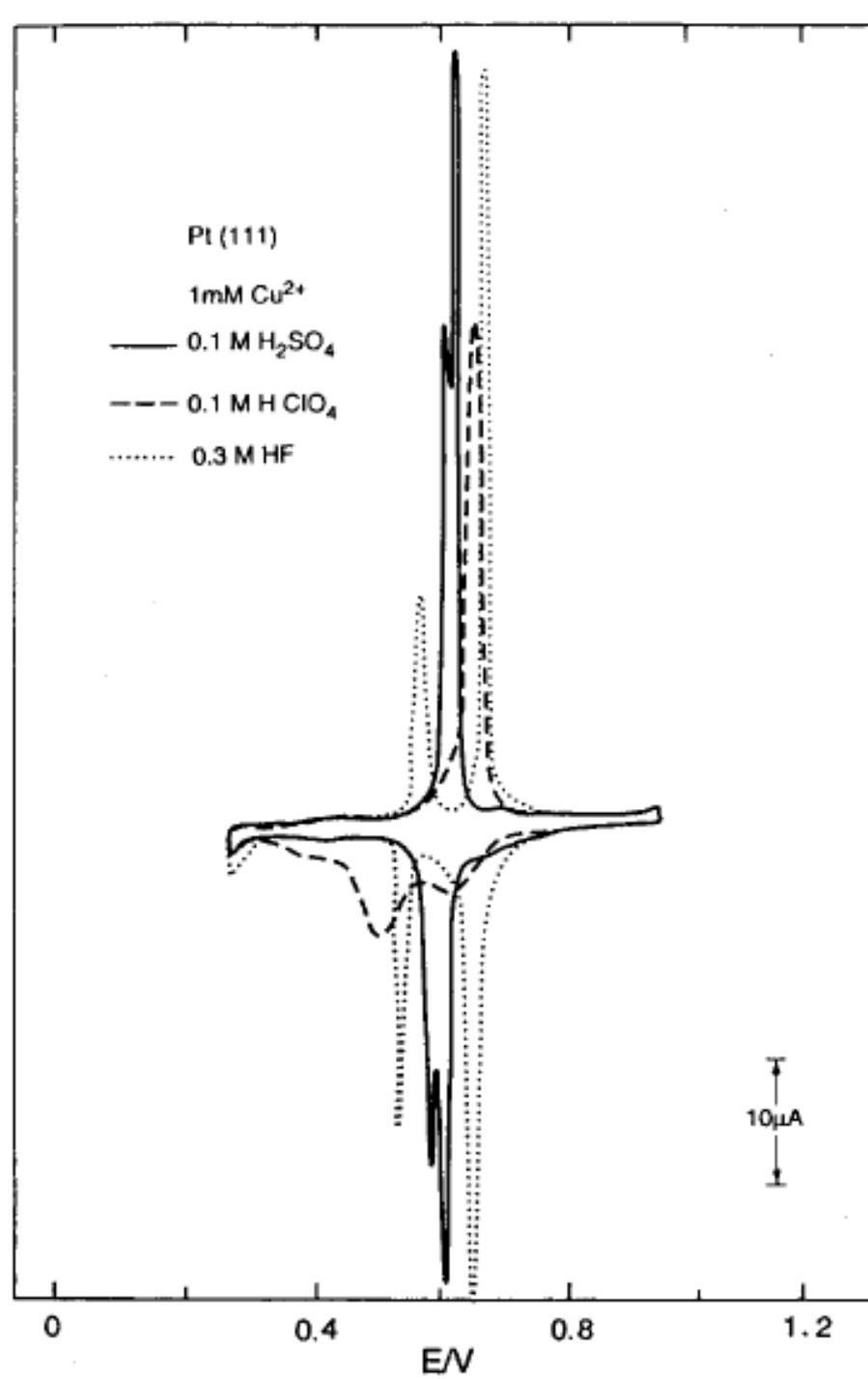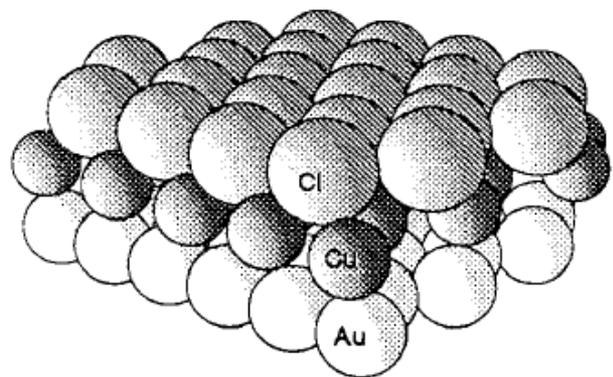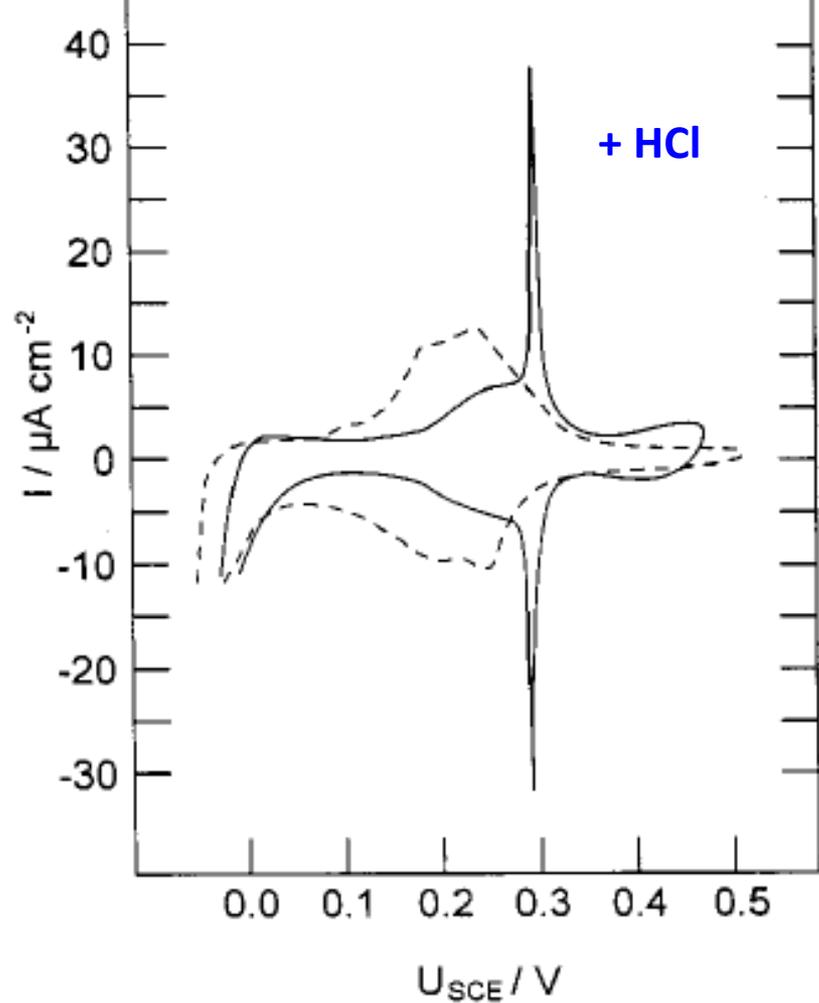
Соадсорбция с кислородом – «upd оксида» (адатомы Tl)
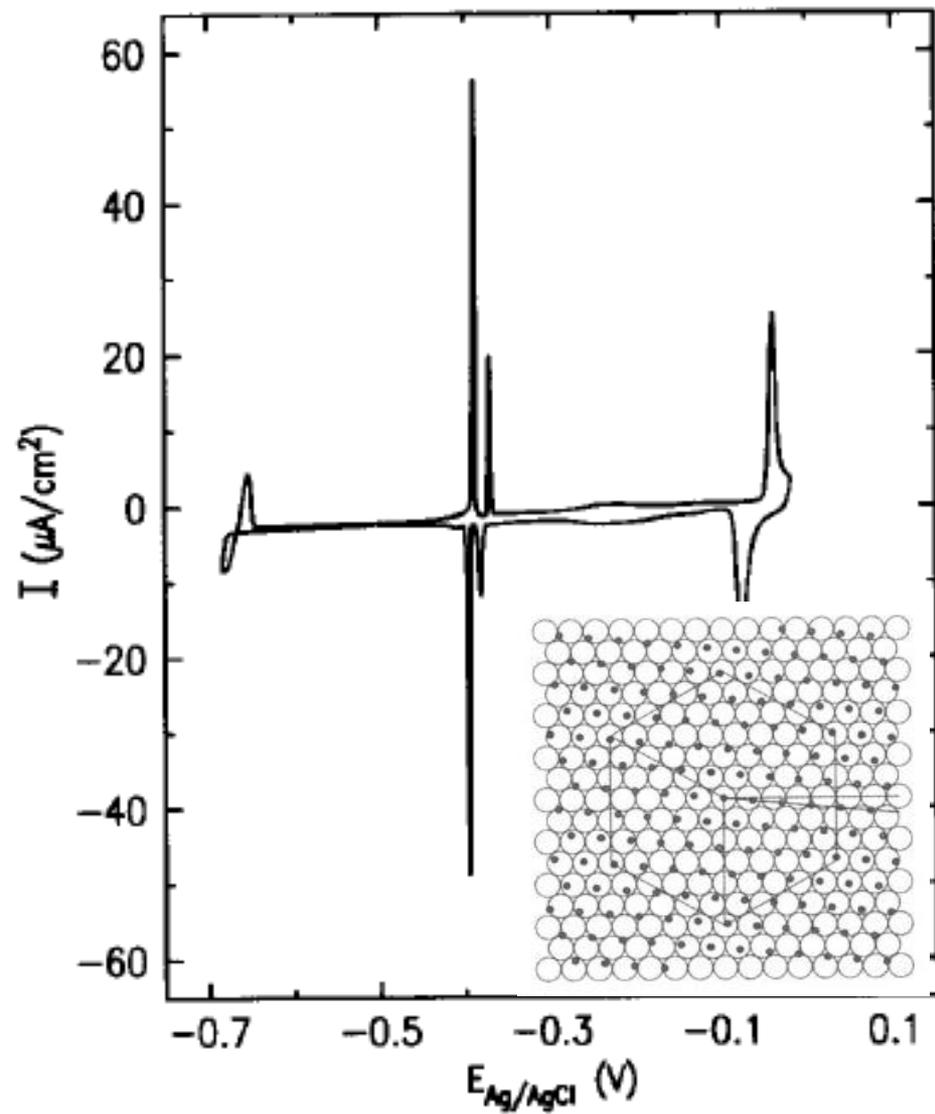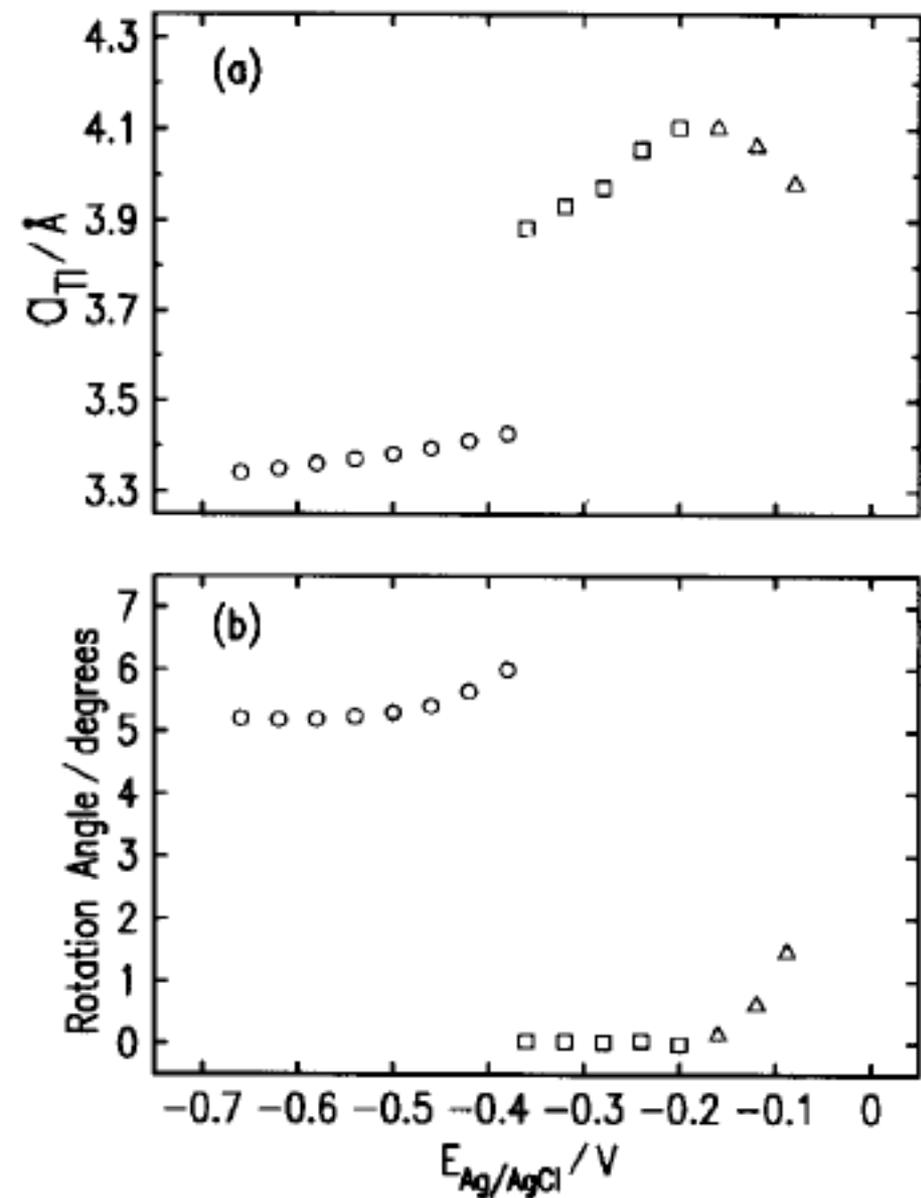
Адатомы меди – осложнения вблизи равновесного потенциала

$$Cu^+ + e^- \Rightarrow Cu$$

$$2Cu^+ \Rightarrow Cu + Cu^{2+}$$

Electrochim. Acta 43 (1997) 733-741.

2.6 Underpotential deposition of metals
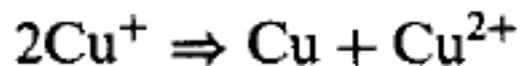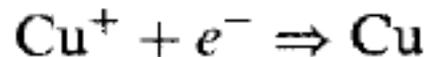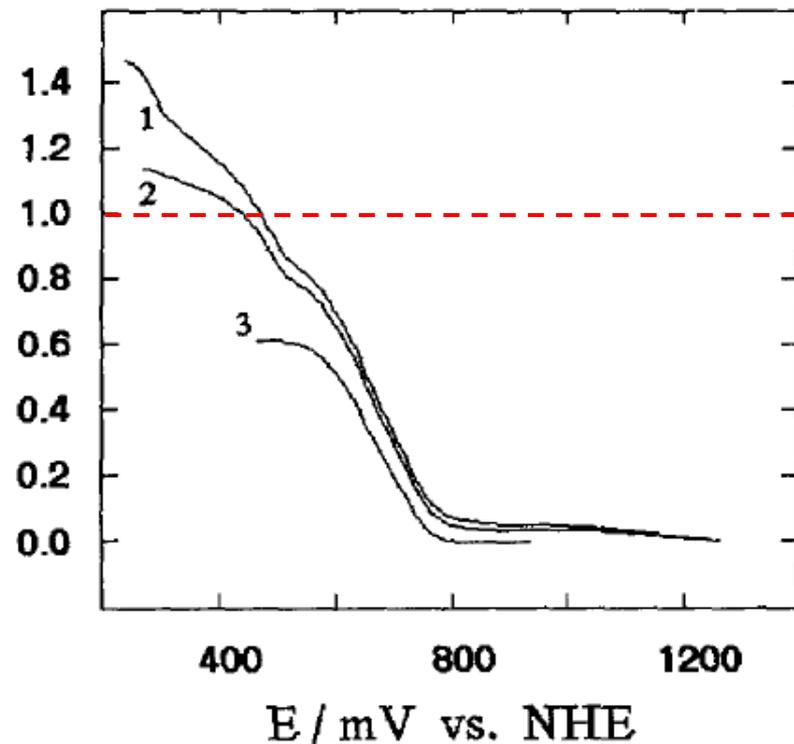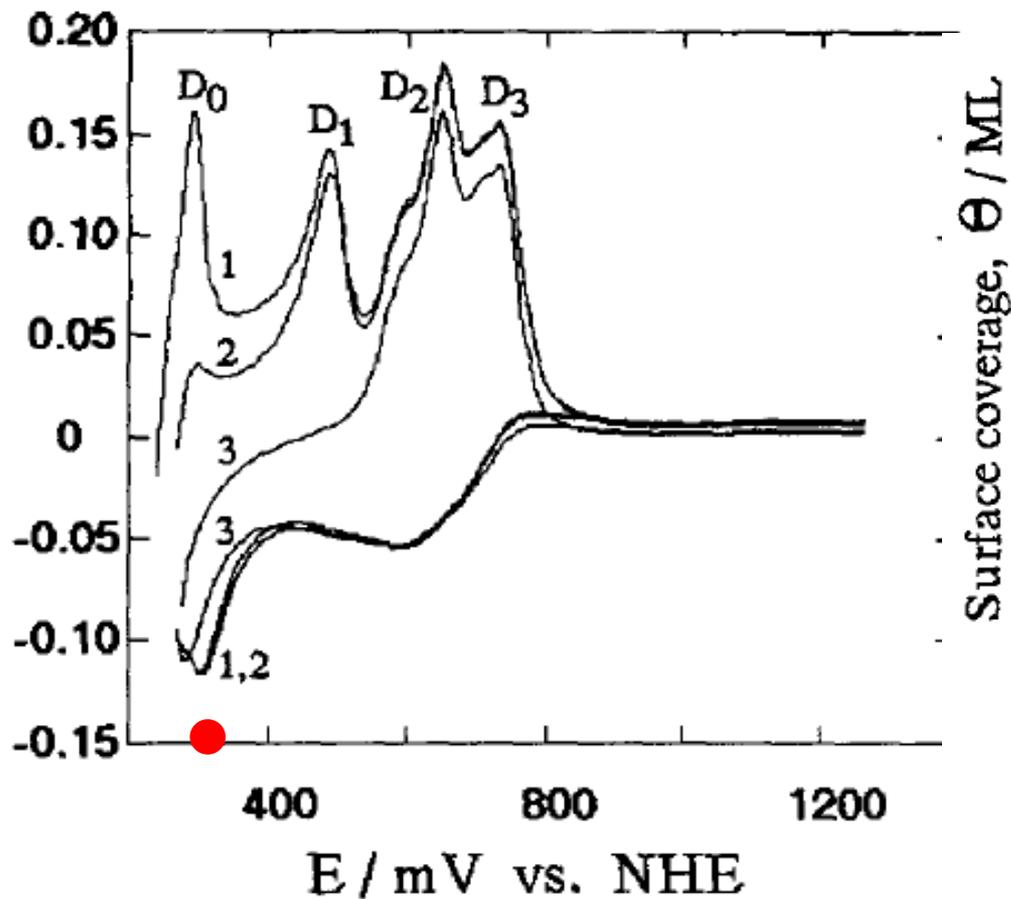
This method has been used for electrodes for which neither of the previous ones can be applied, eg Ag (ref. 57), Cu (ref. 58), and for metals for which a better separation between H and O adsorption cannot be achieved, eg Ru (ref. 59). An advantage of this method over method 4 (hydrogen adsorption) is that no spillover effects are expected, hence selective deposition is possible. Thus, the method may be particularly convenient to determine the (active) surface of supported electrodes where the (inactive) support comes in contact with the solution (ref. 60).

2.6.1 Principles. The charge associated with the underpotential deposition of a suitable metal ion is measured usually by voltammetry. The maximum adsorption in a monolayer is calculated on the basis of a chosen model so that the surface area of the sample is given by:

$$A = Q_M / Q_M^* \qquad (6.1)$$

Usually, Ag and Cu adatoms are used.

2.6.2 Limitations. This method suffers from the same shortcomings as method 4, in particular the correction for double layer charging is arbitrary and the identification of the end point for the metal adsorption is uncertain. In addition, (*i*) the UPD region may interfere with hydrogen or oxygen adsorption, (*ii*) the surface distribution of the UPD species may be unknown, (*iii*) the adatom deposition may occur with partial charge transfer thus making the value of Q_M^* specifically system-dependent, and (*iv*) the usual assumption of one-to-one correspondence with H and O adsorption may not be valid in the case of UPD because the new phase formation may result in more condensed monolayers, multilayers or cluster growth (ref. 61). Thus, in the case of Pb on Cu (111) the coverage has been found (ref. 58) to correspond to a close-packed configuration, while in the case of Pb on Ru the one-to-one correspondence (epitaxial growth) is more probable (ref. 59). The occurrence of the one or the other possibilities depends on a number of factors including size ratio between supporting metal and UPD metal, strength of the bond between overlayer and support in comparison with lateral interactions in the monolayer, etc.

The calculation of Q_M^* for polycrystalline surfaces is based on empirical considerations. The same is also the case of single crystal faces for which the method gives strictly the number of surface active sites rather than the true surface area. The response of the single crystal face is however different from that of the polycrystalline surface of a given metal because of the possible penetration of the discharged atoms into grain boundaries in the latter case.
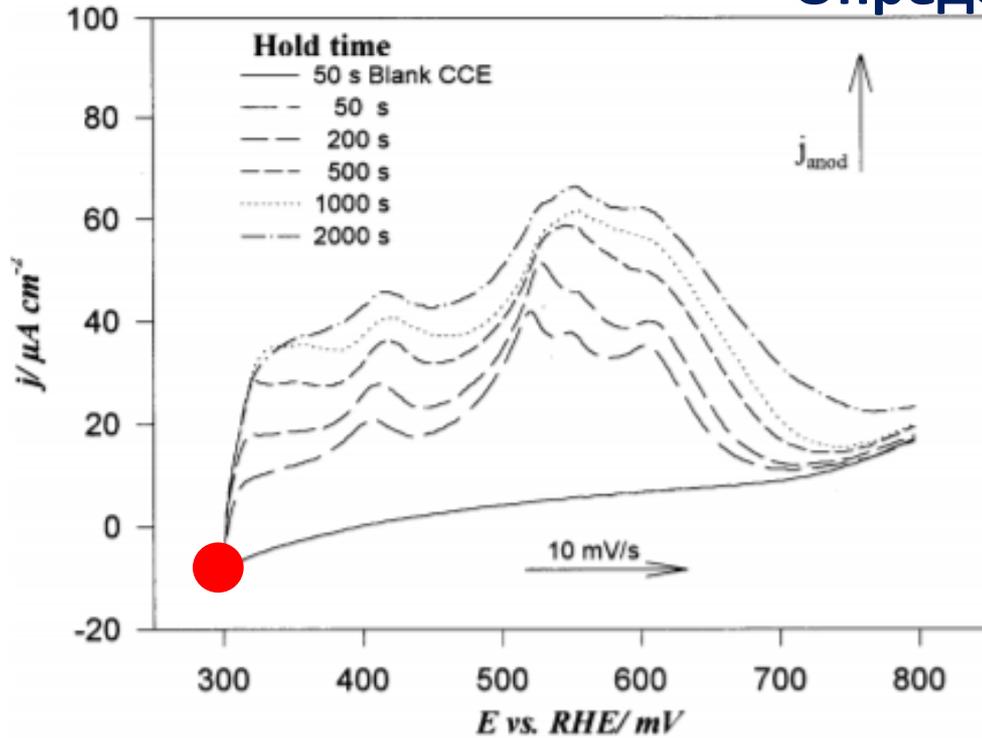
Зависимость от времени выдержки при потениале катодного предела: 🔴

При этом потенциале:
(1) накапливается Cu^+ в растворе,
(2) постепенно достигается предельное заполнение адатомами.
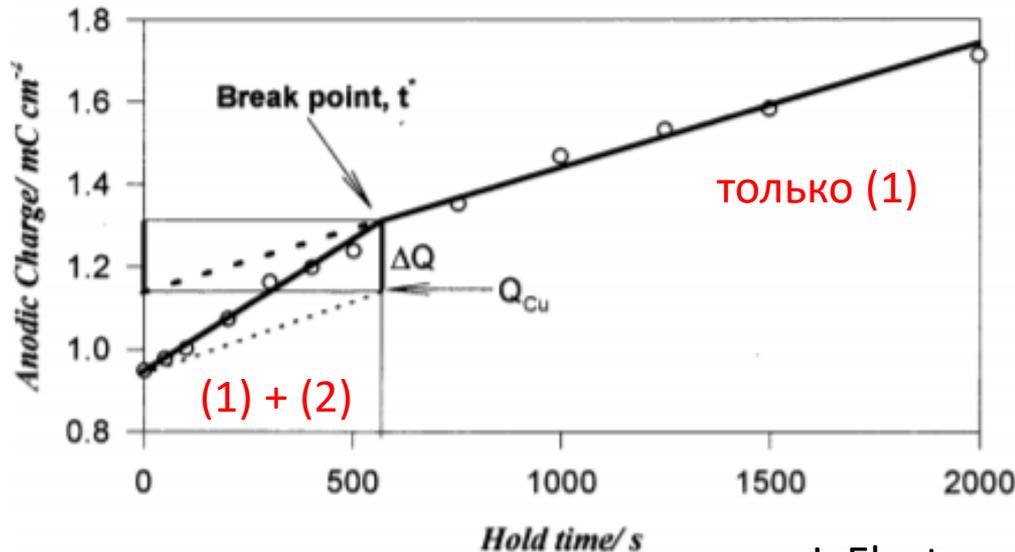
Для Pd нельзя определять поверхность по водороду, т.к. он сорбируется (образуется PdH_x).

Трудно также определять по кислороду, т.к. Pd легко растворяется.

J. Electroanal. Chem. 466 (99) 45
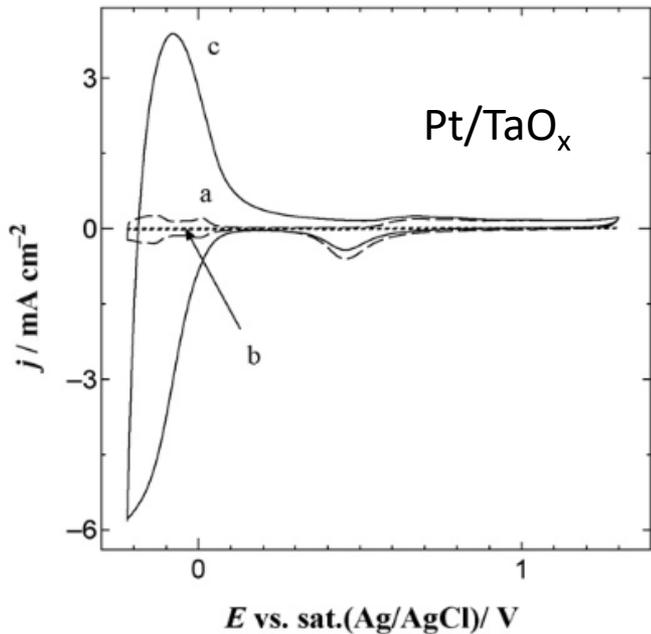
Spill over – распространение адсорбата по инертной подложке.

Зависимость от скорости развертки определяется кинетикой поверхностной диффузии.
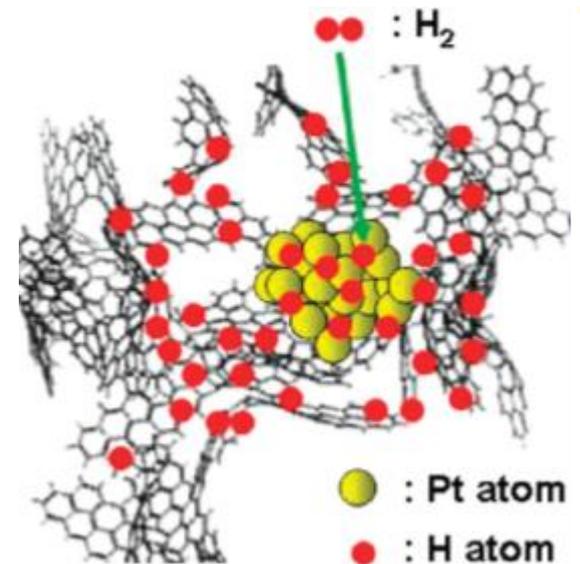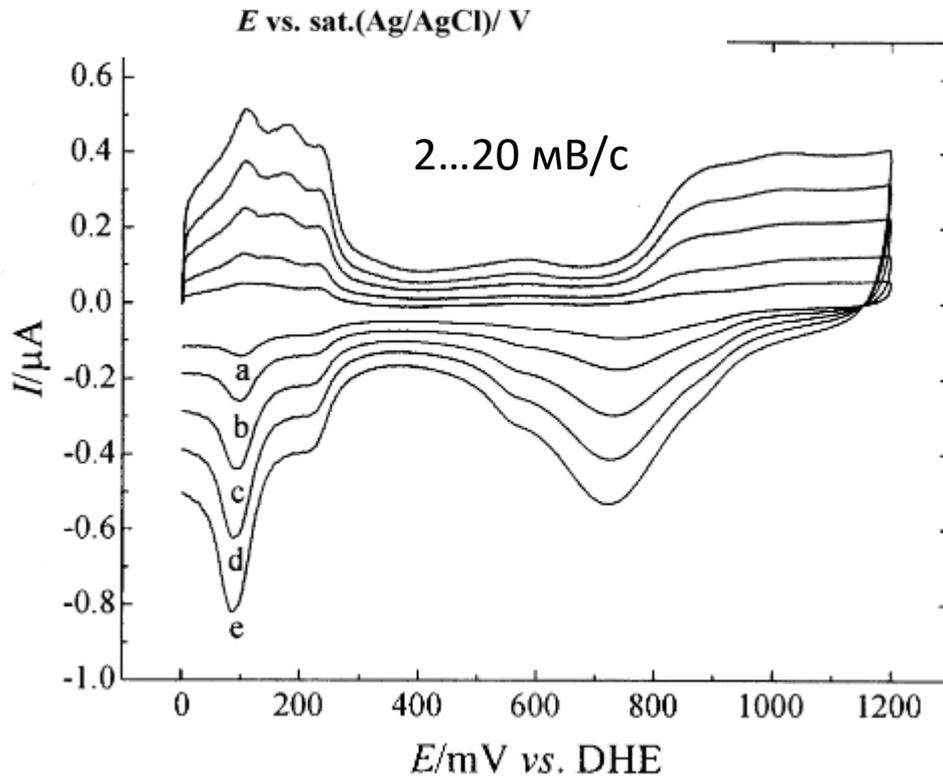
Galvanic replacement

Палладий, 105х105 нм

$$2Cu^0_{UPD} + Pt^{4+}_{solv} = 2Cu^{2+}_{solv} + Pt^0_{depos}$$

nano void

nano cluster

1 nm

0 nm

Emersion potential
E=0.005 V

j / μAcm^{-2}

E / V vs. Cu/0.1 M Cu^{2+}

A

B