

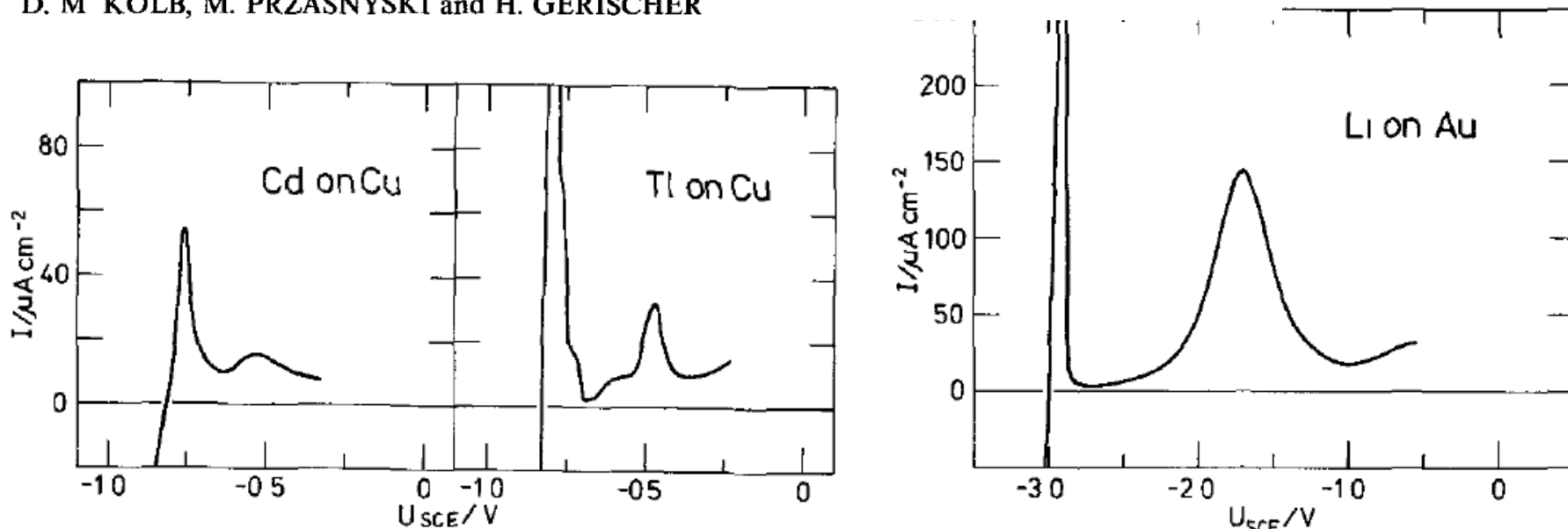
UNDERPOTENTIAL DEPOSITION

(«осаждение при недонапряжении» = «осаждение при потенциале положительнее равновесного», если заряд переносится с электрода на адсорбат, например, катион; «.. при потенциале отрицательнее равновесного», если заряд переносится с адсорбата на электрод, например, анион или молекула воды)

UNDERPOTENTIAL DEPOSITION OF METALS AND WORK FUNCTION DIFFERENCES

J. Electroanal. Chem. 54 (1974) 25-38

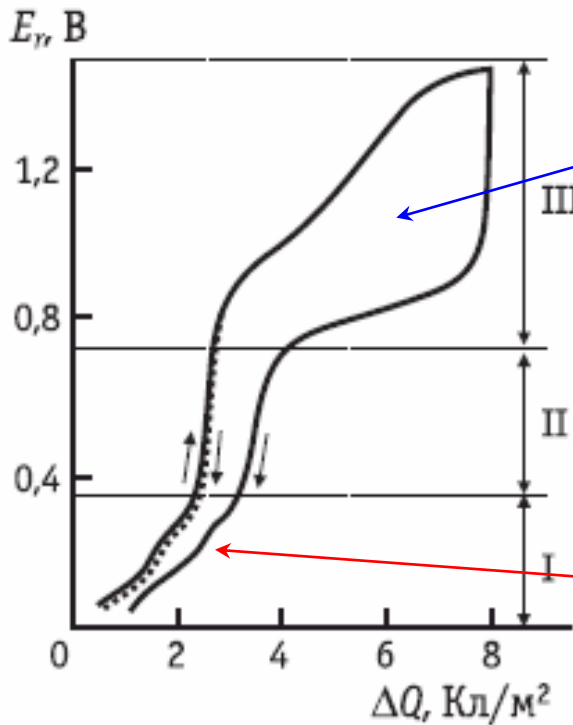
D. M. KOLB, M. PRZASNYSKI and H. GERISCHER



Anodic stripping curves of Cd and Tl deposits on Cu in 1 M Na_2SO_4 [Cd^{2+}] = 5×10^{-4} M [Tl^+] = 1×10^{-3} M. Scan rate = 20 mV s^{-1} .

Anodic stripping curve for Li on Au in acetonitrile (1 M LiClO_4) Scan rate = 100 mV s^{-1}

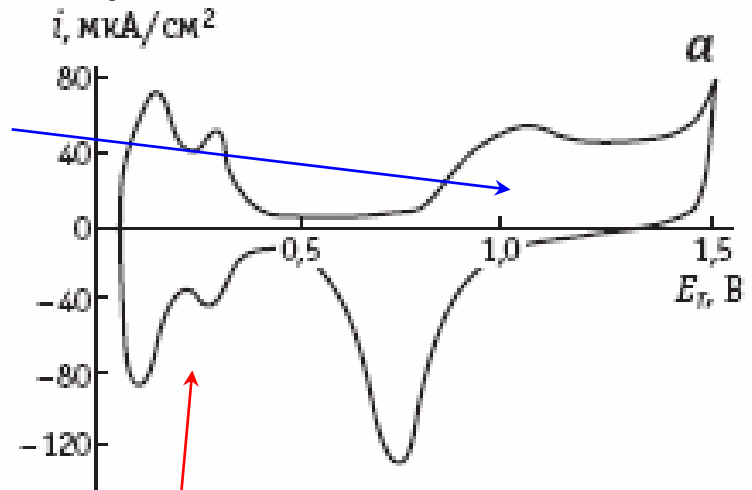
Кривая заряжения



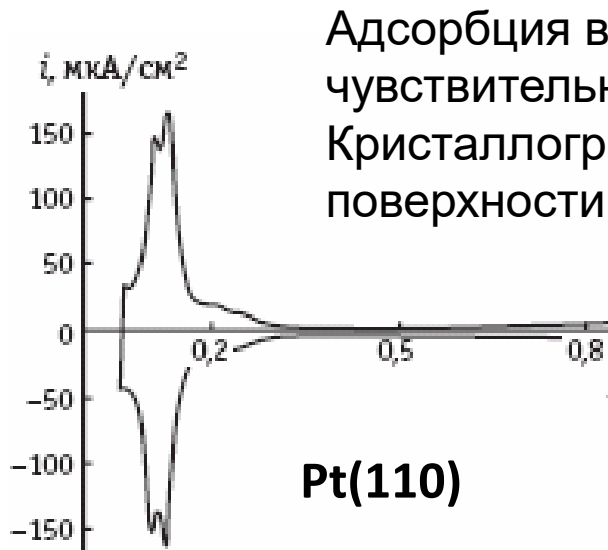
Платиновый электрод

Адсорбция кислорода

Адсорбция водорода

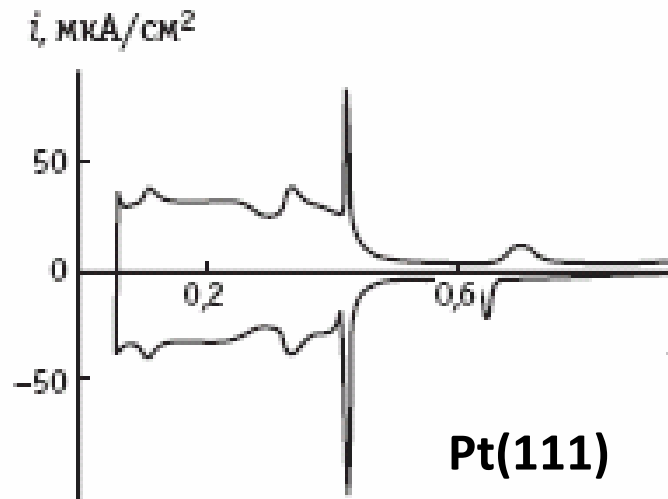


Вольтамперограмма (заряд ΔQ можно рассчитать по площади под кривой)



Адсорбция водорода чувствительна к Кристаллографии поверхности

Pt(110)



Pt(111)

Адсорбционный метод изучения заряженных межфазных границ (определение изменения поверхностной концентрации)

Оценки:

- заряд *идеально поляризуемого* электрода в реальных системах может достигать 30 мкКл/см²;
- полный заряд *совершенно поляризуемого* электрода может изменяться на 200-400 мкКл/см²



Изменение состава раствора в результате формирования адсорбционного слоя на 1 см² истинной поверхности не превышает 1 наномоля

Метод
радиоактивных
индикаторов



Прямое определение адсорбции возможно на электродах с развитой поверхностью из малого объема раствора

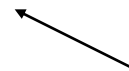
титрование



спектрофотометрия

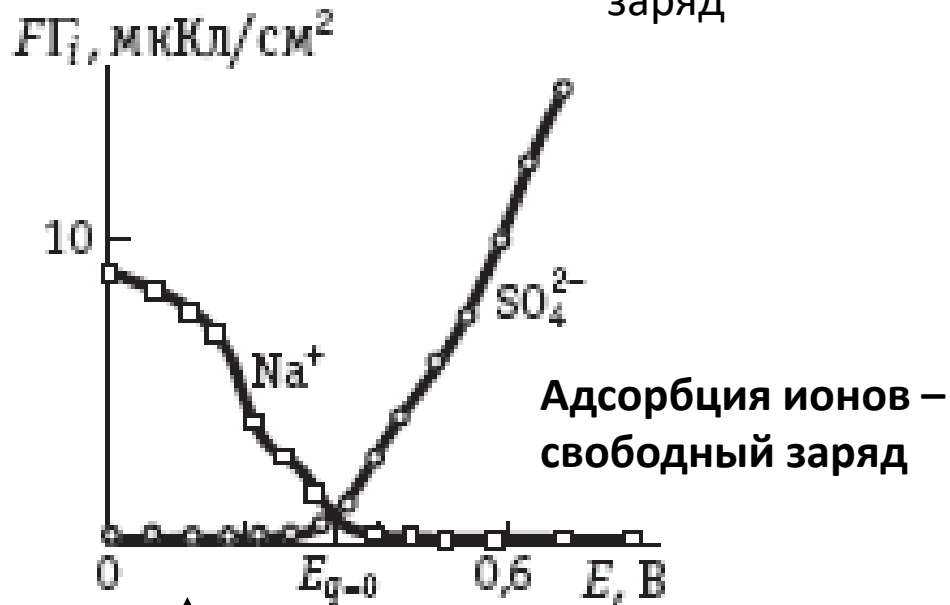


электропроводность



полный заряд $\longrightarrow \Delta Q = \Delta q \pm F \Delta A_i$

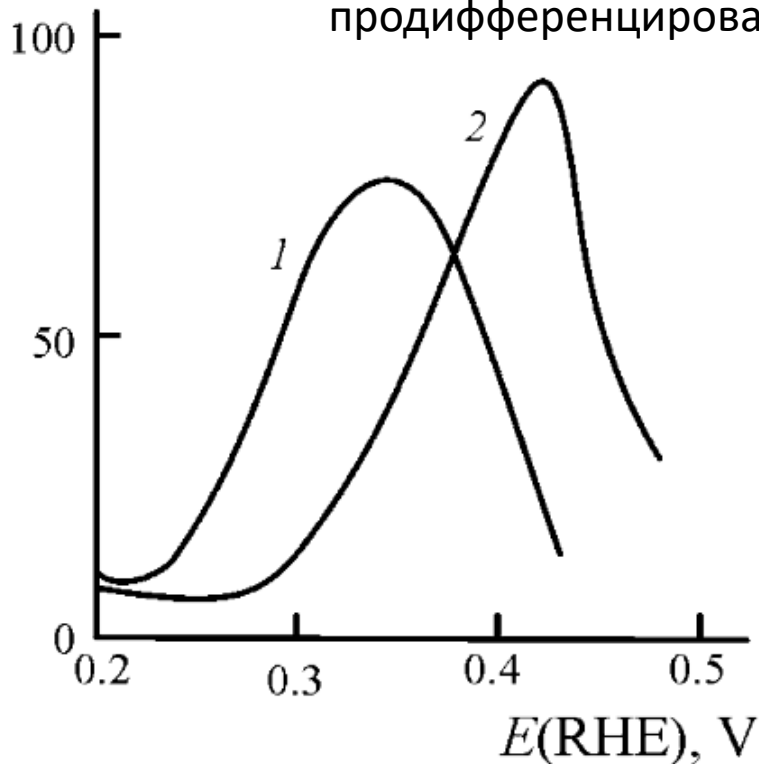
свободный заряд



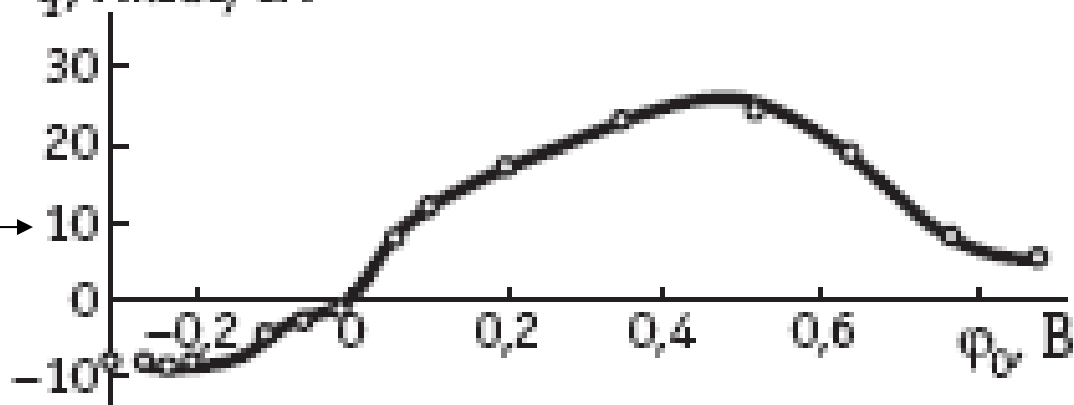
Метод радиоактивных индикаторов

Адсорбционный метод \longrightarrow

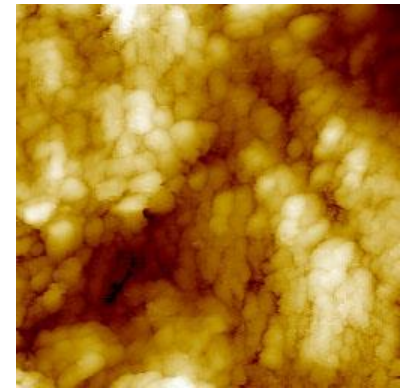
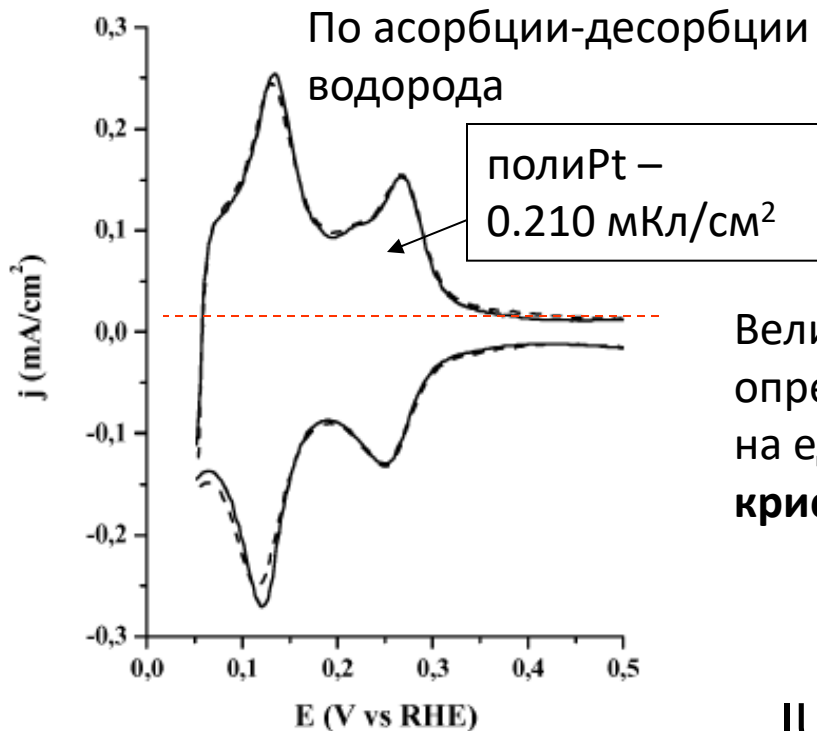
$C_f, \mu\text{F}\cdot\text{cm}^{-2}$ Что получится если продифференцировать:



$q, \mu\text{C}/\text{cm}^2$



Определение истинной поверхности *in situ*



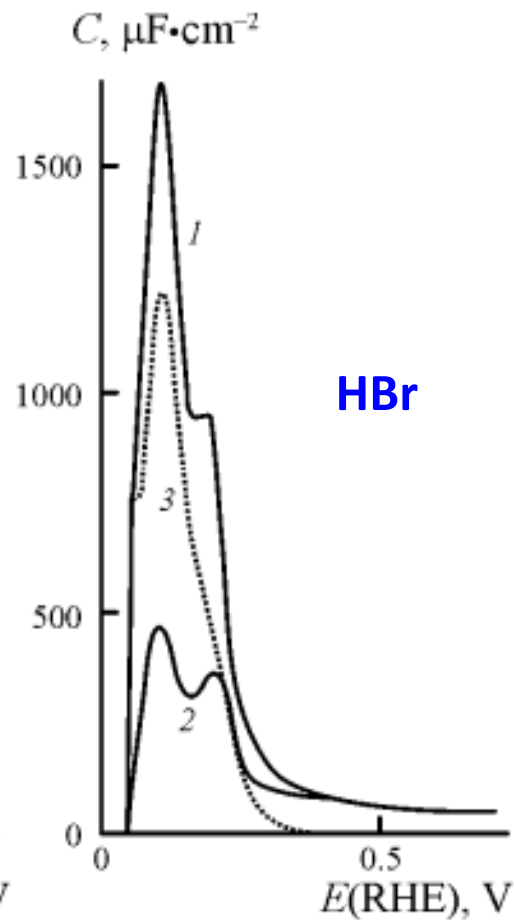
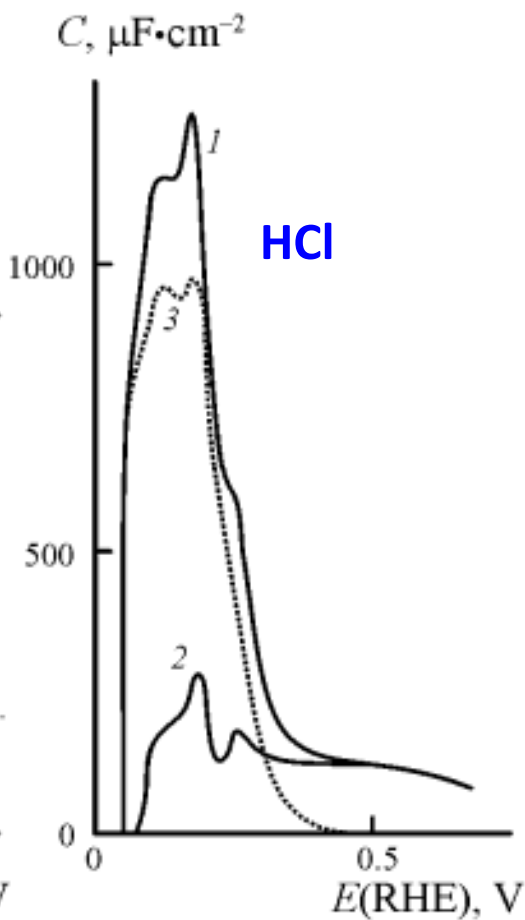
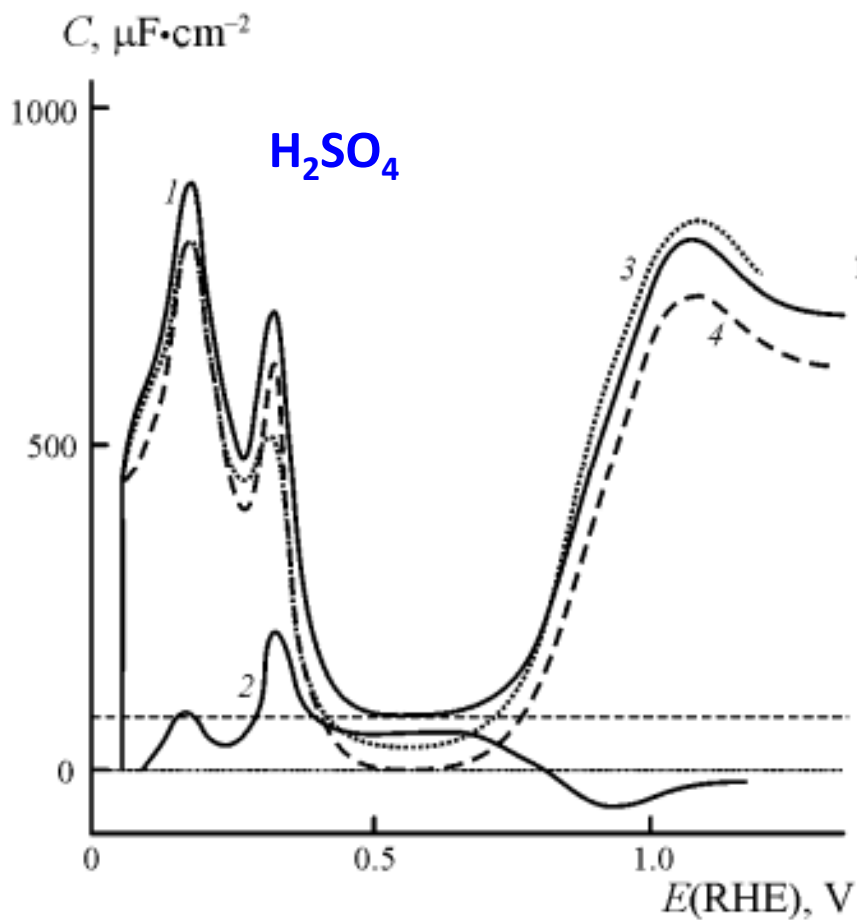
← 300 нм →

Величина удельного заряда определяется числом атомов на единице поверхности, то есть кристаллографией.

IUPAC: Pure Appl. Chem.63 (1991) 711

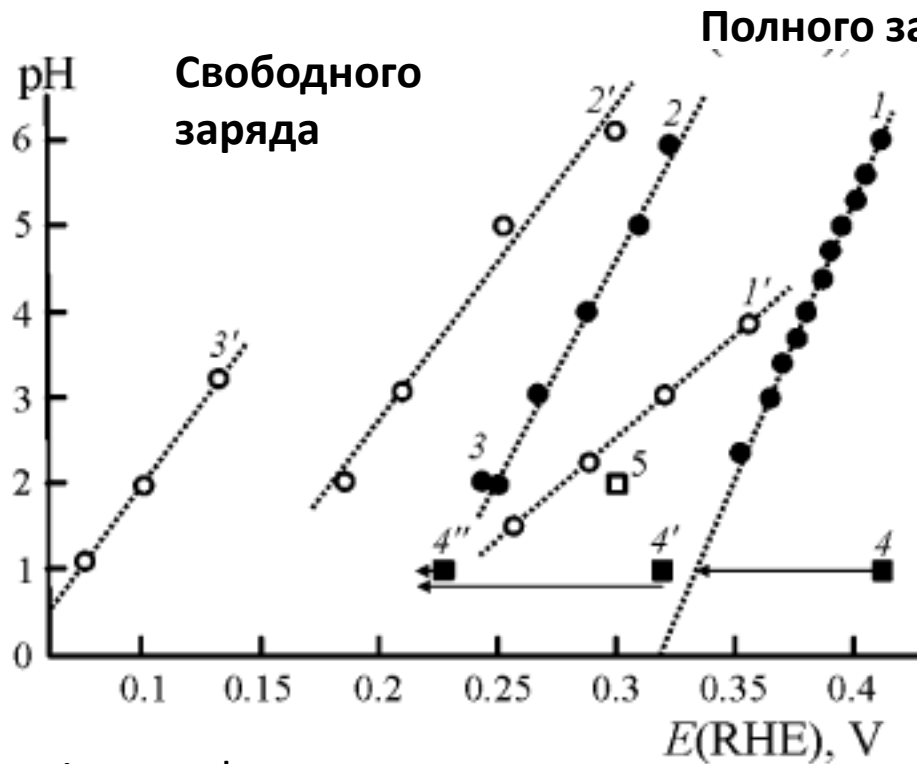
The validity of the method implies that the point where hydrogen adsorption is complete can be exactly identified, and that the coverage is completed before the rate of hydrogen evolution becomes significant. In addition, it rests on the assumption that there is a definite quantitative relation between the charge measured and the amount of substance deposited, i.e. total charge transfer takes place from the adsorbate to the metal. Finally, no alteration of the surface upon adsorption is assumed to take place. These assumptions are common also to methods 5 and 6.

Вклады адсорбции анионов и водорода в общую поляризационную емкость



Ток обмена образования адатомов (реакция Фольмера) $\sim 1 \text{ A}/\text{cm}^2$

Потенциалы нулевого заряда платины



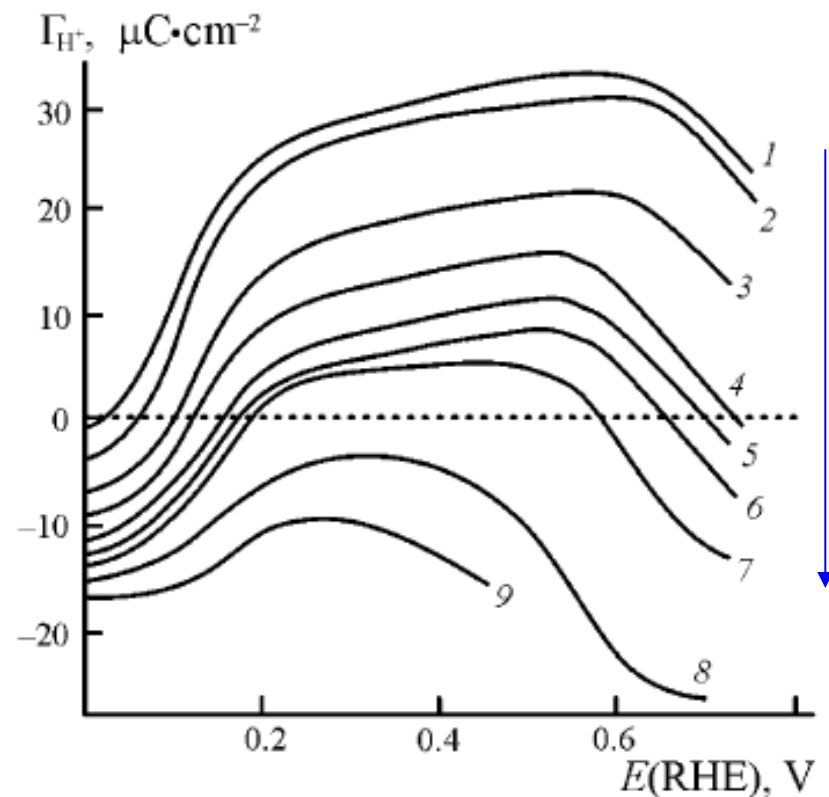
1 – сульфат

2 – хлорид

3 – бромид

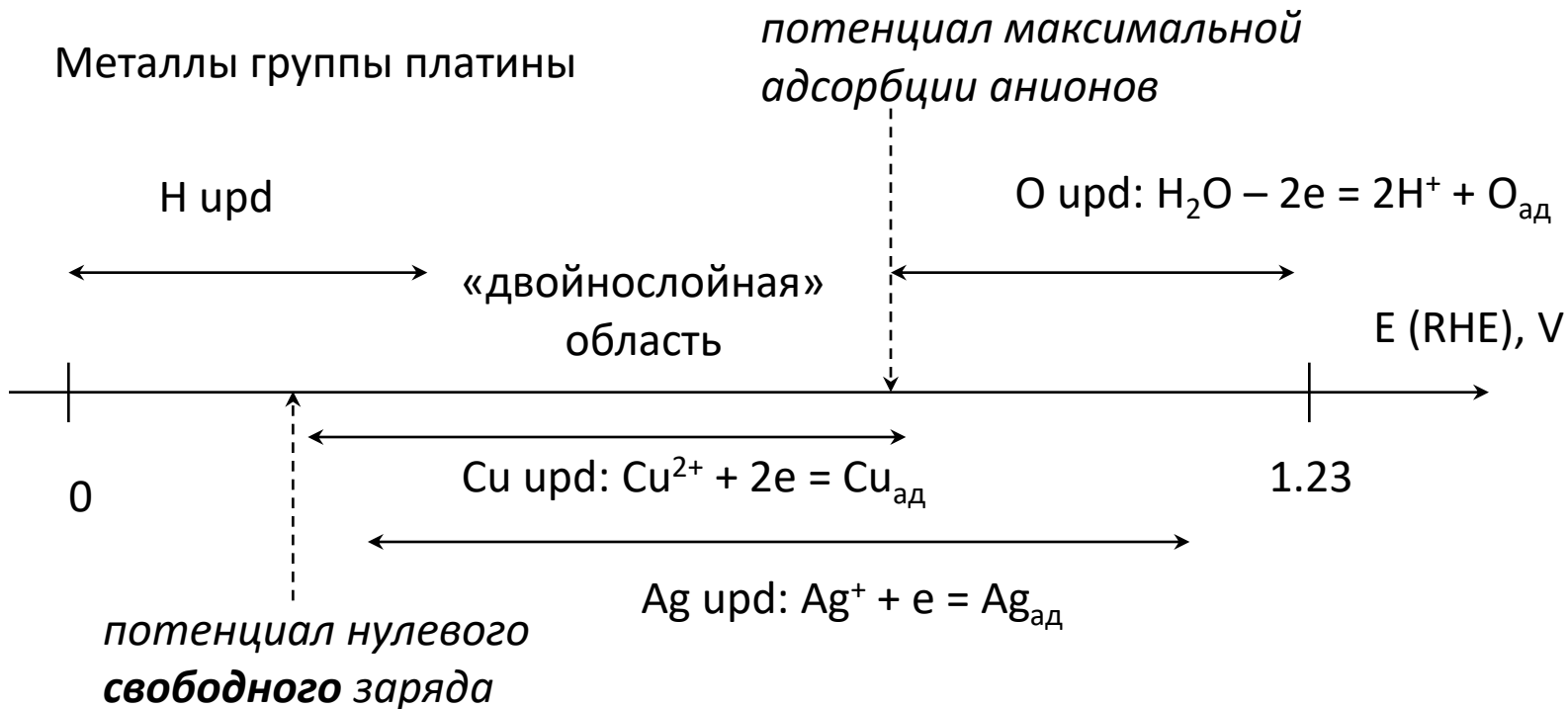
4 – перхлорат,
монокристаллическая Pt

Свободный заряд – зависимость от рН



Совершенно поляризуемые электроды - соадсорбция

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



RHE – reversible hydrogen electrode
(обратимый водородный электрод в том же растворе)

Металлы группы платины

потенциал максимальной адсорбции анионов

H upd

O upd: $\text{H}_2\text{O} - 2\text{e} = 2\text{H}^+ + \text{O}_{\text{ад}}$

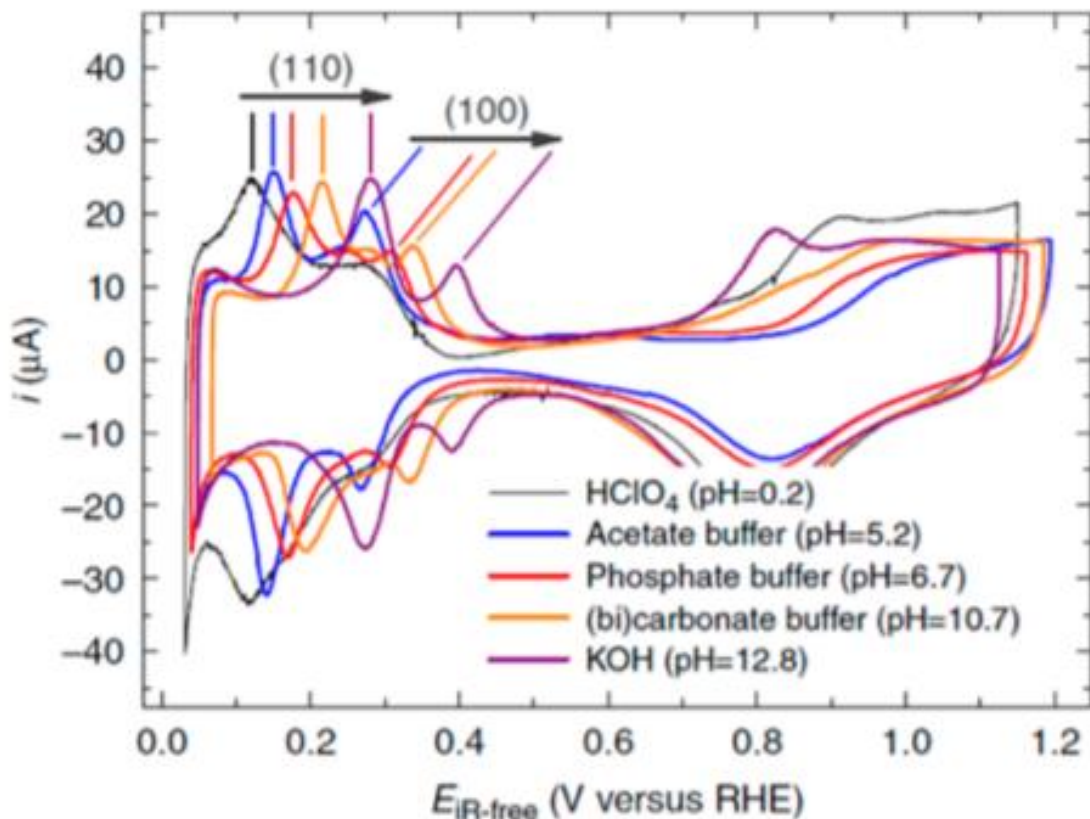
«двойнослойная»
область

E (RHE), V

0

Cu upd: $\text{Cu}^{2+} + 2\text{e} = \text{Cu}_{\text{ад}}$

1.23

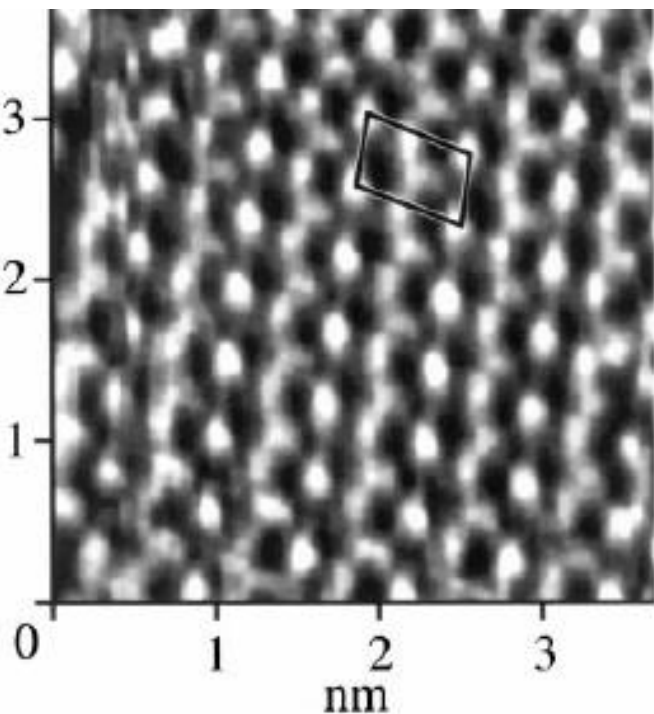


Так – только в кислоте, поскольку H upd и O upd pH-зависимы, а Cu upd не зависит от pH.

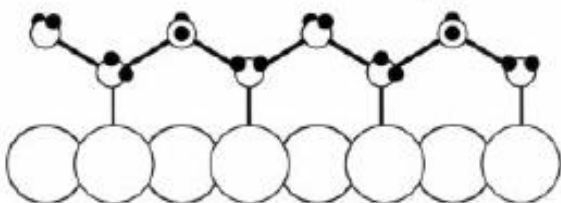
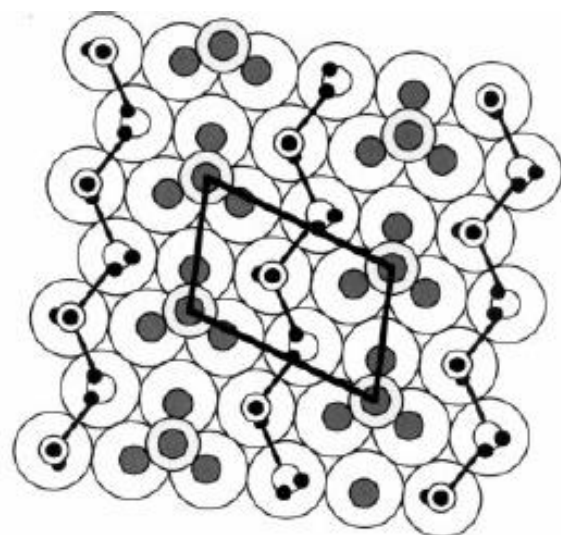
RHE – reversible hydrogen electrode (обратимый водородный электрод в том же растворе, SHE - 0.059pH)

С ростом pH сдвигаются H upd и O upd.

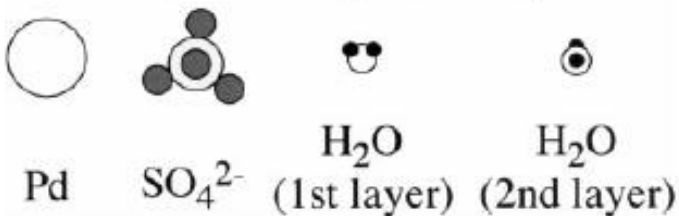
На отклик в области H upd влияет соадсорбция анионов



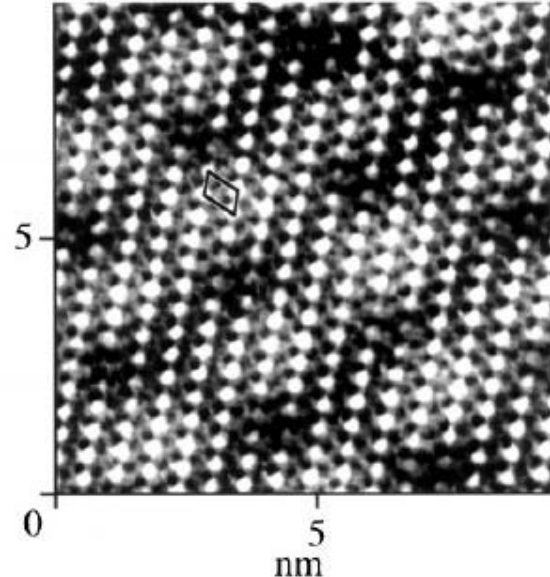
Pd(111)



water chain (side view)

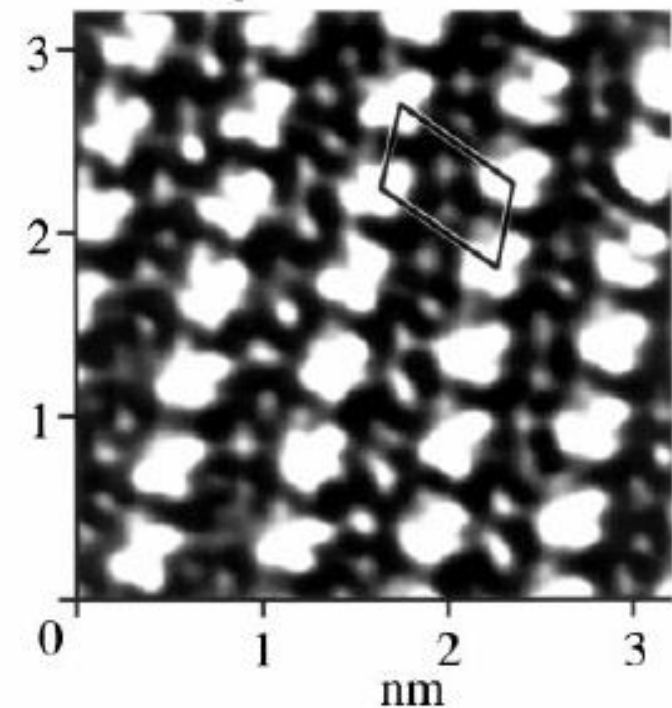


Cu/Pd(111) - монослой

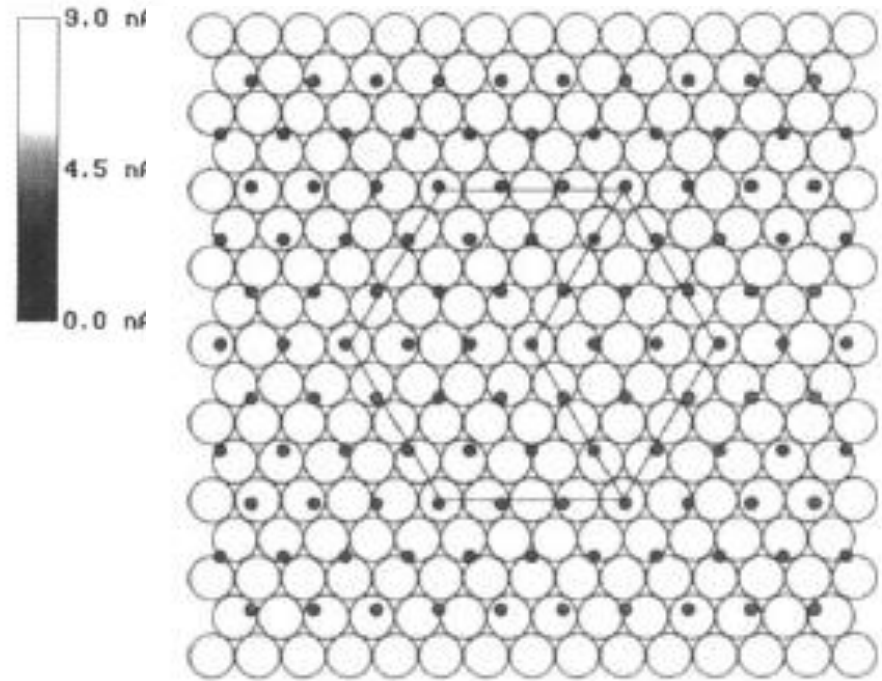
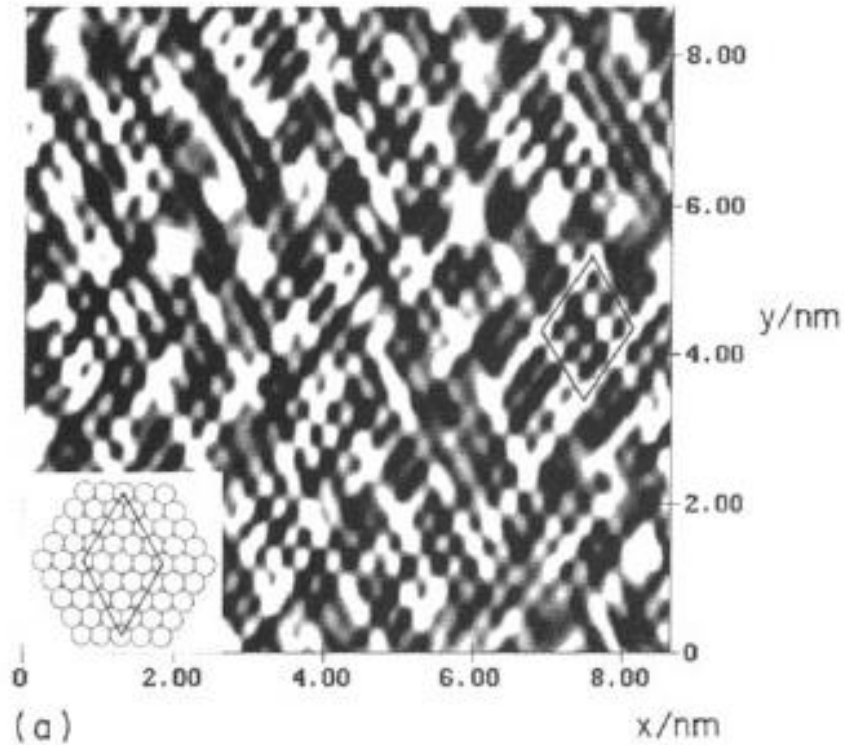


Сu - полислой

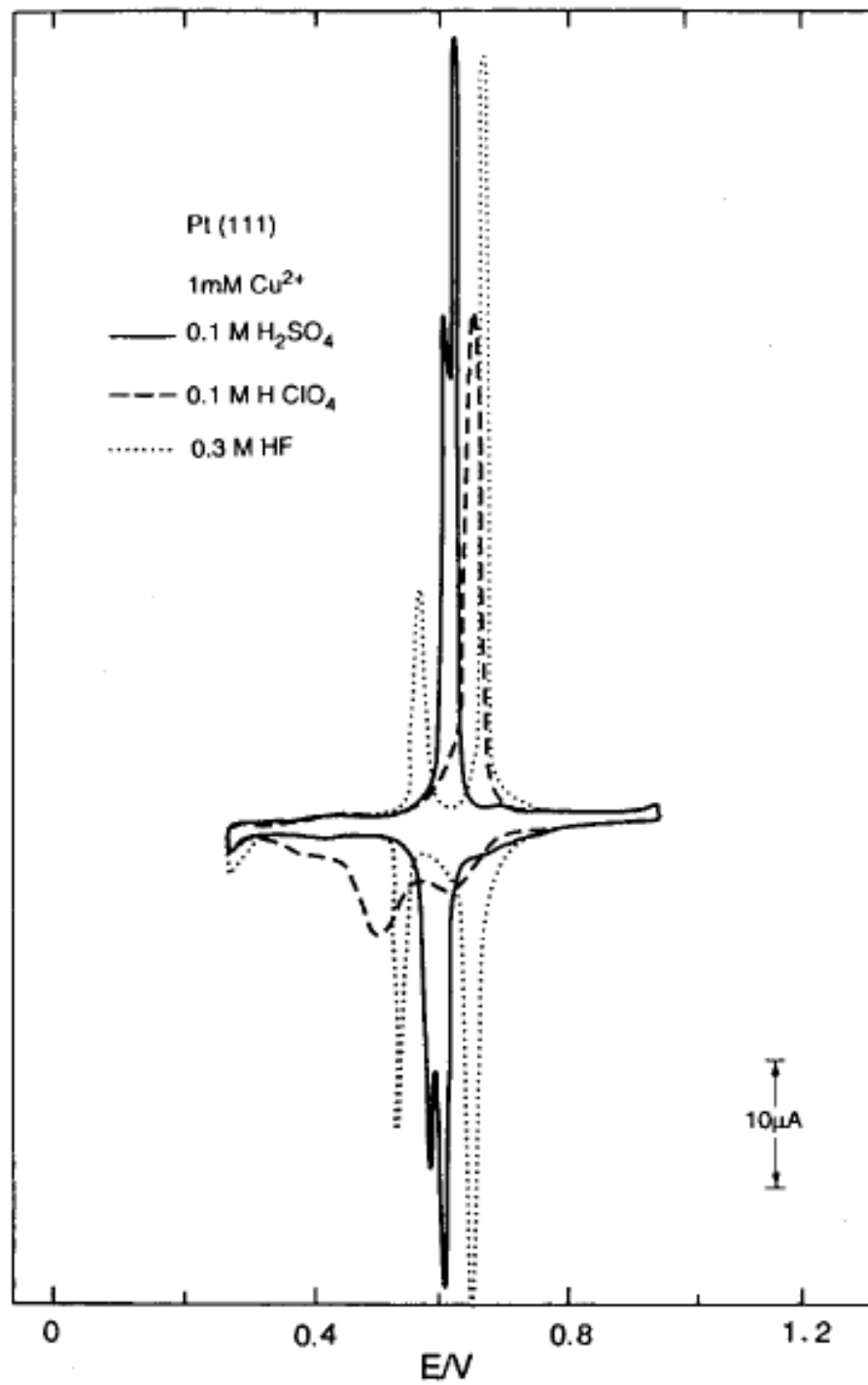
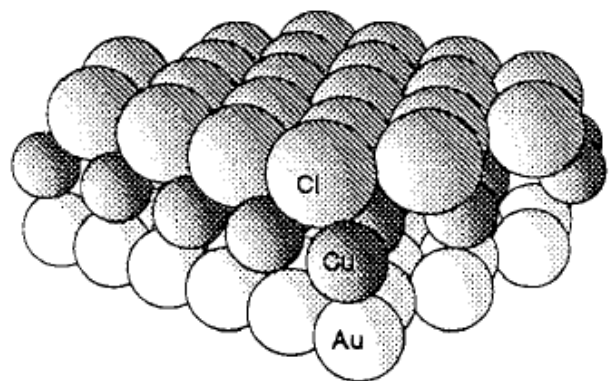
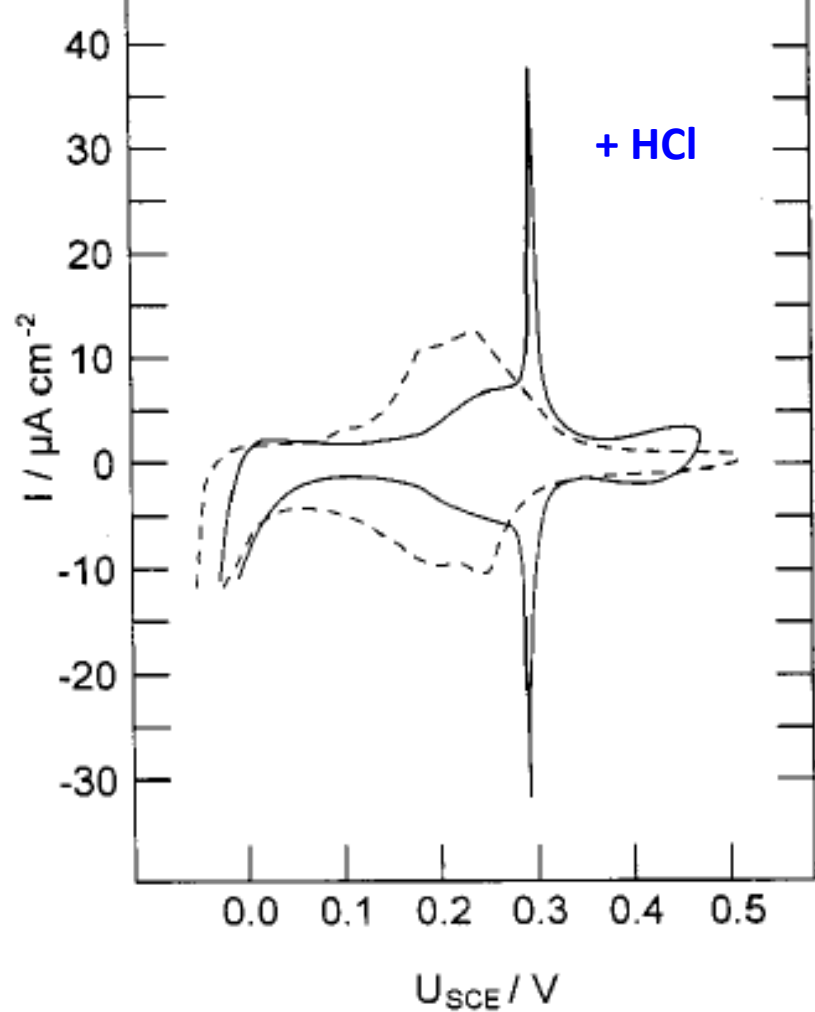
**Commensurated
adlayer**



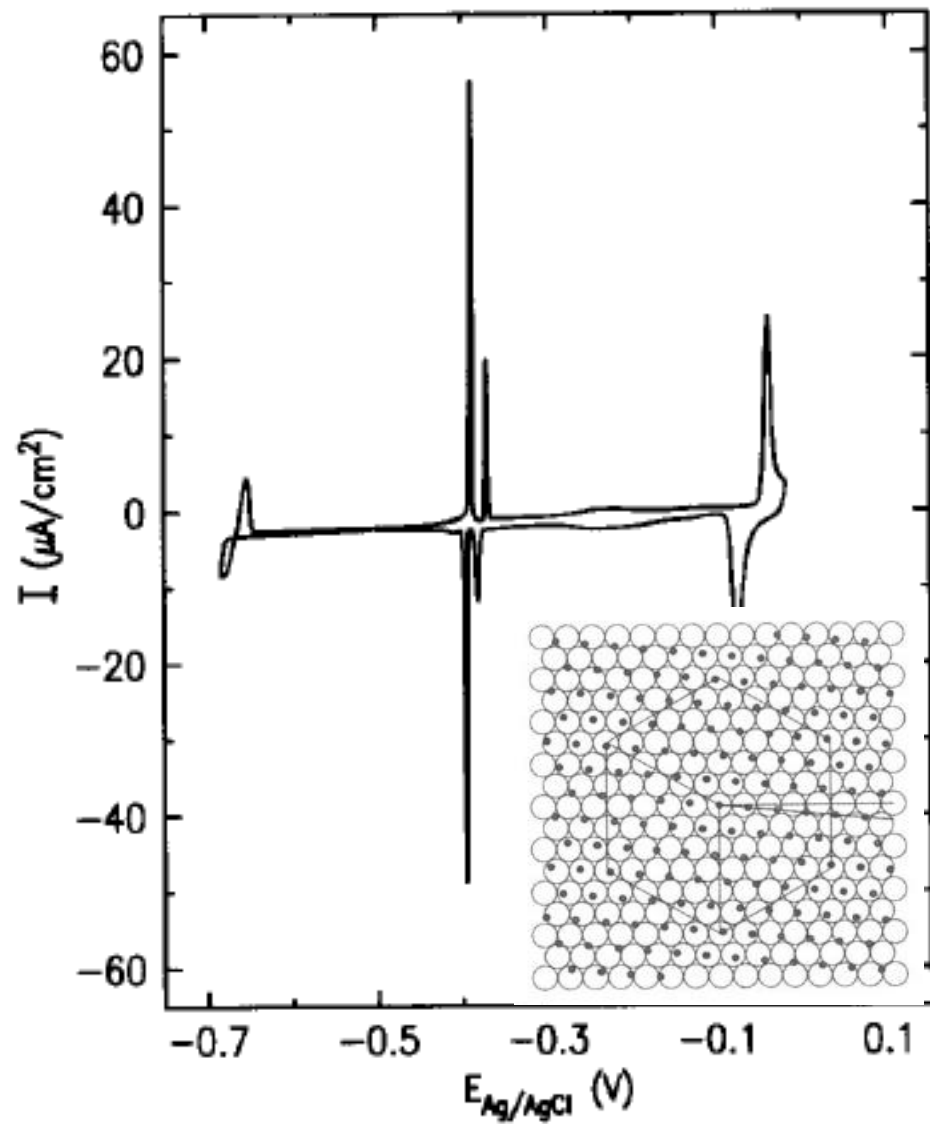
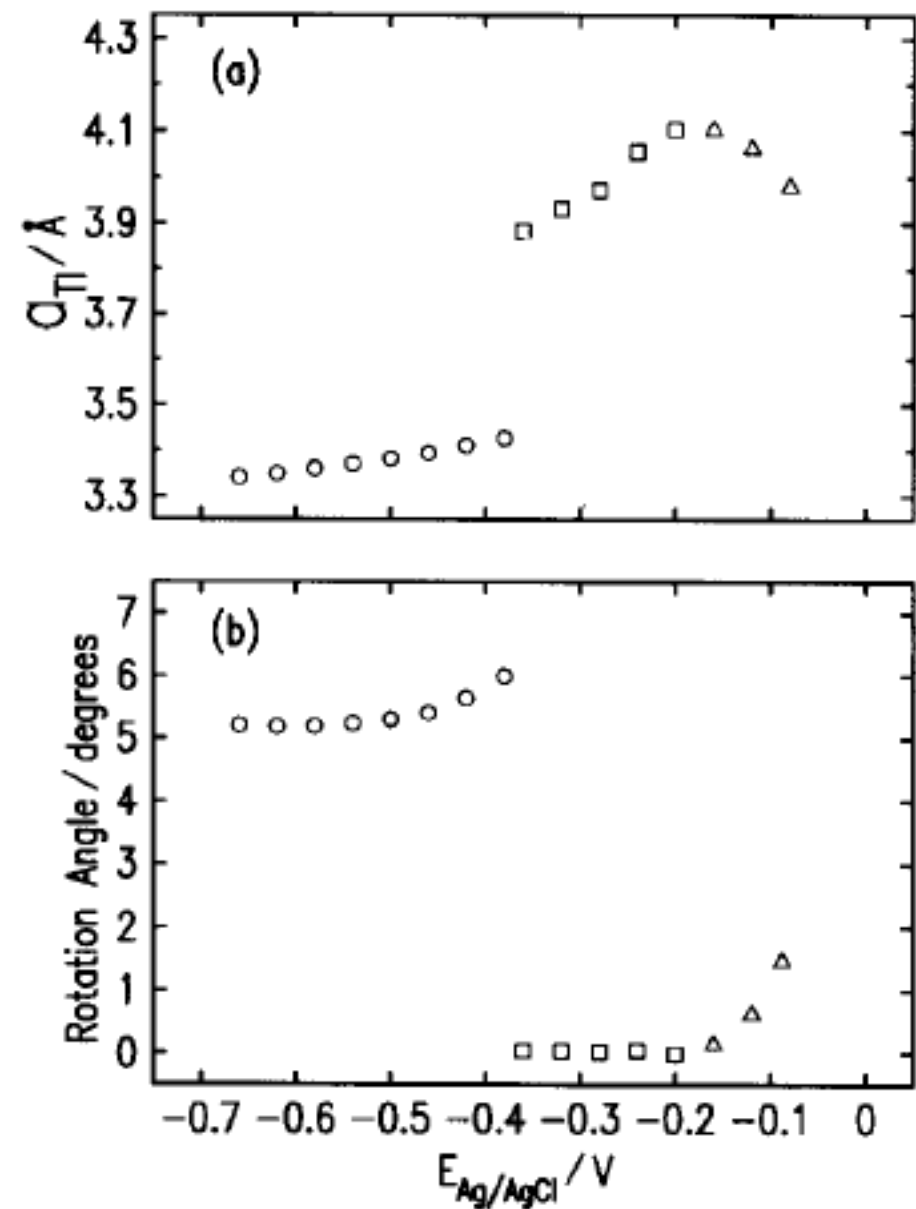
Incommensurated adlayer



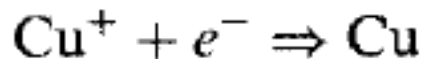
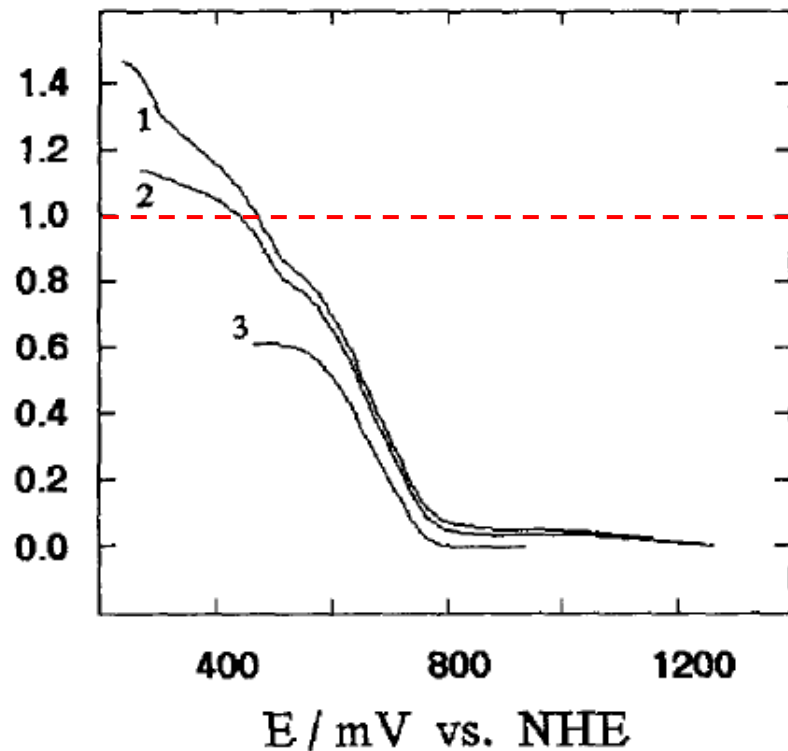
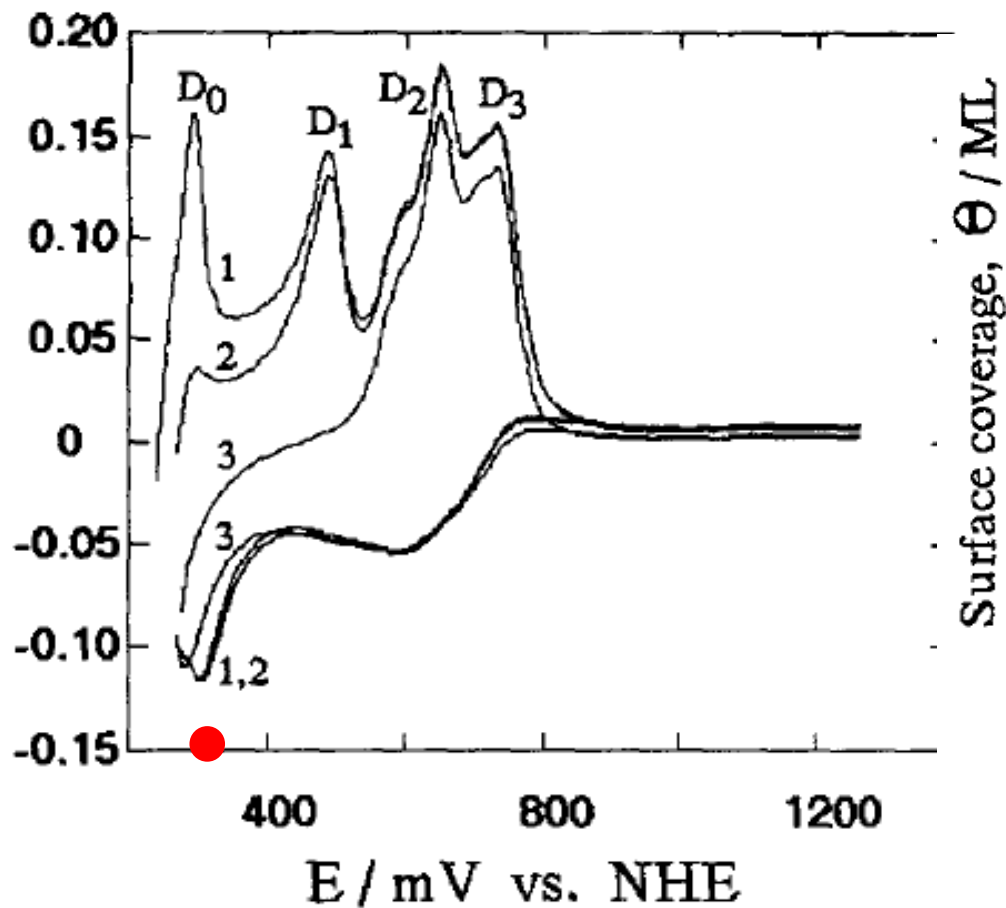
Phase ^a	Tl-Tl separation/Å		Rotation angle/deg		Tl coverage	
	STM	SXS	STM	SXS	STM	SXS
Rotated hexagonal	3.4	3.33	6	5.1	0.74	0.73
Aligned hexagonal	3.8	3.92	0	0	0.56	0.55
Low coverage hexagonal	–	3.92	0	1.5	–	0.5



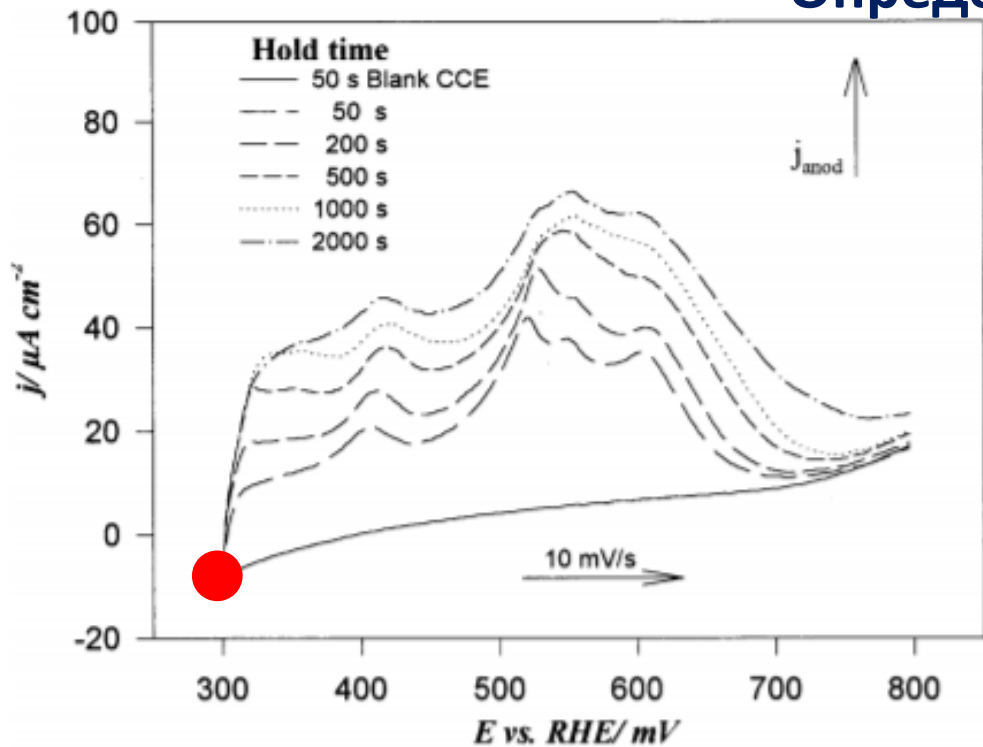
Соадсорбция с кислородом – «урд оксида» (адатомы TI)



Адаптомы меди – осложнения вблизи равновесного потенциала



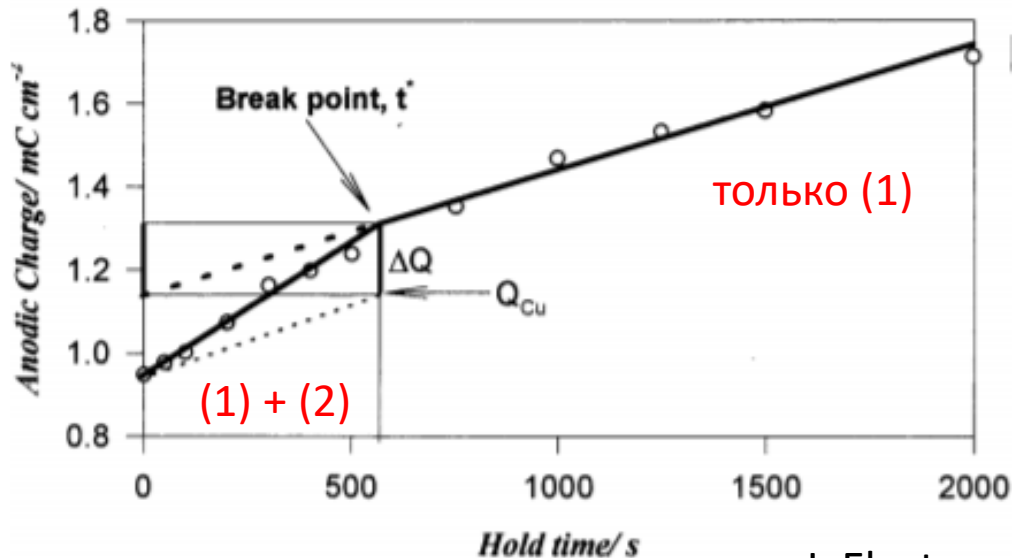
Определение истинной поверхности Pd/C, Cu upd



Зависимость от времени выдержки при потенциале катодного предела: ●

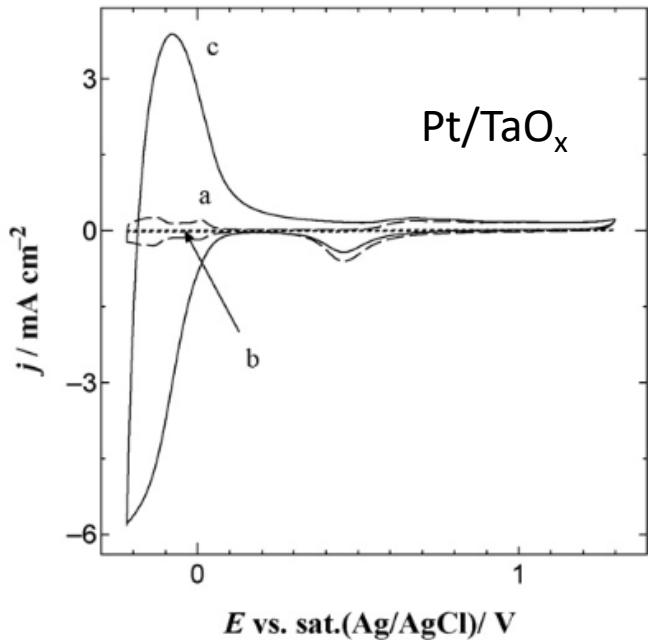
При этом потенциале:

- (1) накапливается Cu^+ в растворе,
- (2) постепенно достигается предельное заполнение адатомами.



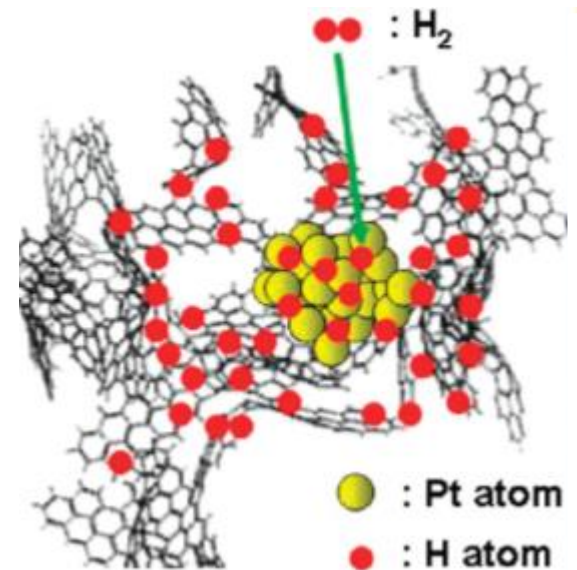
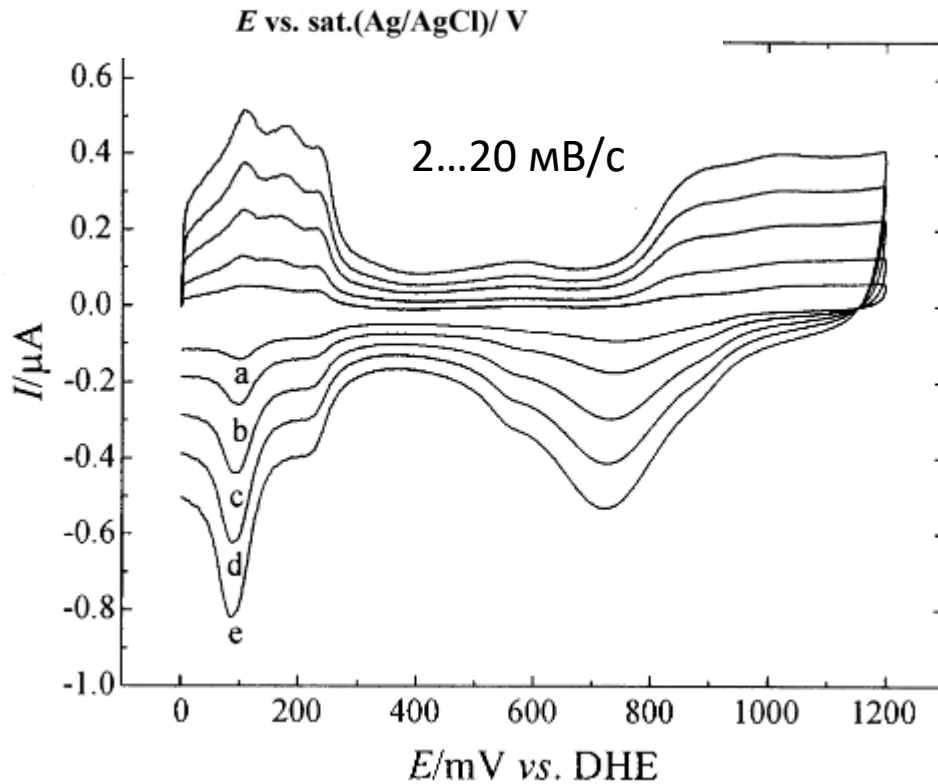
Для Pd нельзя определять поверхность по водороду, т.к. он сорбируется (образуется PdH_x).

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



Spill over – распространение адсорбата по инертной подложке.

Зависимость от скорости развертки определяется кинетикой поверхностной диффузии.



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:

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

Usually, Ag and Cu adatoms are used.

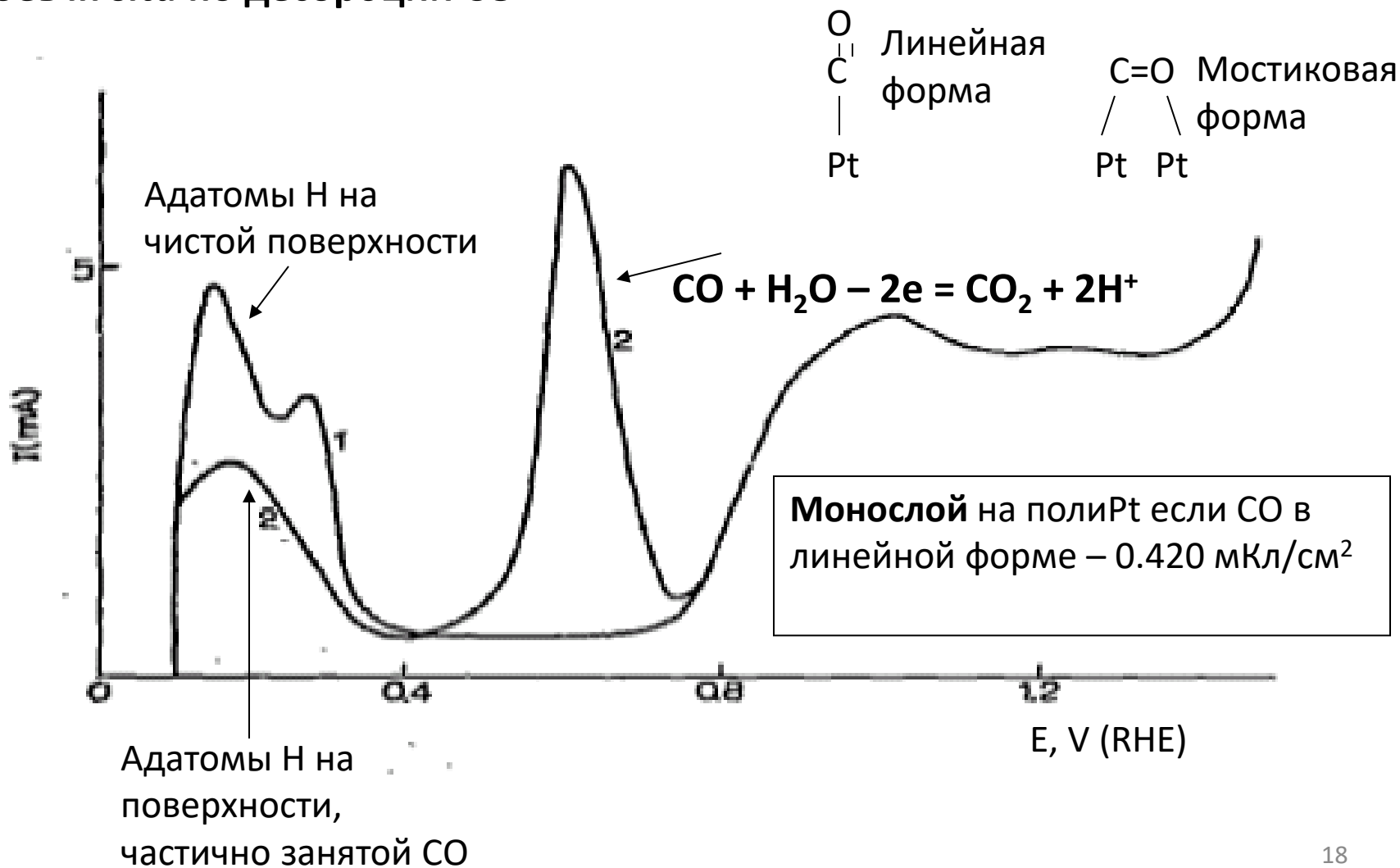
Pure Appl. Chem. 63 (1991) 711-734

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.

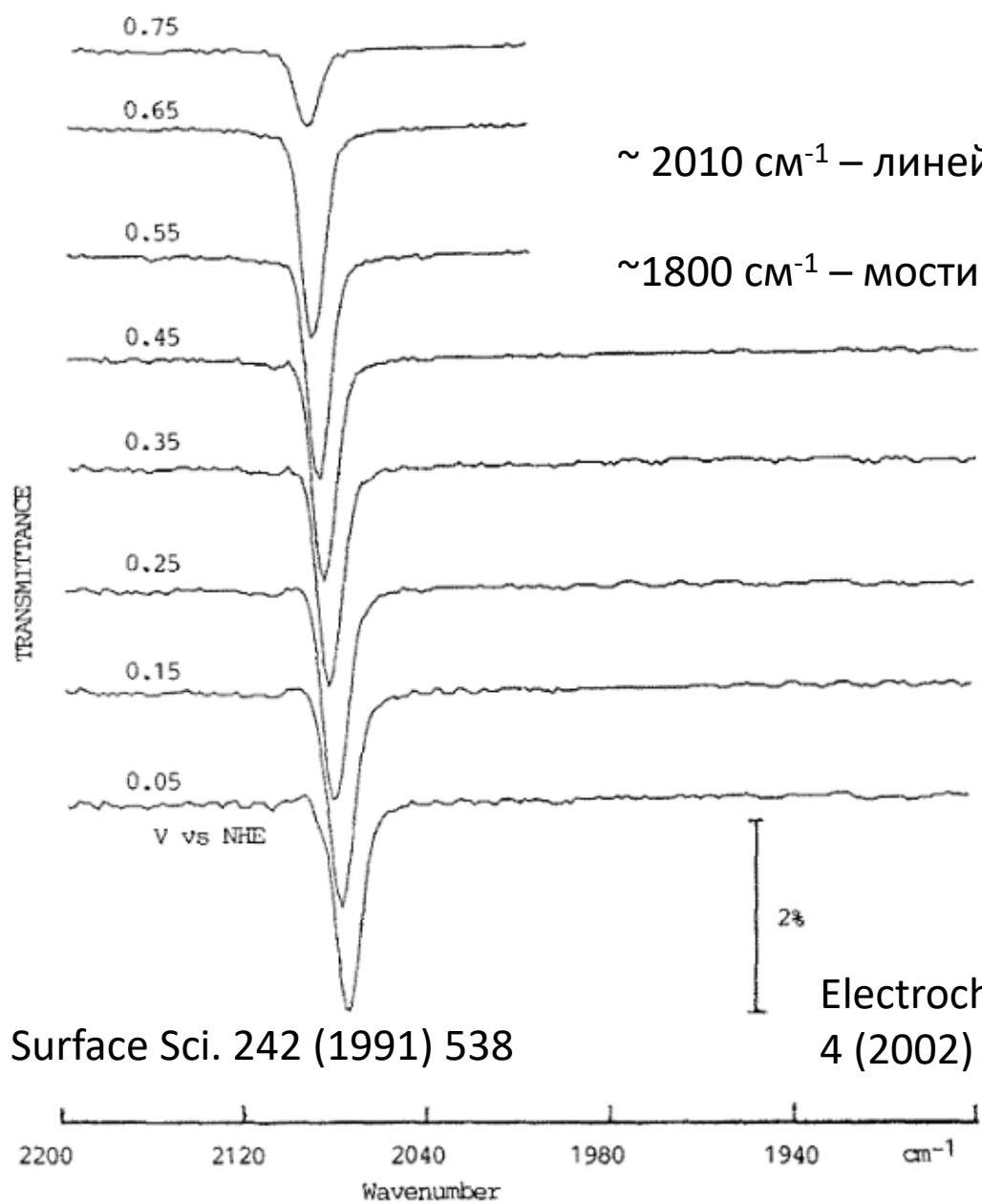
The calculation of Q_M^* for polycrystalline surfaces is based on empirical considerations. The same is also the case of single crystal faces for which the method gives strictly the number of surface active sites rather than the true surface area. The response of the single crystal face is however different 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.

Органические адсорбаты на металлах группы платины – **необратимая** деструктивная) **адсорбция**

Определение поверхности и состава смешанных адсорбционных слоев *in situ* по десорбции CO

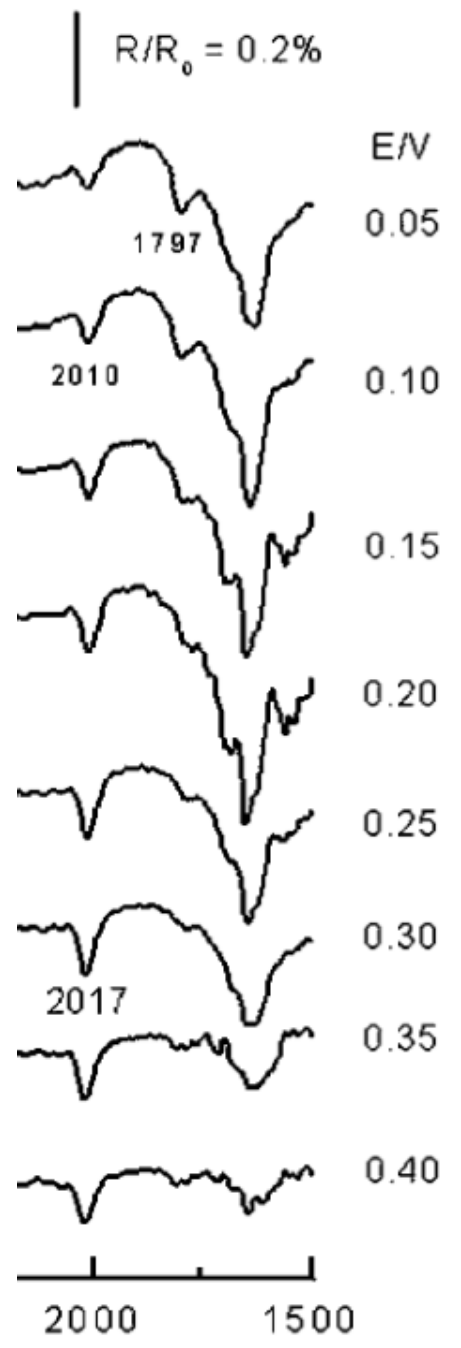


Валентное колебание CO на Pt(110), разные потенциалы



Surface Sci. 242 (1991) 538

Electrochem. Commun. 4 (2002) 959



2.10 Adsorption of probe molecules from solution

The method is usually applied to high surface area and/or disperse solids (refs. 84-86). While ionic species are used as probe species in previous methods, neutral compounds are essentially used here. The amount of adsorbate may be detected directly or indirectly using electrochemical or non-electrochemical techniques.

2.10.1 Principles. A probe molecule is adsorbed on the solid in solution and the extent of adsorption is determined analytically from the depletion in the solution. Dyes, surfactants, fatty acids and polyalcohols are generally suggested as suitable probe molecules (refs. 81,82). From the (apparent) monolayer surface concentration the surface area of the solid is derived by the equation:

$$A = \Gamma_s N_A A^* \quad (10.1)$$

where Γ_s is the saturation coverage in mol cm⁻² and A^* is the projected area assigned to one adsorbed probe molecule.

In the electrochemical variant, for instance, CO and I₂ have been used as probe molecules (refs. 45,89-91). A monolayer of atomic iodine is assumed to form in the case of I₂ adsorption. The amount of adsorption is determined from the charge required to anodically oxidize the adsorbate (anodic stripping).

The electrochemical detection of the adsorbate by "anodic stripping" (in the case of CO and I₂) suffers from the same shortcomings as the methods based on H, O and metal adsorption (methods 4 to 6) with the additional problem that the "background charge" usually includes processes of surface oxidation which may be affected by the presence of the adsorbate. The surface stoichiometry of the adsorbed layer has been found to depend on the metal nature and on the crystallite size in the case of CO (ref. 45). The assumption of a close-packed monolayer of unassociated atoms of iodine or of CO may not be straightforwardly extensible to all systems.