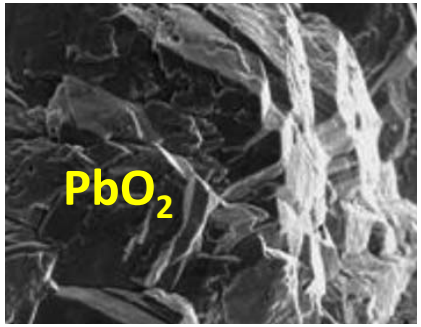
5 - Бинарные

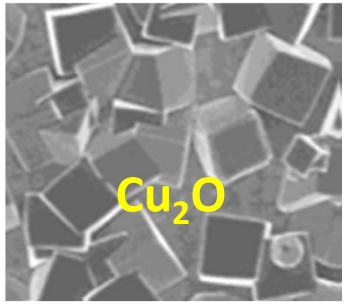
Анодая и катодная **электрокристаллизация оксидов**. Зависимость стехиометрии оксида от потенциала. Электрохимически индуцированное осаждение оксидов, индуцирующие реакции (восстановление нитрата, перекиси, кислорода). Возможности эпитаксии.

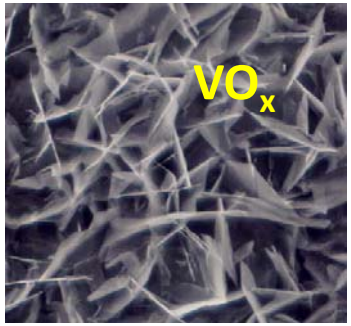
Осаждение бинарных полупроводников. Одно- и двухстадийные схемы осаждения. Процессы восстановления кислородных соединений S, Se, Te. Побочные процессы.

Необходимые условия:

- минимум две степени ненулевых степени окисления;
- среда, в которой соответствующие соединения имеют существенно разную растворимость;
- проводимость осаждаемого оксида.



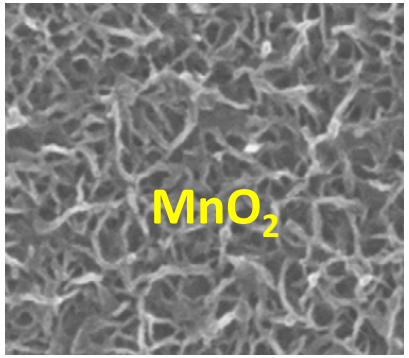


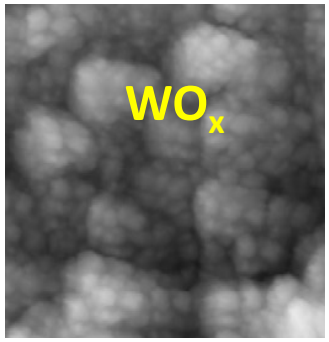


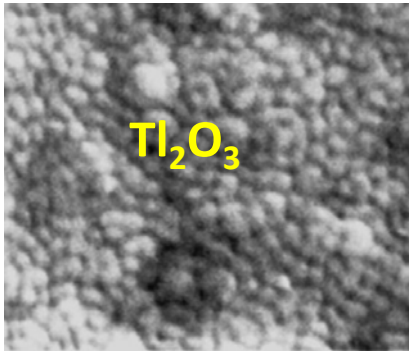
Анодная электрокристаллизация

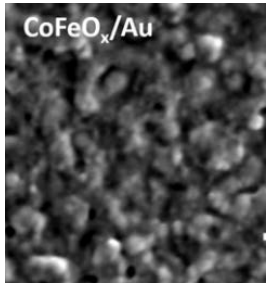
$$[M(OH)_x(H_2O)_y]^{z+}$$

Катодная электрокристаллизация









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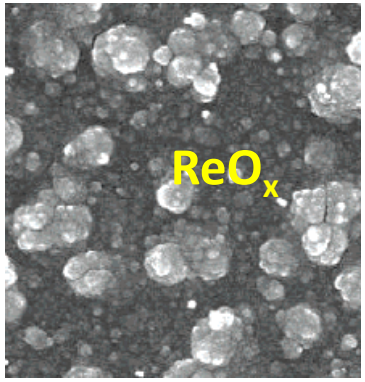


...

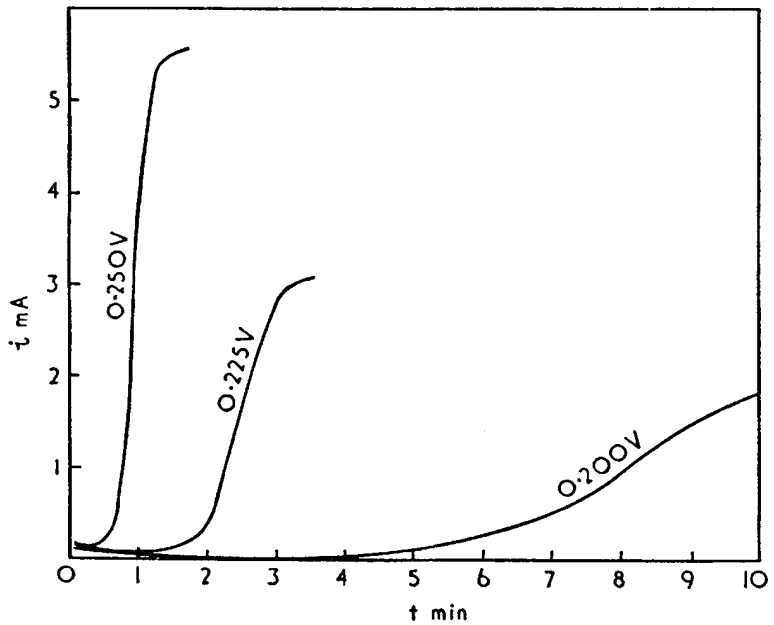
THE ANODIC OXIDATION OF SOLUTIONS OF PLUMBOUS SALTS

PART 1.—THE KINETICS OF DEPOSITION OF α-LEAD DIOXIDE FROM ACETATE SOLUTIONS

Trans. Faraday Soc.
54 (1958) 1370-1381

By M. Fleischmann and (Miss) M. Liler

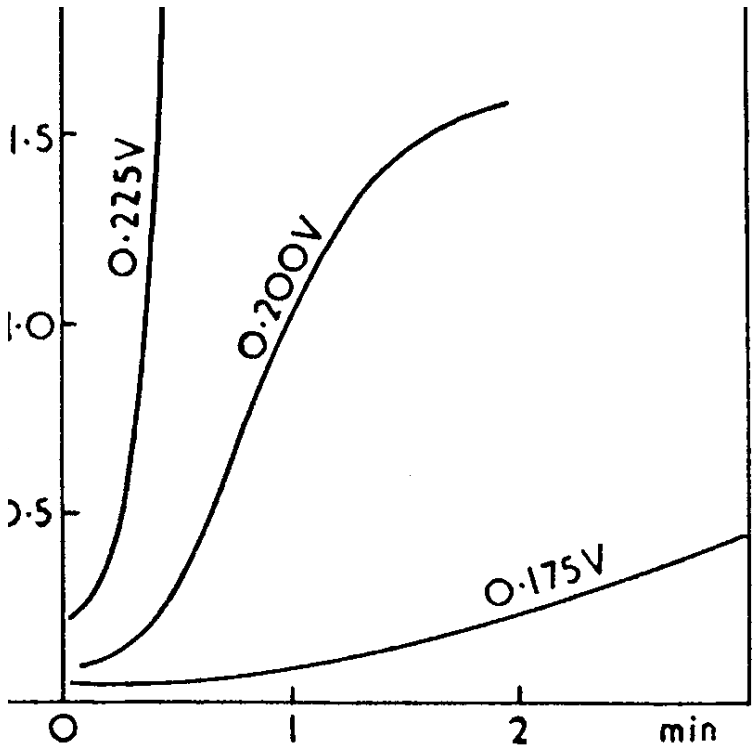
$$Pb^{2+} + OH_{ads} + OH^- - e \rightarrow Pb(OH)_2^{2+} \rightleftharpoons PbO_2 + 2H^+,$$

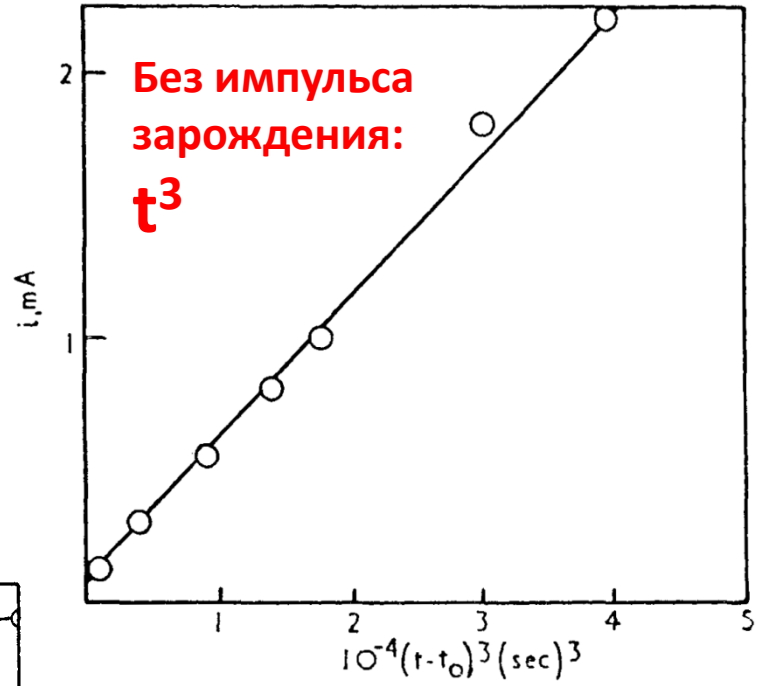


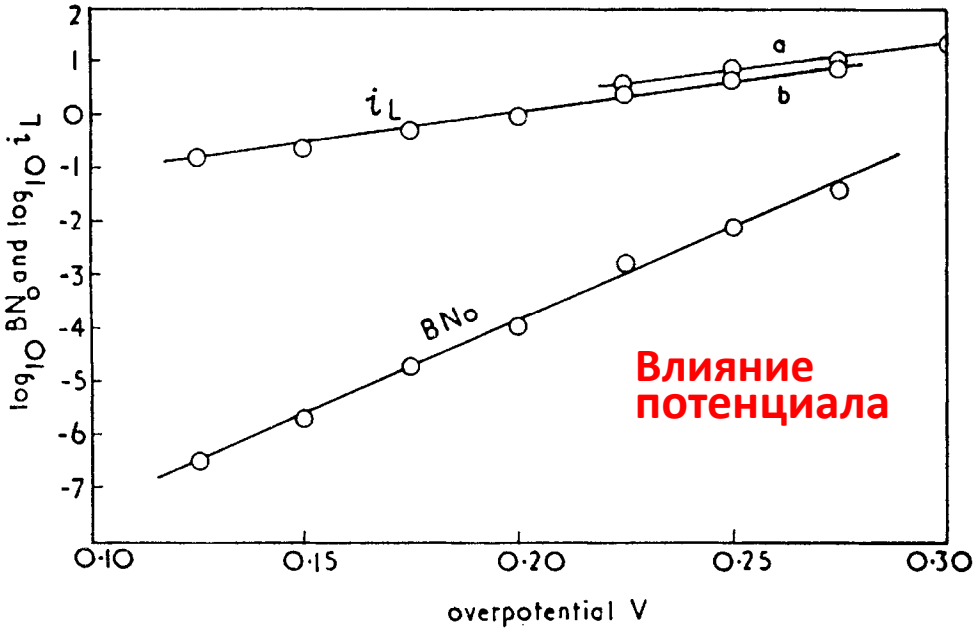
$$N = A't,$$

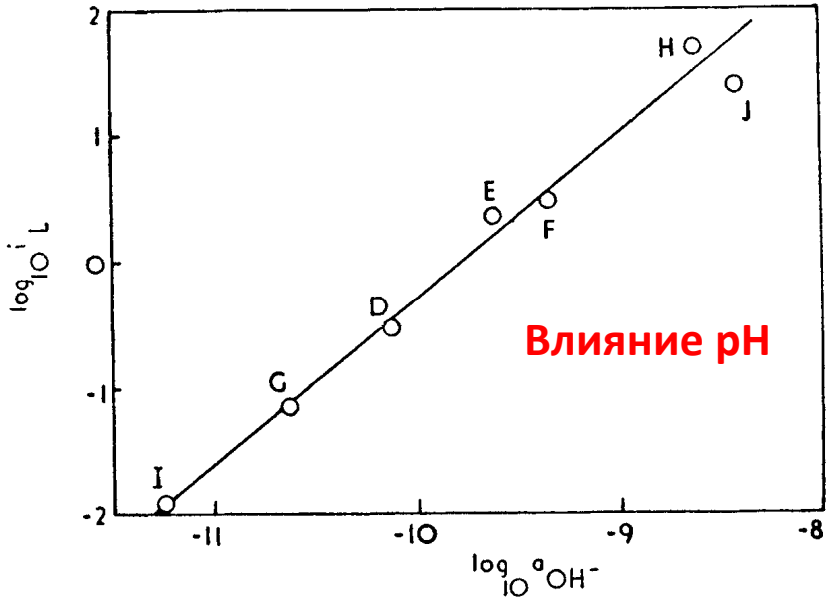
$$i = A'Bt^3/3 \text{ A cm}^{-2}$$

0.1 с
при 0.4 В



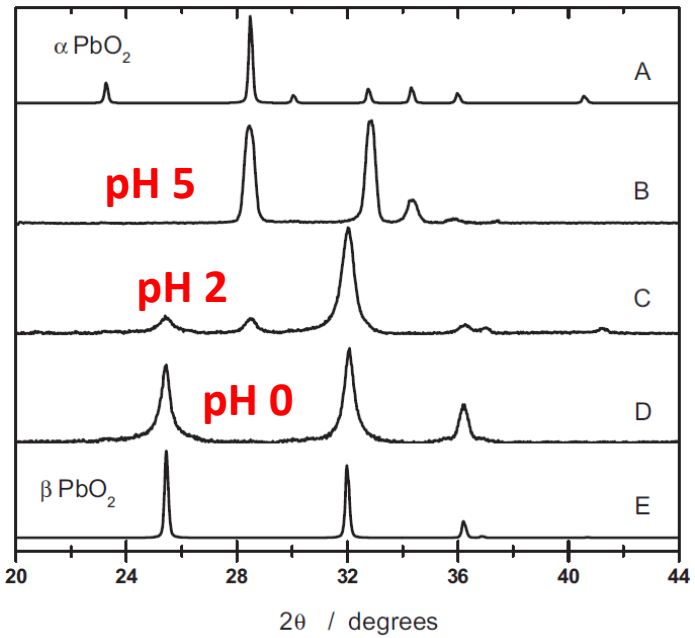






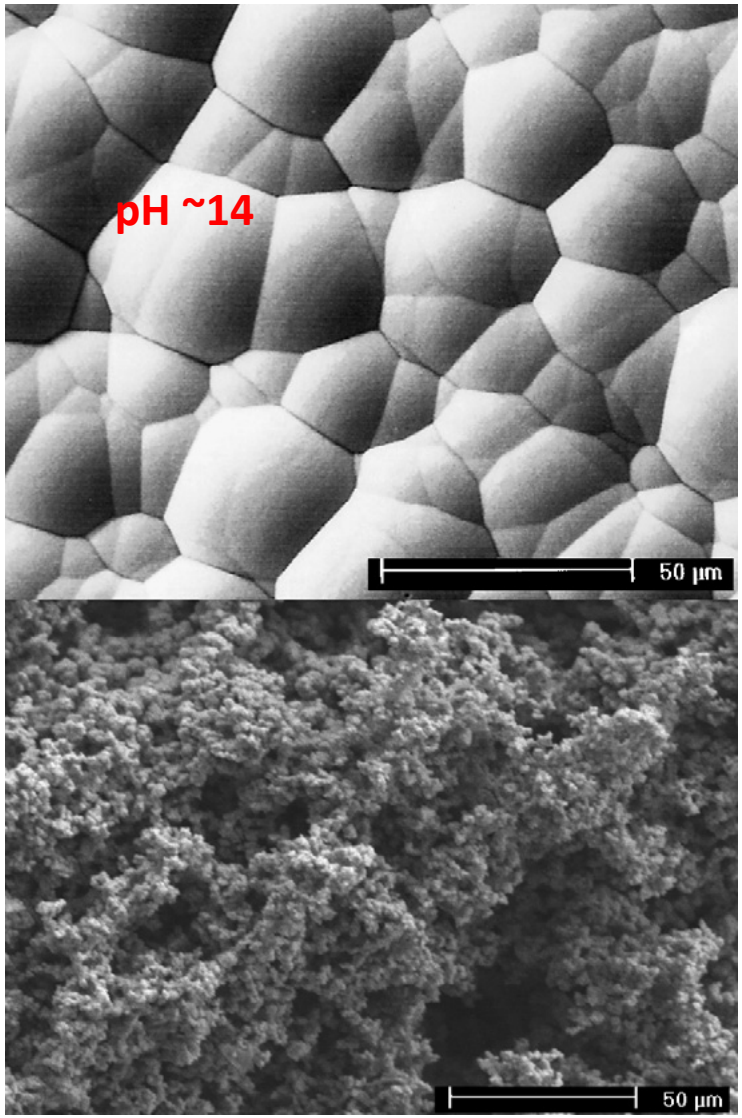
+ уствновлены условия формирования

α- и β-модификаций



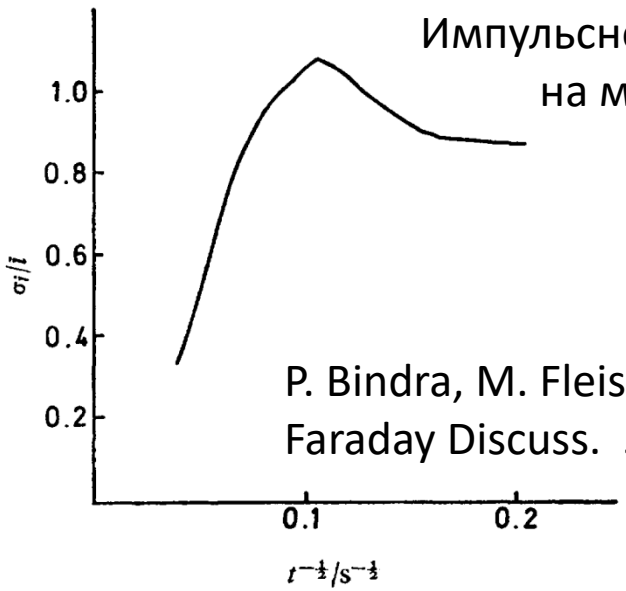
P. Perret et al., J. Electrochem. Soc. 156 (2009) A645-A651

Электрофоретическое соосаждение, дополнительные центры нуклеации



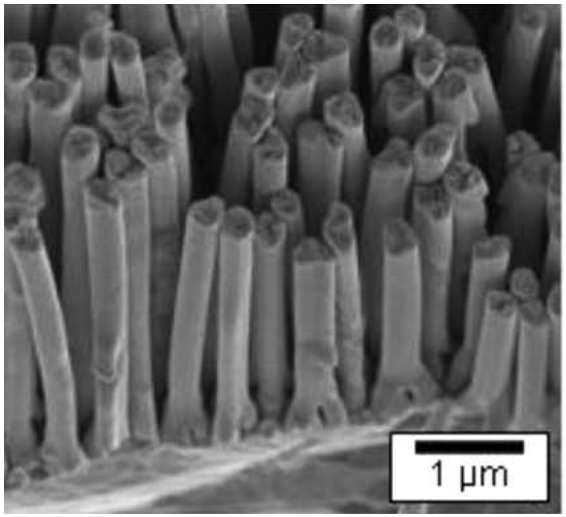
S.Cattarin , M. Musiani, Electrochim. Acta, 52 (2007) 2796–2805

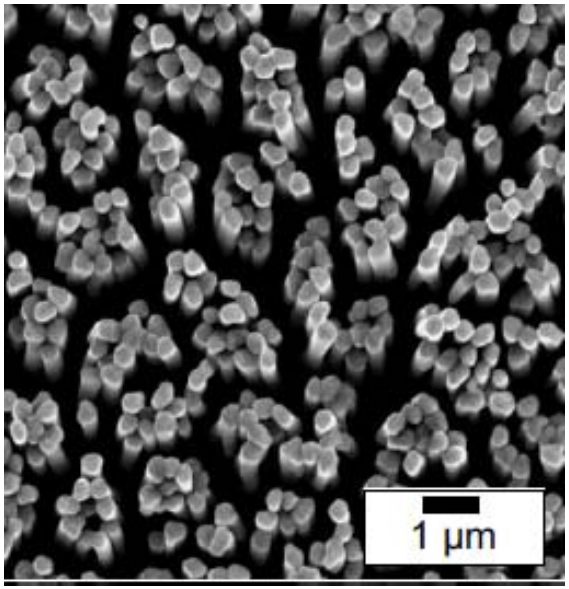
Импульсное зарождение на микроэлектроде ($5*10^{-6}$ см^2).



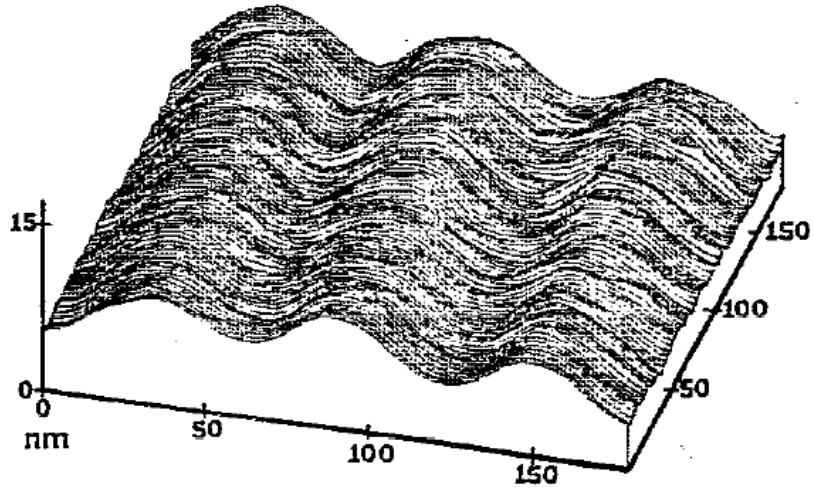
P. Bindra, M. Fleishmann et al., Faraday Discuss. 56(1973)180-198

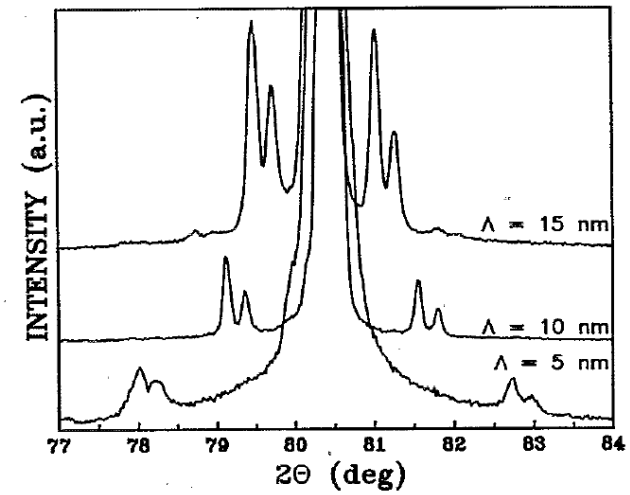
Наноструктуры на основе PbO_2



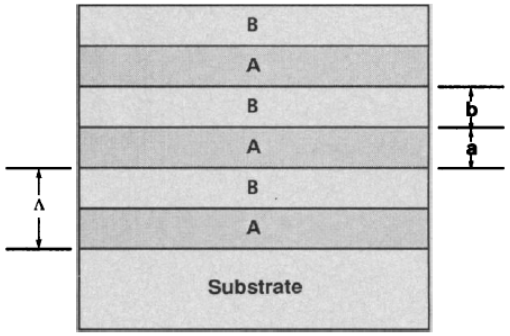


P. Perret et al.,
J. Electrochem. Soc.
156 (2009) A645-A651





$(Pb, Tl)O_x$



J. Switzer et al.:
Science 247 (1990) 444-446;
Appl. Phys. Lett. **63** (1993)
1501 -1503.

Kinetics of Electrodeposition of γ-Manganese Dioxide

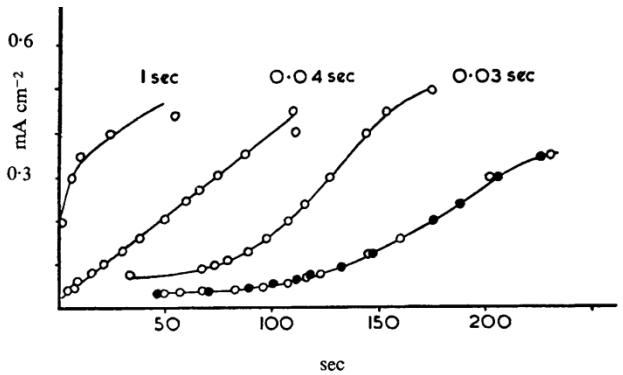
Trans. Faraday Soc.
58 (1962) 1865-1877

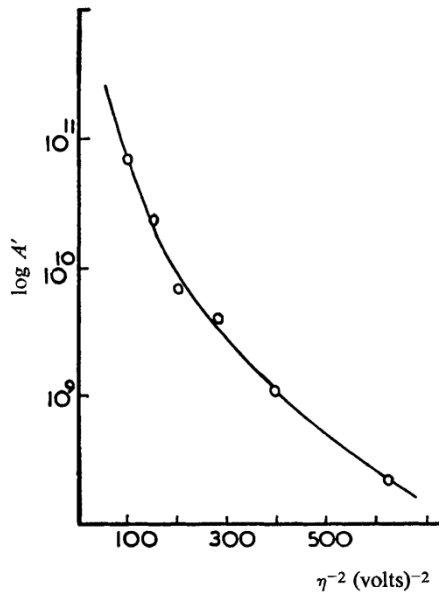
By M. Fleischmann, H. R. Thirsk and I. M. Tordesillas

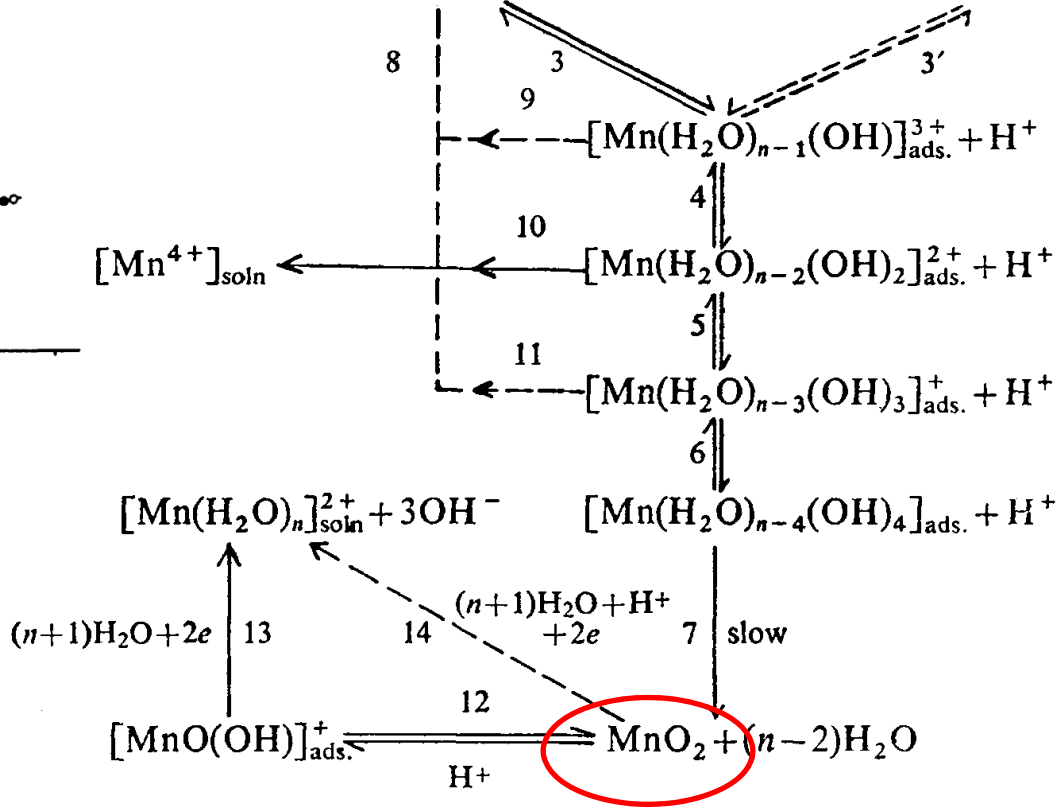
$$[Mn(H_2O)_n]^{2+}_{soln} \overset{1}{\rightleftharpoons} [Mn(H_2O)_n]^{3+}_{ads.} + e$$

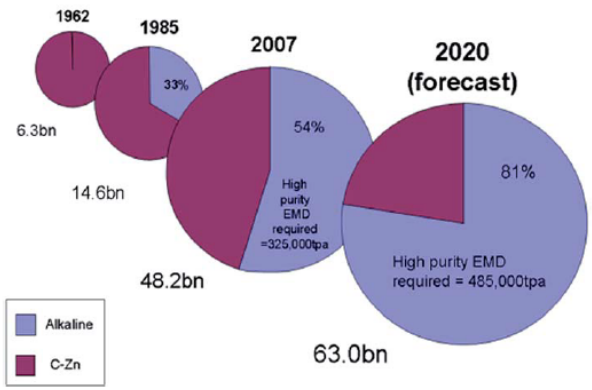
$$[Mn(H_2O)_n]^{3+}_{ads.} + [Mn(H_2O)_n]^{3+}_{ads.} \overset{2}{\rightleftharpoons} [Mn(H_2O)_n]^{2+}_{soln} + [Mn(H_2O)_n]^{4+}_{ads.}$$

$$[Mn(H_2O)_n]^{2+}_{soln} \overset{1'}{\rightleftharpoons} [Mn(H_2O)_n]^{4+}_{ads.} + 2e$$





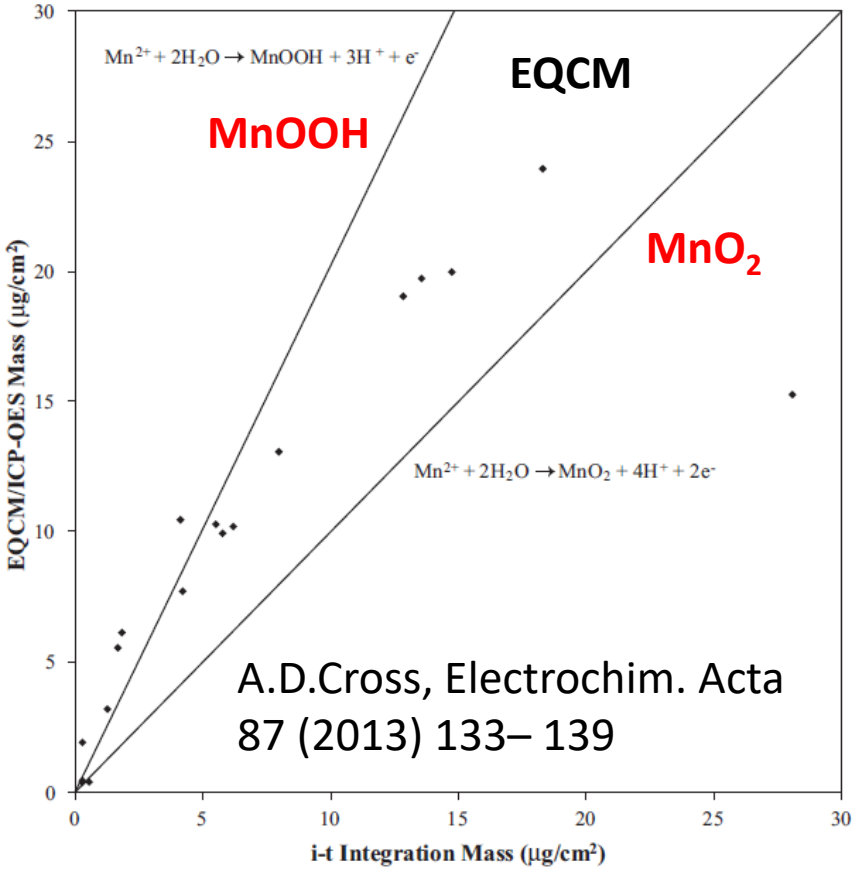




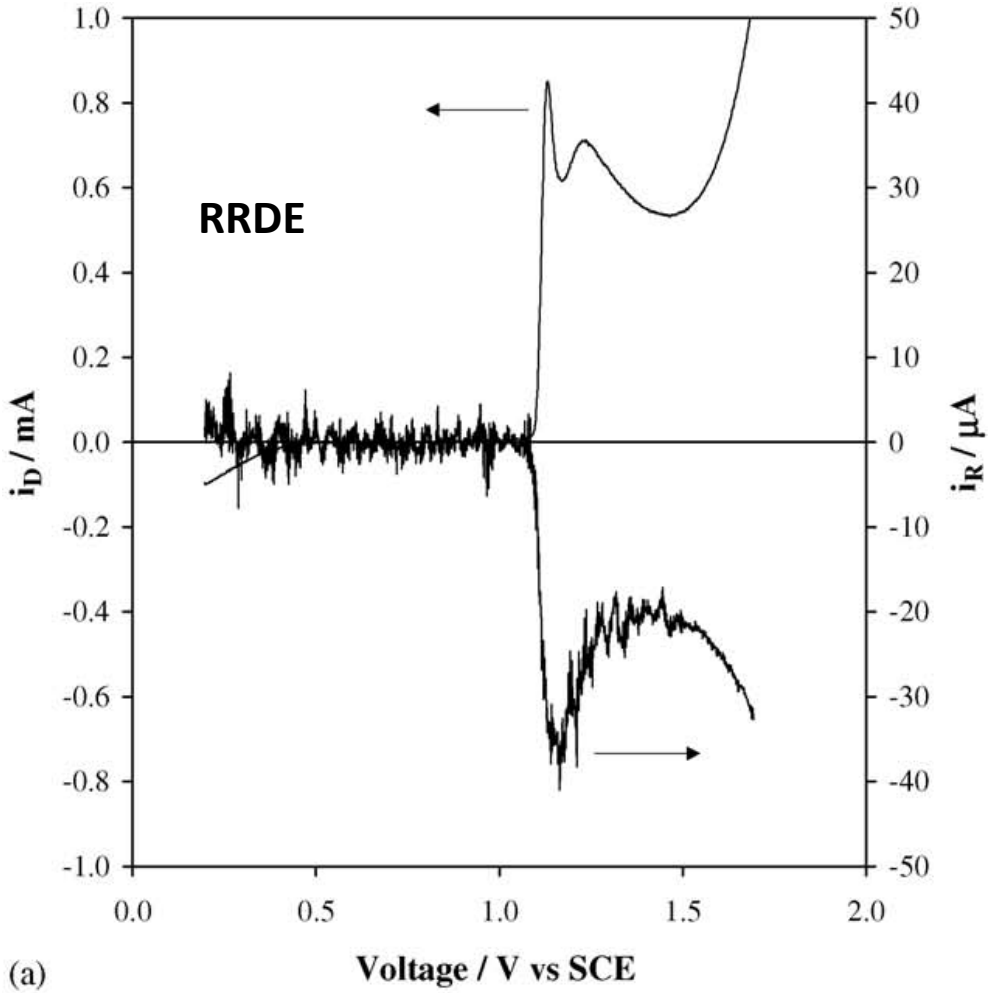
Недавний обзор:

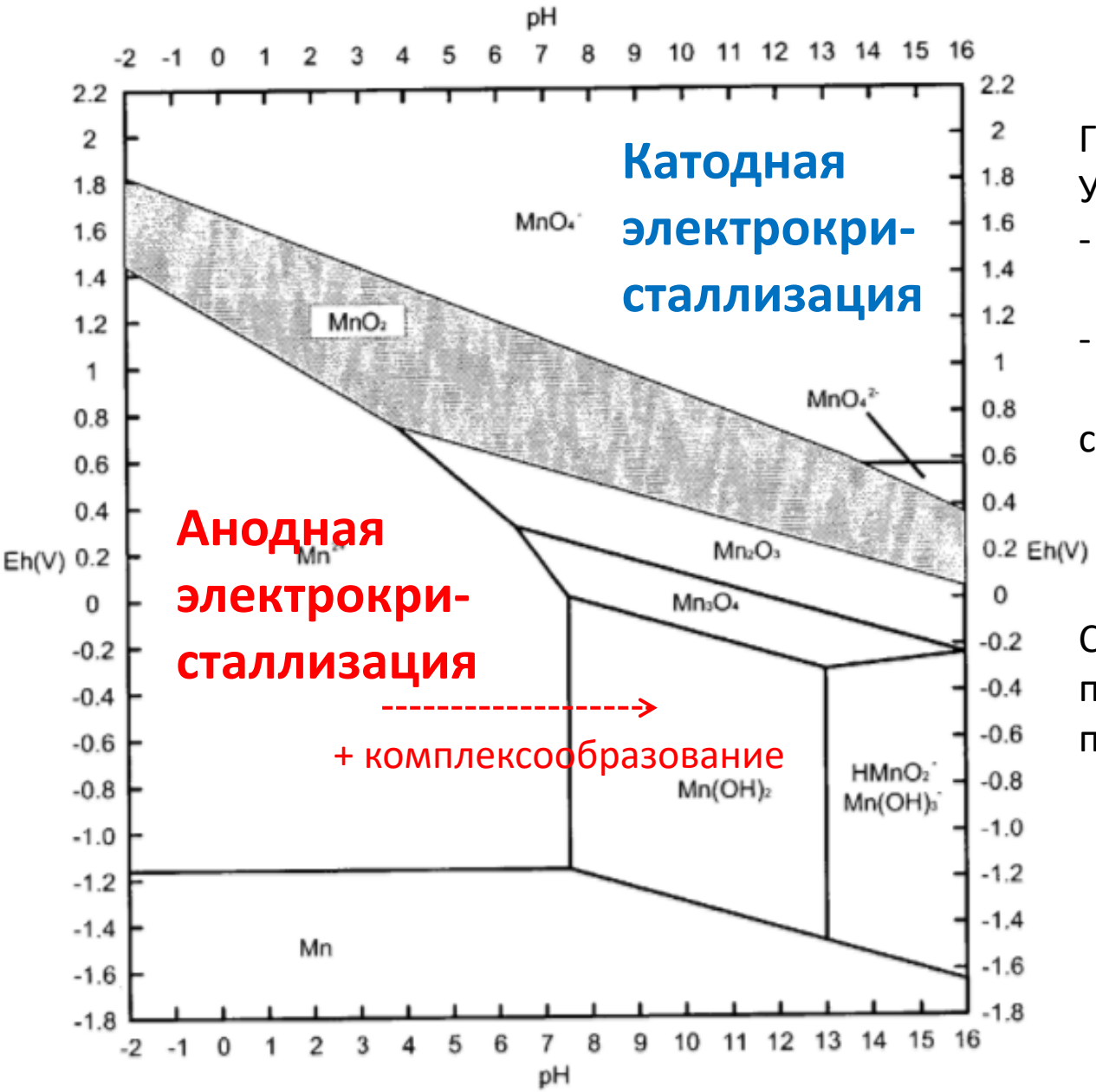
RSC Advances, 5 (2015) 58255-58283

C.J.Clarke, Electrochim. Acta 51 (2013) 5773–5784



A.D.Cross, Electrochim. Acta 87 (2013) 133– 139



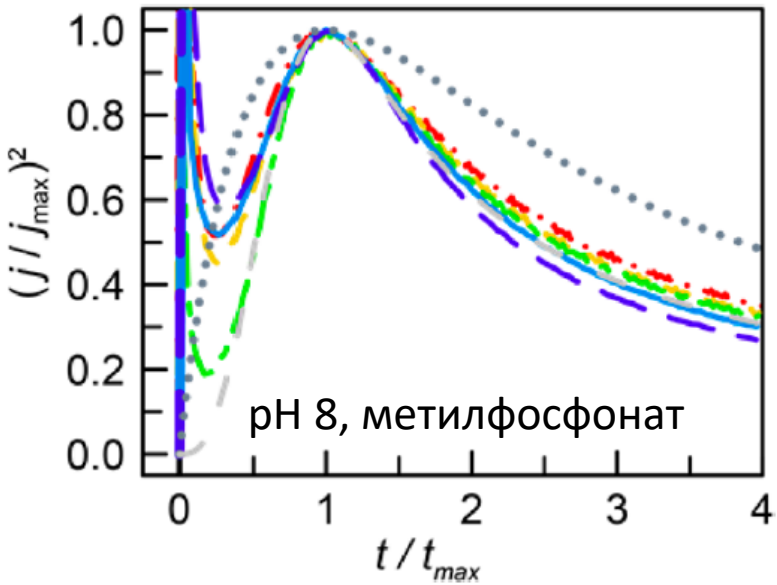


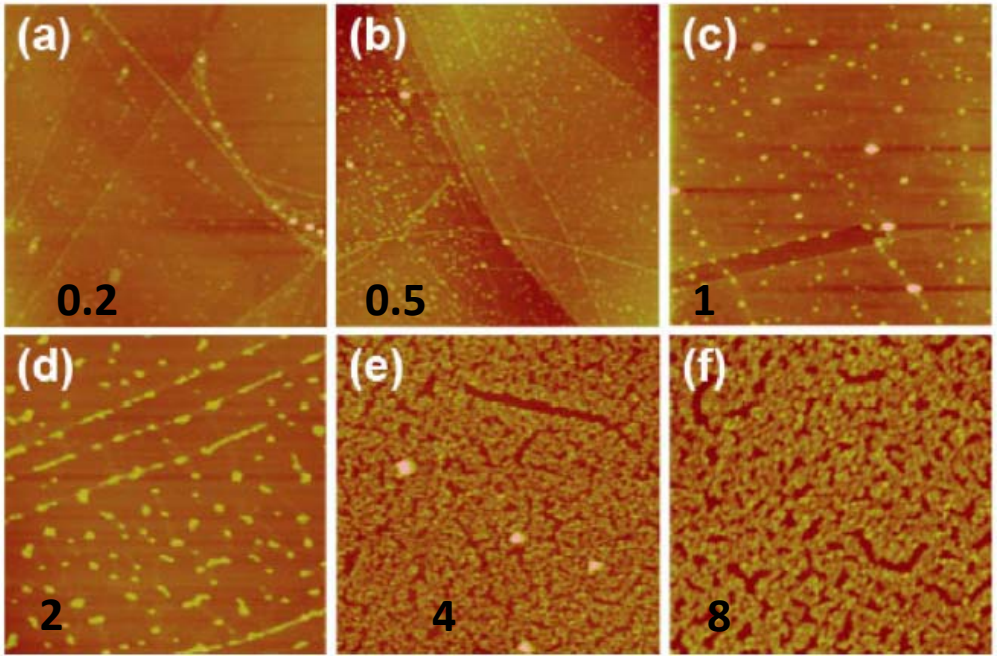
Границы, отвечающие Устойчивости

- разных модификаций диоксида марганца,
- разных гидратированных форм,

строго не известны.

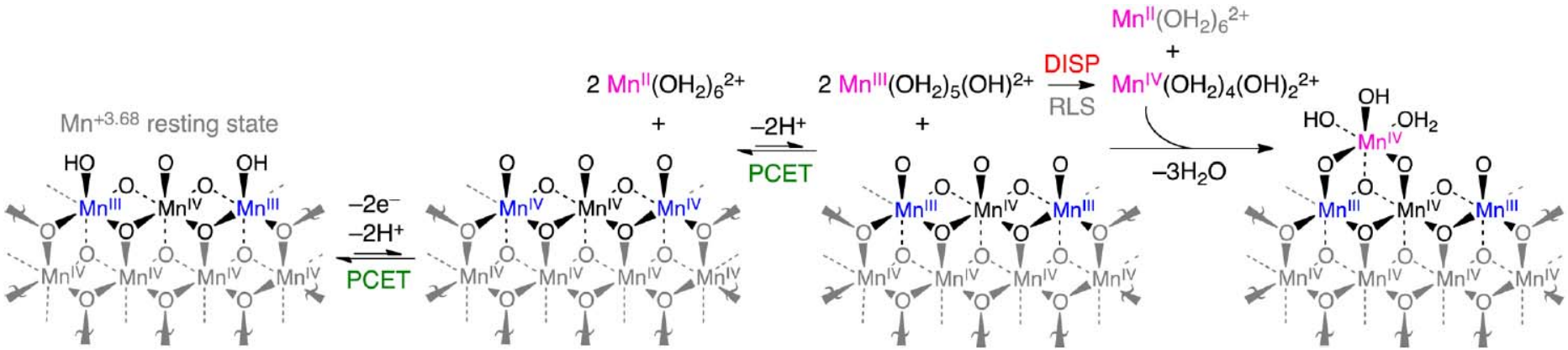
Стехиометрия оксидов плавно изменяется с потенциалом (K. Vetter).

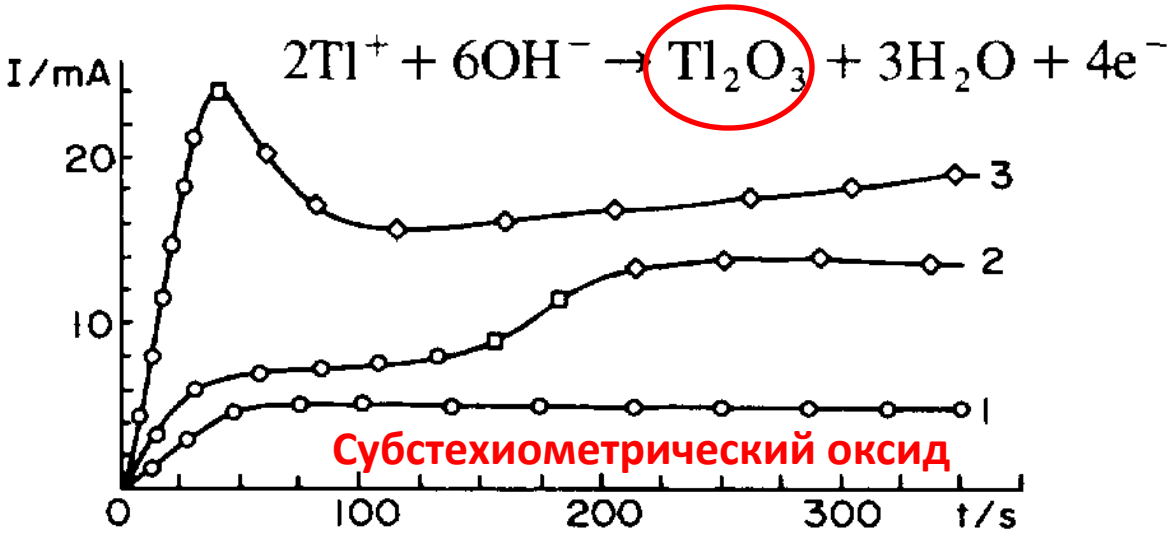




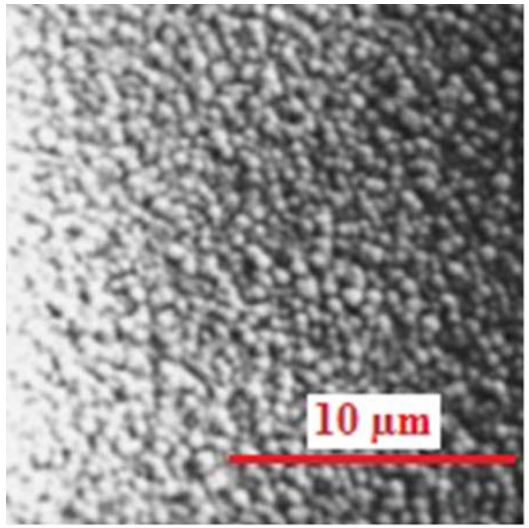
(доли от t_{max})

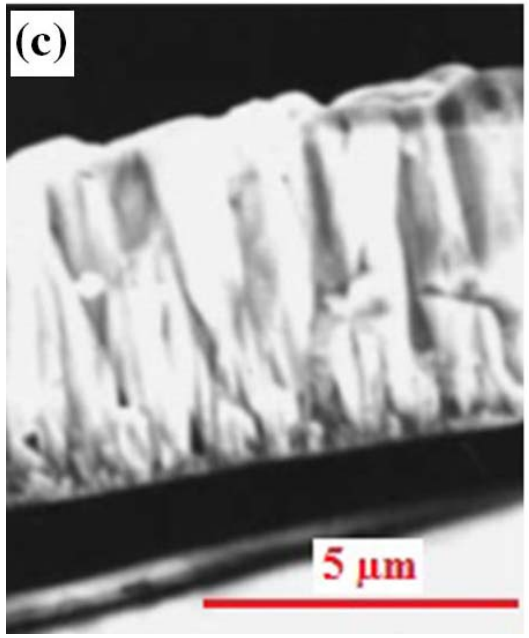
M. Huynh et al.,
J. Phys. Chem. C 118 (2014) 17142−17152





G.A. Tsirlina, O.A. Petrii,
J. Electroanal. Chem. 401 (1996) 33-43





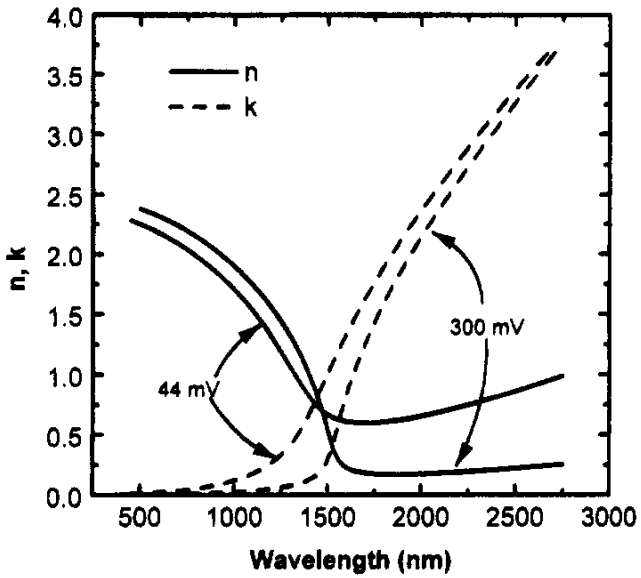
J. F. Liu, Thin Solid Films
298 (1997) 156-159

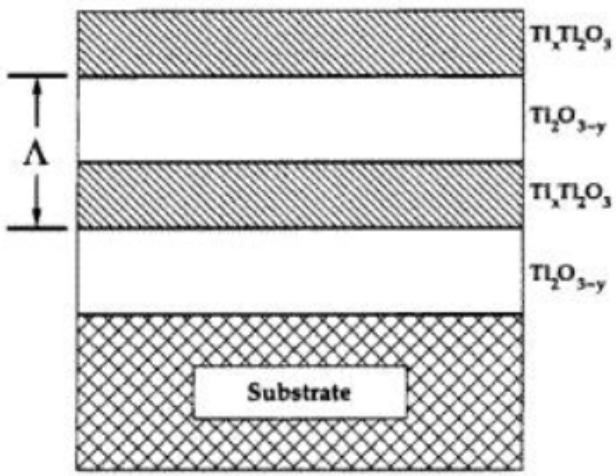
J. Phys. Chem. **1995**, *99*, 15247–15252

Optical and Electronic Transport Properties of Electrodeposited Thallium(III) Oxide Films

Robert A. Van Leeuwen, Chen-Jen Hung, Daniel R. Kammler, and Jay A. Switzer*

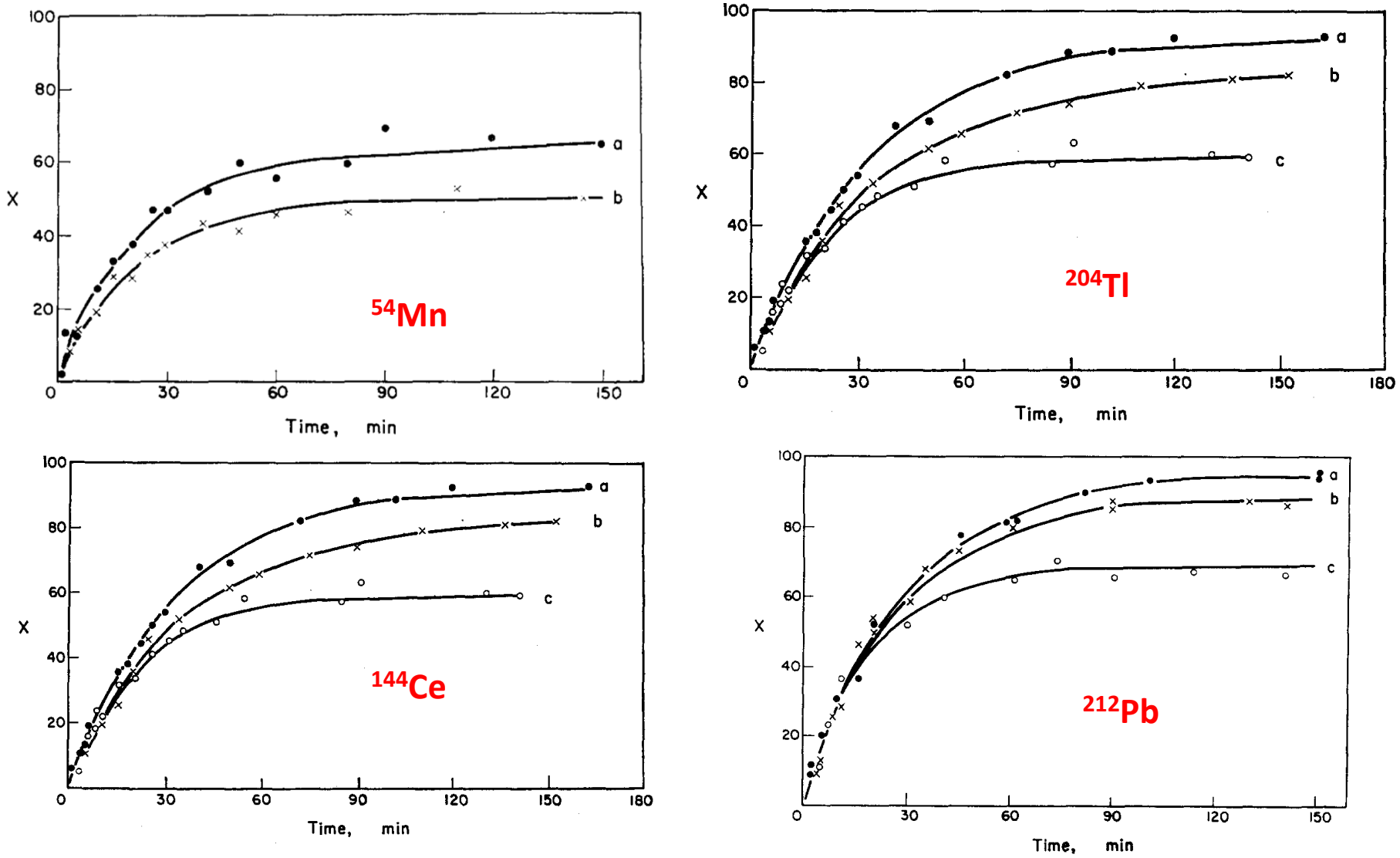
overpotential (mV)	carrier density ($\times 10^{20}$ cm^{-3})	resistivity ($\mu\Omega$ cm)	mobility (cm^2/V s)
535	8.6	86	100
400	8.3	80	94
300	8.7	78	93
220	9.5	75	88
190	9.8	74	86
117	9.5	74	89
90	10.7	130	45
44	11.0	285	27





Сверхрешетка из оксидов разной стехиометрии

Радиохимические приложения



I. Madi, J. Inorg. Nuck. Chem. 28 (1966) 335-345

J. Chim. Phys., Vol. 65 (1968), pp. 2119–2125

Oxydation anodique du curium

Moïse Haissinsky, Jean-Claude Dran, Roger Klein et Élisabeth Pluchet

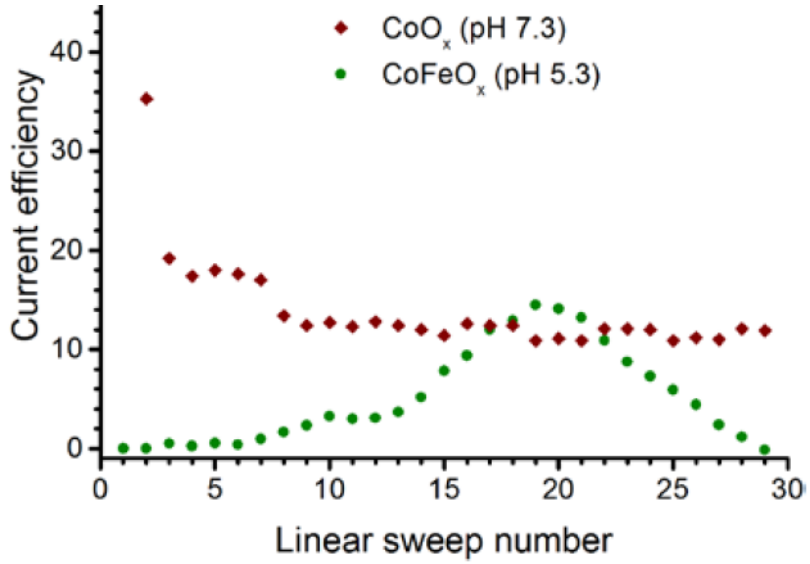
Laboratoire Curie, 11, rue Pierre et Marie Curie, Paris, 5 e France.

Résumé

On précise les facteurs dont dépend le dépôt anodique du curium : concentration, acidité, potentiel, nature de l'anion, agitation, etc. On a examiné le rôle d'un certain nombre de réactifs qui peuvent soit attaquer le dépôt en le portant en solution, soit le favoriser par stabilisation ou même en augmentant sa quantité. On conclut que le dépôt est constitué essentiellement par le bioxyde CmO_2.

After the electrolysis a brown deposit was noted on the anode, containing curium. We observed the appearance of a deposit also in our previous experiments[1] at the oxidation of terbium, praseodymium, and californium: however, in the case of curium the amount of the deposit on the anode was much less. The radiometric analysis de-

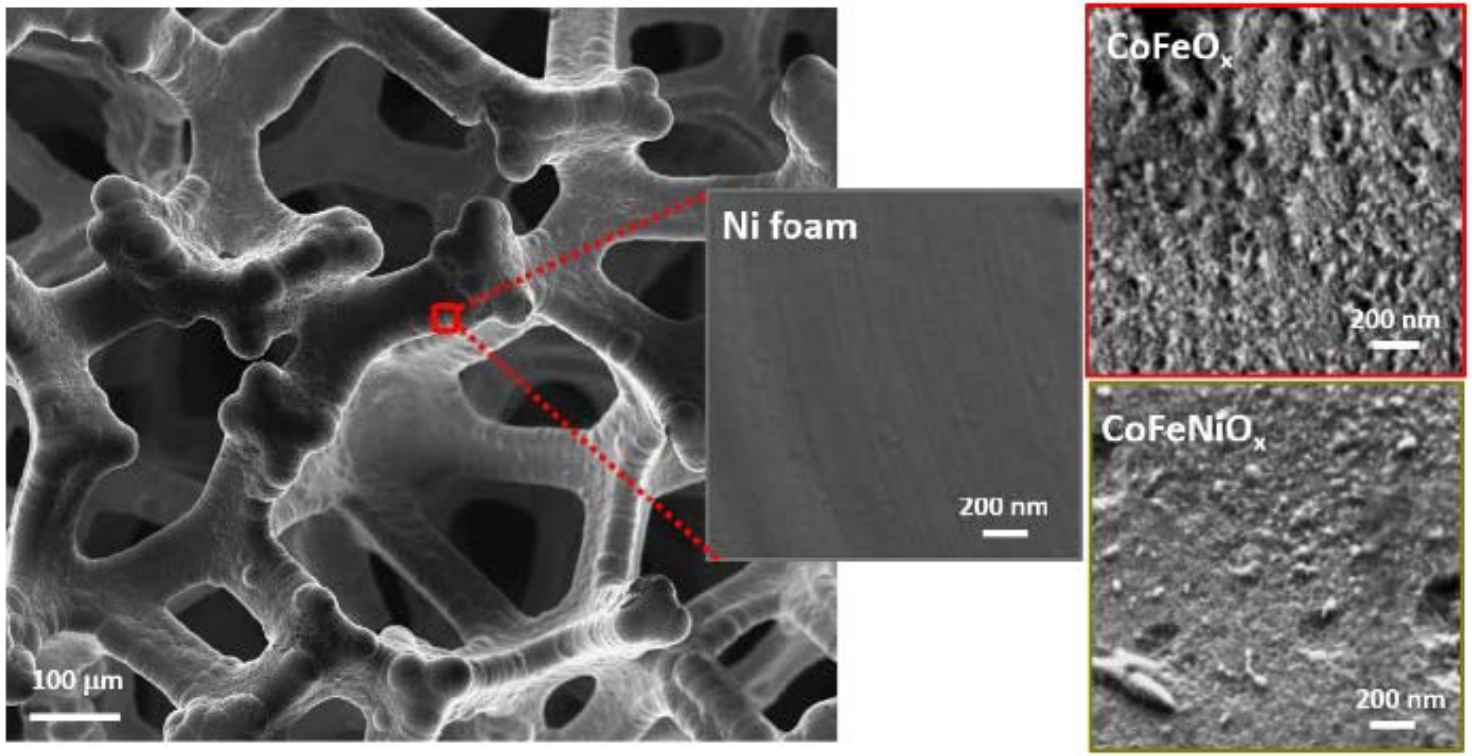
V.Ya. Frenkel et al., J. Radioanal. And Nucl. Chem. Lett. 107 (1986) 159



Электрокаталические приложения (выделение кислорода на оксидах, ‘carbon-free’ электродные композиции):

оксиды металлов группы железа

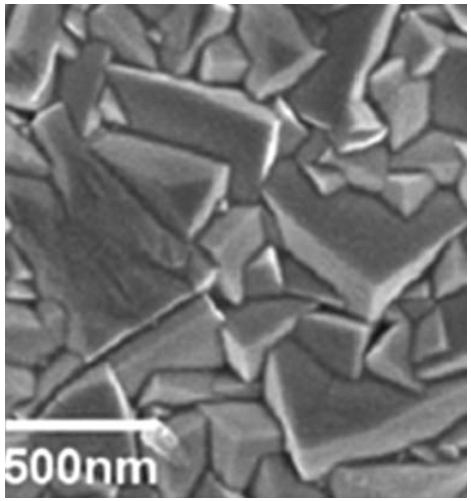
C.G. Morales-Guio, J. Am. Chem. Soc. 138 (2016) 8946–8957.



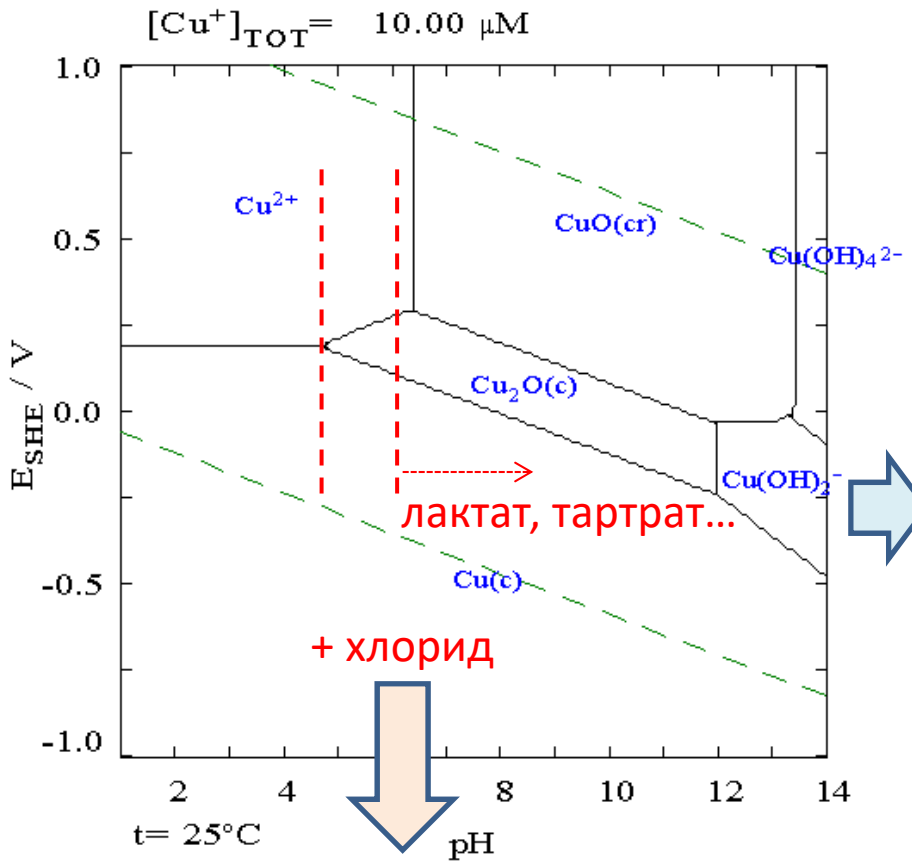
$$Cu^{2+} + e^- \rightarrow Cu^+,$$

$$2Cu^+ + H_2O \rightarrow Cu_2O\downarrow + 2H^+$$

pH 11



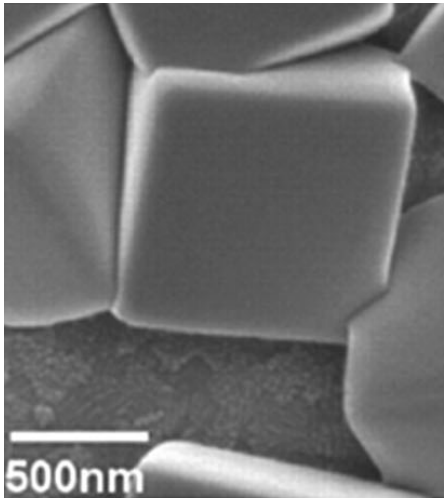
C.M.McShane et al., J. Phys. Chem. Lett . 1 (2010) 2666–2670



n-Cu_2O

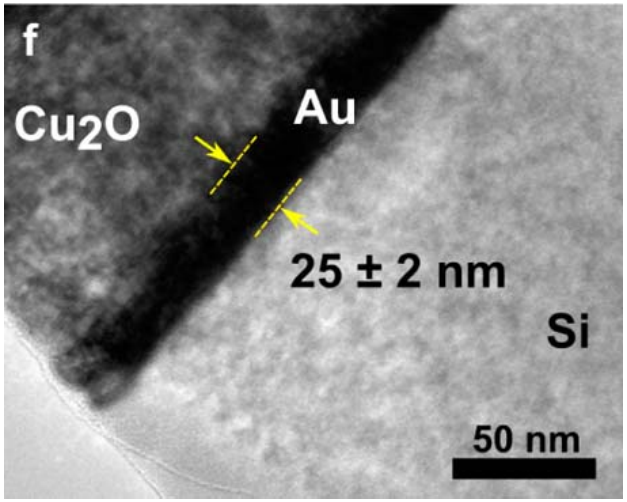
p-Cu_2O

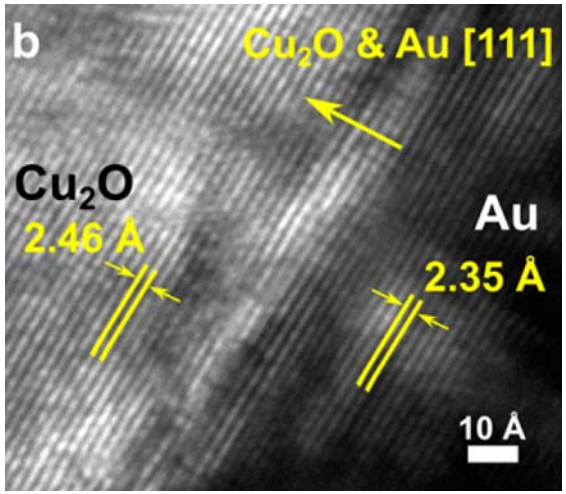
pH 13

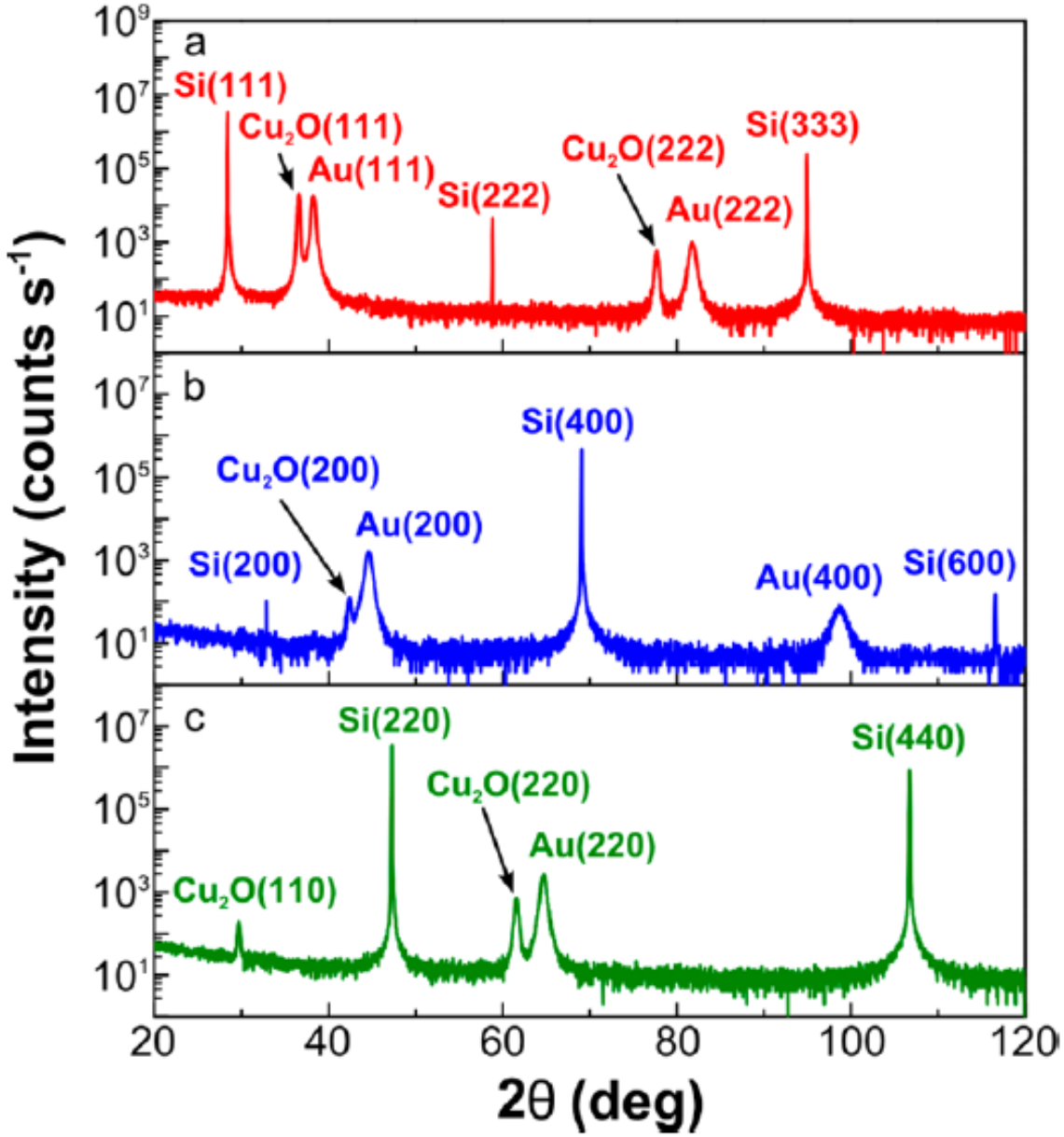


Недавний обзор:
I.S. Brandt et al., J. Solid State Electrochem. 21 (2017) 1999–2020

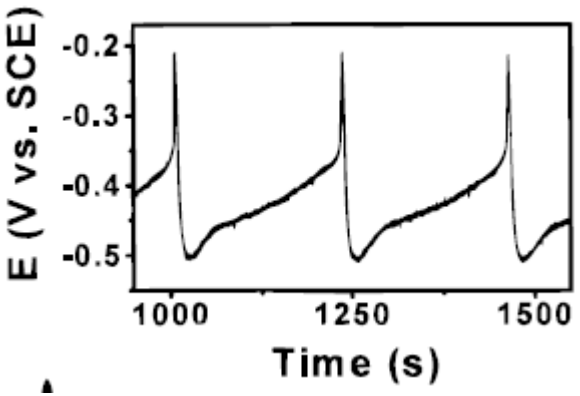
Эпитаксиальное осаждение Cu_2O (**J. Switzer** et al.)





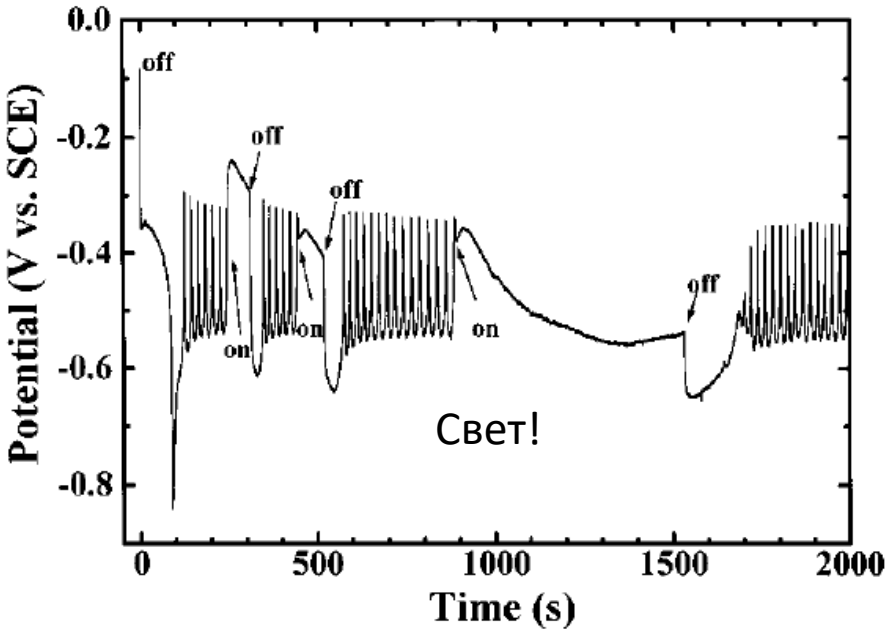


J. Am. Ceram. Soc. 88 (2005) 253–270 ⇨ ACS Appl. Mater. Interfaces 8 (2016) 15828–15837



Самопроизвольные осцилляции потенциала при гальваностатическом осаждении

Cu_2O/Cu слоистые структуры



Наноструктуры на основе Cu_2O

Нити Cu_2O, осаждение в ААО мембрану:
A.Jagminas et al., Appl. Surface Sci. 225 (2004) 302–308

J. Switzer et al.,
J. Am. Chem. Soc. 120 (1998) 3530-3531

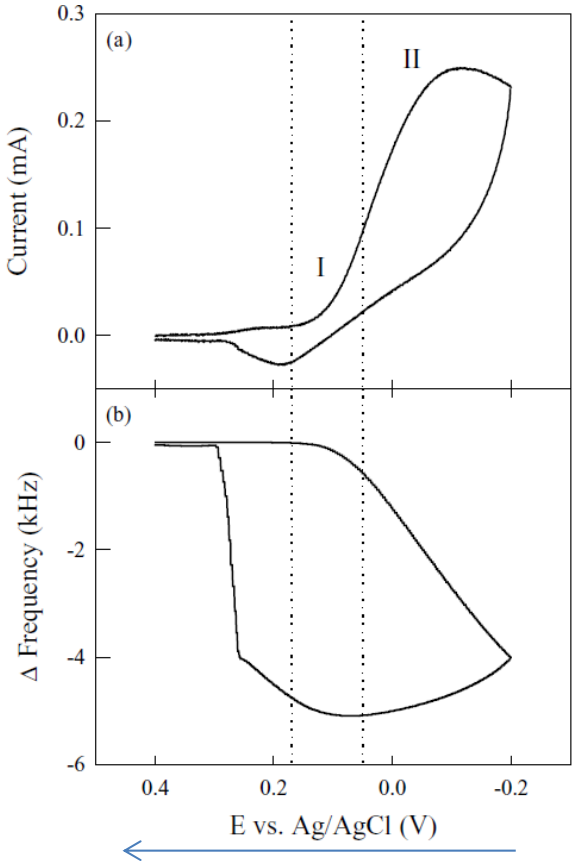
Нестехиометрические оксиды Mo, W и V

$$2W(s) + 10H_2O_2 \rightleftharpoons [W_2(O)_3(O_2)_4(H_2O)_2]^{2-} + 2H_3O^+ + 5H_2O$$

1 - Из пероксокомплексов

$$[Mo_2(O)_3(O_2)_4(H_2O)_2]^{2-} + [H_2MoO_4] + 12[H_3O^+] + 10e^- \rightleftharpoons Mo_3O_{8(s)} + 21H_2O$$

$$[W^{VI}{}_2(O)_3(O_2)_4(H_2O)_2]^{2-} + 14H_3O^+ + 10e^- \rightarrow (W^VO_2{}^+)_2 \cdot 2H_2O(s) + 21H_2O$$



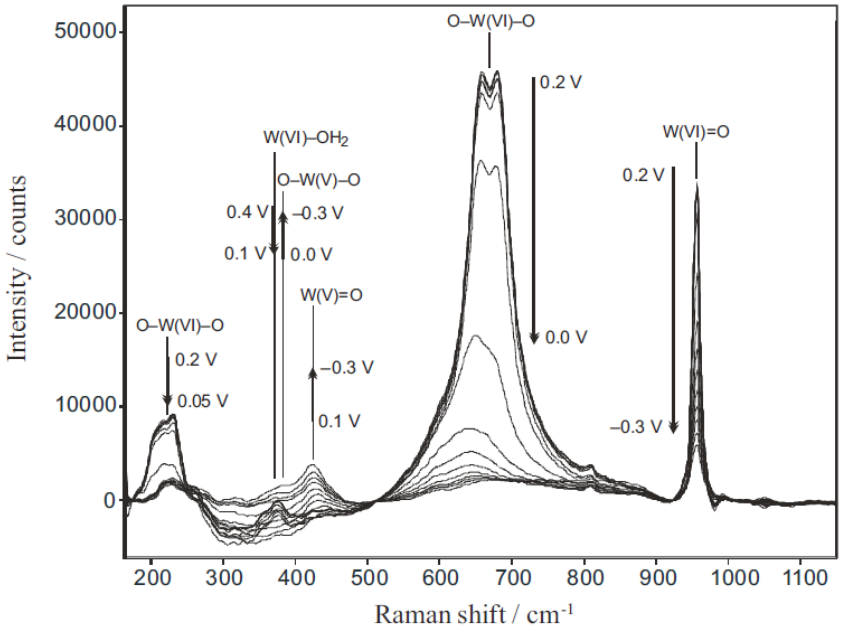
solution comp (mol %)	film comp (est by EDS)
100 W	WO_3
10 Mo/90 W	$Mo_{0.42}W_{0.58}O_3$
20 Mo/80 W	$Mo_{0.55}W_{0.45}O_3$
30 Mo/70 W	$Mo_{0.59}W_{0.41}O_3$
50 Mo/50 W	$Mo_{0.73}W_{0.27}O_3$
100 Mo	α-/β-MoO_3[b]
100 Mo	α-MoO_3
100 Mo	β-MoO_3[b]

T.M.McEvoy, K. J. Stevenson,
Anal. Chim. Acta 496 (2003) 39–51

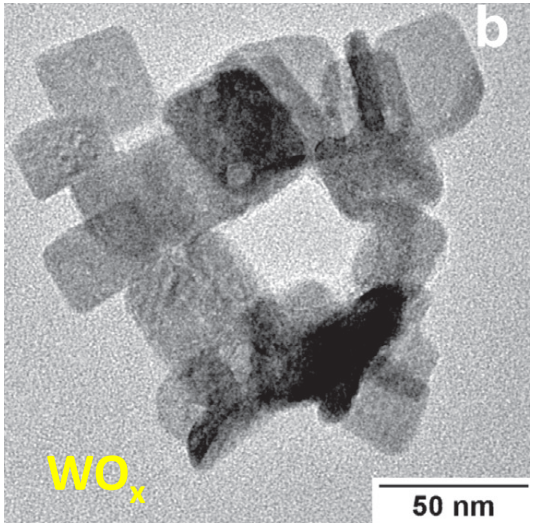
L. Kondrachova et al.,
Langmuir 22 (2006) 10490-10498

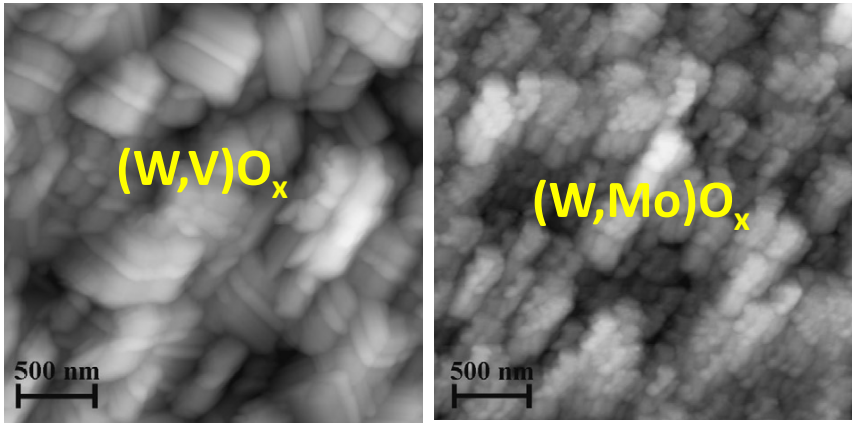
Нестехиометрические оксиды Mo, W и V

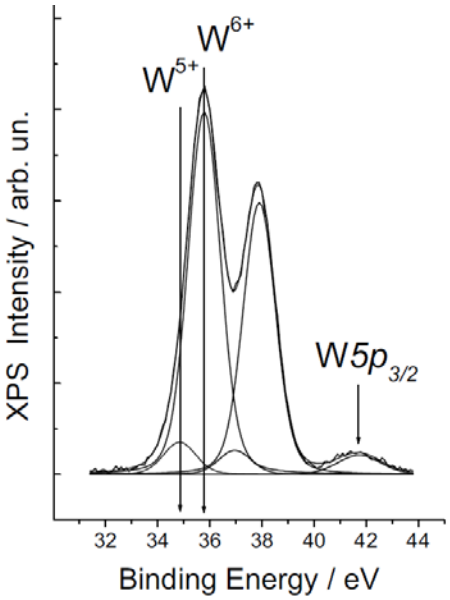
2 - из метастабильных растворов изополисоединений

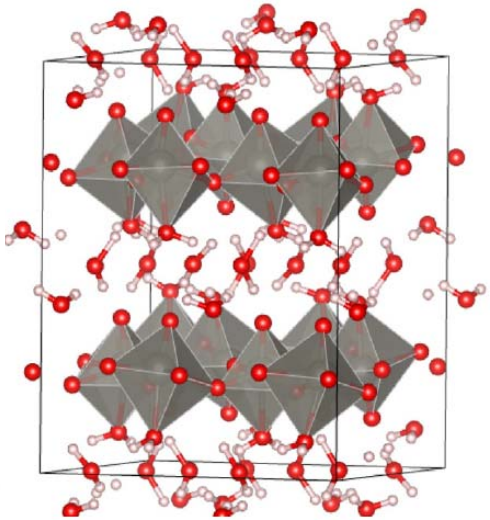


V.K. Laurinavichute, Electrochim.Acta 54 (2009) 5439–5448
56 (2011) 3530–3536









L. Pugolovkin et al., Appl. Surface Sci. 388 (2016) 786–793

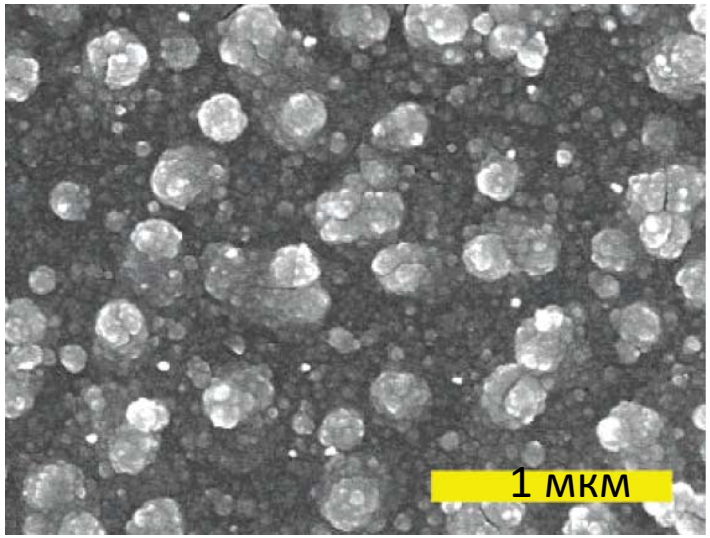
$$2Re^{0} + 9H_2O_2 \rightarrow 2Re^{VII}O_4^{-} + 2H^{+} + 8H_2O + O_2$$

$$Re^{VII}O_4^{-}{}_{(ads)} + 2H_2 \rightarrow Re^{IV}O_2 \cdot 2H_2O \rightarrow Re^{VI}O_3$$

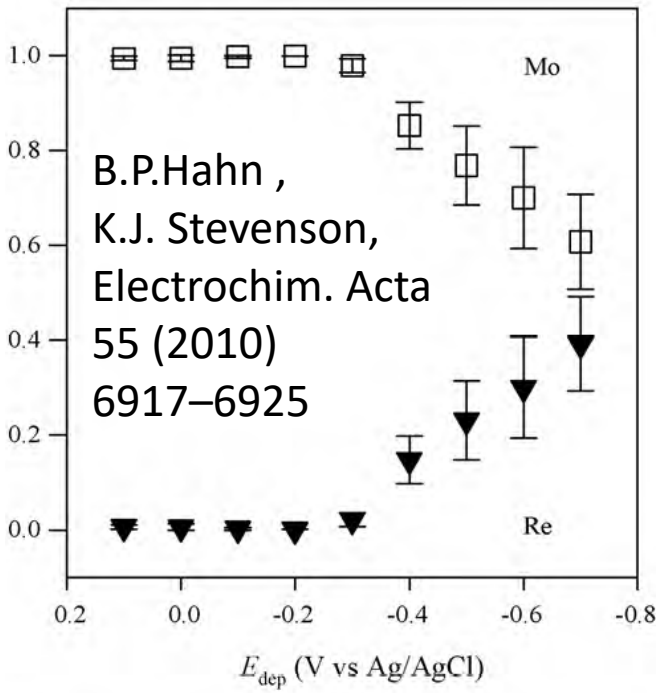
$$4Re^{VII}O_4^{-}{}_{(ads)} + 20H^{+} + 16e^{-} \rightarrow 2Re^{III}{}_2O_3 + 10H_2O$$

B.P.Hahn et al.,
Langmuir 23 (2007)
10837-10845

диспропорционирование

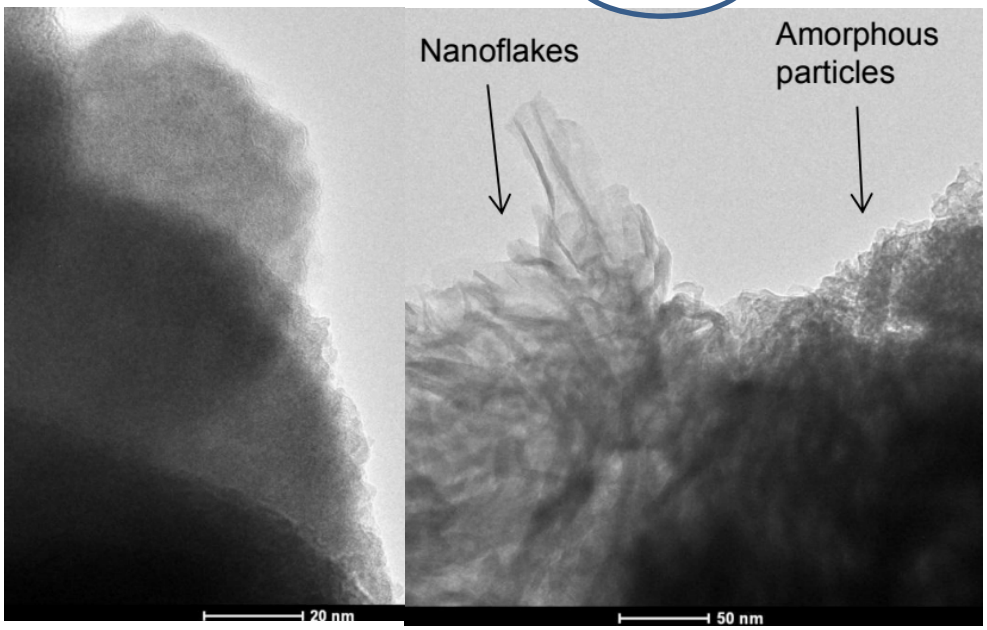


Соосаждение (оксид рения-молибдена)



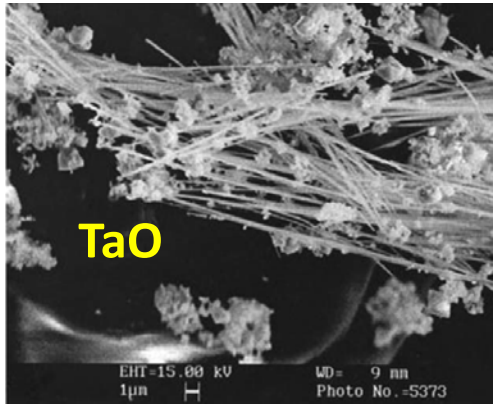
B.P.Hahn ,
K.J. Stevenson,
Electrochim. Acta
55 (2010)
6917–6925

$$KMnO_4 + 3\,e + 2\,H_2O \rightarrow K_xMnO_2 + 4\,OH^-$$

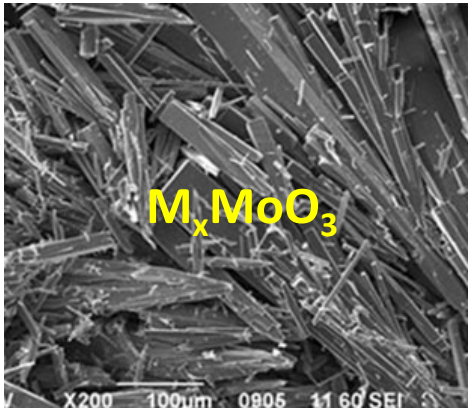


L. Pugolovkin et al., in preparation

Электрокристаллизация оксидов из расплавов

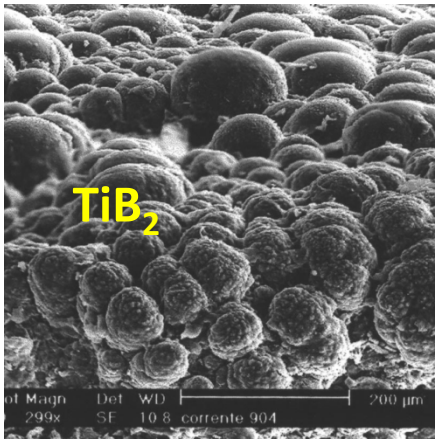


S.A. Kuznetsov,
J. Electrochem. Soc.
164 (2017) H5145-H5149

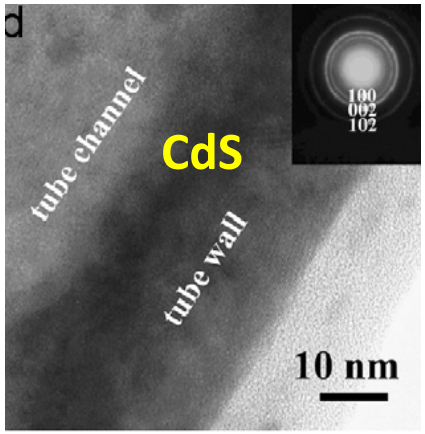


V.K.Laurinavichyute et al.,
J. Solid State Electrochem.
16 (2012) 3515–3528

Электрокристаллизация других бинарных соединений



G. Ett, E.G. Pessine,
Electrochimica Acta
44 (1999) 2859-2870



D. Mo et al., J. Crystal Growth
310 (2008) 612–616

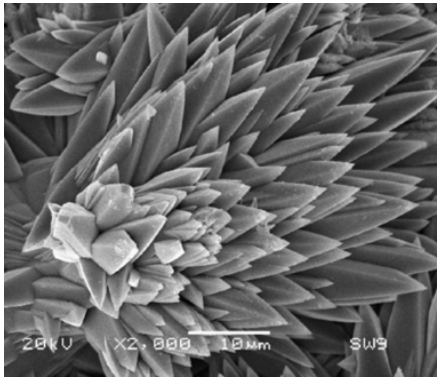
Общие вопросы

- «прекурсоры» в растворах/расплавах
- термодинамика нестехиометрических соединений
- управление природой «активных центров»

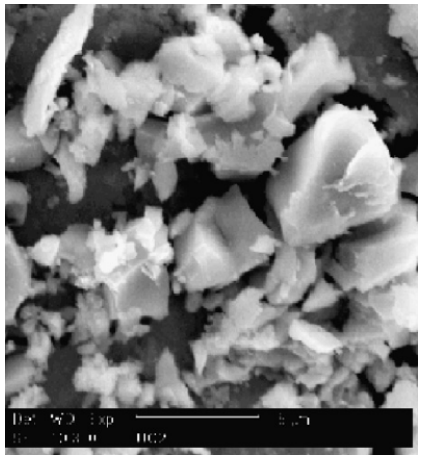
«Неклассические» способы (примеры)

$$W + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^-$$

$$Ba^{2+} + WO_4^{2-} \leftrightarrow BaWO_4$$



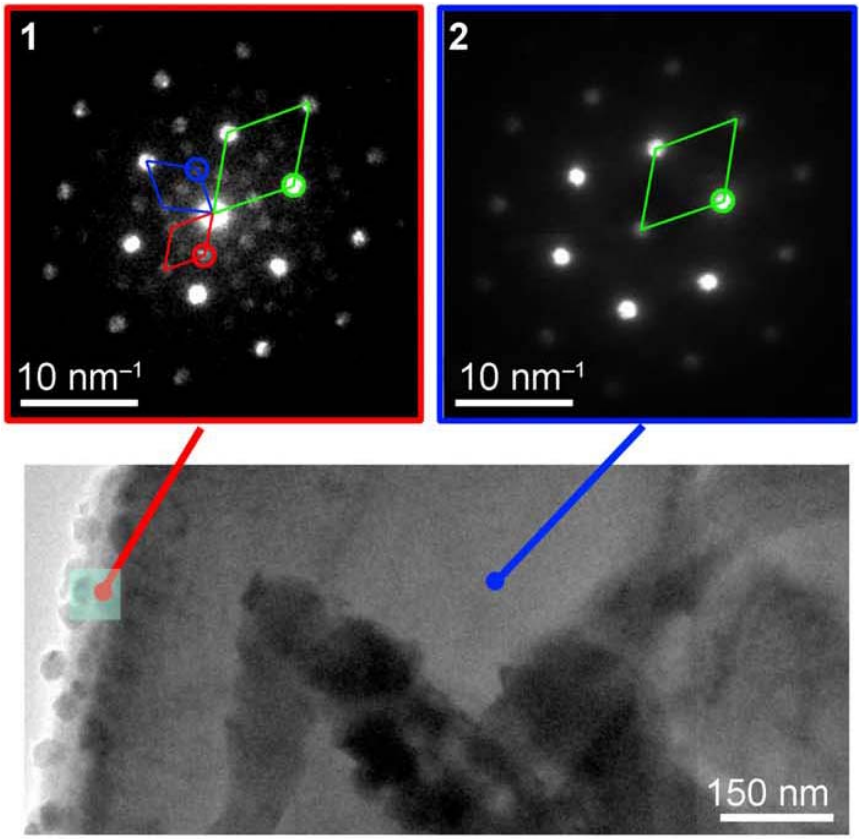
L. Chen, Y. Gao, Materials Chem. Phys. 116 (2009) 242–246



$[UO_2]^{2+}$ / UO_2

в ионной жидкости!

P. Giridhar, Electrochim. Acta 52 (2007) 3006–3012



$LiCoO_2$ в «мокрых» щелочных расплавах

H. Zhang et al., Sci. Adv. 3 (2017) e1602427

Взаимоотношения электрохимии и растворной химии

Электрокристаллизация:

$Tl^{+} - 2e = Tl^{3+}$ или $Cu^{2+} + e = Cu^{+}$

$Tl^{3+} + 3OH^{-} \rightarrow [Tl(OH)_3] \rightarrow Tl_2O_3$ или

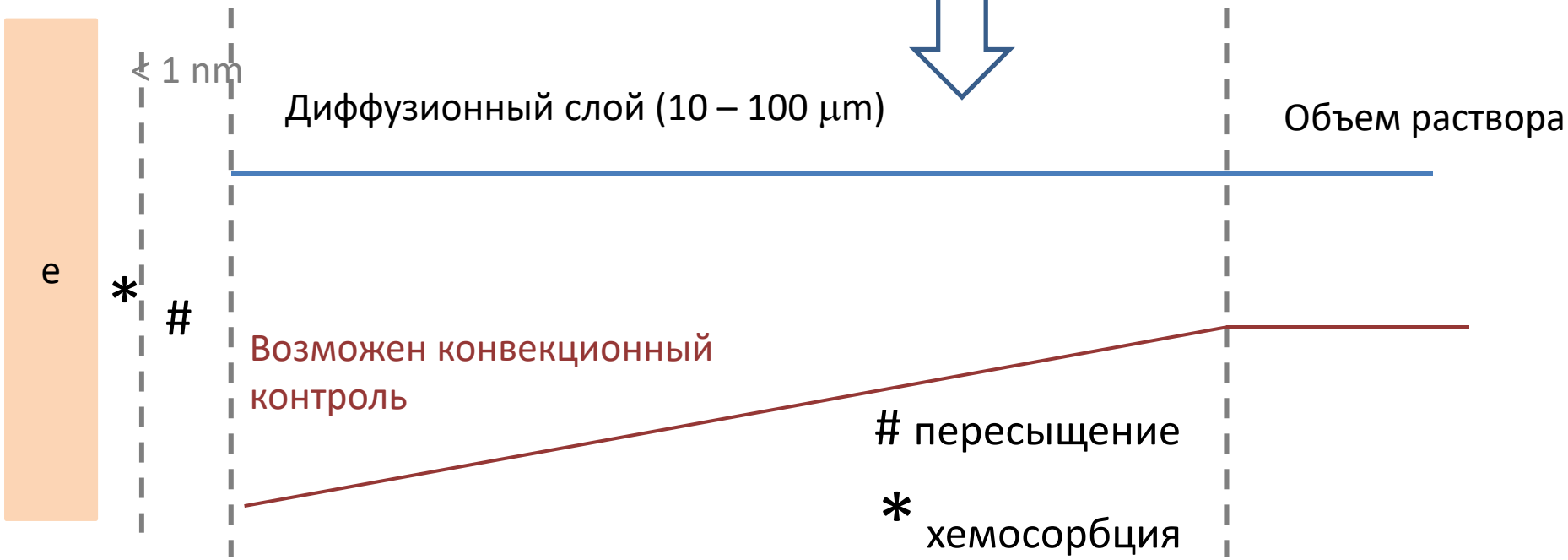
$Cu^{+} + OH^{-} \rightarrow [CuOH] \rightarrow Cu_2O$

Электрохимически **индуцированное** осаждение:

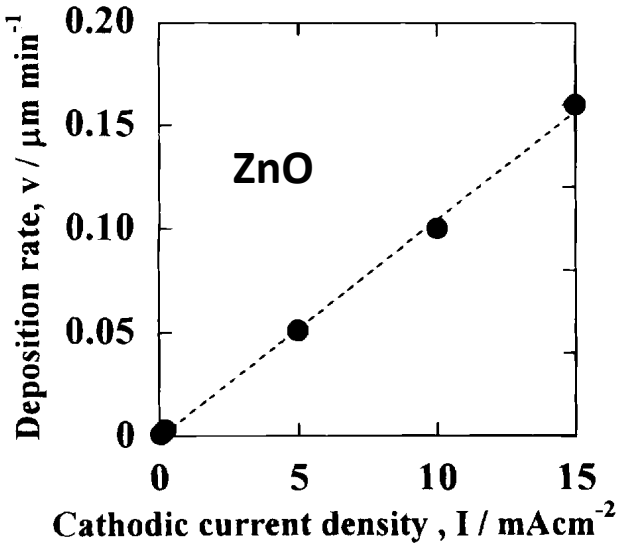
$H_2O_2 + 2e = 2OH^{-}$ или

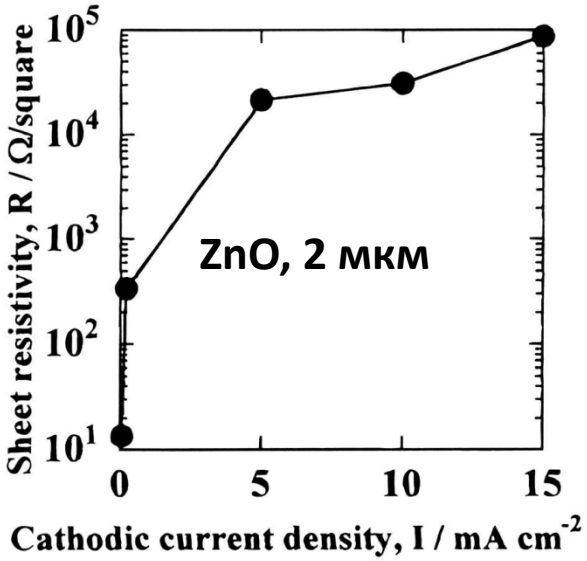
$NO_3^{-} + H_2O + 2e = NO_2^{-} + 2OH^{-}$

$Zn^{2+} + 2OH^{-} = Zn(OH)_2$

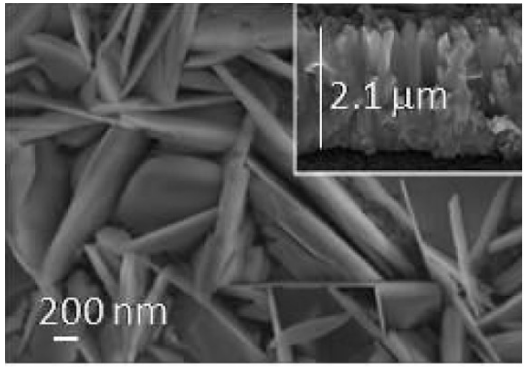


ZnO

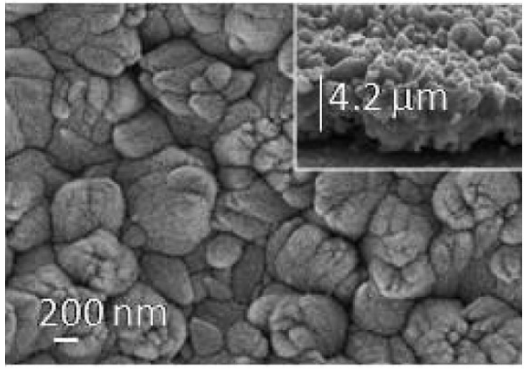




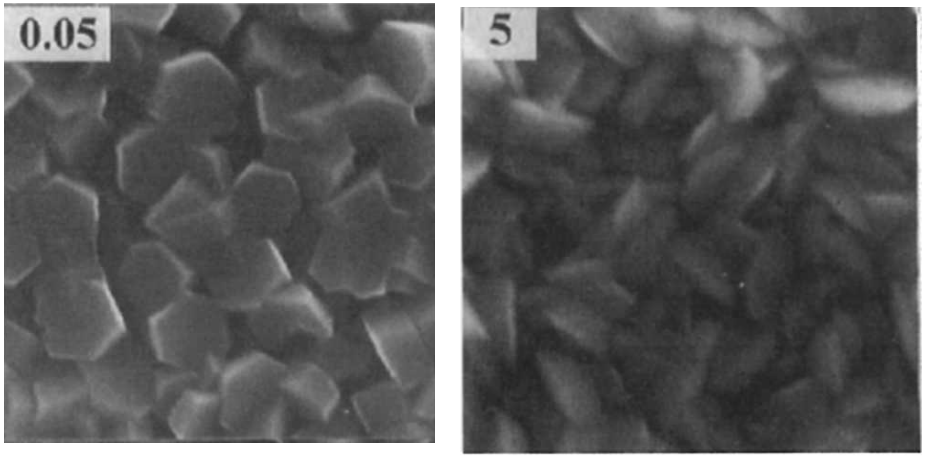
Без добавки



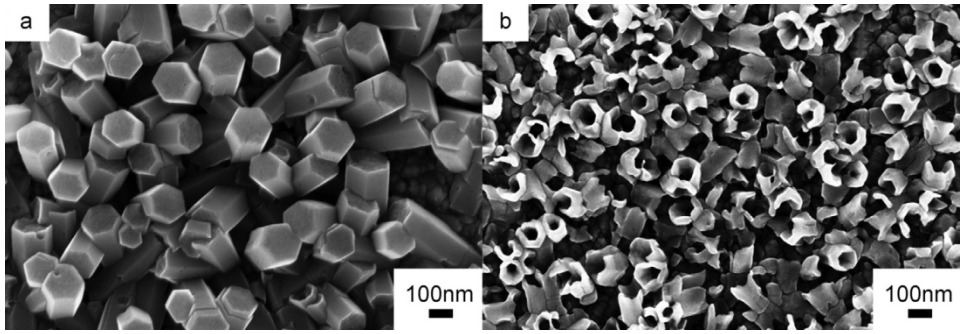
С тиомочевиной



Electrochim. Acta 178 (2015) 225



J. Electrochem. Soc. 144 (1997) 1949



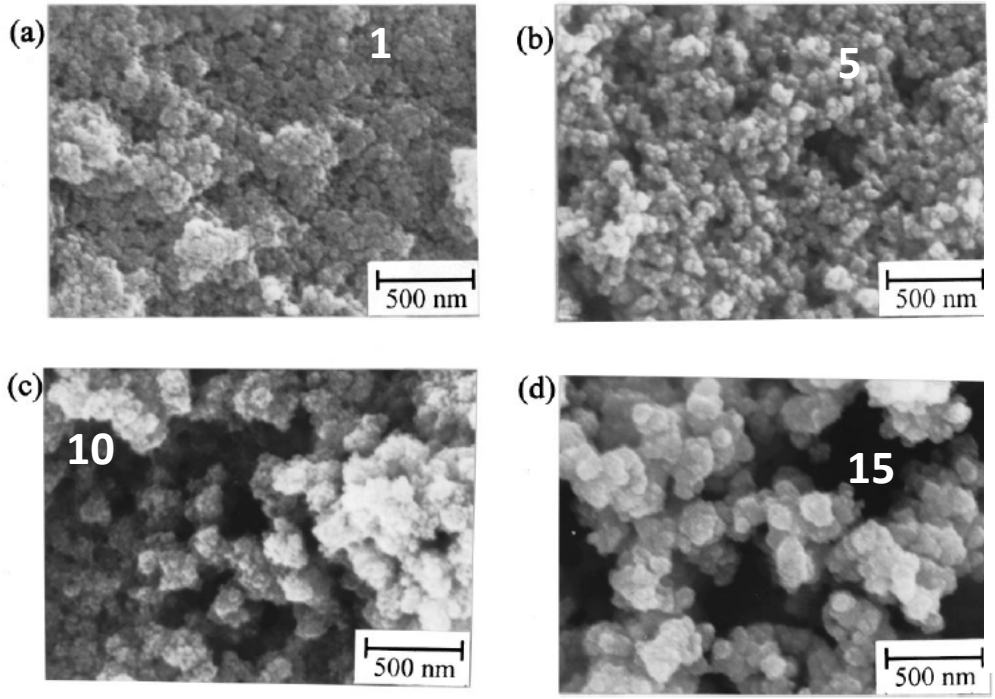
На некоторых подложках – рост монокристаллических стержней, иногда трубок.

Electrochim. Acta 132 (2014) 370

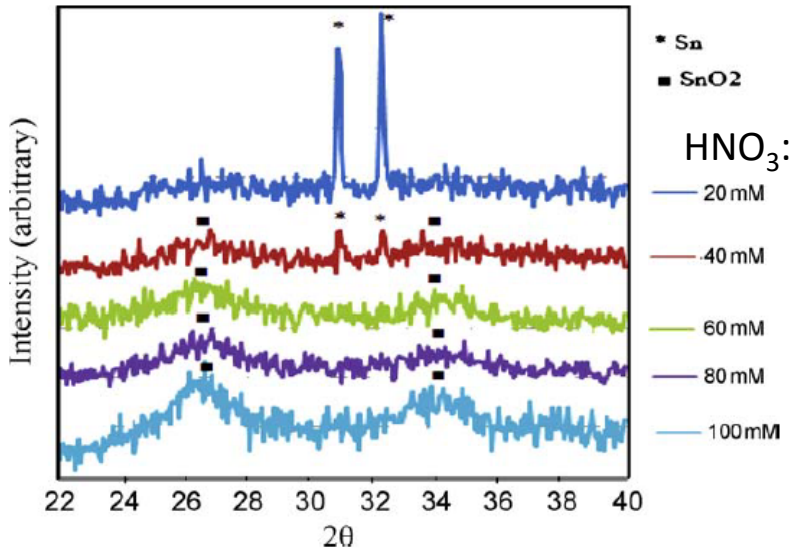
Electrochem. Solid State Lett. 5 (2002) C71

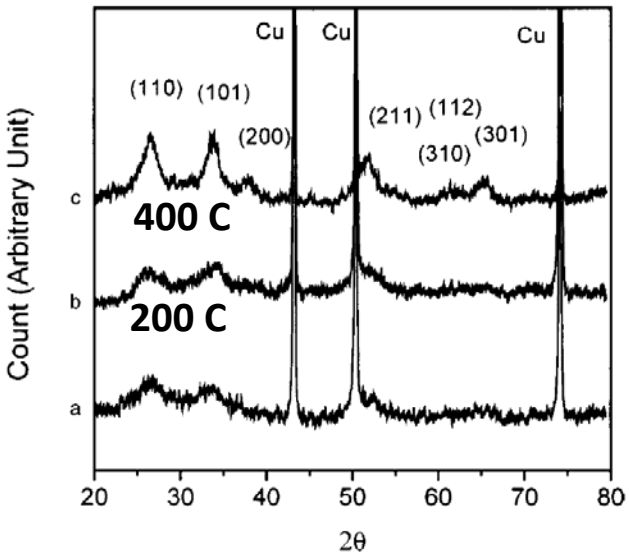
SnO_2 (катодное)

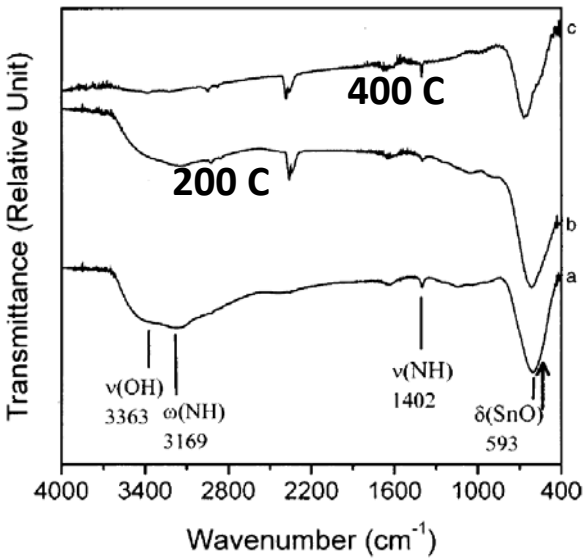
Морфология при разных плотностях тока (мА/см2):

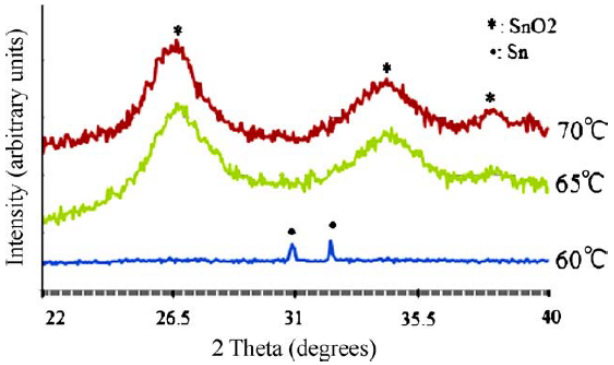


Конкуренция осаждения металла и оксида









Mater. Res. Bull.
45 (2010) 2006–2011

SnO_2 (анодное)

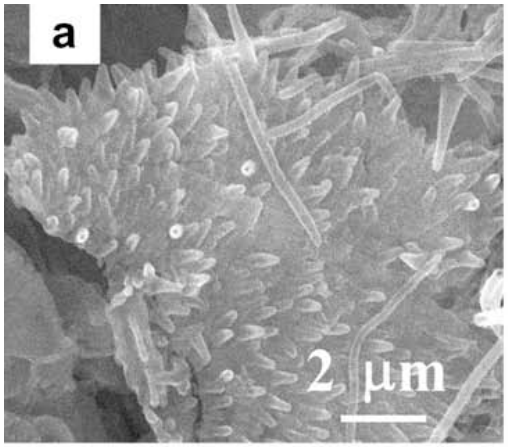
Electrochem. Commun. 11 (2009) 242

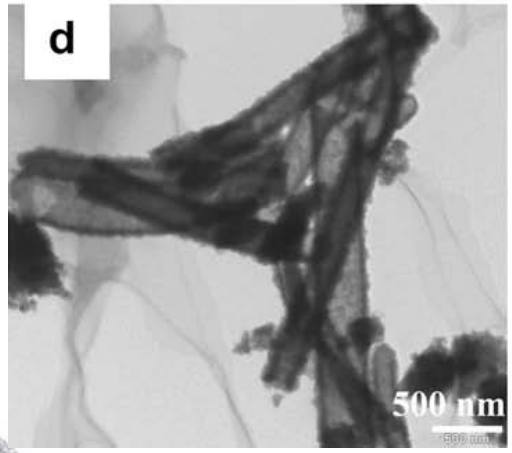
$$Sn^{2+} + 4H_2O \rightarrow Sn(OH)_4 + 2e^- + 4H^+$$
$$Sn(OH)_4 + Sn(OH)_4 \leftrightarrow Sn_2O(OH)_6 + H_2O \leftrightarrow 2SnO_2 + 4H_2O$$

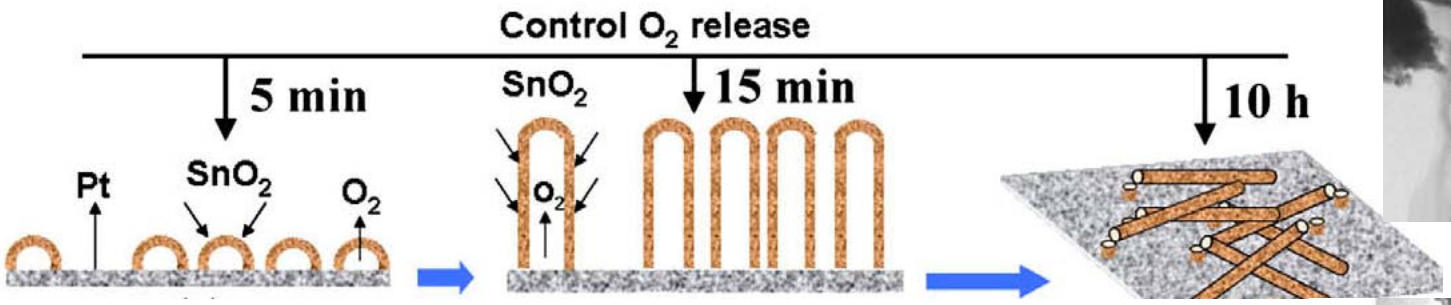
(*так могла бы протекать анодная электрокристаллизация*)

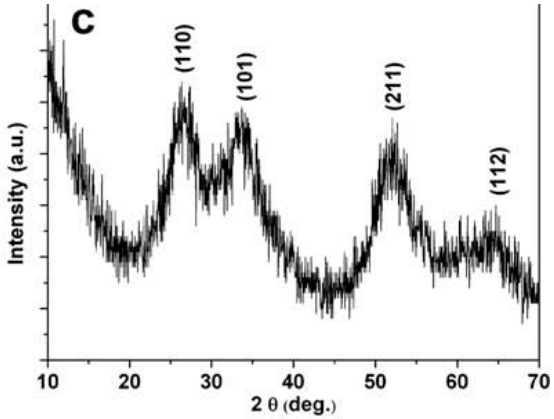
При высоких анодных потенциалах:

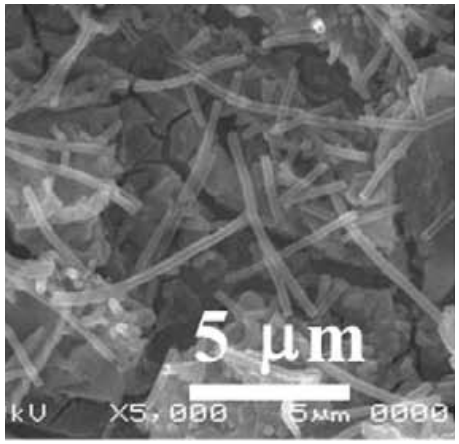
$$2H_2O \rightarrow O_2 \uparrow + 4H^+ + 4e^-$$
$$2Sn^{2+} + O_2 + 6H_2O \leftrightarrow 2Sn(OH)_4 + 4H^+$$
$$Sn(OH)_4 + Sn(OH)_4 \leftrightarrow Sn_2O(OH)_6 + H_2O \leftrightarrow 2SnO_2 + 4H_2O$$

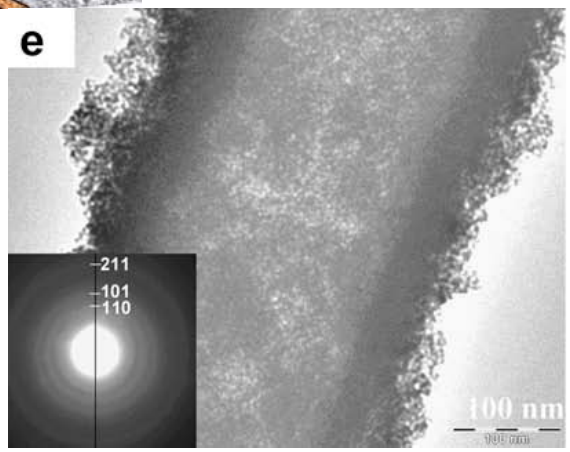








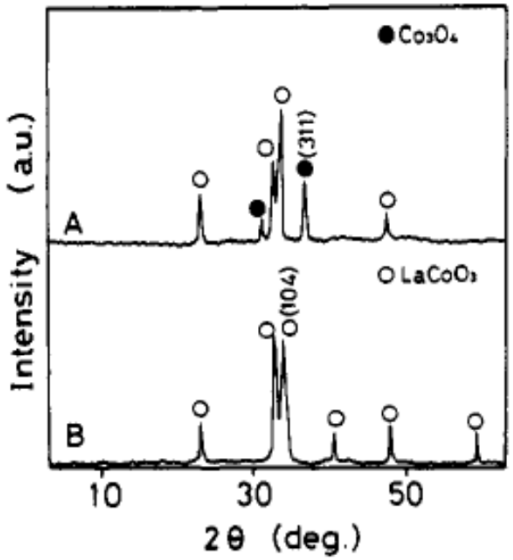


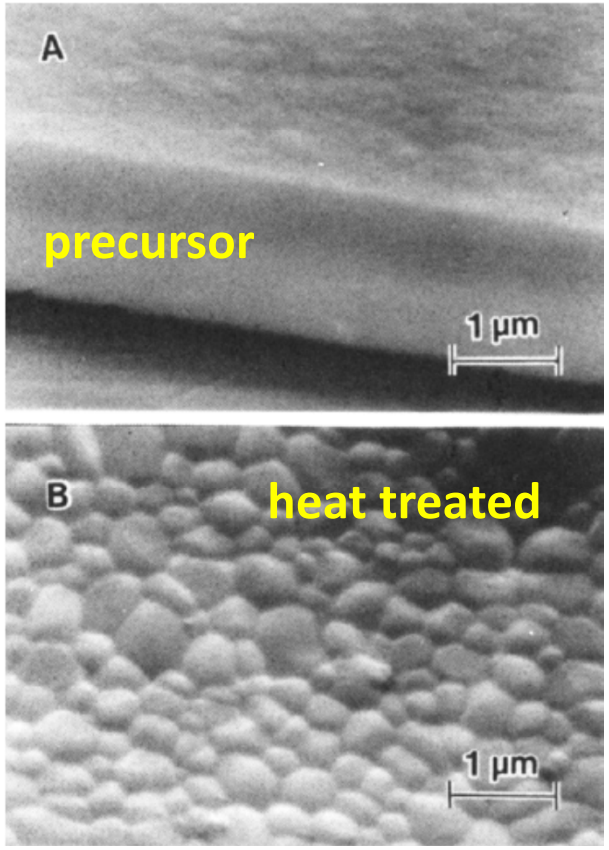


Электрохимически индуцированное осаждение многокомпонентных оксидов (их прекурсоров?)

electrolyte[a]	applied potential, V	immersion time in water, min	I_{LaCoO_3}	La/Co ratio
$Co(CH_3COO)_2$ $La(NO_3)_3$	0.95	30	0.9	1.0
$Co(CH_3COO)_2$ $La(NO_3)_3$	0.95	1	1.0	1.1
$Co(NO_3)_2$ $La(NO_3)_3$	0.70–0.95	1	1.0	1.1
$CoSO_4$ $La(NO_3)_3$	0.70–0.95	1	1.0	0.9

[a] Ratio of $[Co^{2+}]/[La^{3+}]$ is fixed to be 0.02 M/2.0 M.

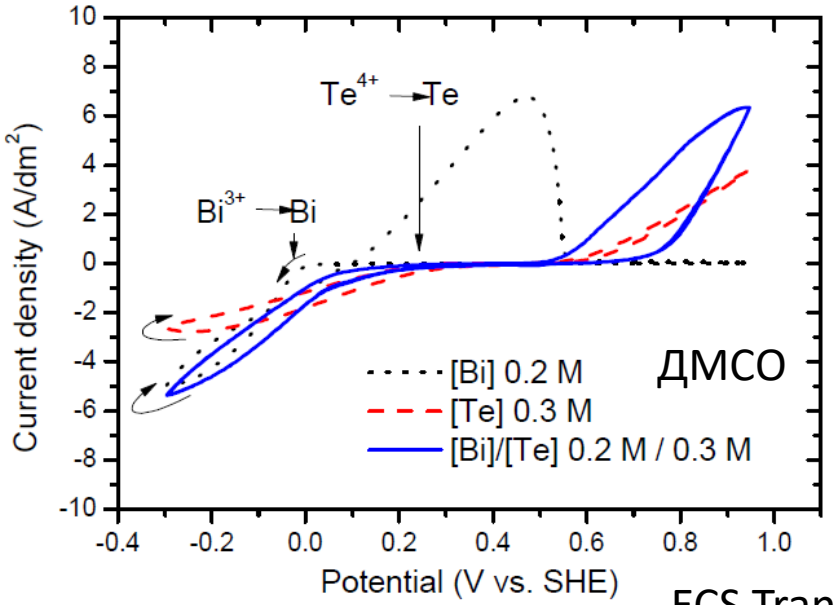


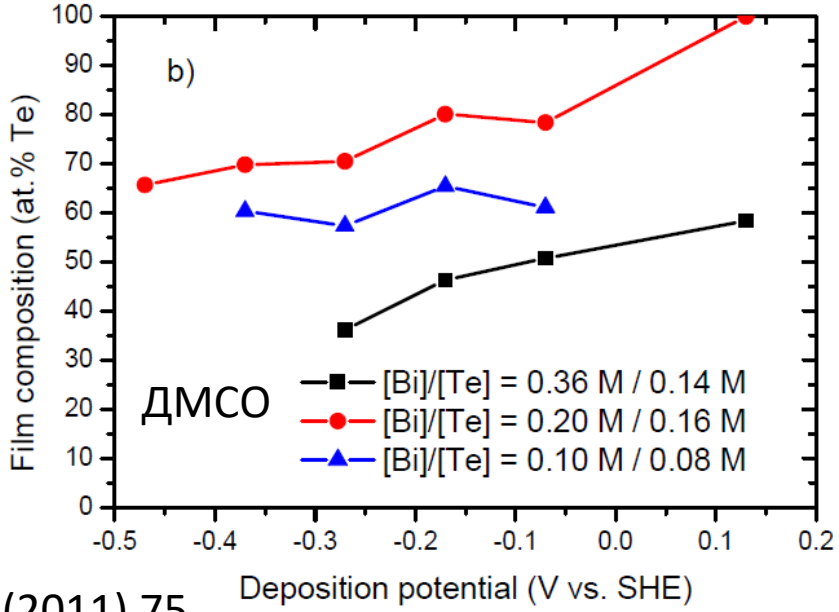


В большинстве случаев термообработка, необходимая для получения однофазного многокомпонентного материала, требует температур всего на 100-150° ниже, чем при твердофазном синтезе.

Бинарные полупроводники – две возможности:

(1) по аналогии с осаждением сплавов (восстанавливаются оба компонента);





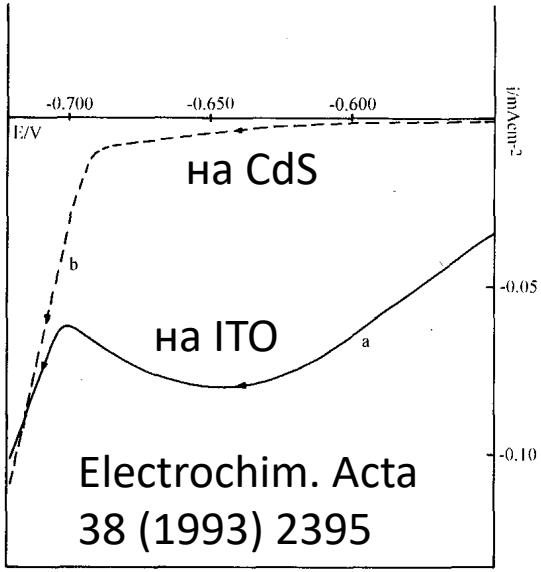
ECS Trans. 33 (2011) 75

(2) по аналогии с электрокристаллизацией оксидов (восстанавливается один компонент, второй присоединяется в химической реакции).

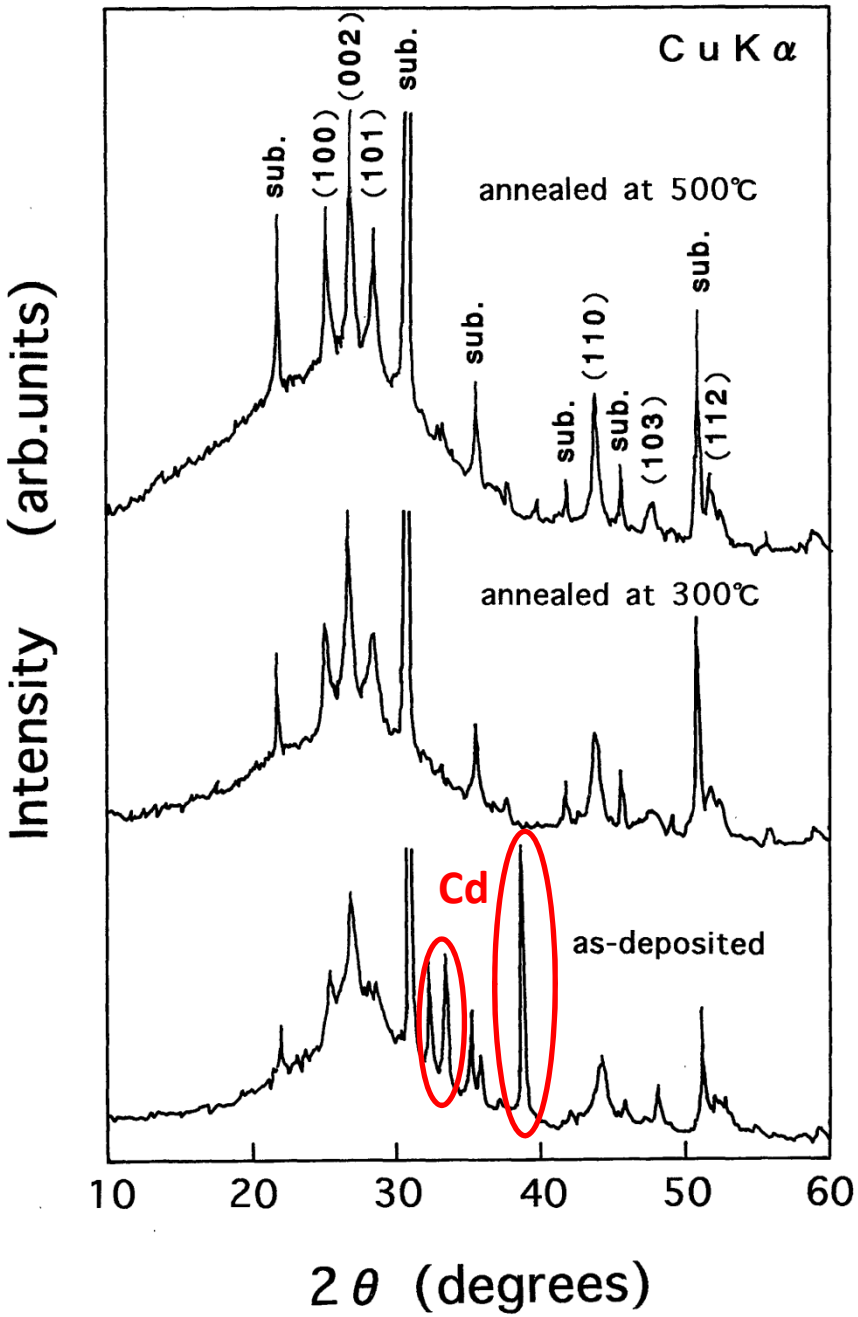
$$S_2O_3^{2-} + 2H^+ \rightleftarrows S + H_2SO_3$$

$$Cd^{2+} + S + 2e^- \rightleftarrows CdS$$

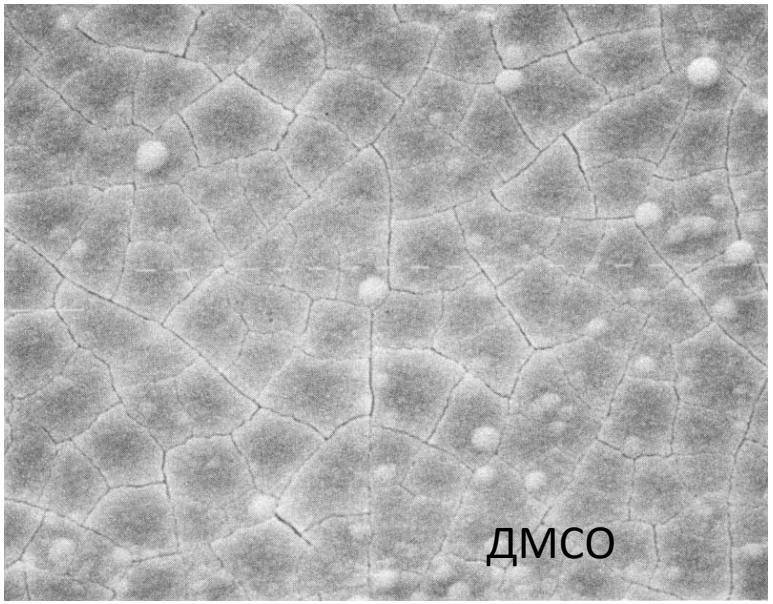
Побочный процесс - восстановление катиона



Electrochim. Acta 38 (1993) 2395



Jap. J. Appl. Phys. 35 (1996) 2057



Electrochim. Acta 32 (1987) 139