Электроосажденные оксиды: обратимые изменения стехиометрии, гидратация, структурные несовершенства

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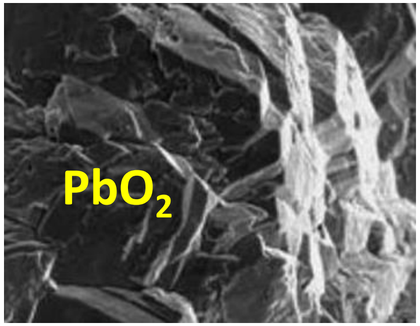
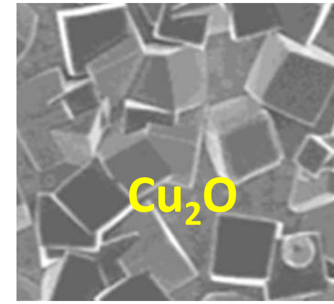
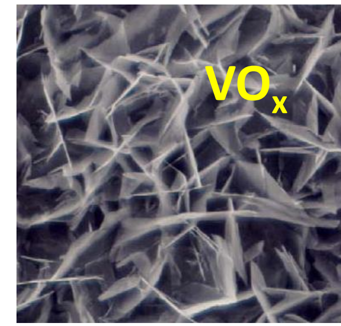


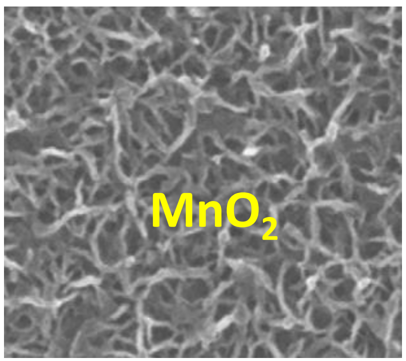
Requirements:

- at least two non-zero oxidation states;
- essential difference in solubility of the reduced and oxidized states in certain the solvent/medium;
- conductivity of the resulting solvent.



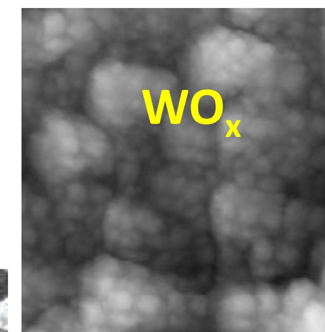


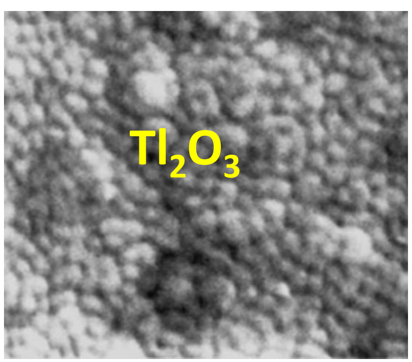
Anodic electrocrystallization

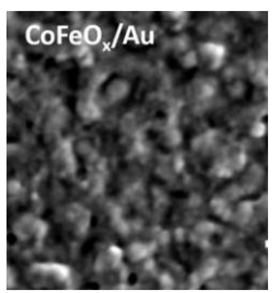


$$[M(OH)_x(H_2O)_y]^{z+}$$

Cathodic electrocrystallization







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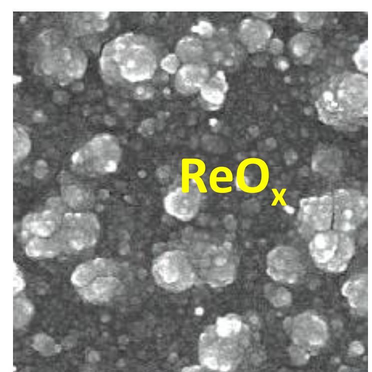

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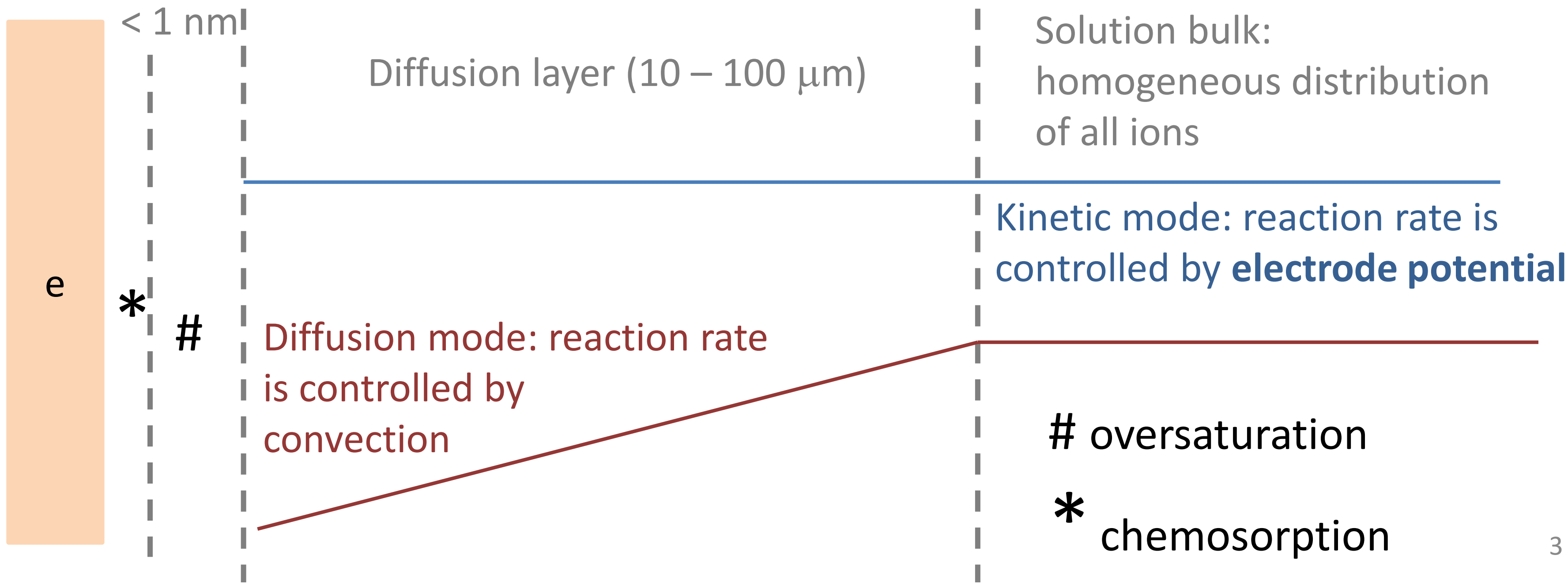
Electrochemistry starts, solution chemistry continues

Oxide-forming ions undergo electrode reaction (either oxidation or reduction) in the close vicinity of the interface, e.g.

$$\mathbf{Tl^{+} - 2e = Tl^{3+}} \quad \text{or} \quad \mathbf{Cu^{2+} + e = Cu^{+}}$$

Reaction products form insoluble solid compound with hydroxyl ions and/or other anions from the medium. Solids are formed just at the interface (**heterogeneous nucleation**) and undergo partial or complete dehydration:

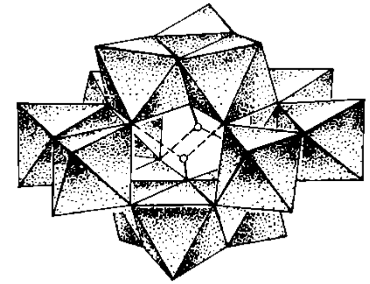
$$\mathbf{Tl^{3+} + 3OH^{-} \rightarrow hydrolysis} \rightarrow [Tl(OH)_3] \rightarrow Tl_2O_3 \quad \text{or} \quad \mathbf{Cu^{+} + OH^{-}} \rightarrow [CuOH] \rightarrow Cu_2O$$



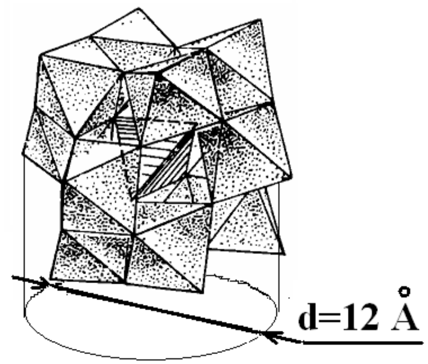
Cathodic deposition of non-stoichiometric tungsten oxides

Molecular Precursors

$[WO_4]^{2-}$

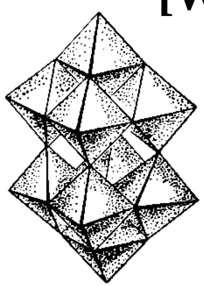


$[H_2W_{12}O_{42}]^{10-}$

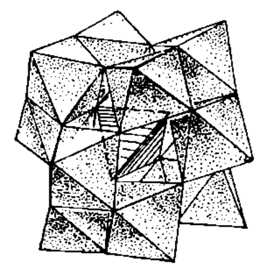


$[H_2W_{12}O_{40}]^{6-}$

$[W_{10}O_{32}]^{4-}$



and also



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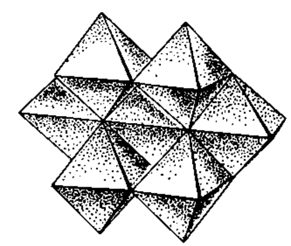
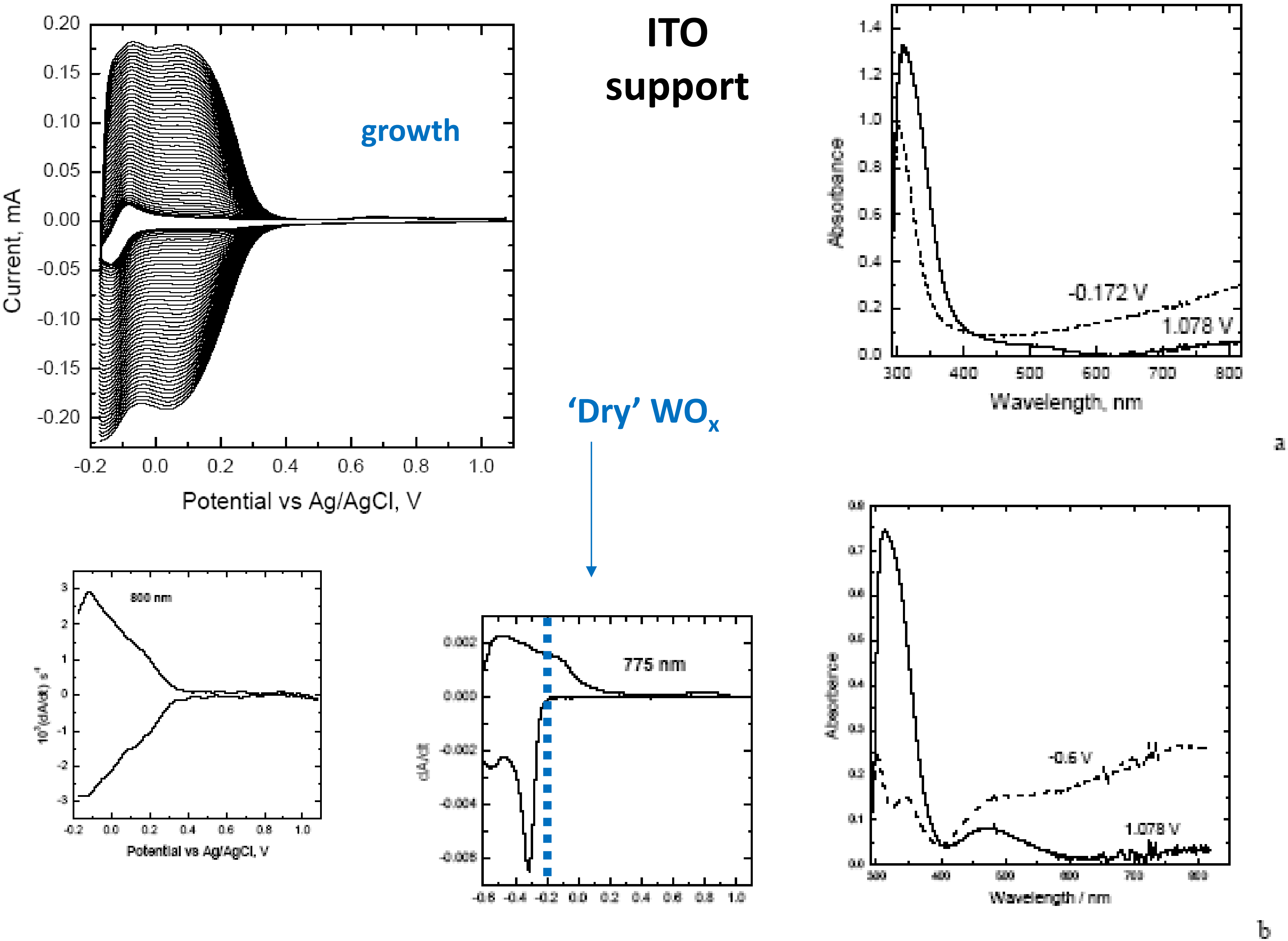


, etc

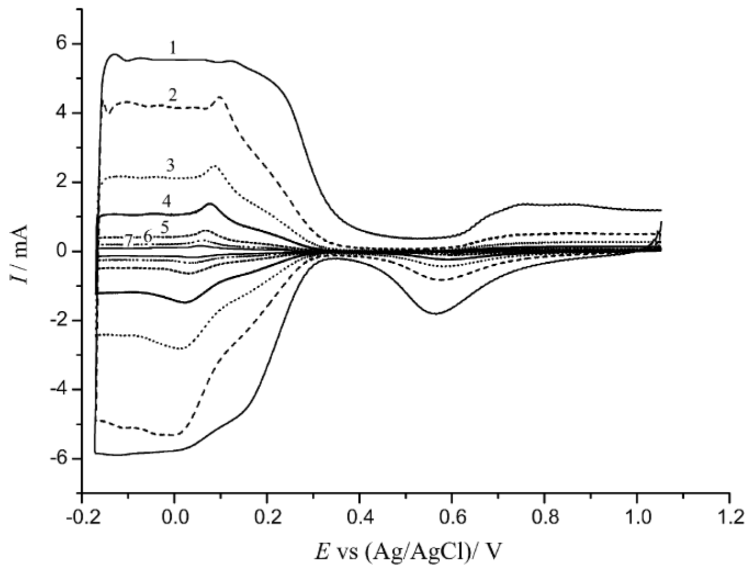
For all these W(VI) isopolyanions, W(V) containing mixed valence species can be generated under cathodic polarization.

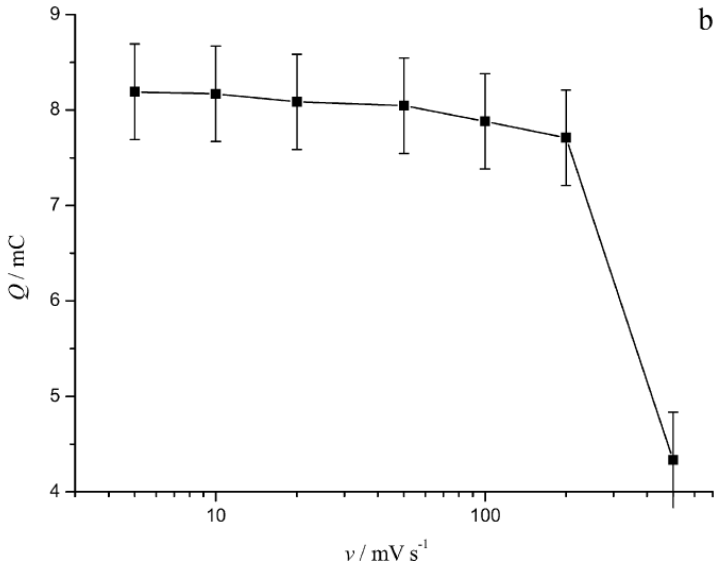

ITO support
growth
Current, mA
Potential vs Ag/AgCl, V
'Dry' WO_x
Absorbance
Wavelength, nm
-0.172 V
1.078 V
a
800 nm
10^3(dA/dt) s^{-1}
Potential vs Ag/AgCl, V
775 nm
dA/dt
-0.6 V
1.078 V
Wavelength / nm
b

Recharging in supporting solution

~ 10% W^{V}

	Charge, mC	W, $*10^7$, mol (from ICP-MS)	e per W atom	d, nm
Pt / film	2.7	2.26	0.12	60
Pt / film	14.3	14.15	0.11	390
FTO / film	6.3	9.75	0.07	140
Pt / aged film	7.2	7.67	0.10	160

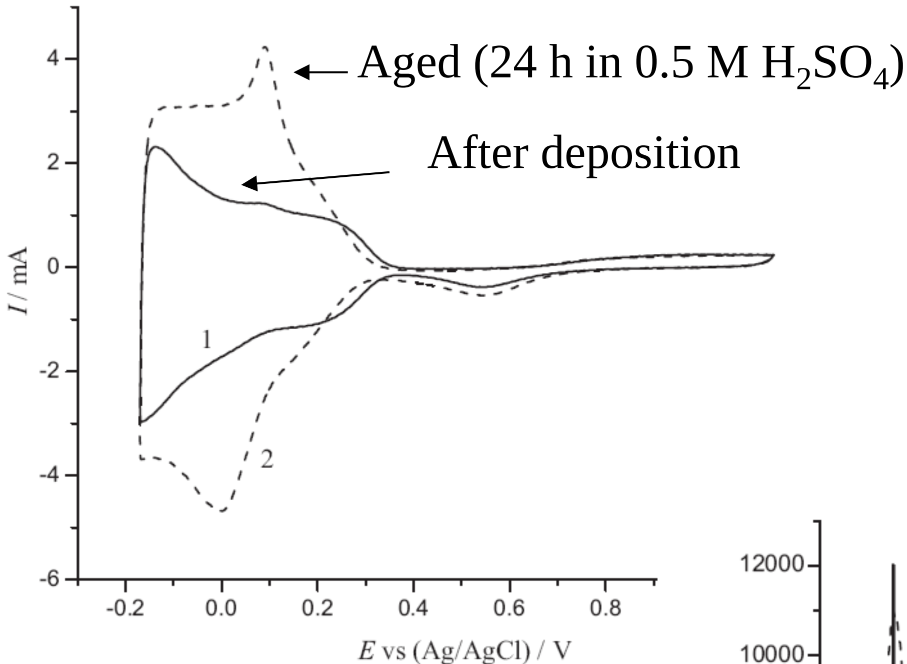


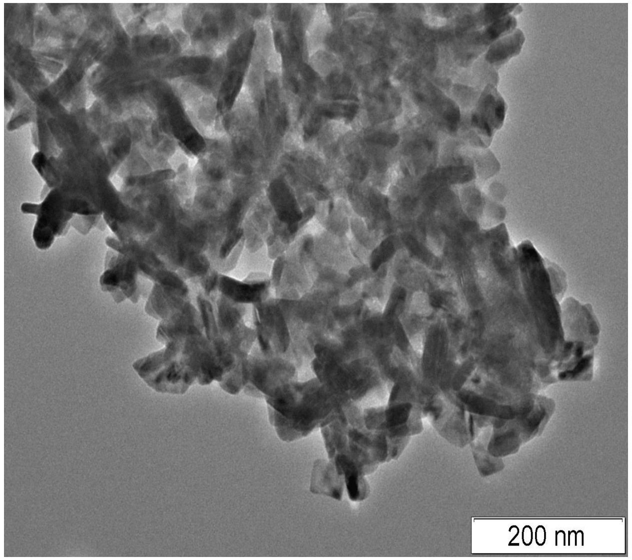


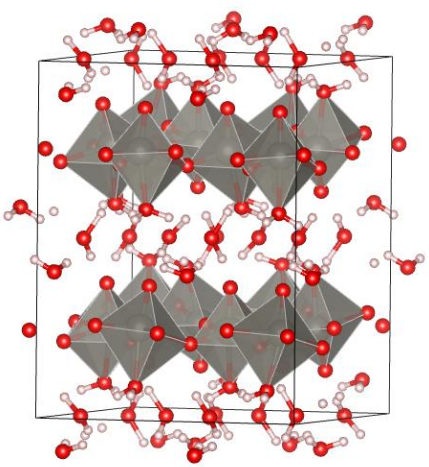
Our data: D ~ 10^{-6} cm^2 s^{-1}

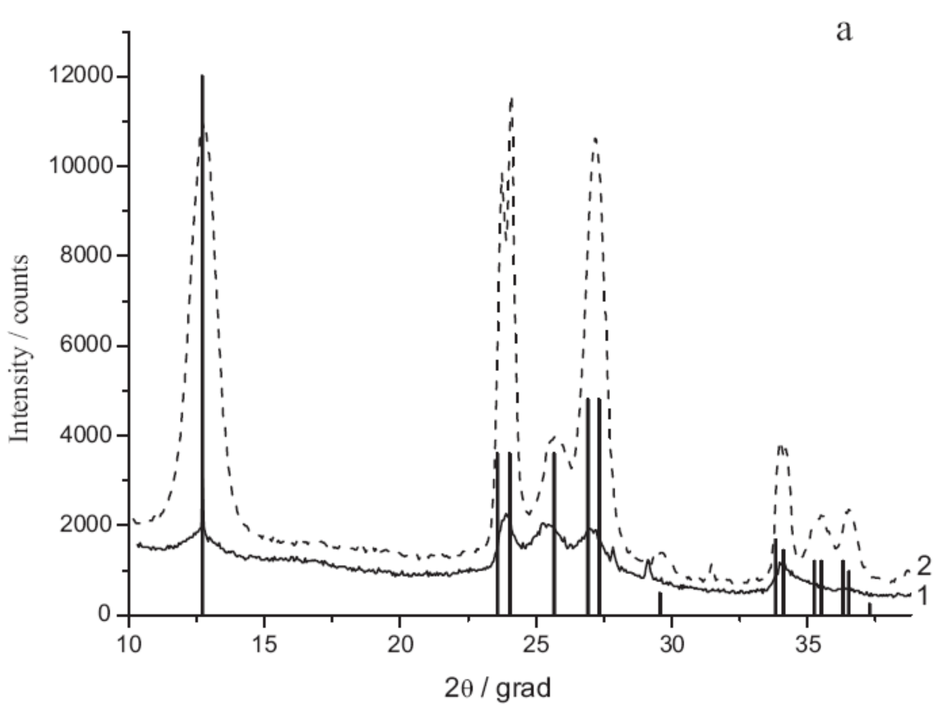
For anhydrous WO_3: D ~ 10^{-8} – 10^{-12} cm^2 s^{-1}

Ageing: 'development of crystallinity'

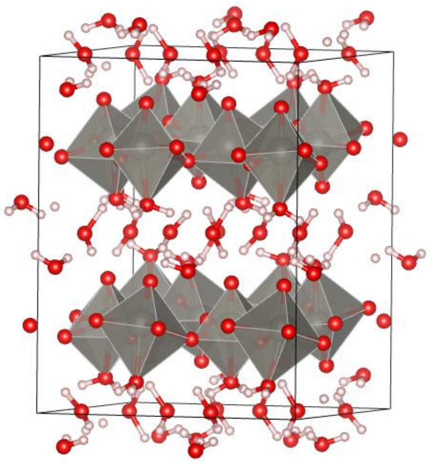


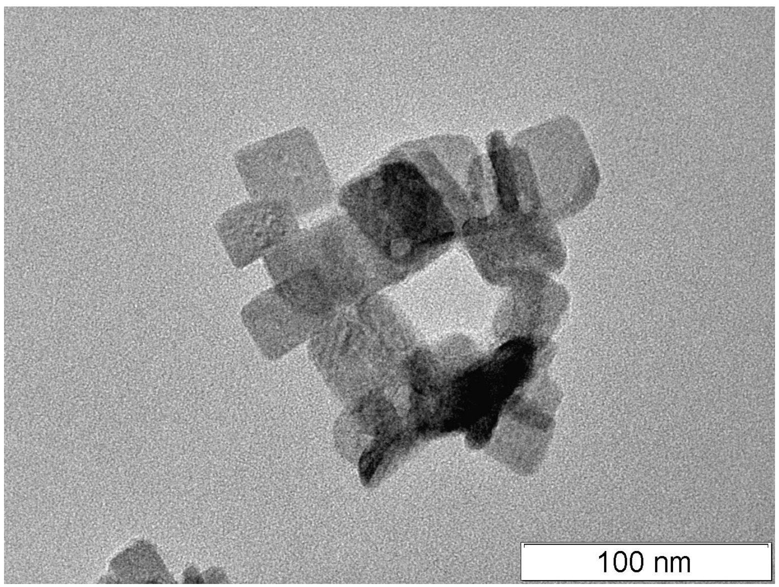


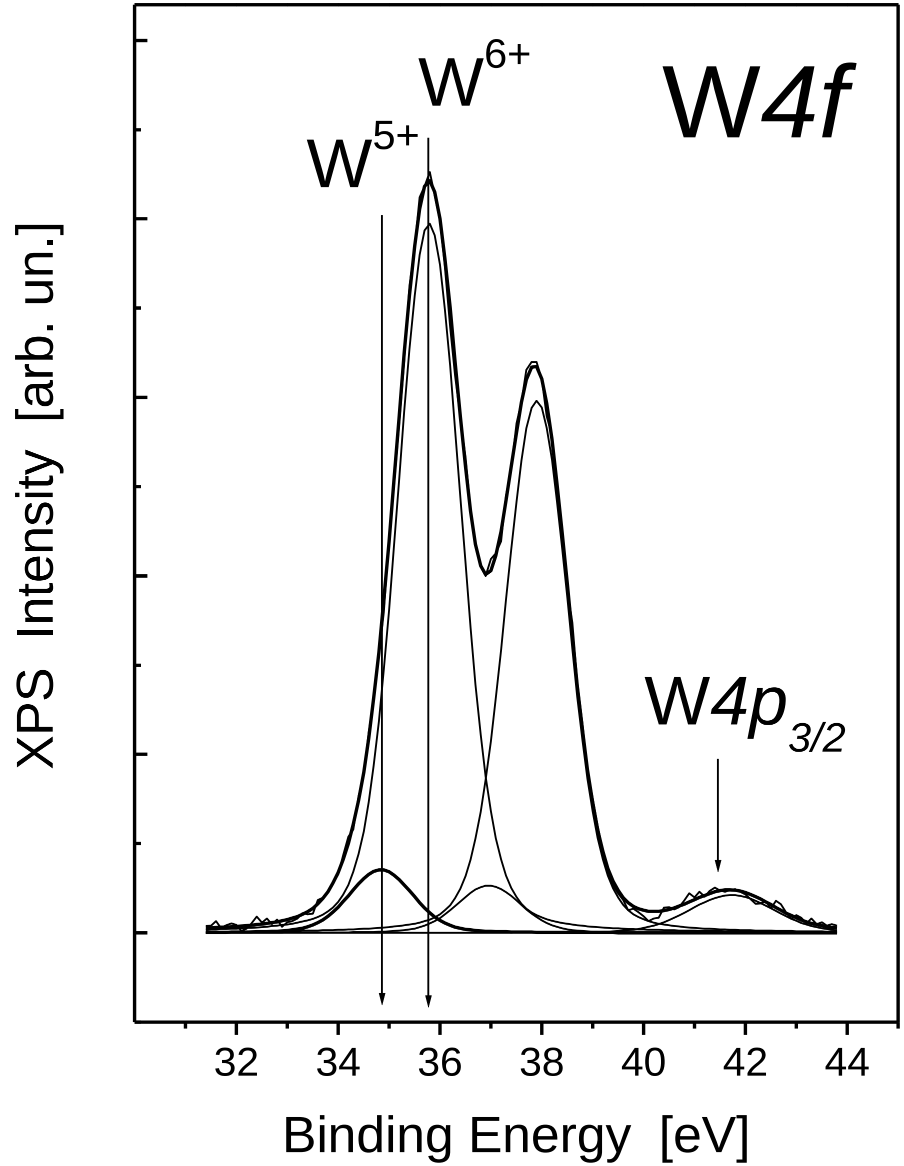




Ageing:
ca. 8% of tungsten keep 5+ oxidation state even in air





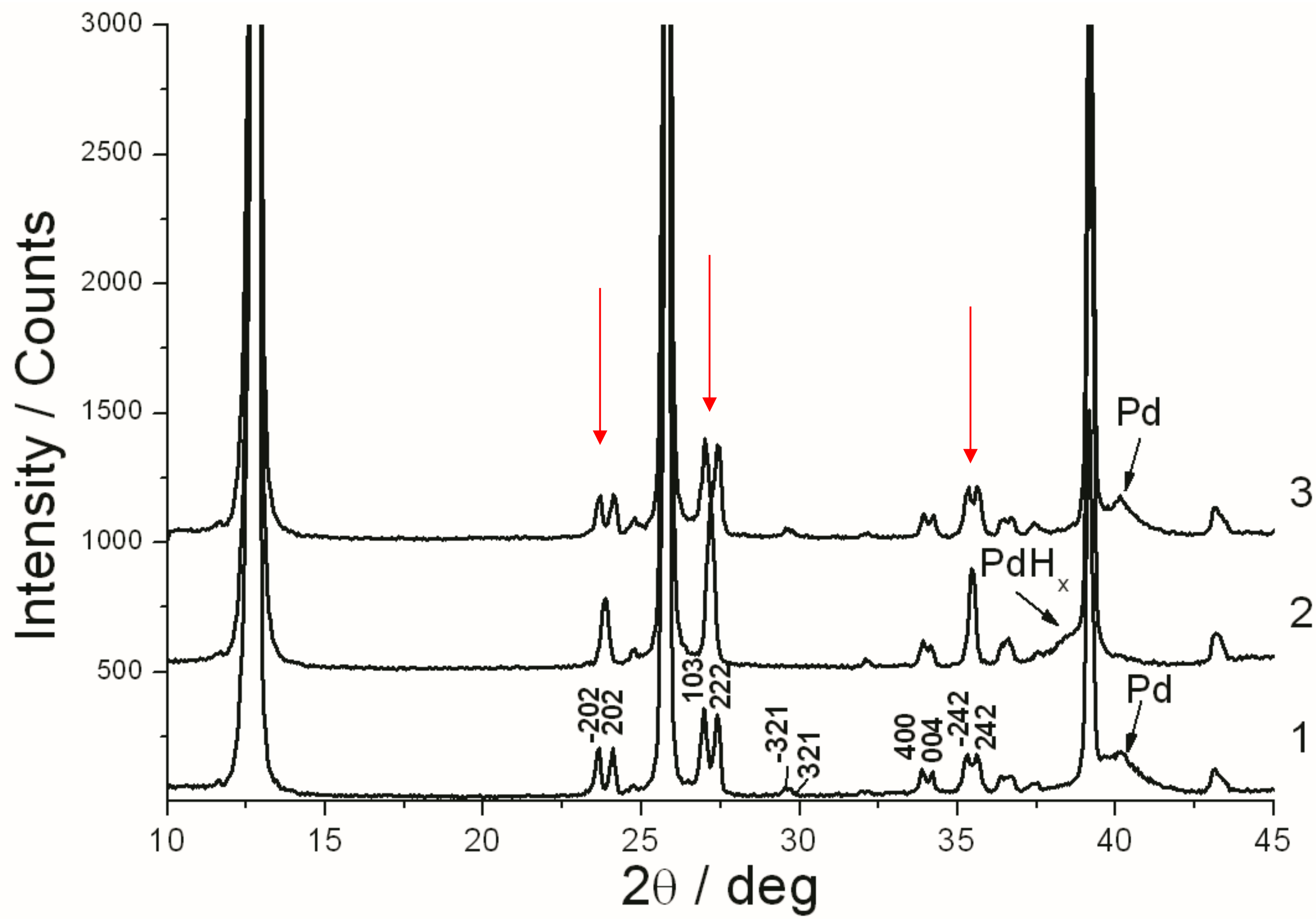


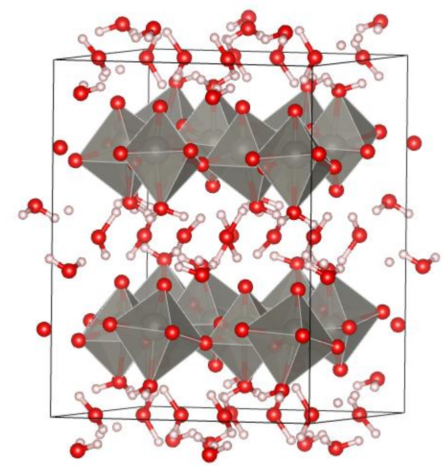
Reversible cycling in the gas phase:

Model experiments with tungstic acid powder

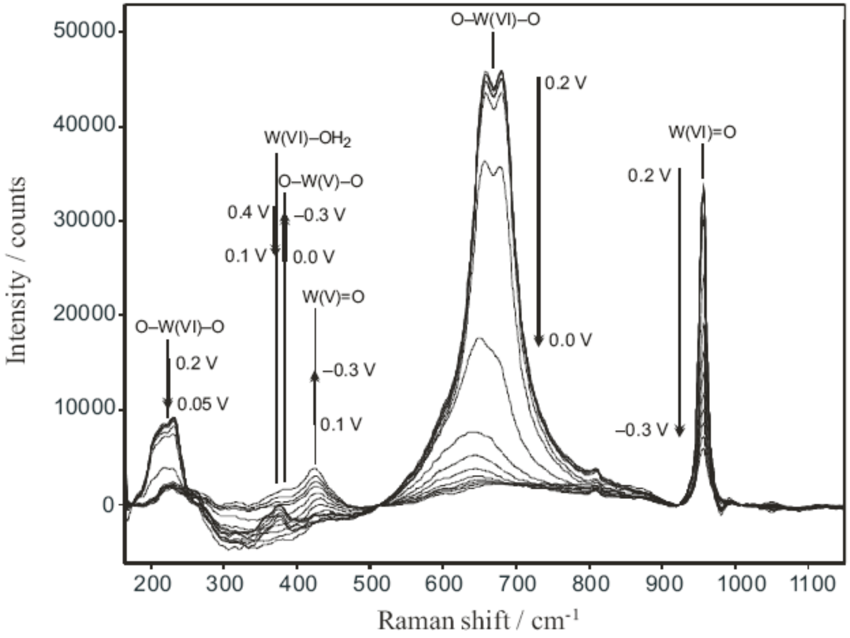
H_2 – He – H_2, Pd catalyst

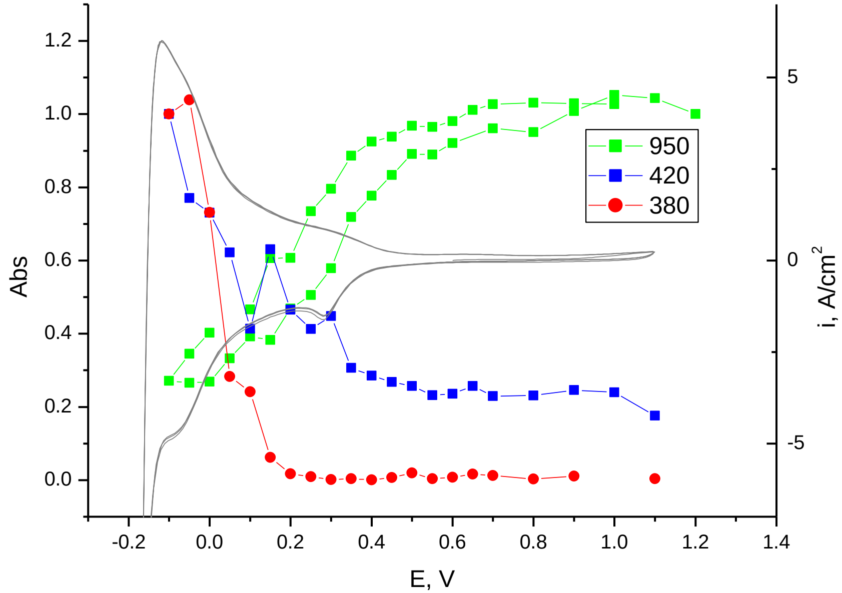
monoclinic/orthorhombic





In- situ Raman





E < 0.3 V — ↓ $956\ cm^{-1}$ W(6)=O (WO_3*$2H_2O$)
— ↓ $670\ cm^{-1}$ O-W(6)-O;

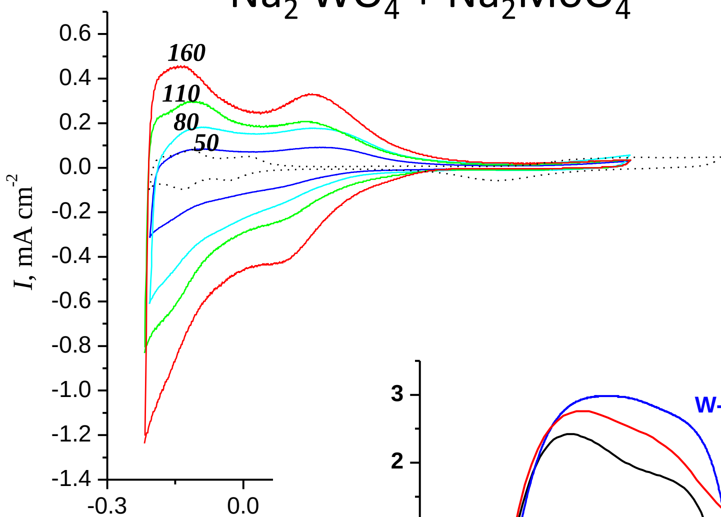
E < 0.2 V — ↑ $380\ cm^{-1}$ O-W(5)-O

E < 0.3 V — ↑ $425\ cm^{-1}$ W(5)=O

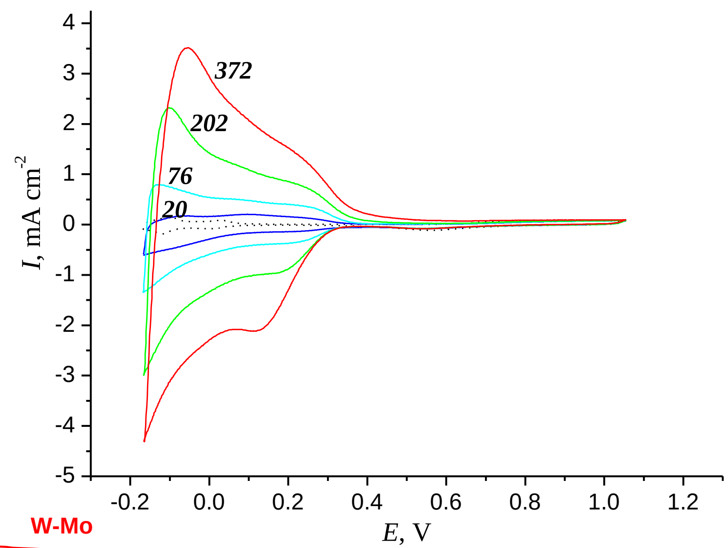
Deposition of tungsten-based doped oxides

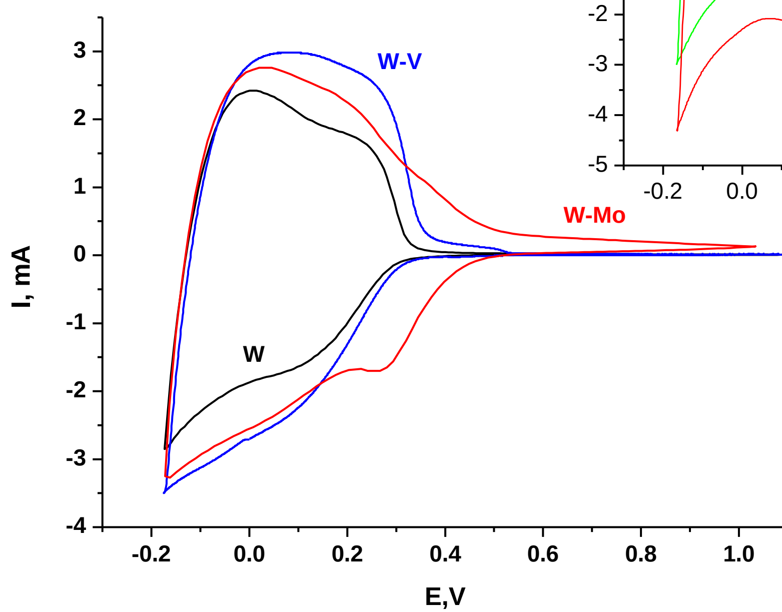
200-700 cycles in Na_2WO_4 metastable solution or mixtures (12 mM total concentration) in 0.5 M H_2SO_4

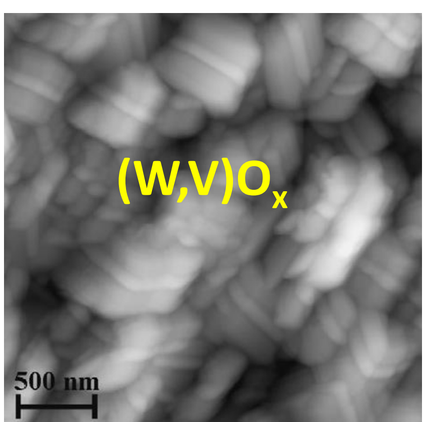
$Na_2\ WO_4 + Na_2MoO_4$

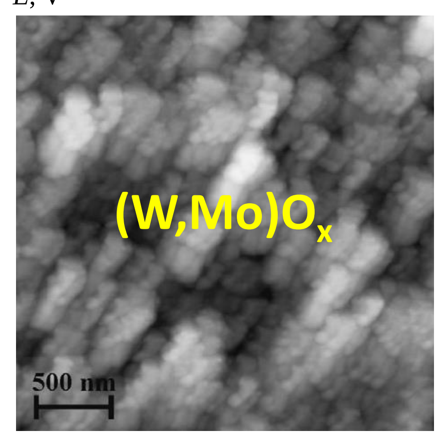


$Na_2WO_4 + NaVO_3$



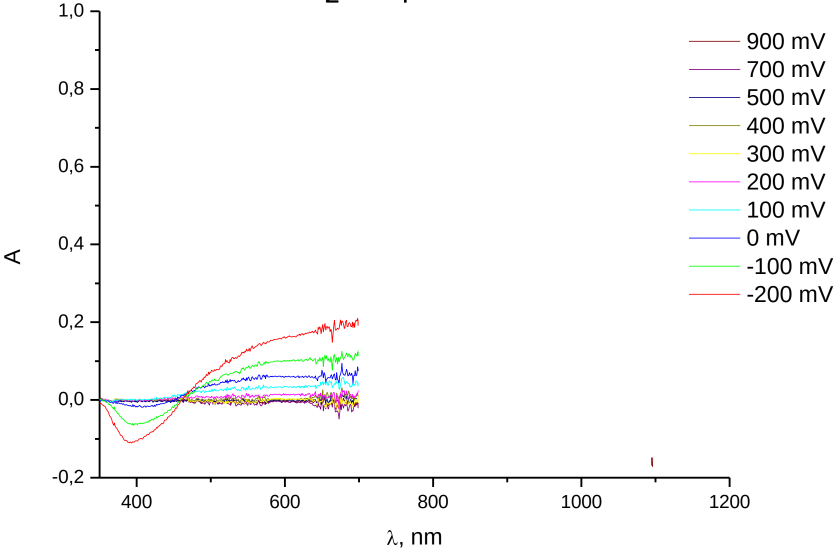


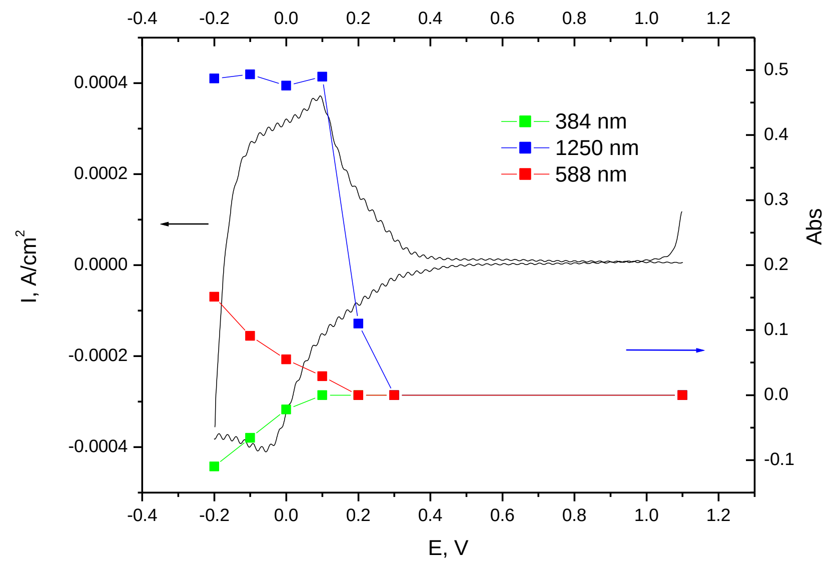


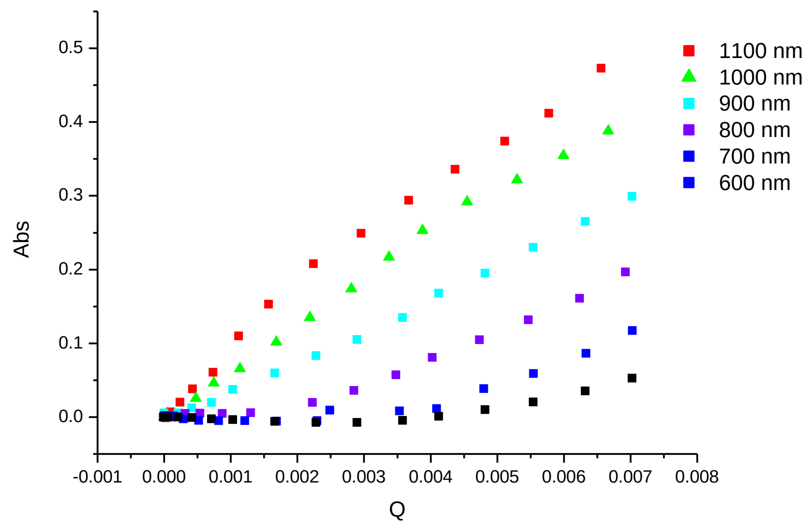


In-situ UV-VIS characterization (W-V film)

($2\ M\ H_2SO_4$)

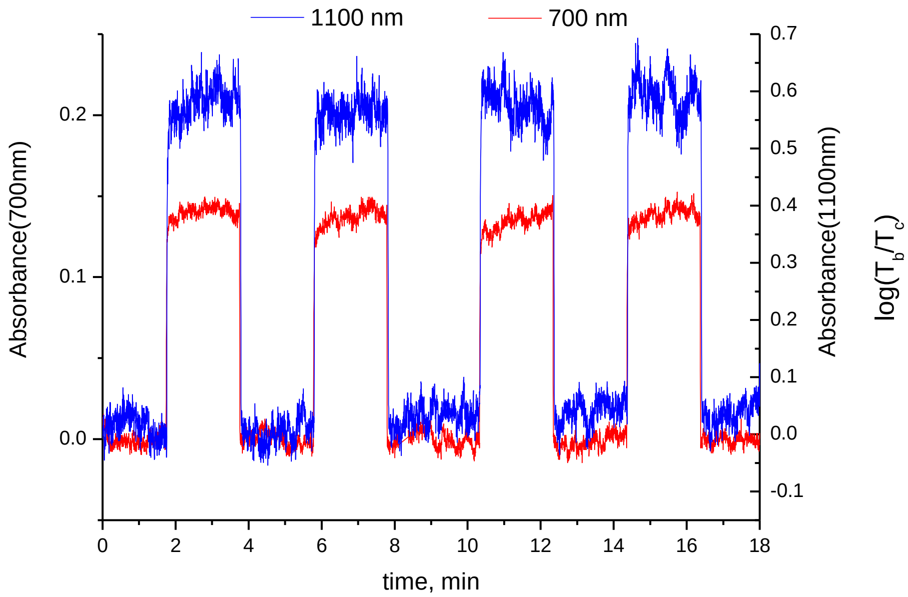




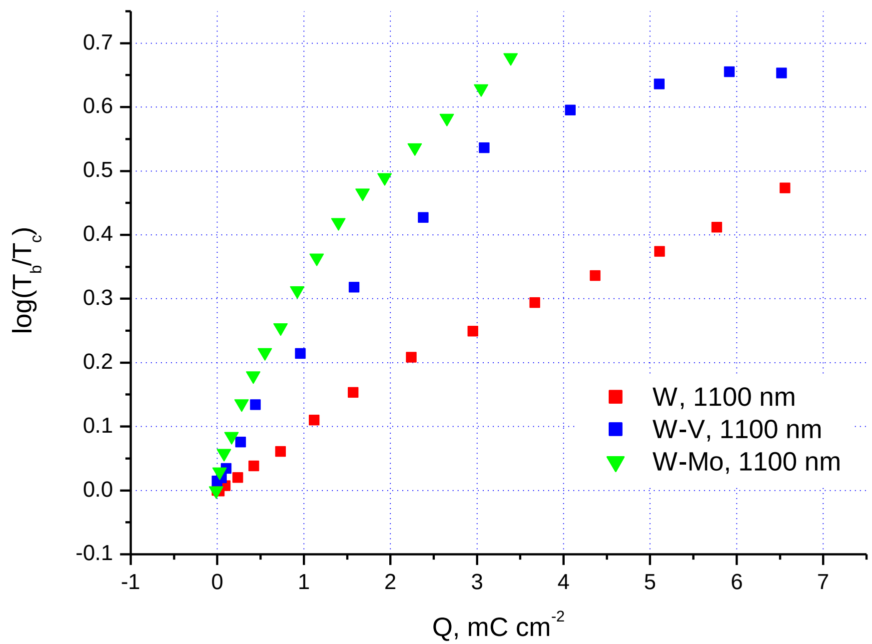


- ~400 nm - α-WO_3
- 620 -700 nm – W5/W6 or V4/W6 ?
- 1000 nm – charge transfer W5/W6 or V4/W6

Coloration efficiency (1100 nm) and response time, 2 M H_2SO_4



●CE=1/Q log(Tb/Tc)



700 nm:

τ (0,5 M H_2SO_4) ≈ τ (2.0 M H_2SO_4)

τ (700 nm) > τ (1100 nm)

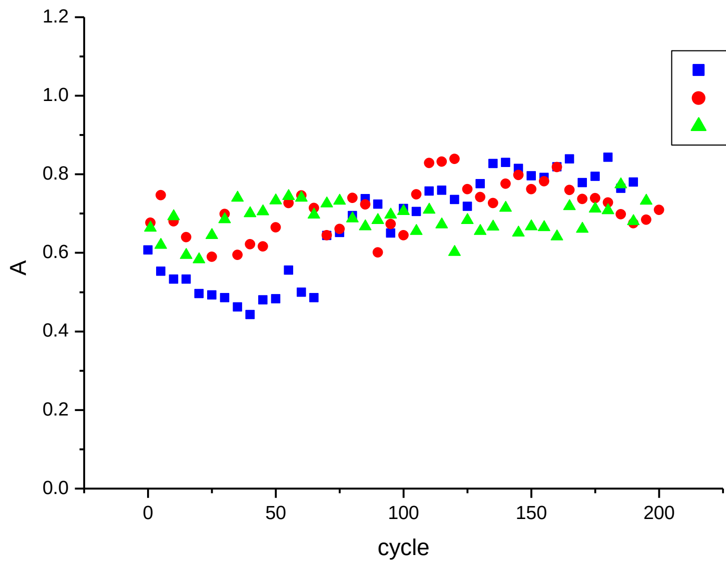
Small charges (< 2–4 mC cm^{-2}):

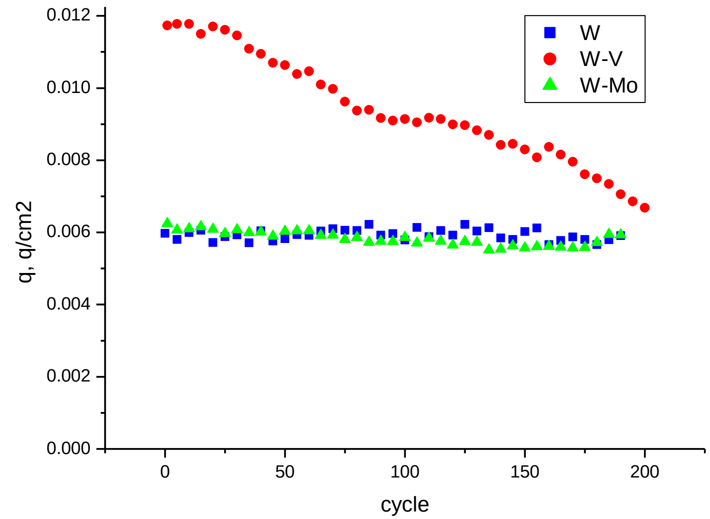
- CE (W) = 95 $cm^2\ C^{-1}$
- CE (V-W) = 269 $cm^2\ C^{-1}$
- CE (Mo-W) = 183 $cm^2\ C^{-1}$

Higher CEs at 1100 nm

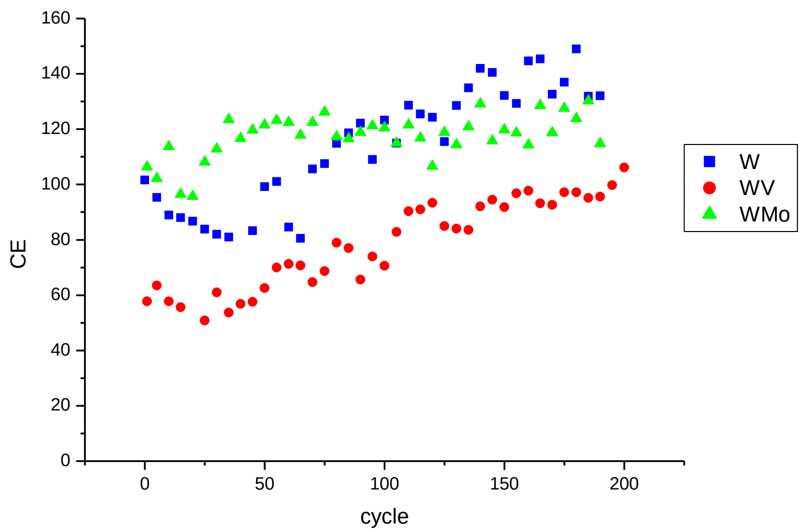
Higher CEs for doped films

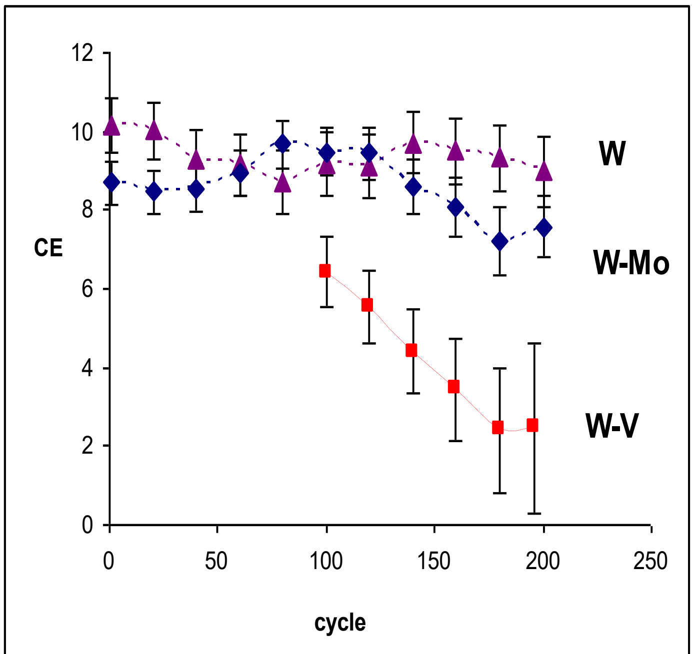
Cycling stability in 2.0 M H_2SO_4





2.0 M H_2SO_4 vs. 0.5 M H_2SO_4



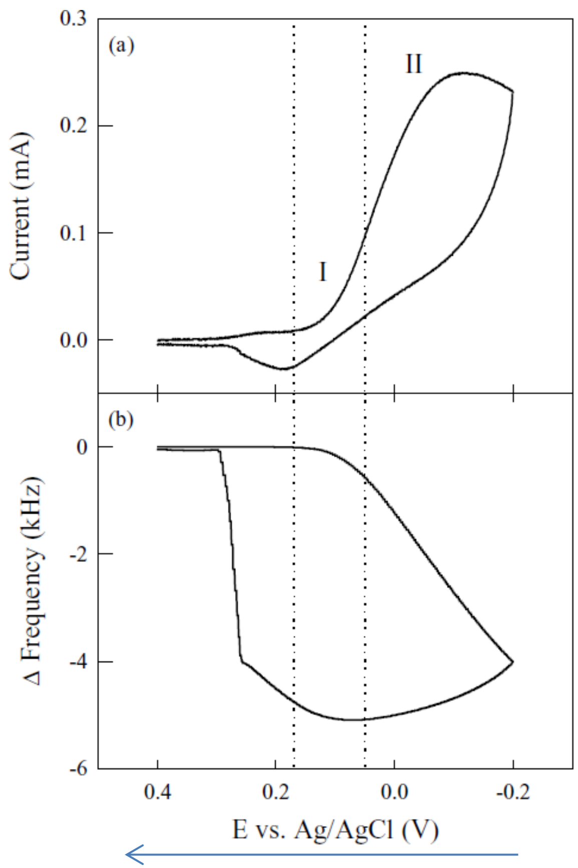


Alternative way: deposition from peroxo-complexes

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

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

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

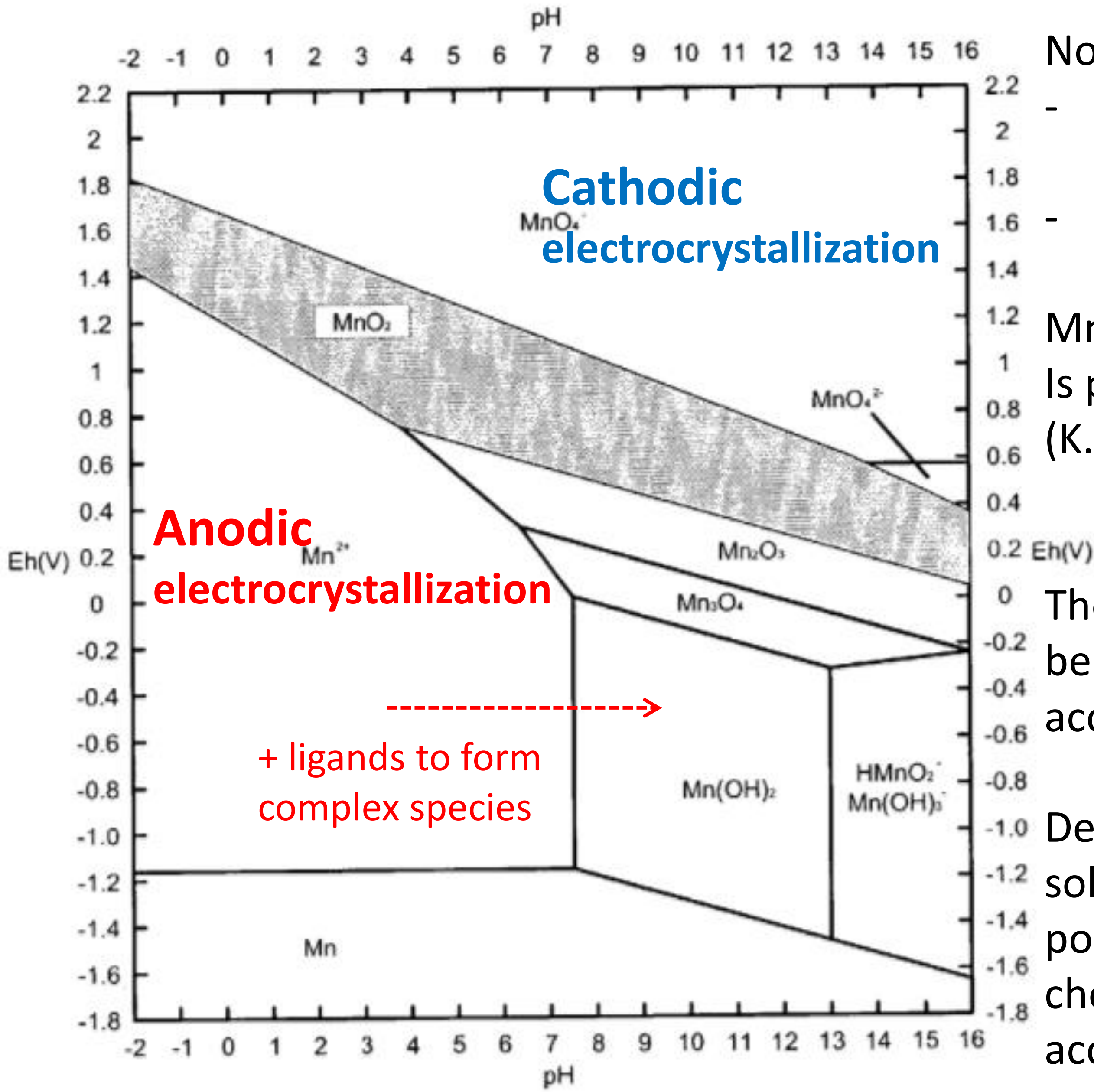


T.M.McEvoy, K. J. Stevenson,
Anal. Chim. Acta 496 (2003) 39–51

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]

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

Any synthesis starts from Pourbaix diagram (as the first approximation)



No exact thermodynamic data

- for various MnO_2 crystal modifications ,
- for various oxohydroxides.

$MnO_{2-\delta}$ oxygen stoichiometry Is potential-dependent (K. Vetter).

The slopes of E, pH lines can be slightly different if one accounts for δ.

Despite of these uncertainties, solution composition and potential interval can be chosen with a reasonable accuracy.

Kinetics of Electrodeposition of γ-Manganese Dioxide

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

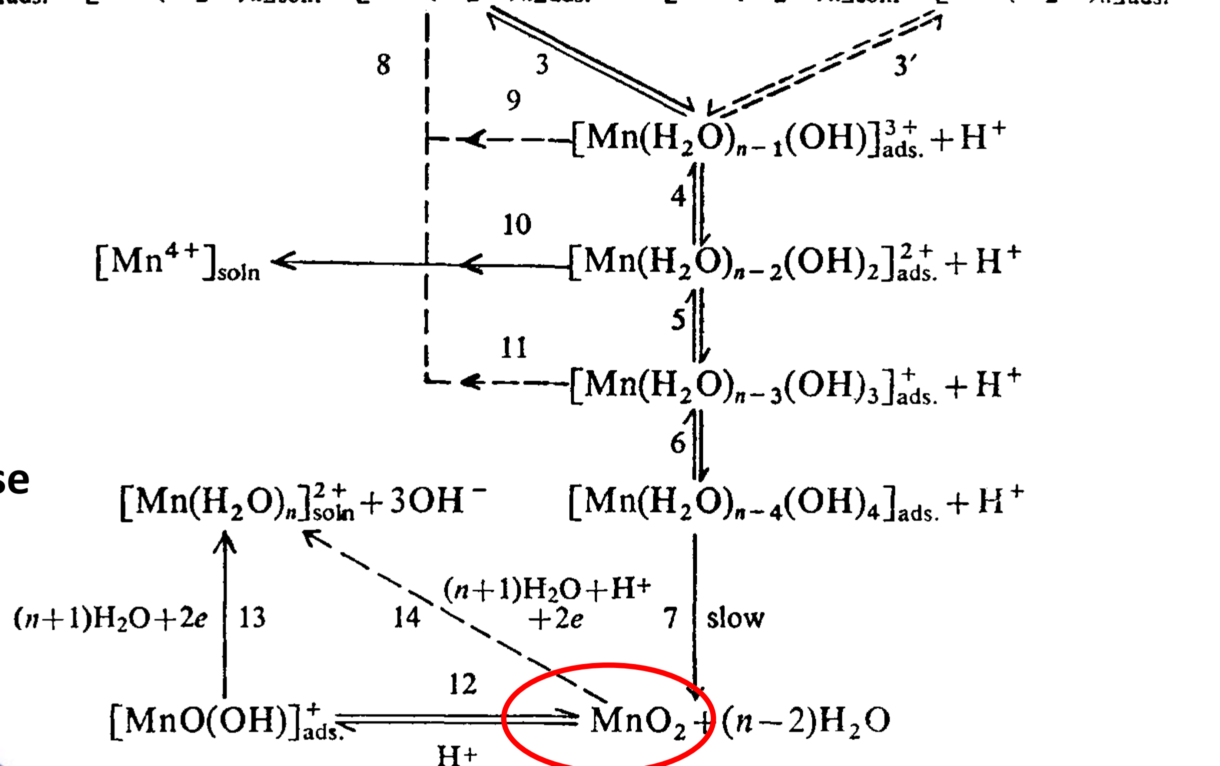
By M. Fleischmann, H. R. Thirsk and I. M. Tordesillas

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

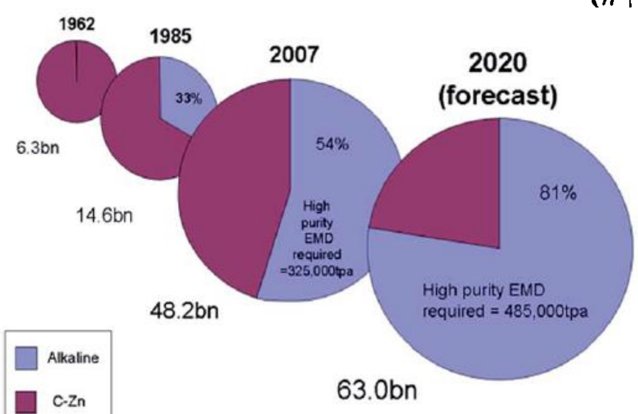
$$[Mn(H_2O)_n]^{3+}_{ads.} + [Mn(H_2O)_n]^{3+}_{ads.} \overset{2}{\rightleftharpoons} [Mn(H_2O)_n]^{2+}_{soln} + [Mn(H_2O)_n]^{4+}_{ads.}$$

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

The principle industrial process:
β-MnO_2 from acidic bath



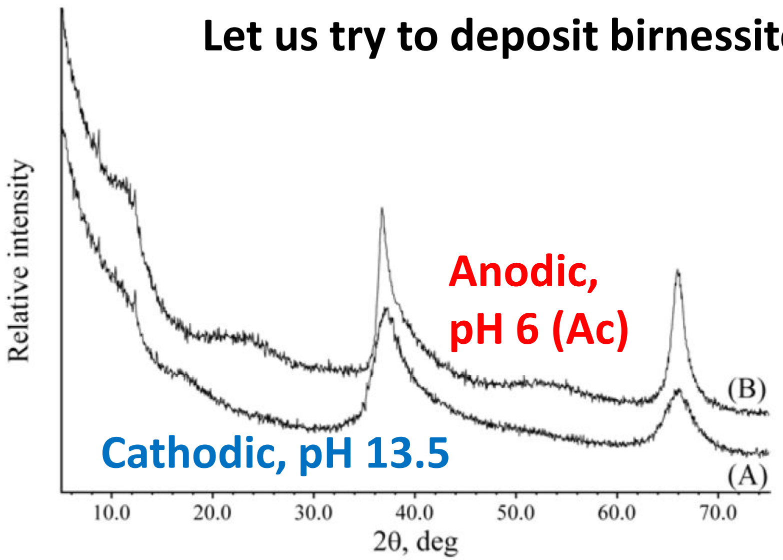
EDM (electrolytic manganese dioxide) demand:



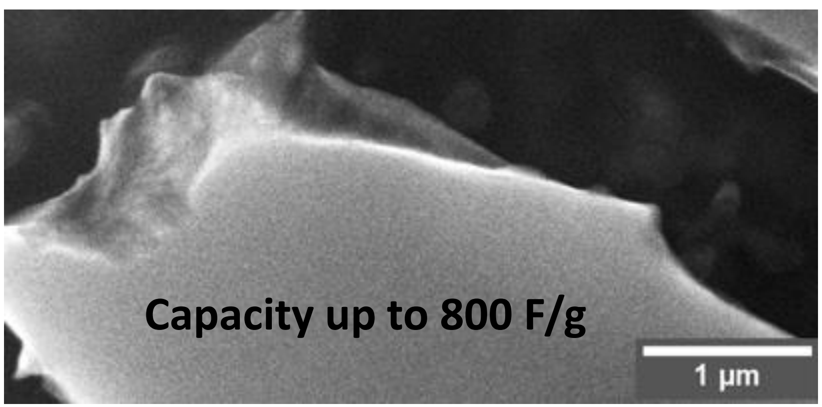
Recent review:
RSC Advances, 5 (2015) 58255-58283

The principle industrial process: β-MnO_2 from acidic bath. *However* the material operates in alkaline medium, and birnessite formation is unavoidable.

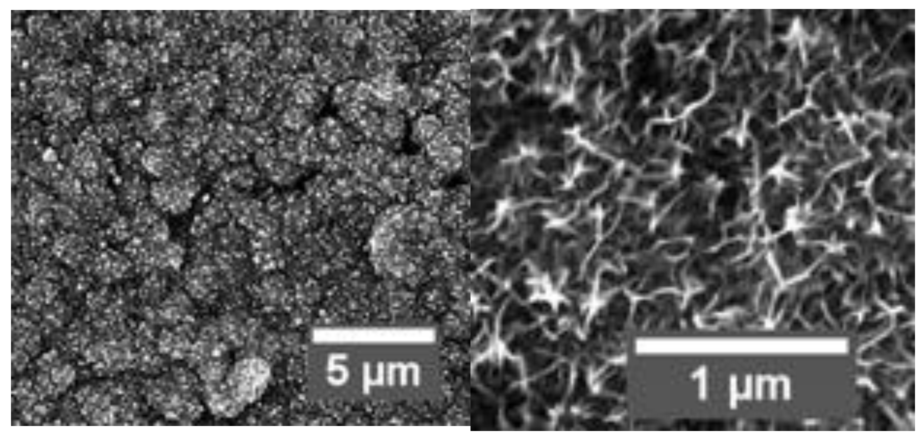
Let us try to deposit birnessite directly? $KMnO_4 + 3\ e + 2\ H_2O \rightarrow K_xMnO_2 + 4\ OH^-$



Loading, µg/cm		ORR current A/g
91	Anodic	10.5
85	Cathodic	28
91	Chem. synth. with C-binder	24



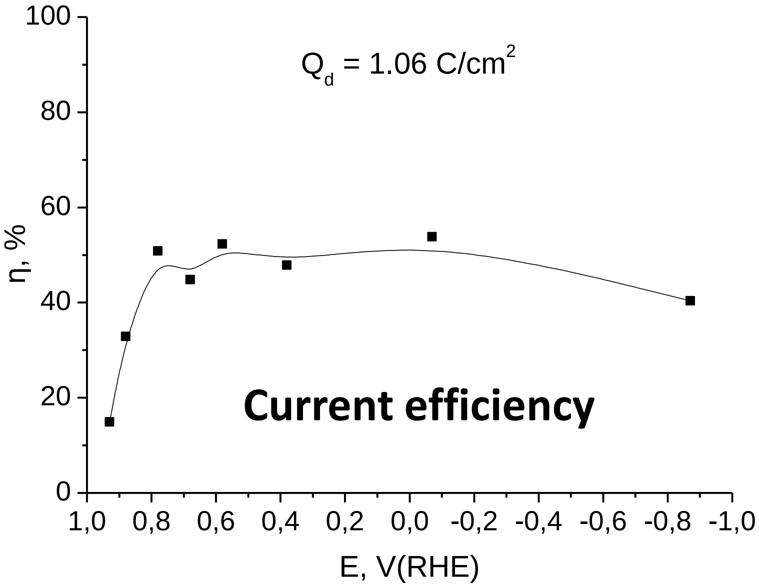
Slow **cathodic** deposition (**kinetic mode**) allows to obtain the compact, but highly dispersed material.

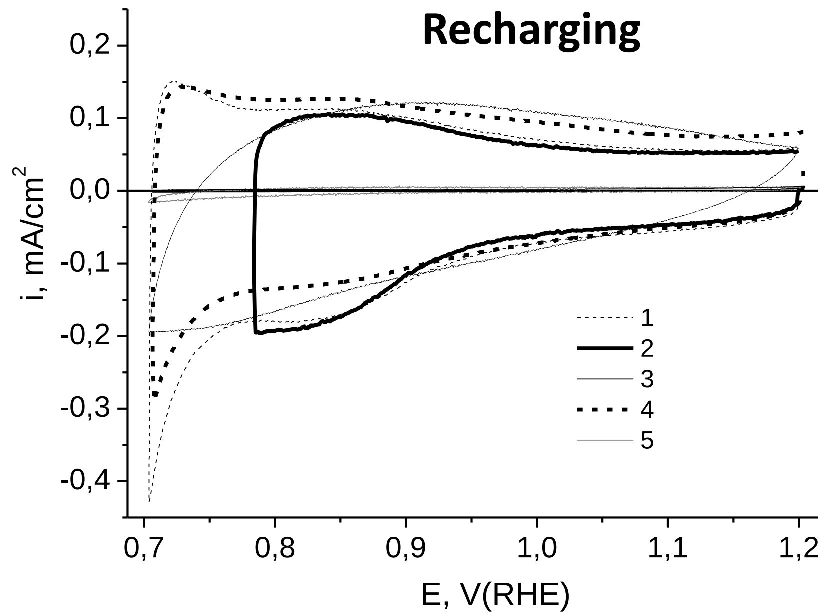


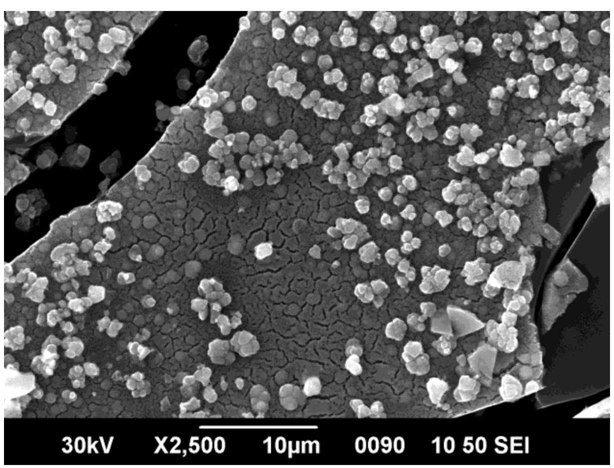
Anodic deposition, as well as cathodic deposition under diffusion control result in formation of resistive flakes.

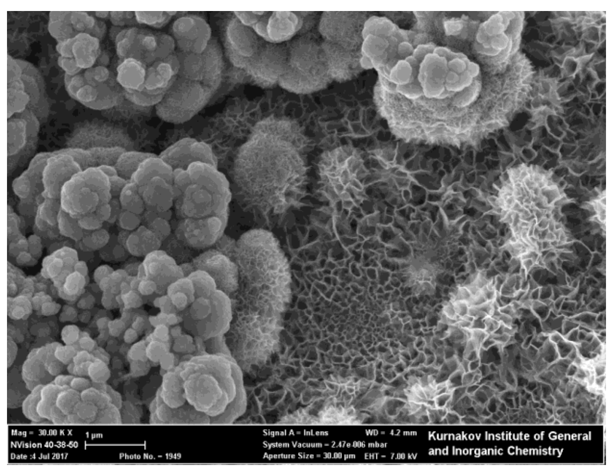
L.V. Pugolovkin et al, ECS Trans. 85 (2018) 137-145

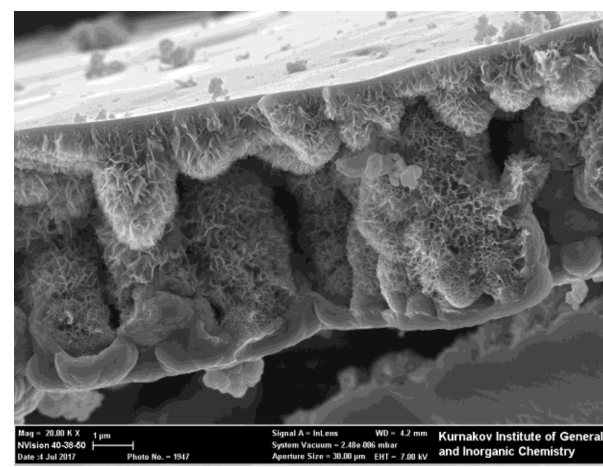
Cathodic deposition from permanganate: less usual technique



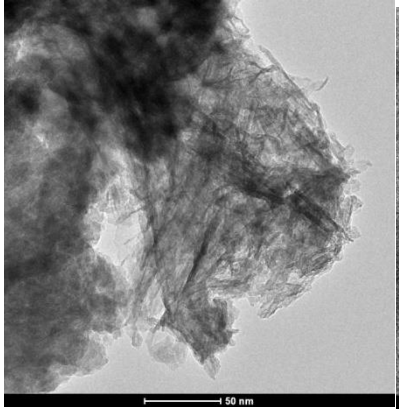


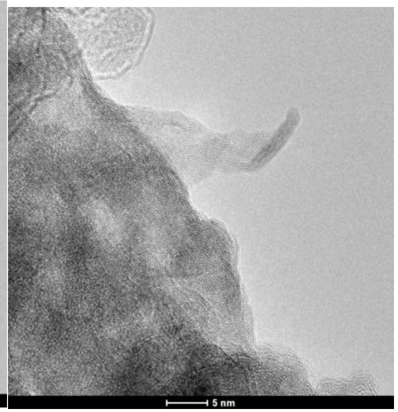




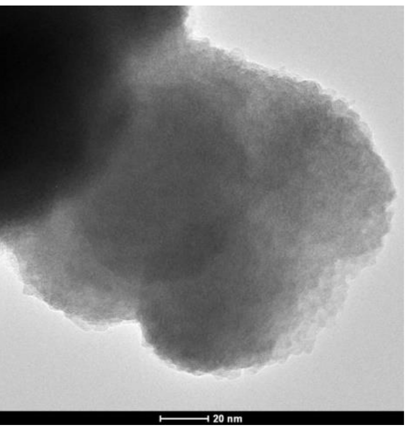


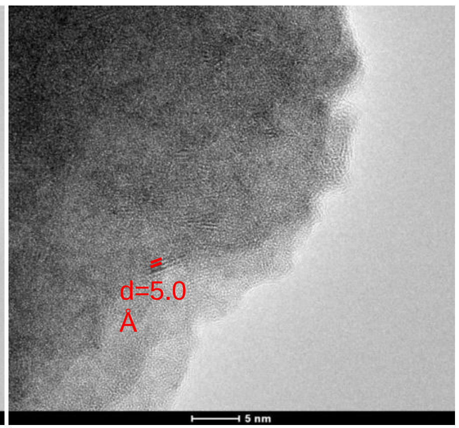
TEM (Antwerpen: Joke Hadermann, Maria Batuk)





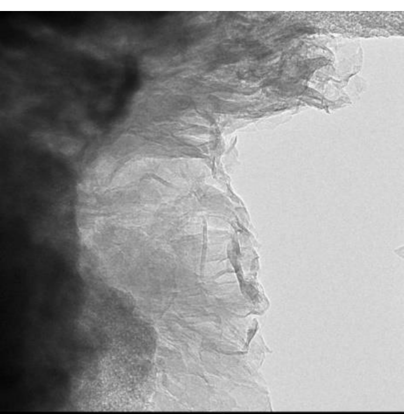
Anodic deposition

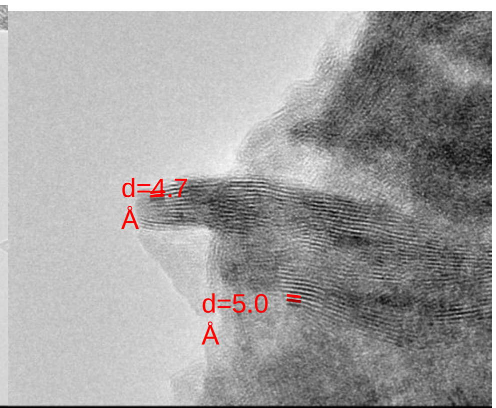




Cathodic deposition at low overvoltage,

good recharging





Cathodic deposition at higher overvoltage,

bad recharging

Задачи для in situ структурного экспермента:

- Мониторинг роста
- Эволюция после осаждения при разомкнутой цепи
- Мониторинг перезаряжения

Сложности:

- Сильное разупорядочение, вплоть до рентгеноаморфности
- Ограниченность толщин осадков и площади электродов
- Наличие кристаллических подложек