Second International Workshop on Durability and Degradation Issues in PEM Electrolysis Cells and its Components , february 16th, 2016

Corrosion Protective Coatings for Bipolar Plates and Current Collectors in PEM Electrolysers

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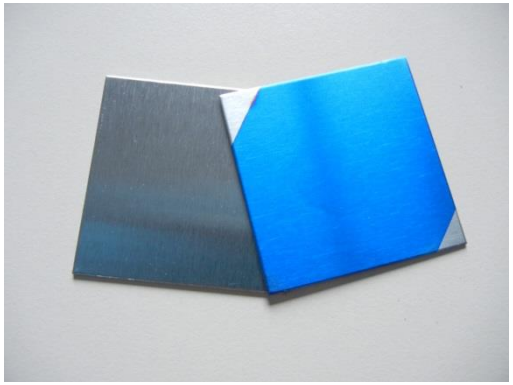


"Novel materials and system designs for low cost, efficient and durable PEM electrolysers"

agenda

- passivation of uncoated titanium
  - valve metal properties, high field model
  - electrochemical methods of ex-situ characterization: LSV, CA
  - interfacial contact resistance (ICR)
- method of deposition: sputtering
- coated bipolar plates
- stack tests

passivation of titanium

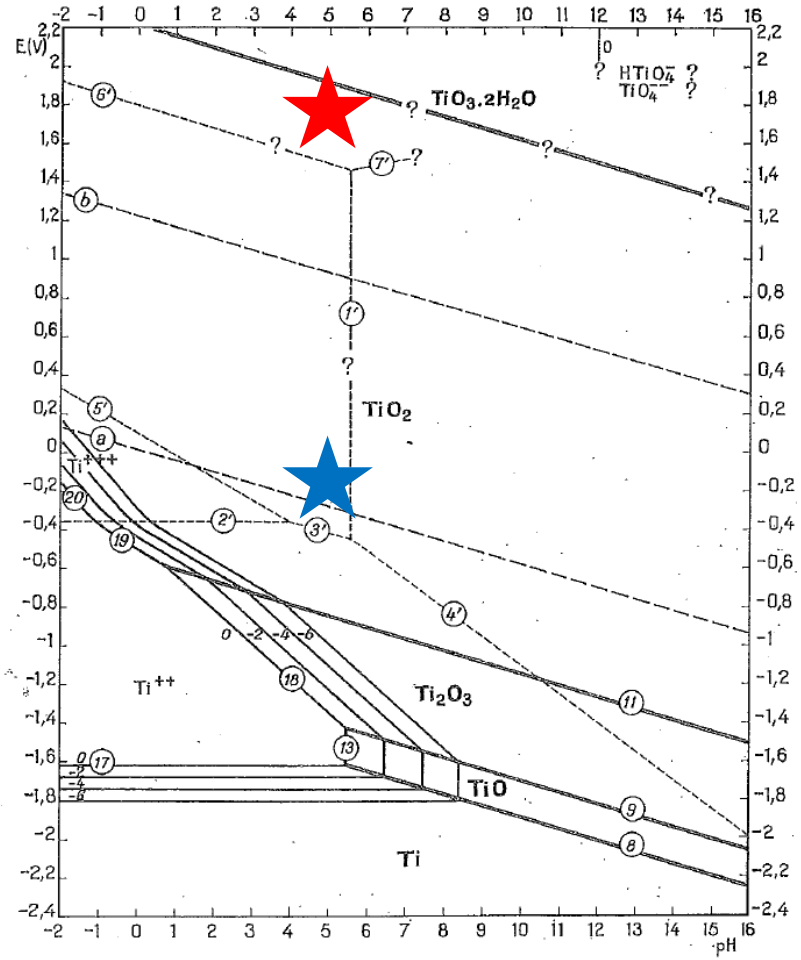


FIG. 1. Potential–pH equilibrium diagram for the system titanium–water, at 25°C. [Figure established by considering, as derivatives of tri- and tetravalent titanium, the anhydrous oxides Ti_2O_3 and TiO_2 (rutile).]

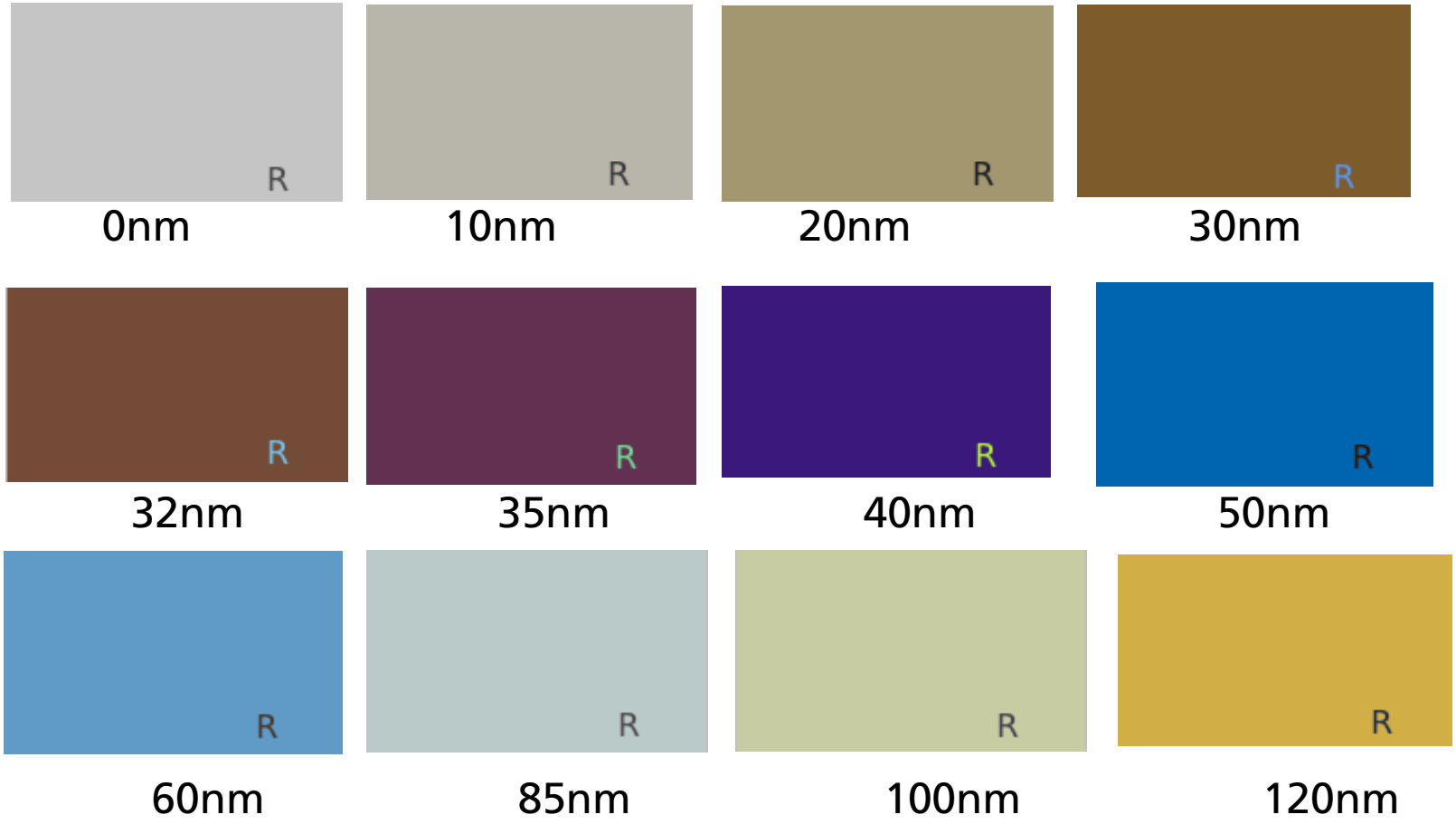
anode

cathode

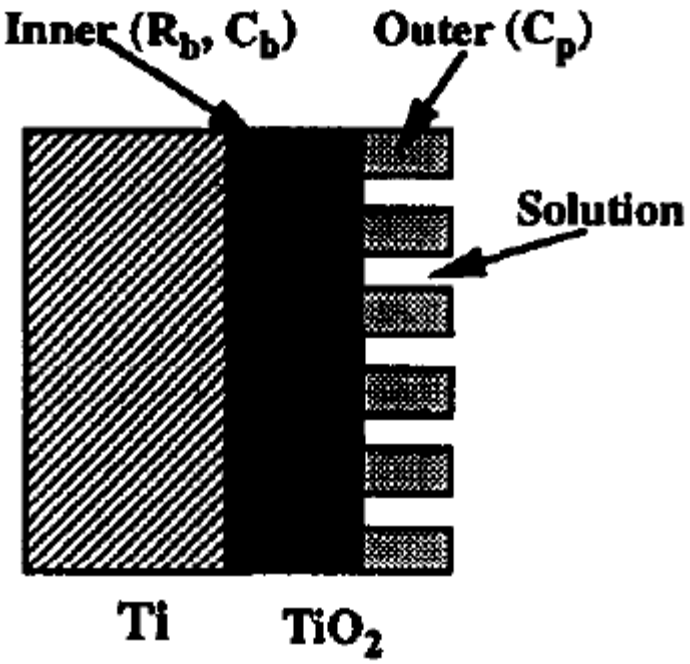
roughly 10..20nm of TiO_2 on Ti

passivation of titanium: colour corresponds to thickness

- reflectance: optical simulation :



passivation of titanium

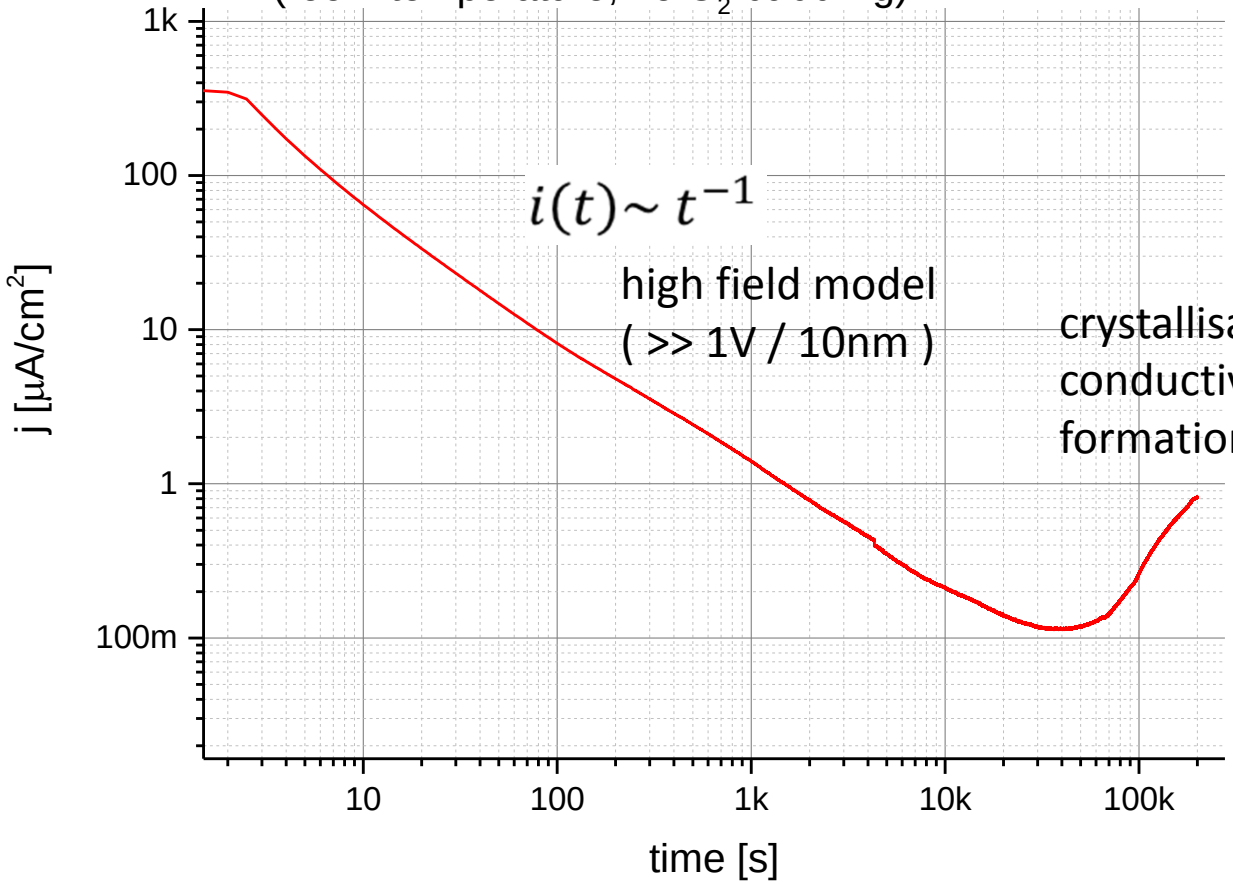


in general:
inner (compact) and outer (porous) oxide layer

Pan, J., Thierry, D., & Leygraf, C. (1996). Electrochemical Impedance Spectroscopy Study of the Passive Oxide Film on Titanium for Implant Application. *Electrochemica Acta, 41*, 1143-1153.

passivation of titanium: “valve metal”

Chronoamperometry on uncoated Ti at 2V vs. SHE
(room temperature, no O_2 bubbling)



crystallisation of TiO_2
conductive for electrons
formation of O_2

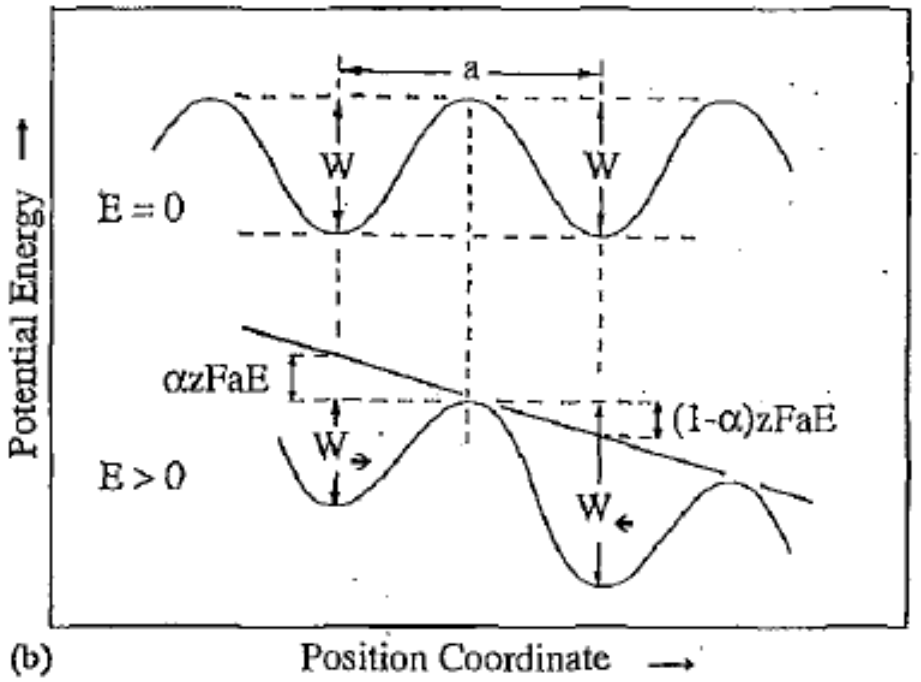
passivation of titanium: high field model

high field model:

hopping process of ions in between interstitial lattice sites
(Ti^{4+} as well as O^{2-})

high activation energy has to be overcome by high electrical field

Kinetical description similar to Butler Volmer equation

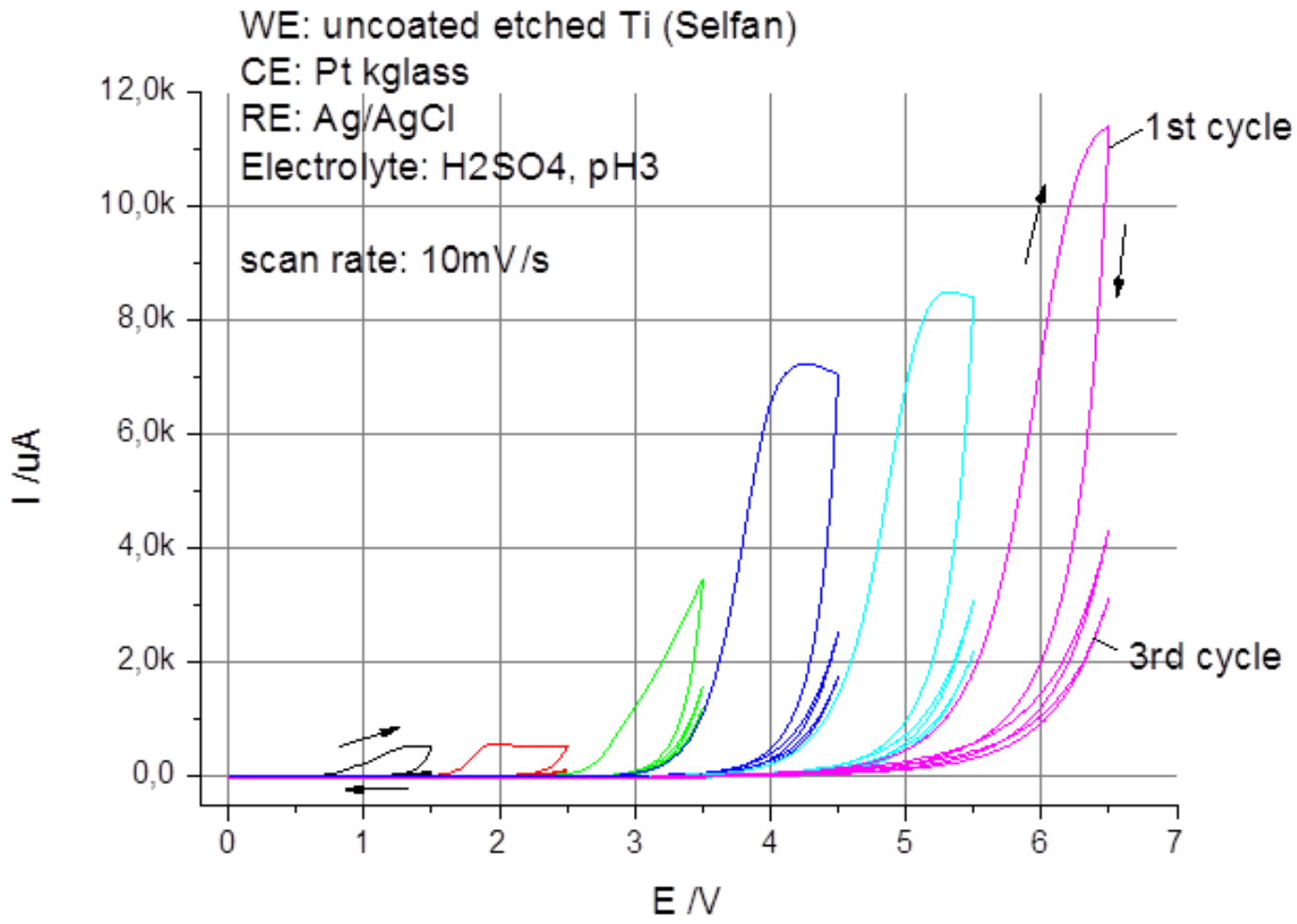


Neglection of hopping back: („high overpotential“ <-> high electrical field $\Delta\varphi$ / d)

$$i = i_0 \exp\left(\frac{\alpha z F}{RT} \cdot \frac{\delta}{a} \cdot \Delta\varphi\right) \quad \Rightarrow \quad i(t) \sim t^{-1}$$

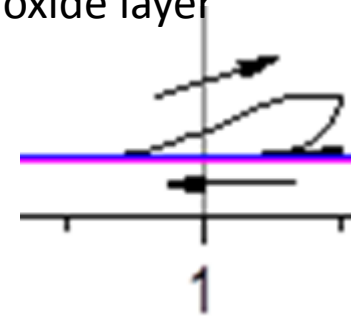
Low electrical field: $$i(t) \sim \frac{1}{\sqrt{t}} = t^{-0.5}$$

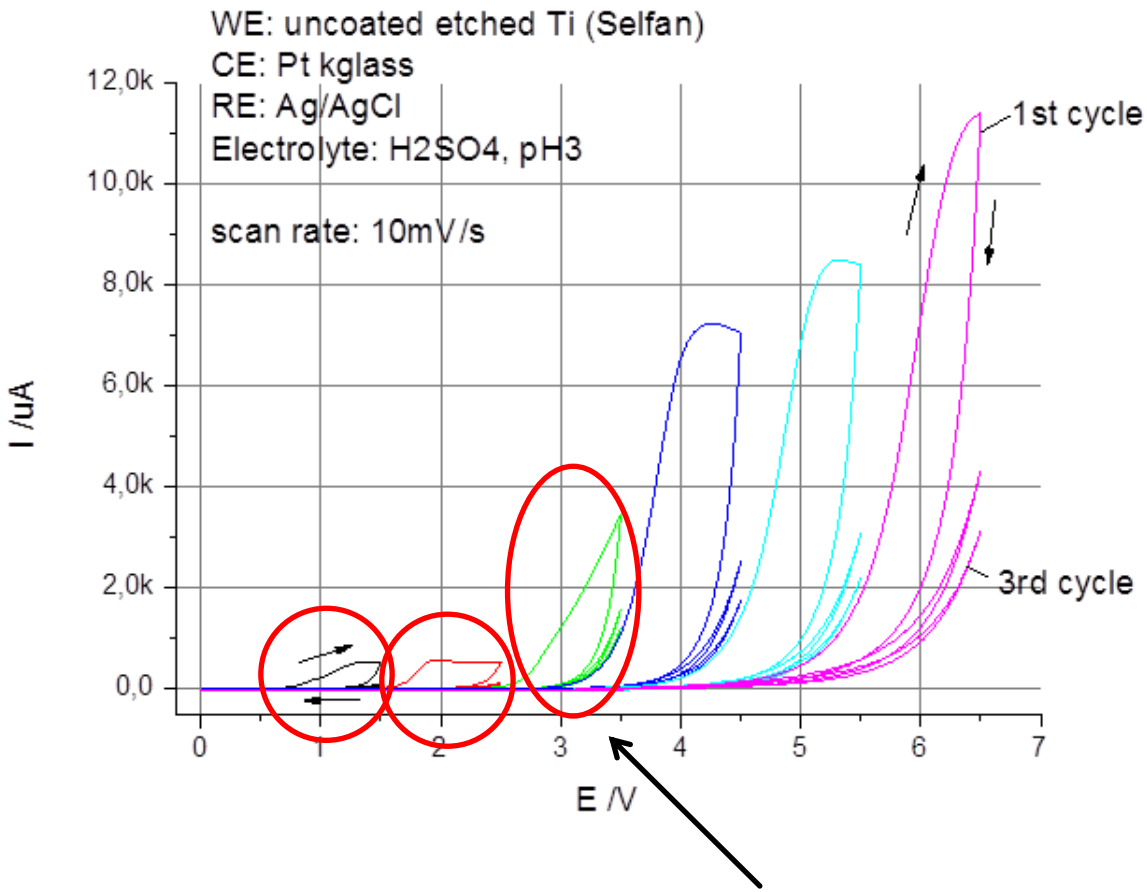
passivation of titanium: valve metal



passivation of titanium: valve metal

„critical“ field strength needed for „high“ current depending on thickness of already existing oxide layer



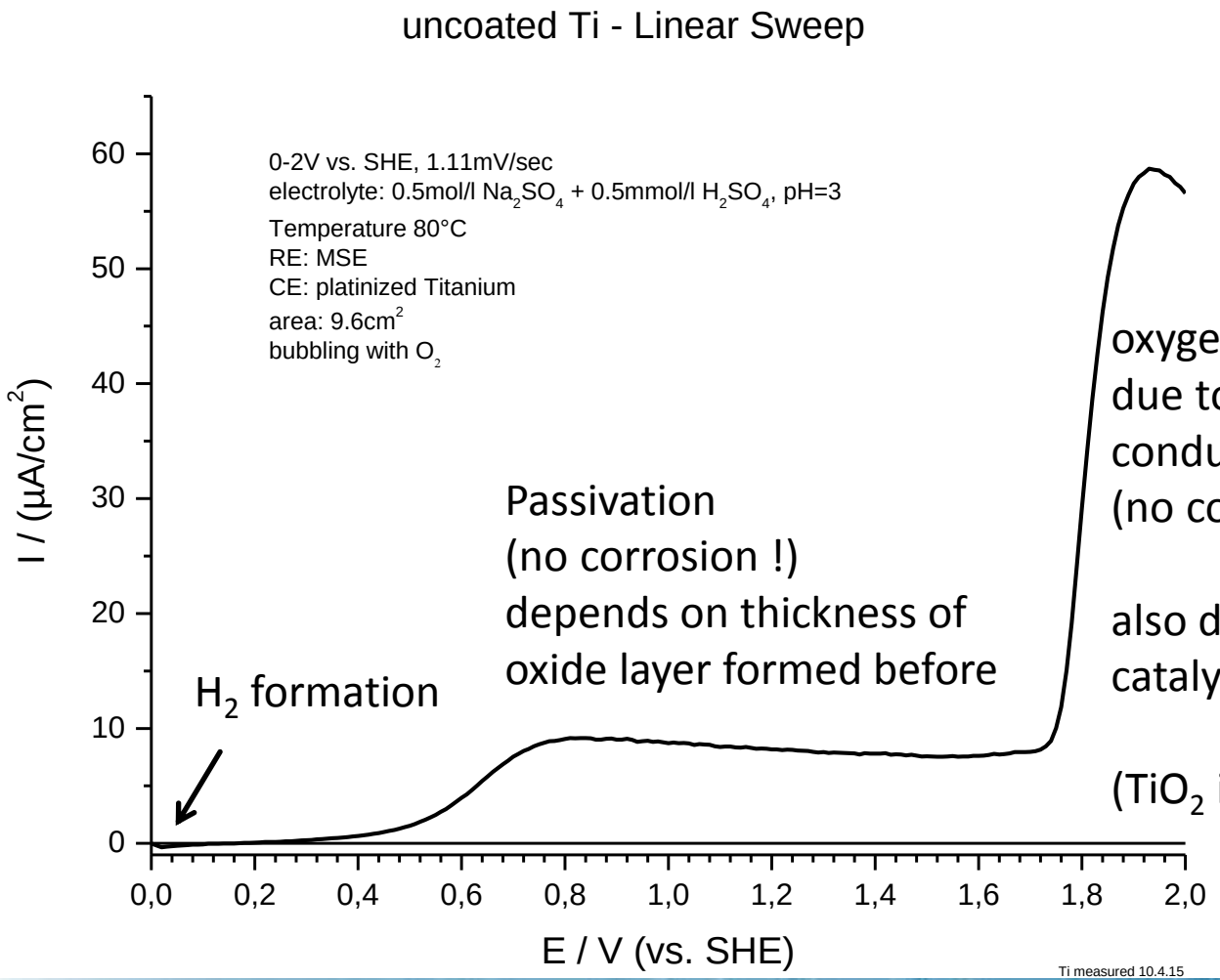


constant current on LSV on first cycle

low current on second cycle

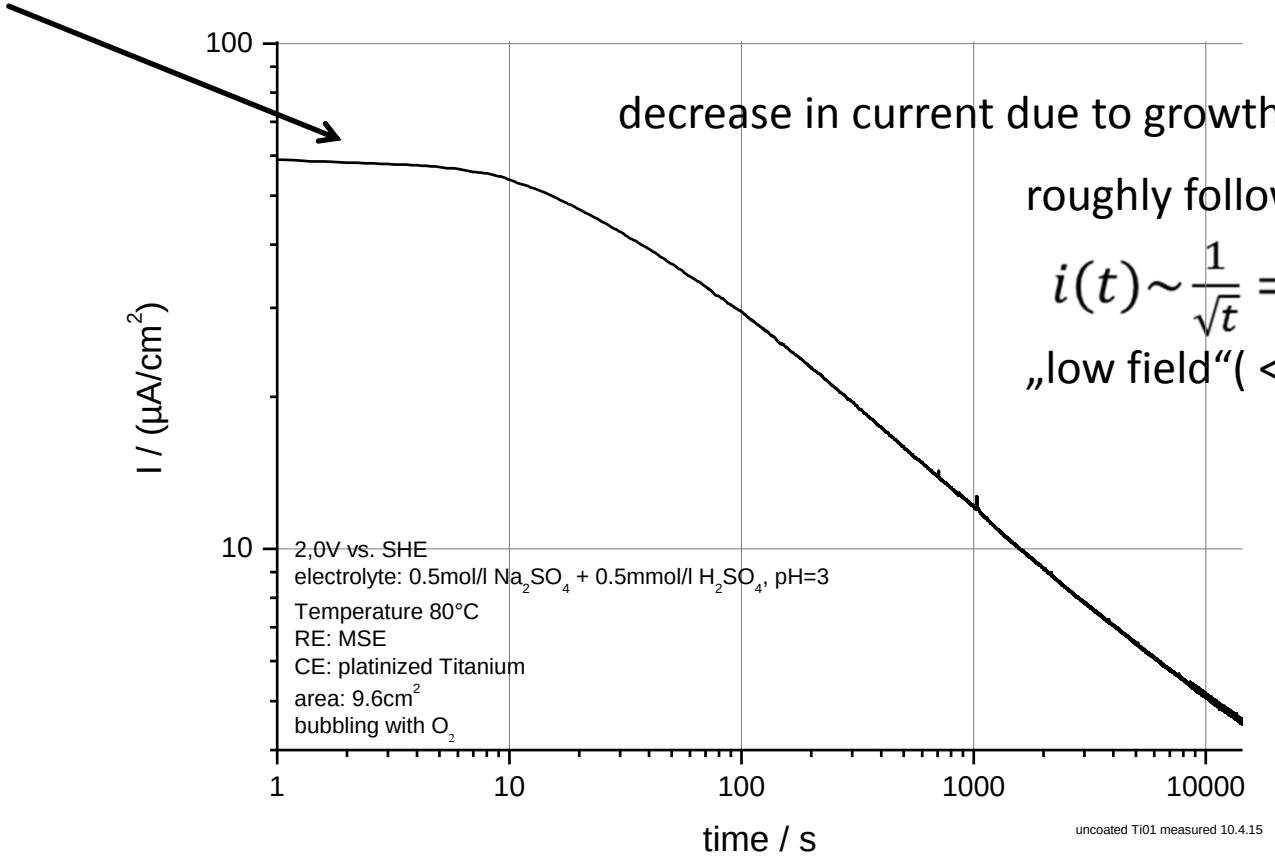
in case of Ti: formation of Ti-peroxides for potentials >= 3V

Linear sweep on uncoated Ti



Chronoamperometry on uncoated Ti (2V vs. SHE)

constant current due to oxide layer formed before



decrease in current due to growth of oxide layer

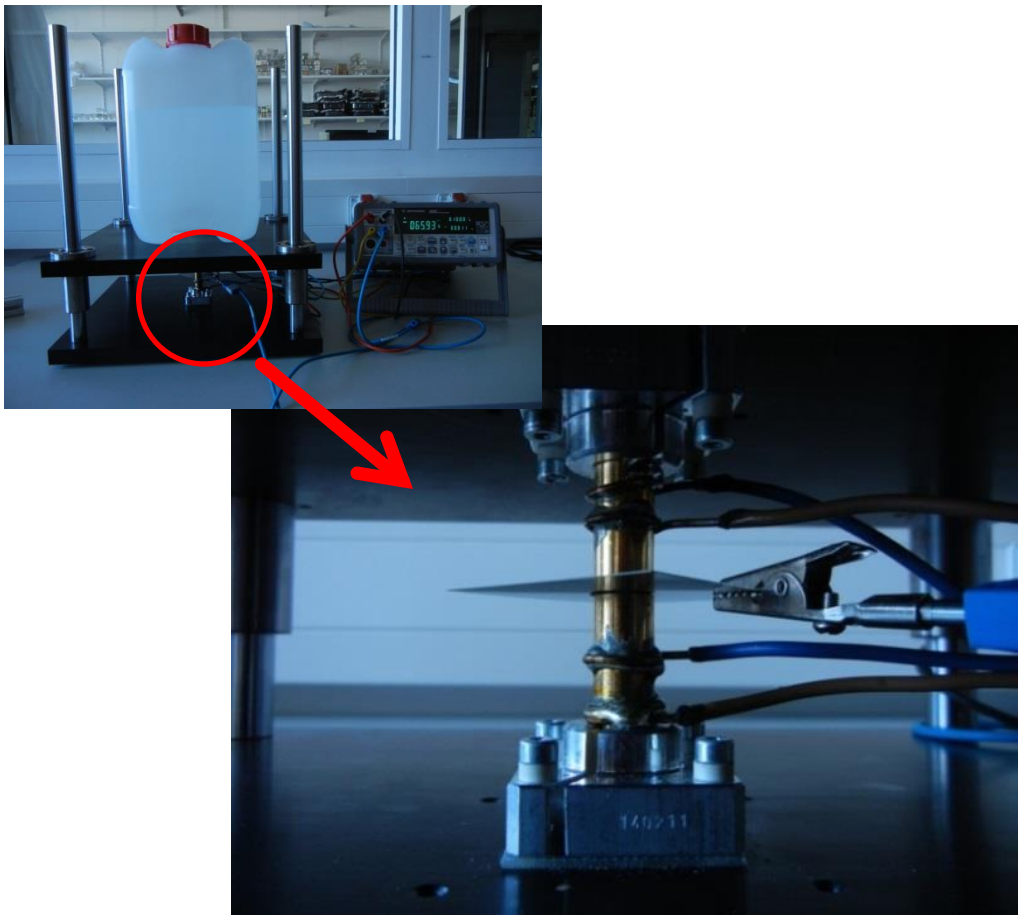
roughly following

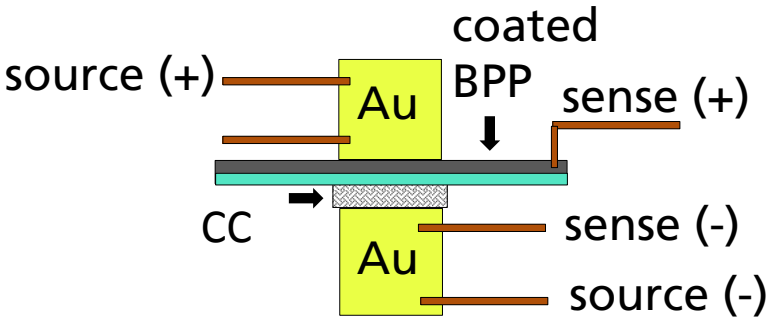
$$i(t) \sim \frac{1}{\sqrt{t}} = t^{-0.5}$$

„low field“(<< 1V / 10nm)

Interfacial contact resistance (ICR)

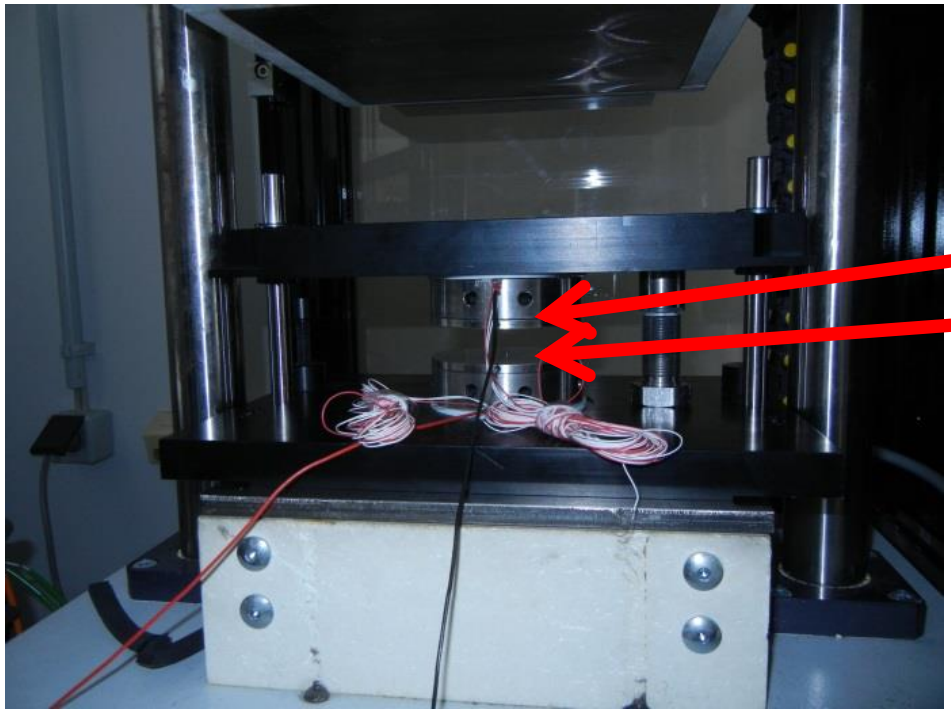
ICR: potential drop in between bipolar plate and current collector

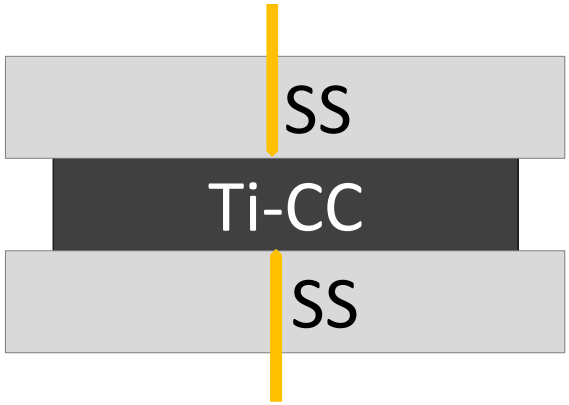




Interfacial contact resistance (ICR)

bulk resistance of current collector





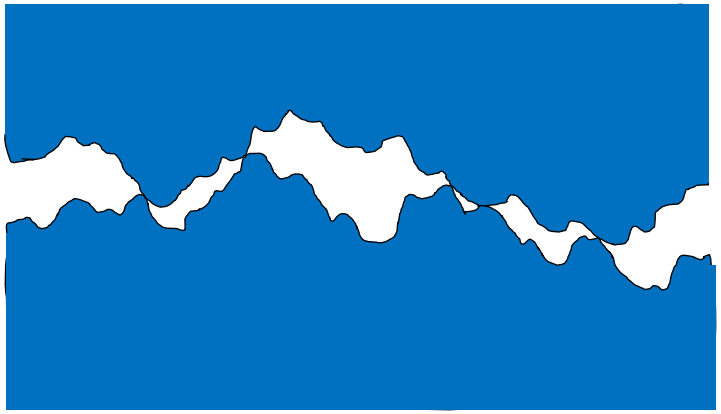
Interfacial contact resistance (ICR)

microscopic contact points

„interfacial“

depends strongly on current collector

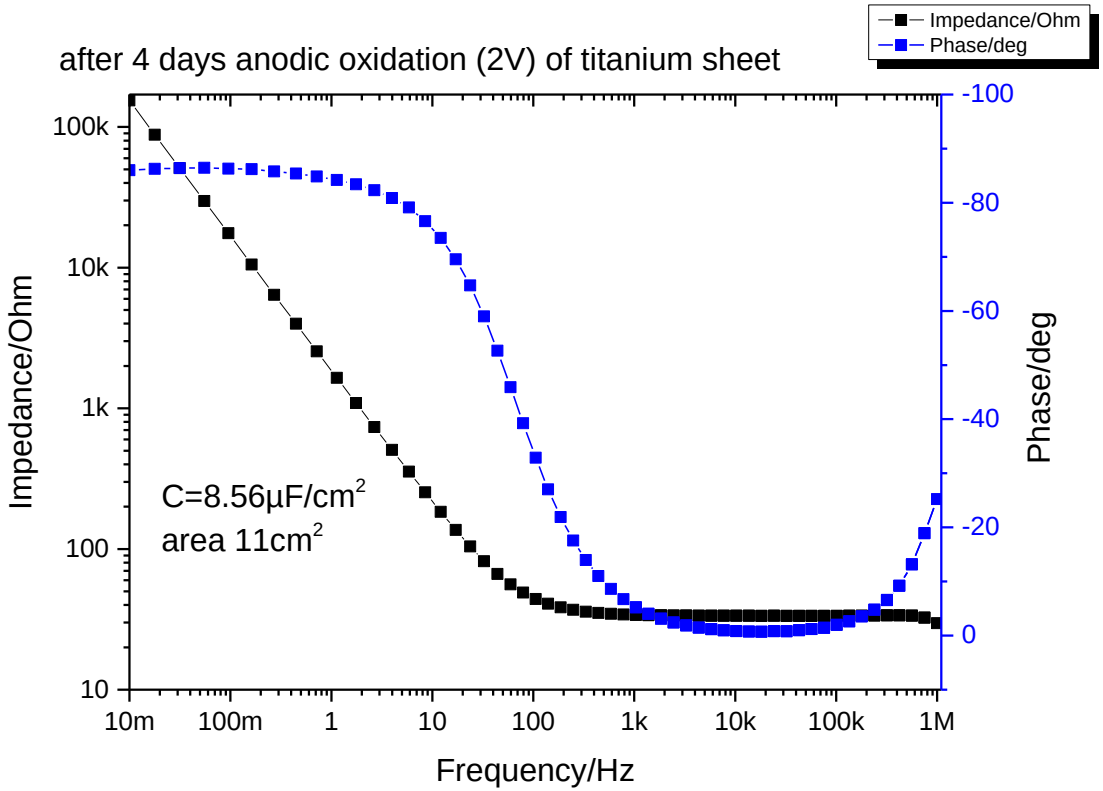
e.g. oxidized titanium plate



ICR vs. Carbon paper GDL: 810 mΩ cm^2
vs. Ti-sinter current collector: 7,7 mΩ cm^2

Interfacial contact resistance (ICR):

Electrochemical methods show high impedance of passivation layer,
Example: EIS: impedance: > 2MΩ*cm^2



but ICR is below 1 Ω*cm^2

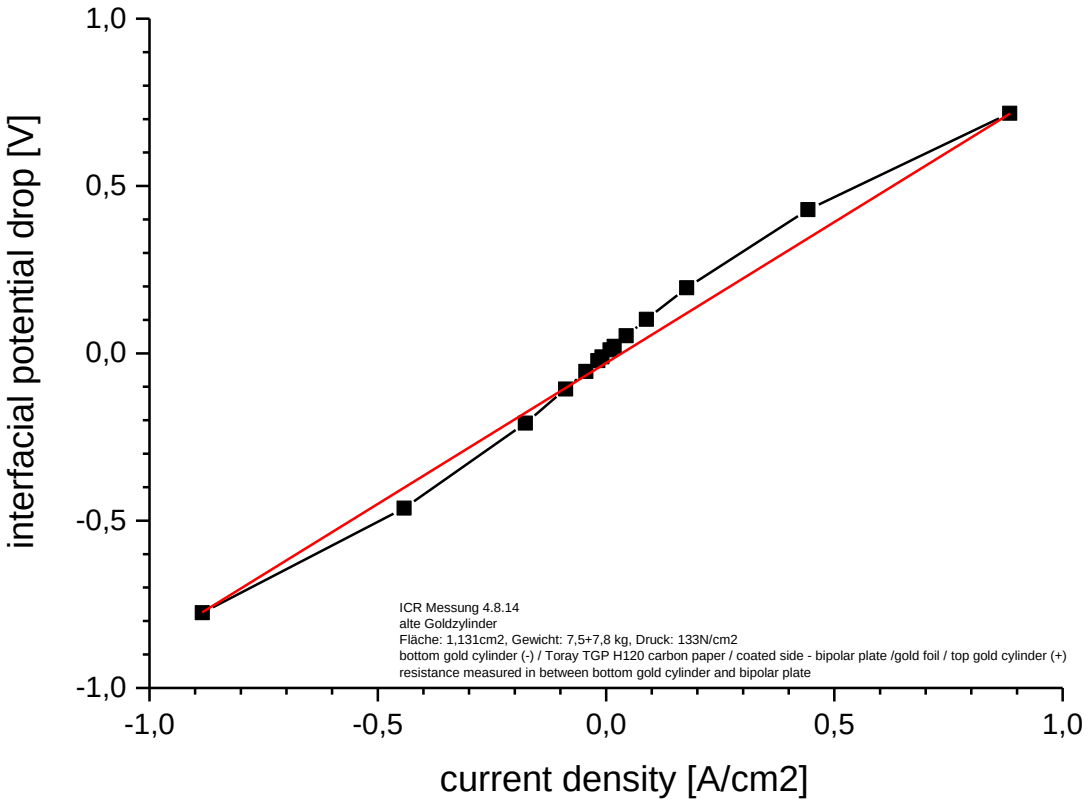
EIS: double layer or TiO_2 ?

TiO_2: n-type semiconductor

Interfacial contact resistance (ICR)

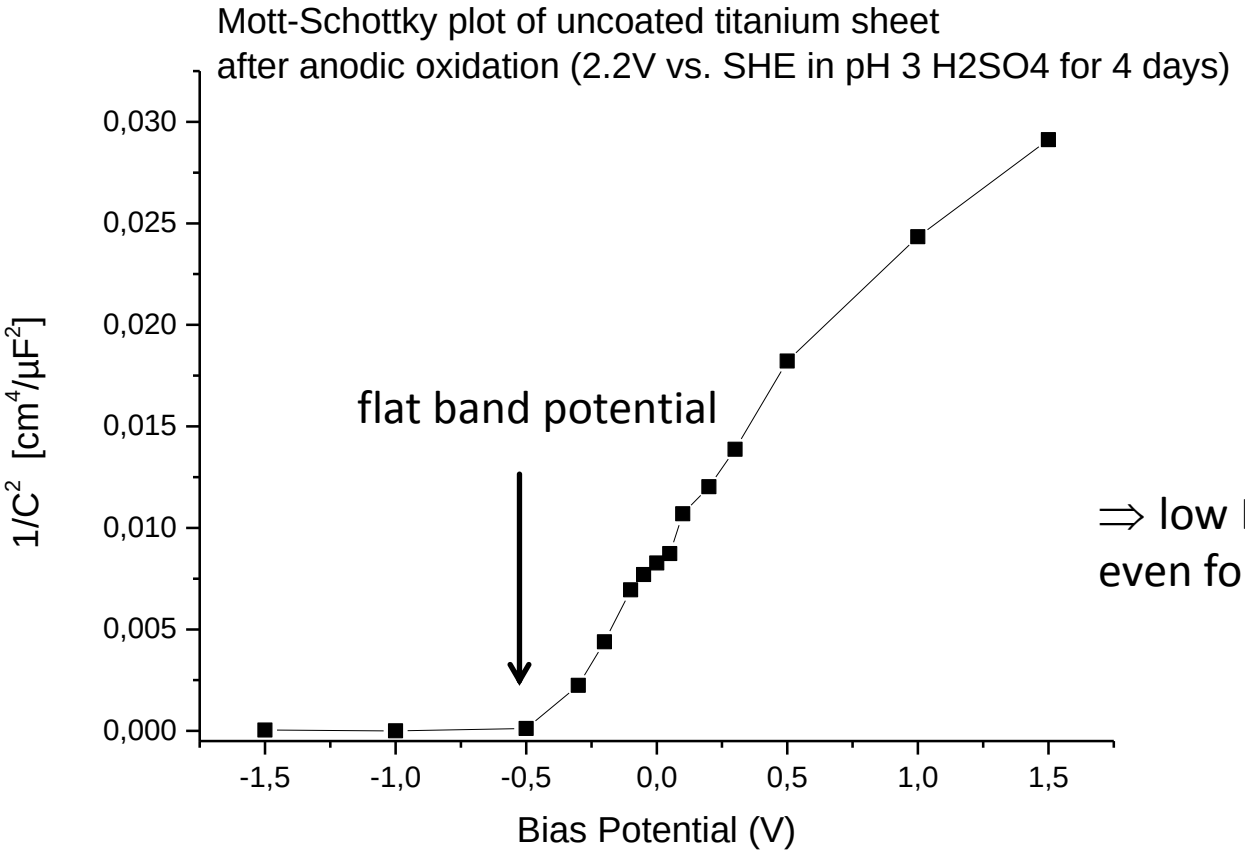
Interfacial contact resistance should follow properties of n-type semiconductor:
This is not the case !

anodized titanium (2V vs. SHE, 1 week, pH=5, room temperature)



Interfacial contact resistance (ICR)

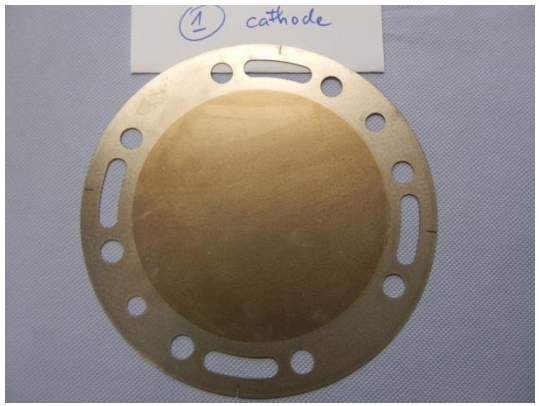
however, EIS measurements confirm n-type semiconducting properties, with flat band potential fitting to TiO_2



⇒ low ICR due to scratching, even for soft carbon paper

passivation of titanium: cathode

Bipolar plates out of titanium had been in use in electrolyzers as anode and as cathode for 300 hours



Optical evaluation
Increase in thickness of passivation layer
about 10nm

ICR, (mΩ cm²)	Ti-sinter	Toray
Anode, non-corroded area	0,57	35
Anode, corroded area	7,7	810
Cathode, non-corroded area	0,87	39
Cathode, corroded area	6,8	540

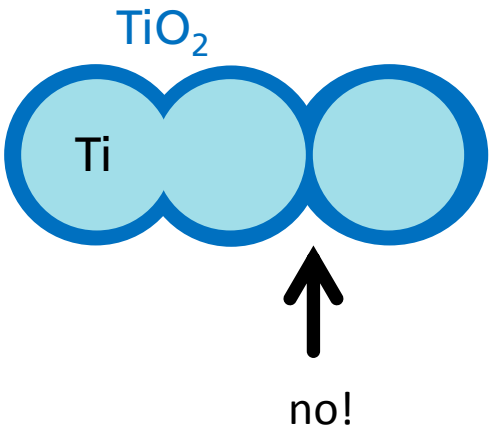
high ICR (vs. carbon paper) also for cathode

=>

protective coating needed also for cathode

ICR: current collectors out of Ti

- passivation of sinter-Ti current collector after 192h of service
- yellow colour: thickness of passivation layer about 10nm
- increase in ICR (vs. Titanium BPP: 1mΩcm^2 -> 23 mΩcm^2)
- => protective coatings needed on current collector
- difficult for ex-situ measurements:
  ICR in between CC and catalyst
- no significant change in bulk resistance !



Saturation of oxidation of uncoated titanium plates (ex situ)

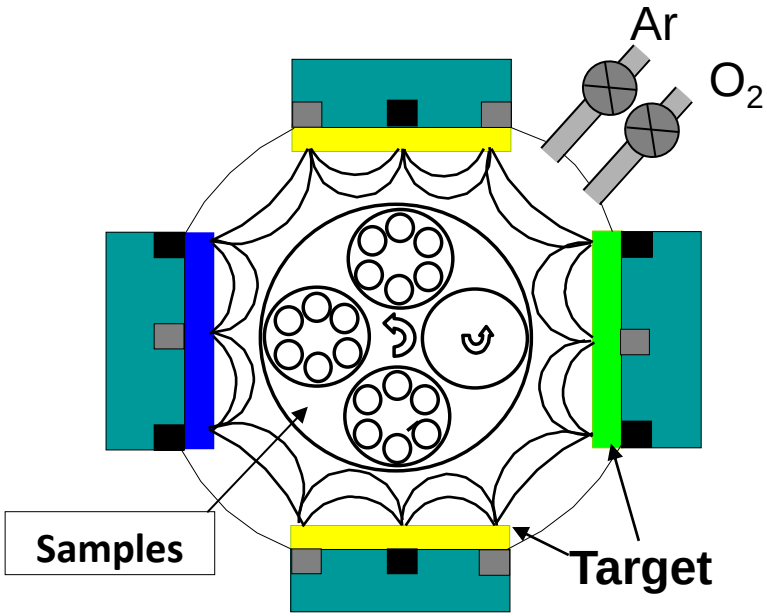
comparison of change in capacity (C, by impedance spectroscopy), thickness of passivation layer (by reflectance R) and contact resistance (ICR) before and after anodic oxidation of uncoated titanium (2V vs SHE)

	Before	1 day	2 days	4 days
EIS: C (µF/cm2)	99	6,8	6,6	8,6
Thickness (nm) by C (ε=60)	0,5	8	8	6
Thickness (nm) by R(λ) (n=2.6)	<=5	13	13	13
ICR (m Ωcm2)	19	387	472	502

=> no further increase in thickness of passivation layer after one day

Sputtering process

Sputter coater at Teer Coating Ltd.



Closed field unbalanced magnetron sputter ion plating (CFUBMSIP)

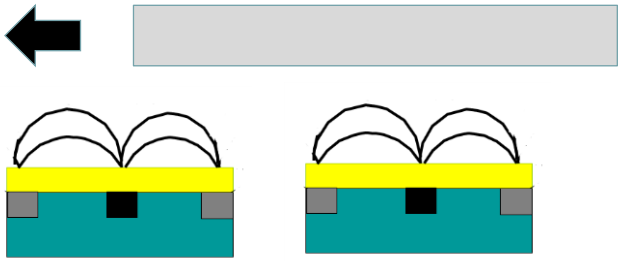
Sputtering process

Sputter coater at Teer Coating Ltd.

Inline coater for upscaling

Sputtering process

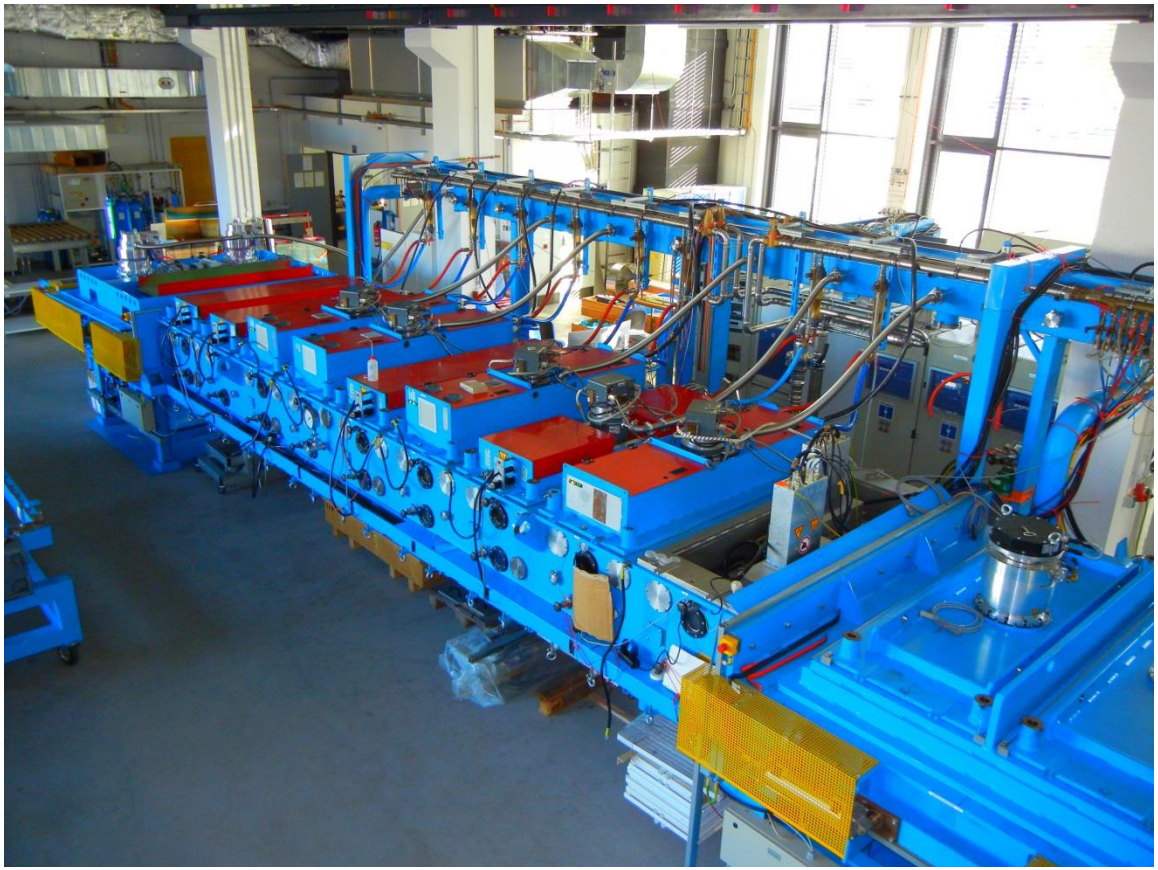
Sputter coater at Fraunhofer ISE



Vertical Inline Sputter Coater, balanced magnetrons

Sputtering process

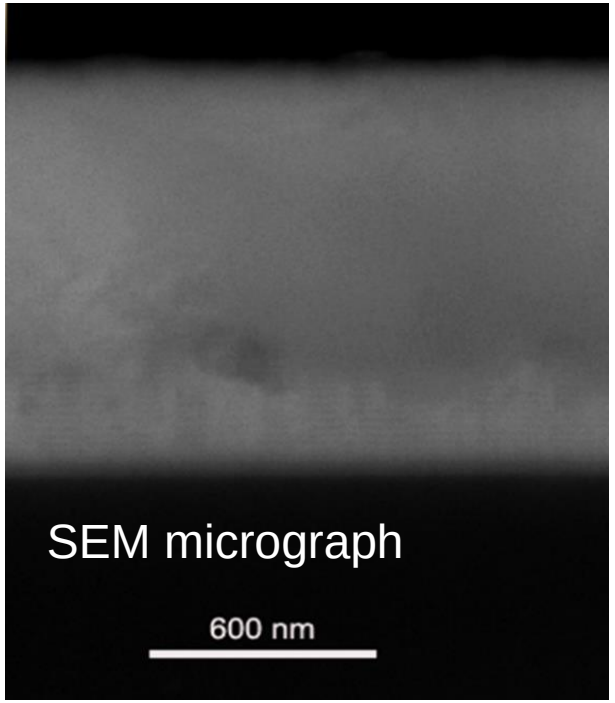
Sputter coater at Fraunhofer ISE



Horizontal Inline Sputter Coater, balanced magnetrons

Coated bipolar plates

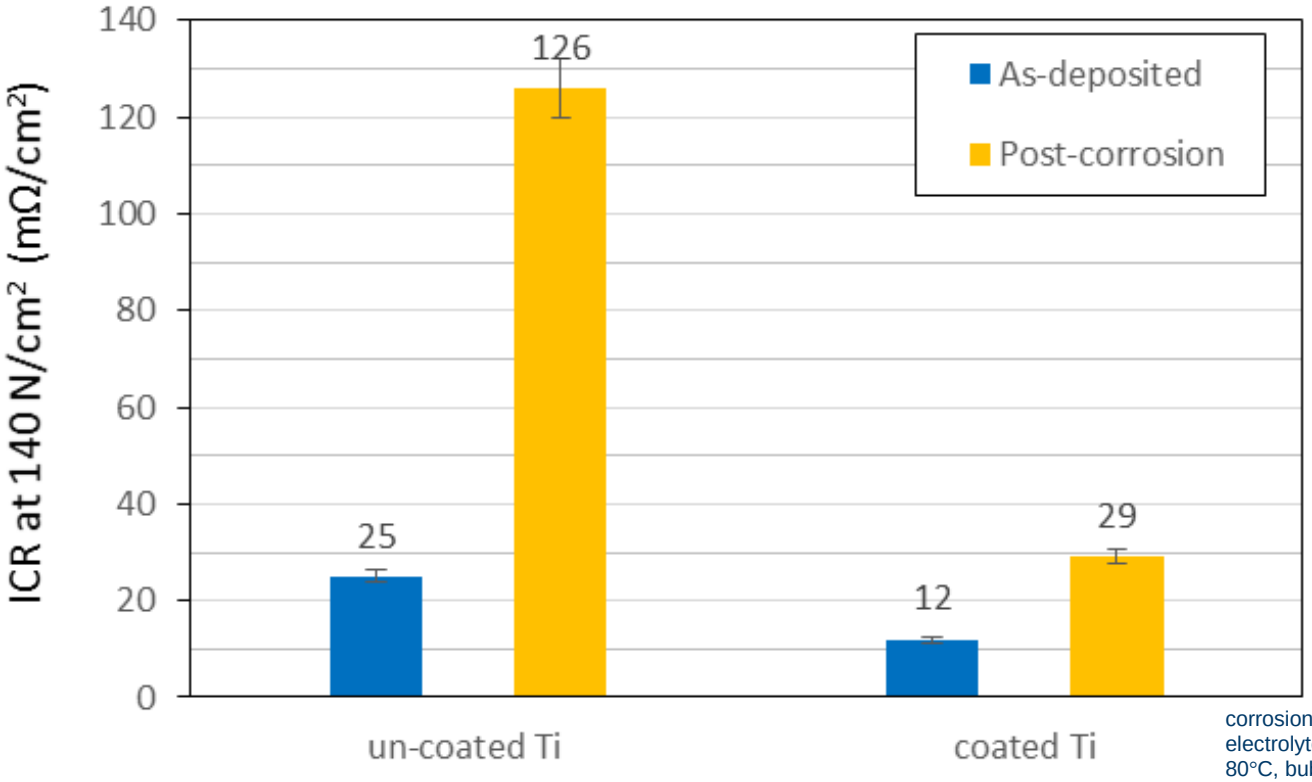
- Protective coatings have been sputtered at Teer Coatings Ltd. on bipolar plates for anode and cathode as well as on current collectors
- Rockwell indentation test demonstrates excellent adhesion
- SEM micrographs of the edge of the coating confirm a compact layer structure



Coated bipolar plates

Coated at Teer Coatings Ltd

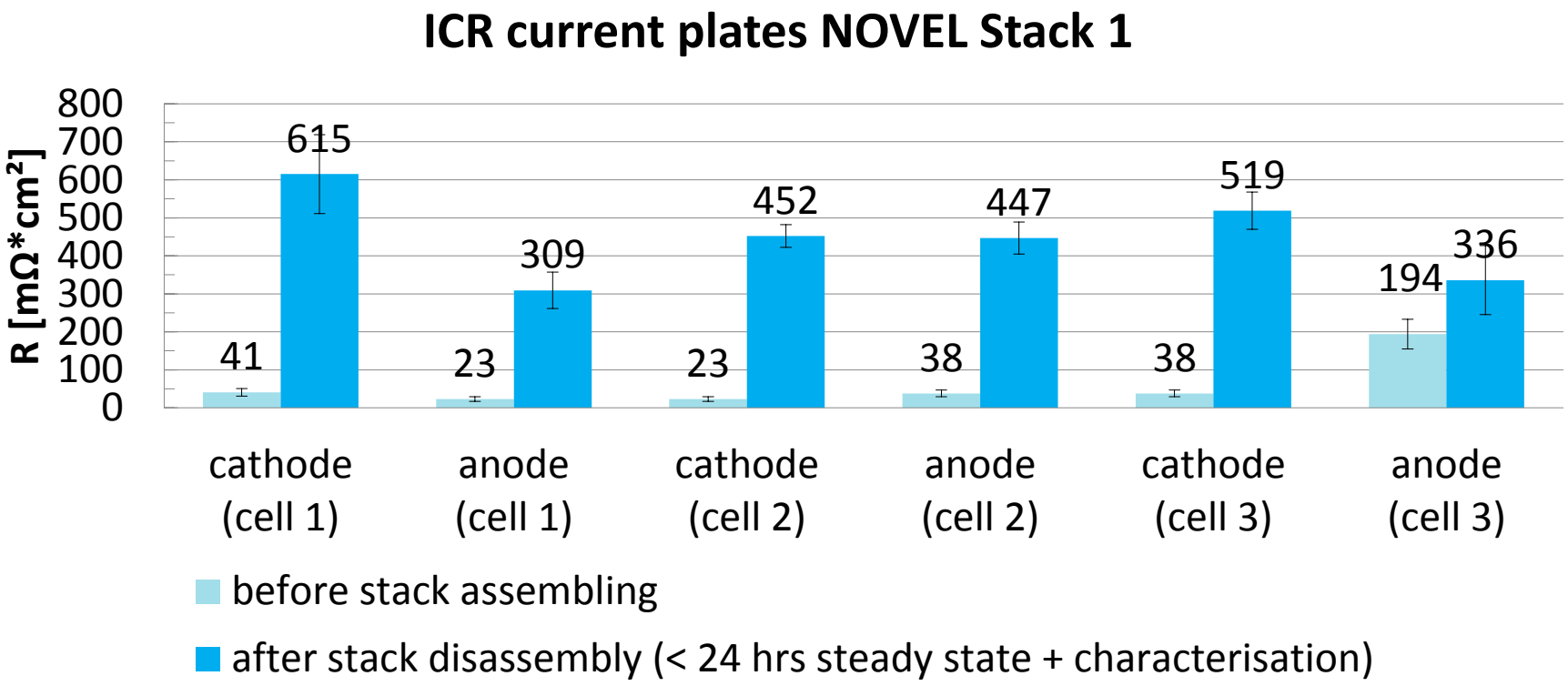
- ICR of coated Ti is ½ & ¼ that of un-coated Ti for as-deposited & post-corrosion samples respectively



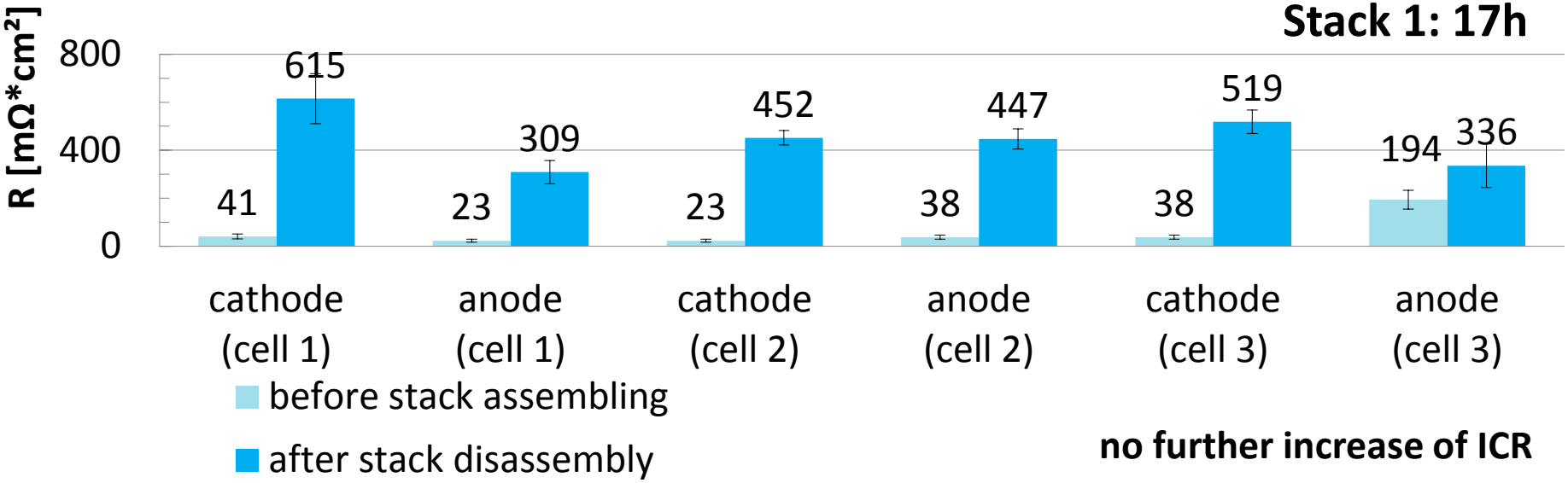
corrosion test:
electrolyte: 0.5mol/l Na_2SO_4 + 0.5mmol/l H_2SO_4, pH=3
80°C, bubbling with O_2
LSV, 1.1mV/s (0..2V vs. SHE)
CA, 1.4V vs. SHE, 1 hour
CA, 2.0V vs. SHE, 4 hours

Stack: titanium bipolar plates (uncoated)

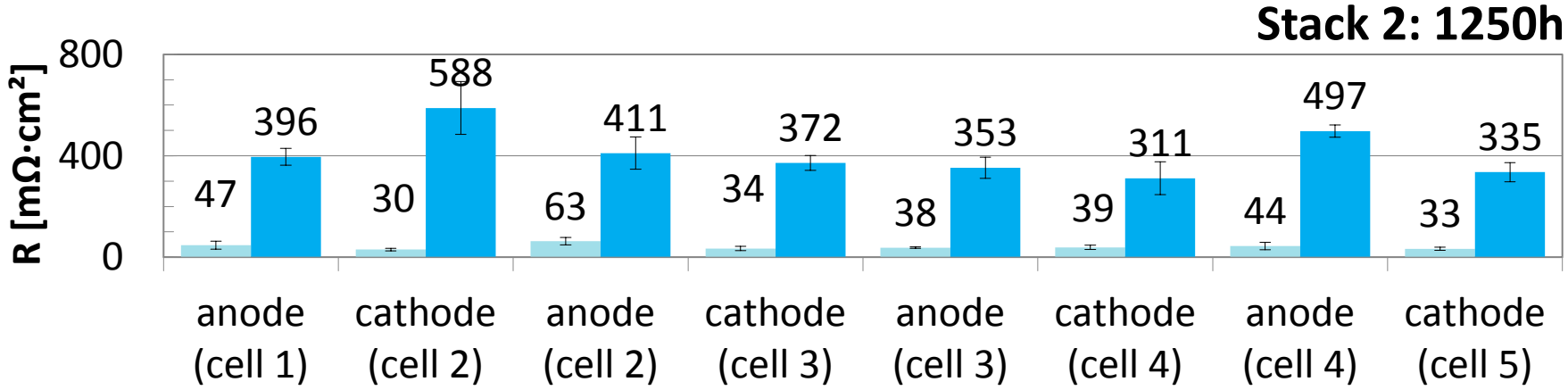
17 h operation: already high ICR also on cathode (ICR measured vs. carbon paper)



Stack: titanium bipolar plates (uncoated)



no further increase of ICR



Conclusions

- uncoated titanium forms highly resistive oxide layer, also on cathode
- growth of oxide layer can be described by valve-metal behaviour
- high resistance of anodically formed n-type TiO_2 reduced to low contact resistance values due to scratching in contact with current collector
- anodic oxidation of sinter-Ti current collector does not involve the bulk resistance
- indications for saturation of growth of oxide layer on titanium
- protective coatings are recommended for anode and cathode,
  for bipolar plate and current collector
- protective coating prepared by Teer Coating Ltd. shows low contact resistance also after corrosion test
- stack tests confirmed formation of highly resistive passivation layers on cathode "saturation"
- stack tests with coated plates are running

Thank you!