Redox Sensors for the Control of Process and Waste Waters

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Outline

- Introduction
- New approach for redox potential measurement
- Fabrication of redox electrode glass and glass paste incl. characterisation
- Fabrication of the electrodes
- Electrode test (laboratory)
- Field operation (Control of Process and Waste Waters)
- Outlook
- Conclusion
- Acknowledgement

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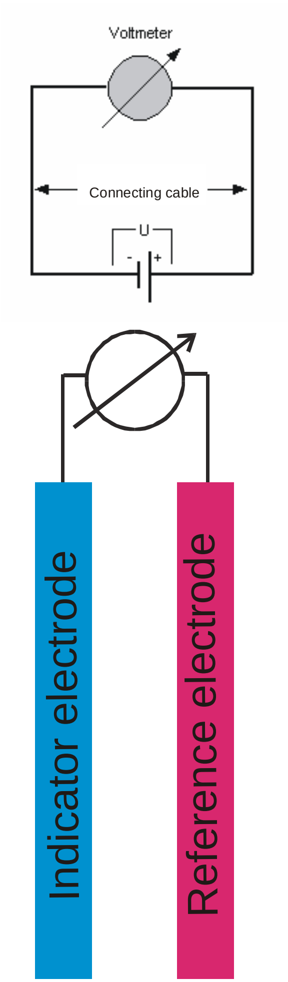
Reduction potential (also known as redox potential, oxidation / reduction potential, ORP, pE, ε, or E_h) is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. Reduction potential is measured in volts (V), or millivolts (mV). Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced. ORP is a common measurement for water quality.

Trevor V. Suslow: Extension Research Specialist, Department of Vegetable Crops, University of California, Davis

$$\varepsilon = \varepsilon_0 + \frac{RT}{nF} \ln\left(\frac{a_{Ox}}{a_{Red}}\right) + \frac{m}{n} \ln a_{H^+}$$

ε ... single potential; ε_0 ... standard potential; a_{Ox}, a_{Red} ... ion activities;
n ... number of electrons ; m ... number of protons

Potentiometry



Scheme of the measuring chain

Determination of redox potentials

↓

Non-specific measurements

Partial specific measurements ← **Measurements with oxidic electrodes**

Selective measurements

↑

Measurements with Ion Selective Electrodes

MEINSBERG KSI

measuring instrument

Pt, Au

redox electrode

SHE

SSE

reference electrode

Drawbacks

reducing solutions:
formation of hydrides

catalytic poisons, e.g. SO_2 or other sulfur compounds, contaminate their surface:
electrodes become unusable

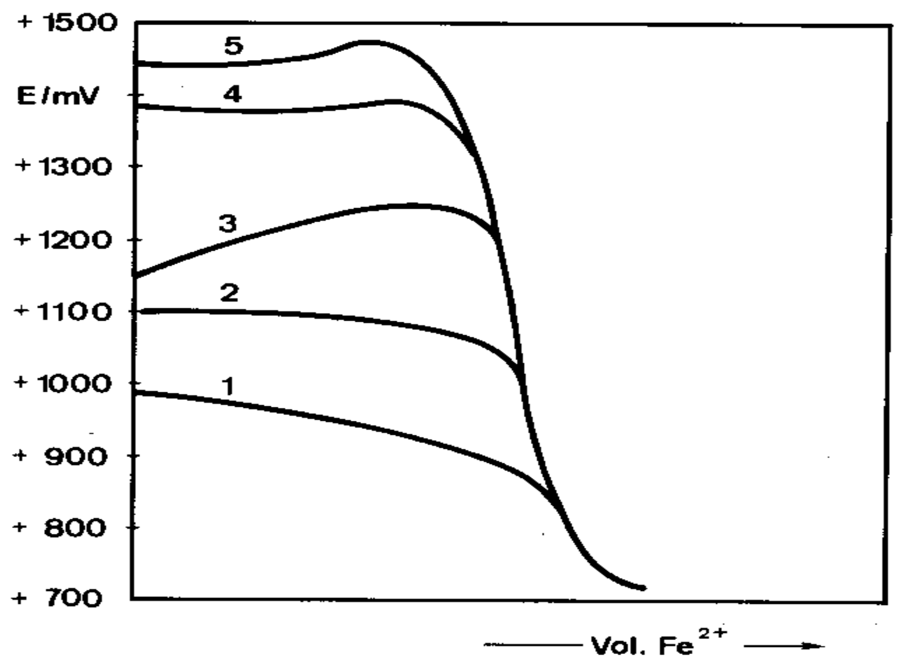
presence of gaseous oxygen and hydrogen:
influences the half cell potential

metals themselves can act as catalysts in certain redox media

Pt, Au

under certain circumstances:
responds to chlorides and cyanides

Measuring errors of ±25 mV are considered normal.



$Cr_2O_7^{2-}$ + 6 Fe^{2+} + 14 H^+ $\longrightarrow$ 6 Fe^{3+} + 2 Cr^{3+} 7 H_2O

1 cathodically polarised (5 min)

2 untreated

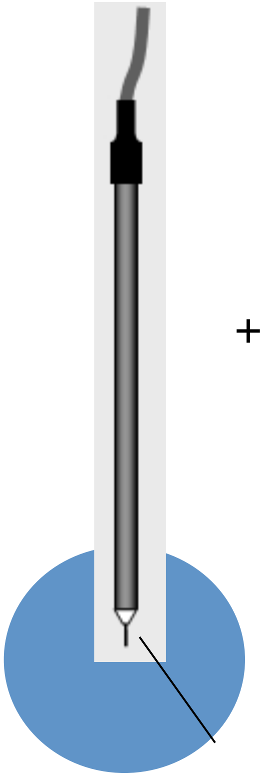
3 annealed at 900 °C

4 anodically polarised (1 min)

5 anodically polarised (5 min)

F. Oehme: G-I-T 20 (1976) 20

Redox sensor

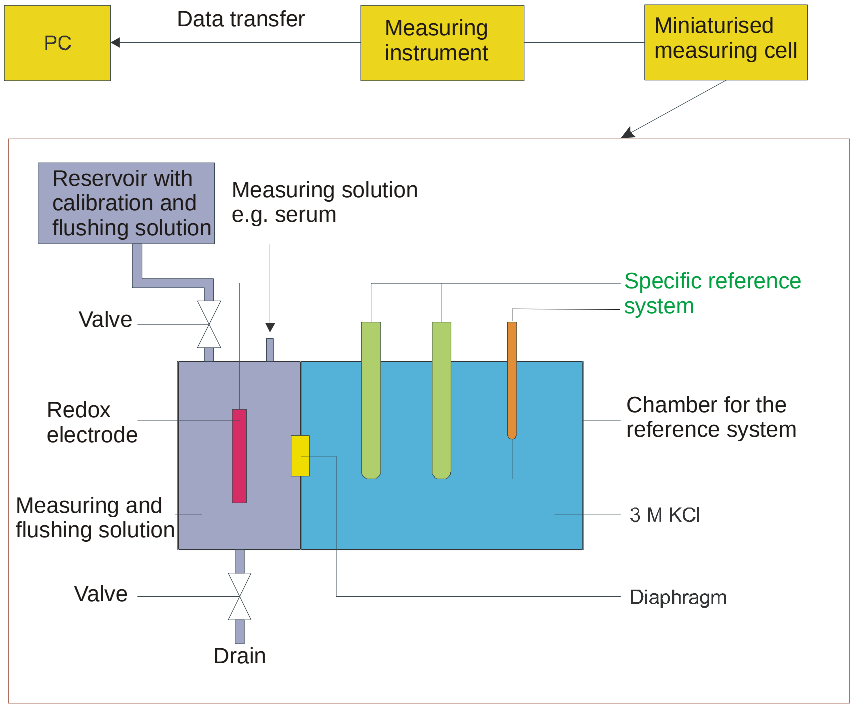


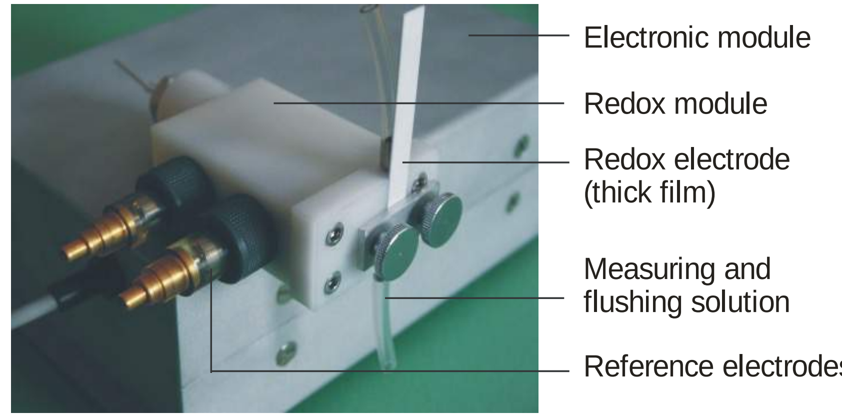
+ reference electrode

platinum
gold
(wire, sheet, …)

Only little volume of blood available
(capillary blood)

Redox electrodes in thick film technology (Au, Pt, ...)



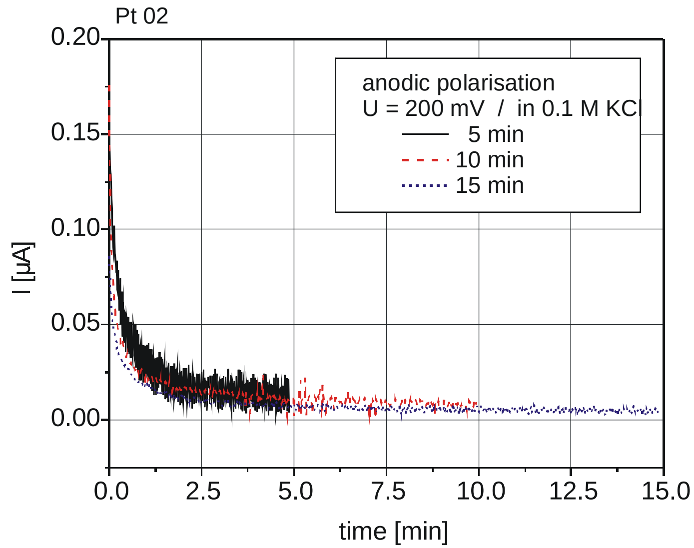


System to condition, measure and calibrate redox measuring chains

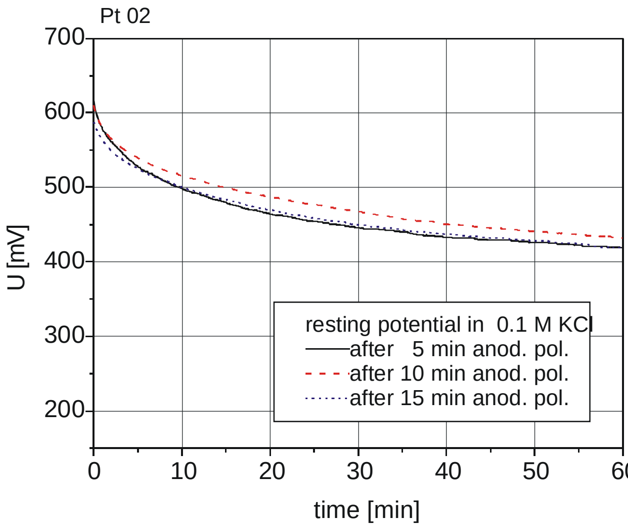
Schematic assembly of the flow through measu-ring system to determine redox potentials in smal-lest quantities of biological liquids for fundamental investigations to estimate measurements with different electrode materials

Herrmann, S.; Berthold, F.; Vonau, W.; Mayer, M.; Bieger, W.: Elektrochemischer Redoxchip für bioanalytische Messungen. In: R. Poll, J. Füssel (Hg.): Dresdner Beiträge zur Medizintechnik, Band 1: 1. Dresdner Medizintechnik-Symposium – Innovation durch Einheit von Therapie und Monitoring. Dresden, TUDpress 2006, S. 55-60

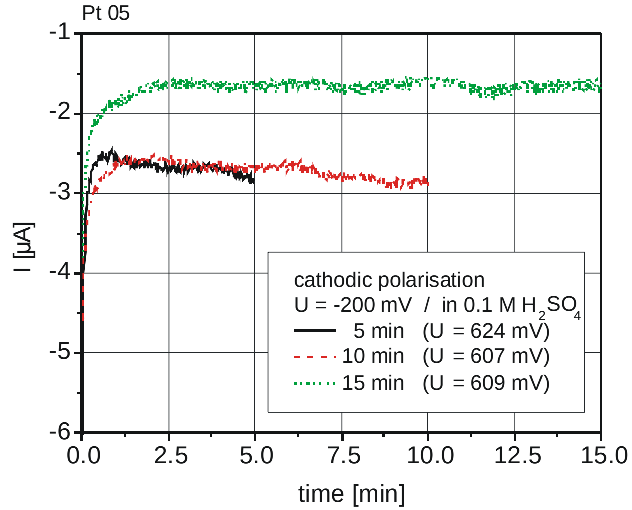
Examples of electrode conditioning



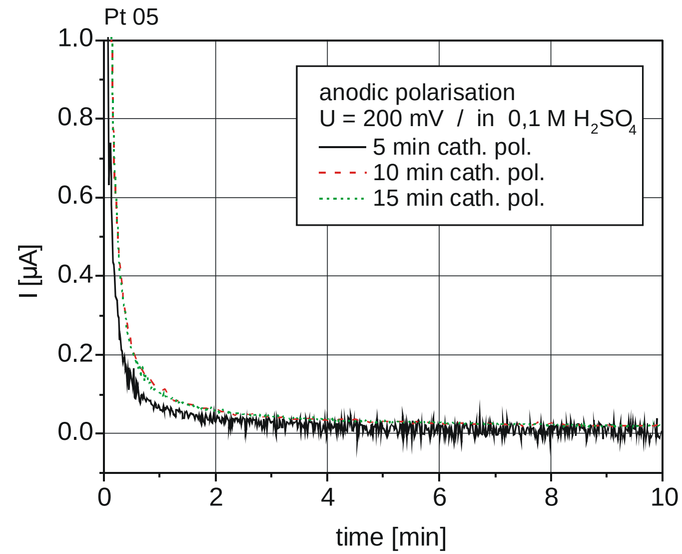
Flow of the current during anodic polarisation



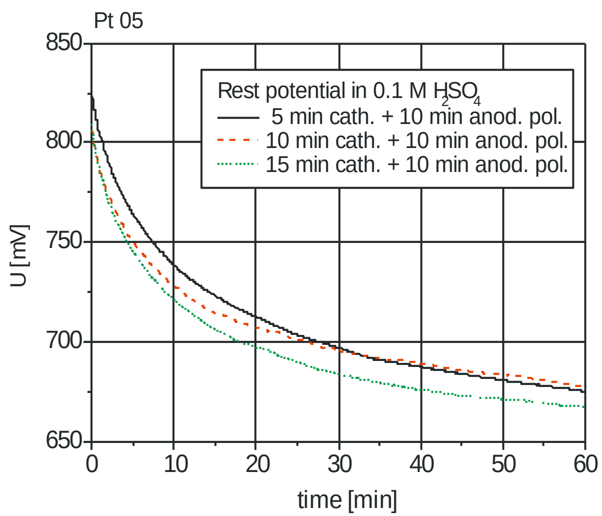
Potential run at platinum after conditioning by anodic polarisation



Cathodic polarisation, flow of the current

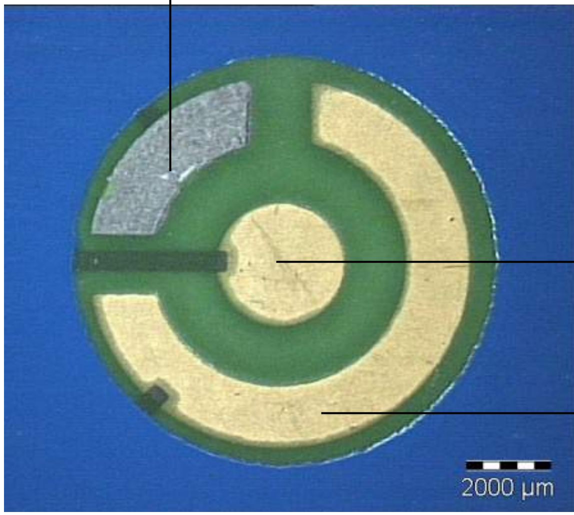


Anodic polarisation, flow of the current



Potential curve of Pt after cathodic/anodic polarisation

Reference electrode

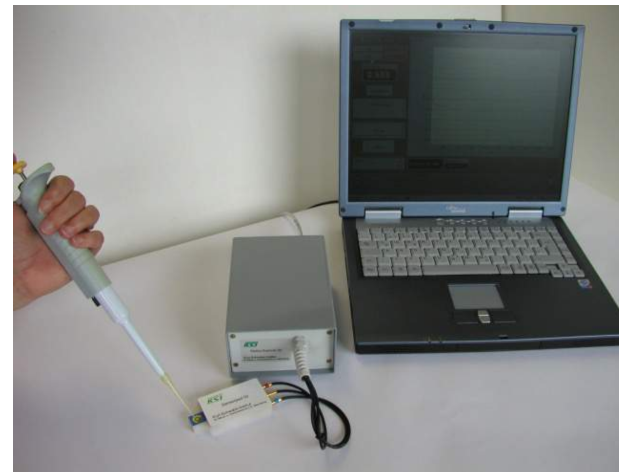


Redox electrode

Counter electrode

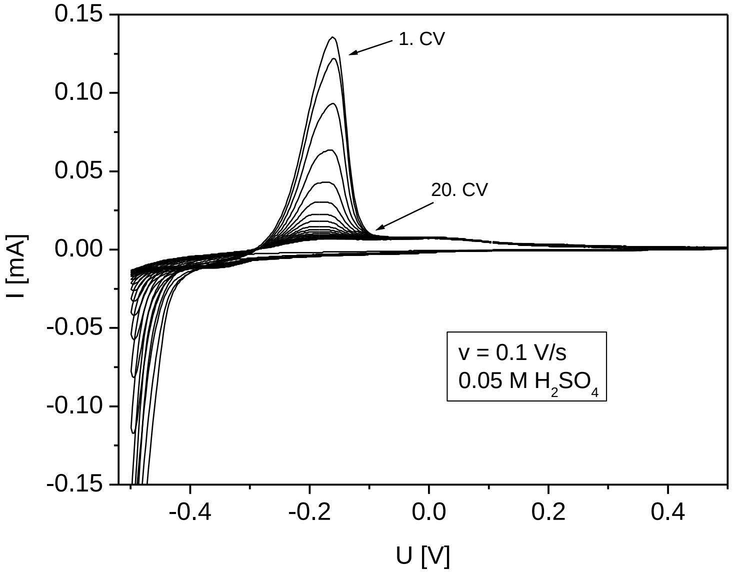
Sensor chip with 3-electrode-measuring system
for the determination of the redox potential
(fabricated in thick film technology)

Sensor pad to contact and keep the redox chips

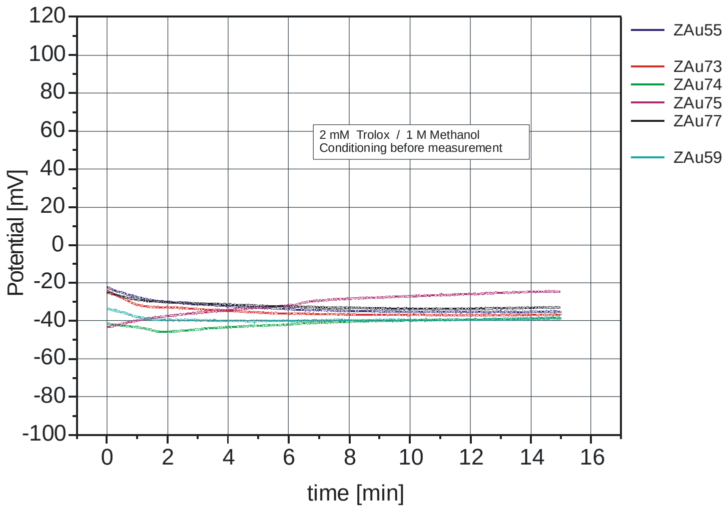


„Redox scanner 04“ and „Sensor pad 02“
with sensor chip as PC coupled device
for quick determination of redox poten-
tials in blood/serum

Vonau, W.; Herrmann, S.;Berthold, F.; Mayer, W.; Bieger, W.:
Chemie Ingenieur Technik 2007, 79. No. 9, 1385

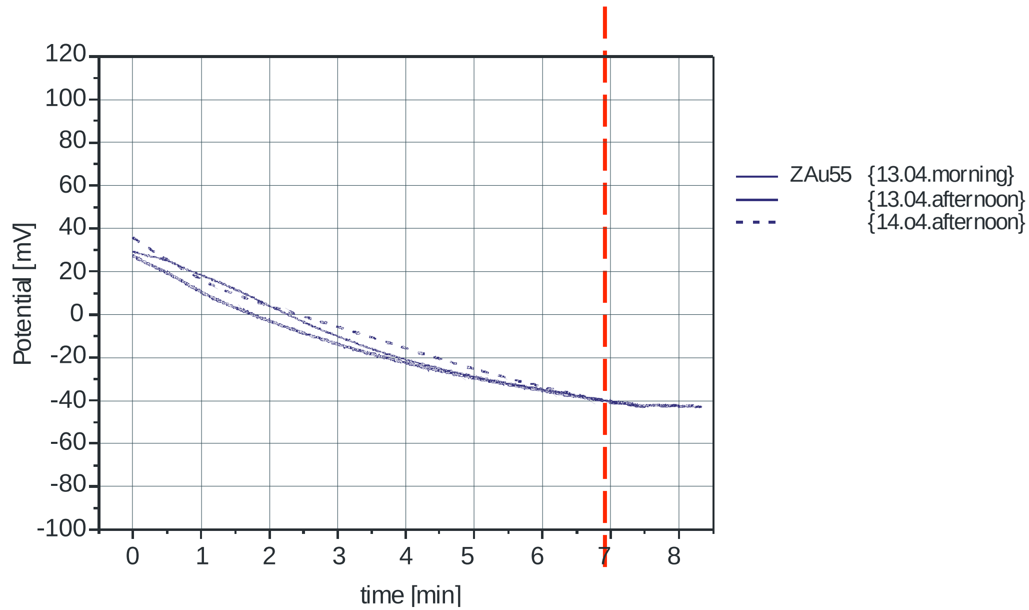


Conditioning of the surface of Au electrodes in thick film technology by cyclic polarisation (20 cycles)



Redox measurement in Trolox reference solution

Berthold, F.; Bieger, W.P.; Herrmann, S.; Vonau, W.:
DE 10 2004 054 521 (2004)



Redox measurement in serum (person Bk)

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Use of glass based (amorphous) electrode membranes instead of noble metals

oxidic glasses

siliceous glasses:
quartz glass
sodium lime glass (pH, pNa, pK)
semiconducting glass (redox potential)

mixtures of several basic glasses:
borosilicate glass

non-siliceous glasses:
borate glass
phosphate glass

non-oxidic glasses

saline glasses:
nitrate glass
fluoride glass

chalcogenide glasses
(mono and polyvalent ions)

metallic glasses

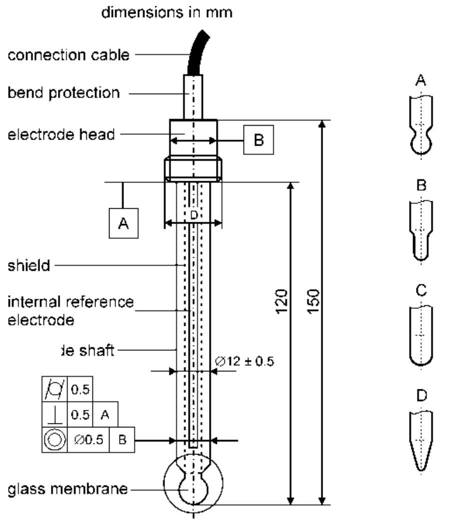
Polymer glasses:
PS
PMMA

GLASS-FORMING SYSTEMS

An **amorphous solid** is a solid in which there is no long-range order of the positions of the atoms.

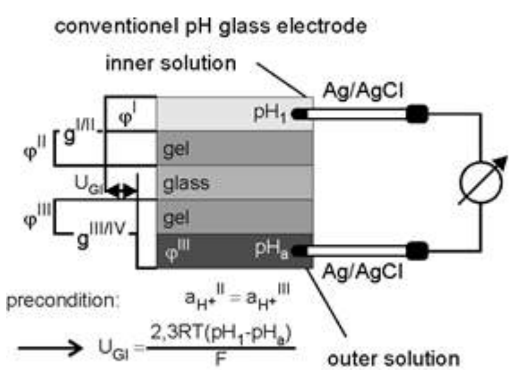
electrodes with amorphous membranes (e.g. pH-glass, chalcogenide glass or redox glass)

Ion conducting glasses



pH glass electrode according to GERMAN STANDARD DIN 19 263

Glass composition:
e.g. 72% SiO_2, 22% Na_2O; 6% CaO



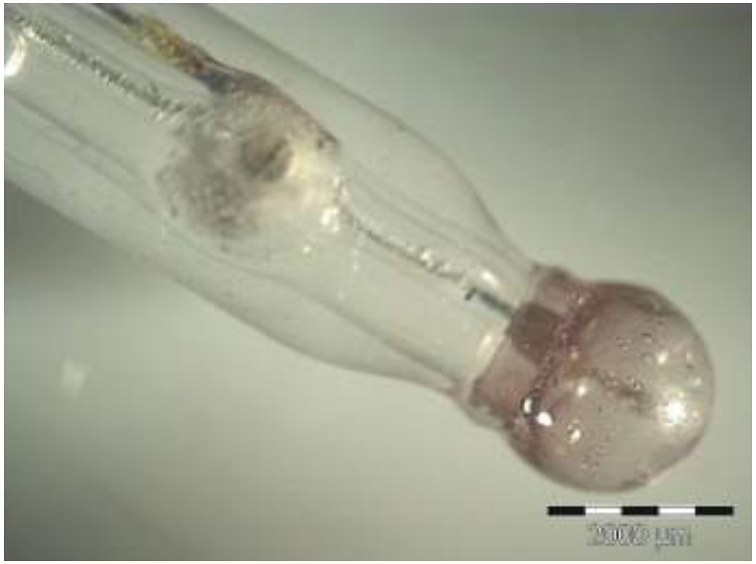
Drawbacks of chemical sensors with liquid components

- ❒ position dependence when stored and used
- ❒ pressure and temperature dependence
- ❒ mechanical instability
- ❒ limitations concerning the miniaturisability
- ❒ impractically applicable for measurements on surfaces
- ❒ costly because of many manual production steps

→

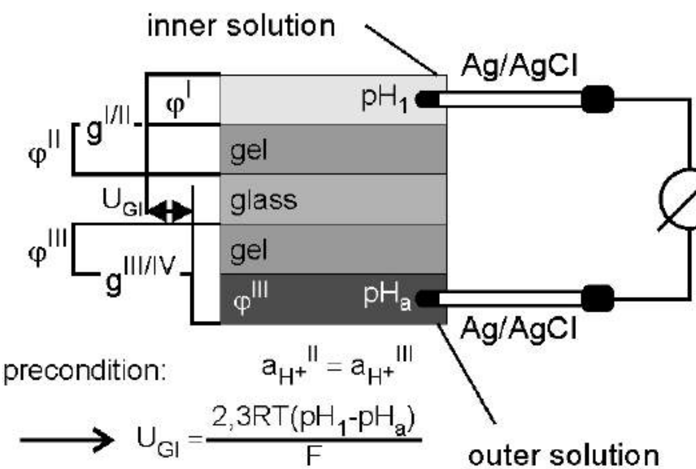
All solid state (glass based) electrode

pH-glass based electrodes

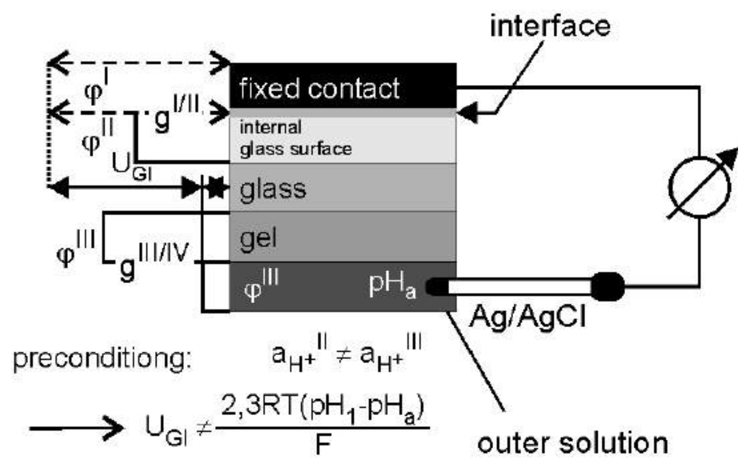


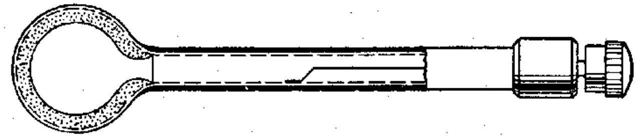
pH glass	ion conducting
metal	electron conducting

conventionel pH glass electrode

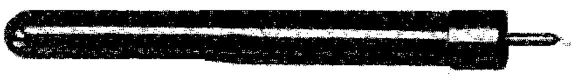


all-solid-state pH glass electrode

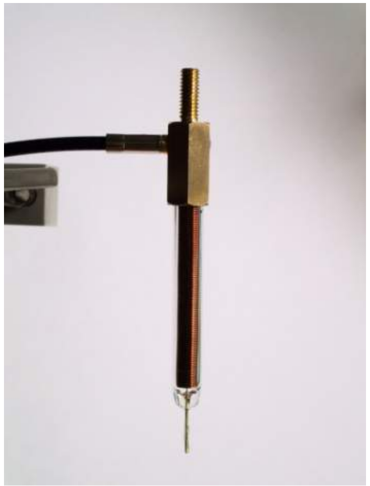




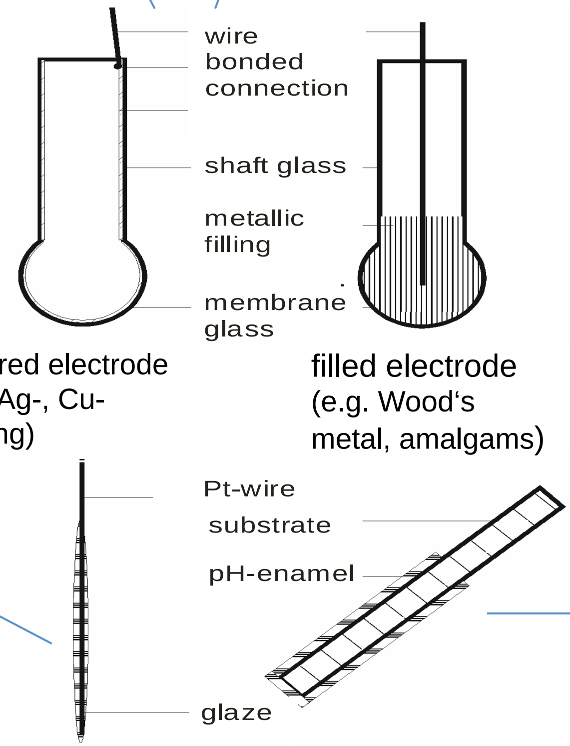
Jenaer flask electrode with metal coating and elastically supported membrane according to KRATZ



Metallised pressure resistant glass electrode according to LIENEWEG and NAUMANN



KSI



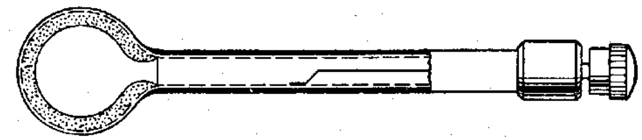
mirrored electrode (e.g. Ag-, Cu-coating)

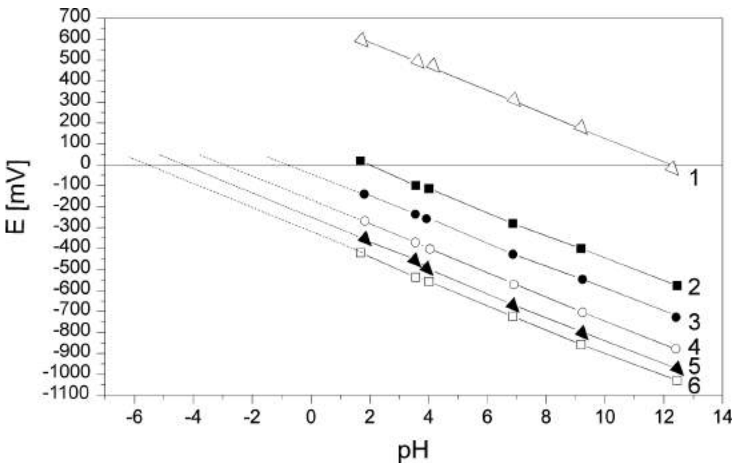
filled electrode (e.g. Wood‘s metal, amalgams)

glazed wire

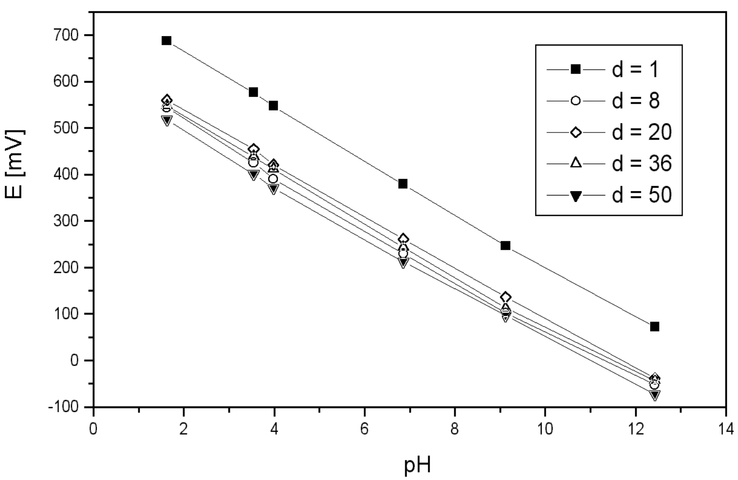
vitreous enamelling

Pfaudler



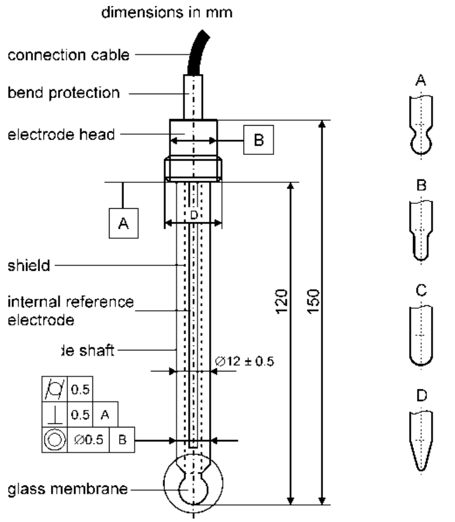


Electrode of all solid state pH electrodes vs. Ag/ AgCl, sat.. KCl at 25 °C in NBS- buffer solutions (solid contact: 1 ... Ag, 2 ... Pb/Bi-alloy, 3 ... WOODs metal, 4 ... Zn-alloy, 5 ... Sn-alloy, 6 ... Cd-alloy



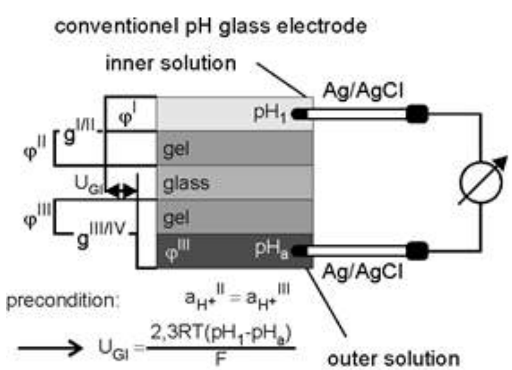
Electrode function of an all solid state pH glass electrode with silver contact vs. Ag/ AgCl, sat. KCl at 25 °C at several days d

Ion conducting glasses

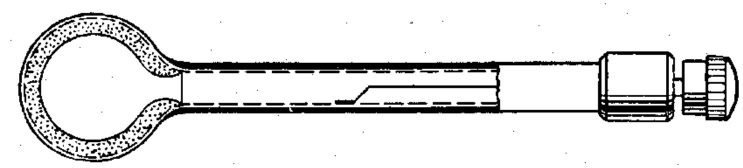


pH glass electrode according to GERMAN STANDARD DIN 19 263

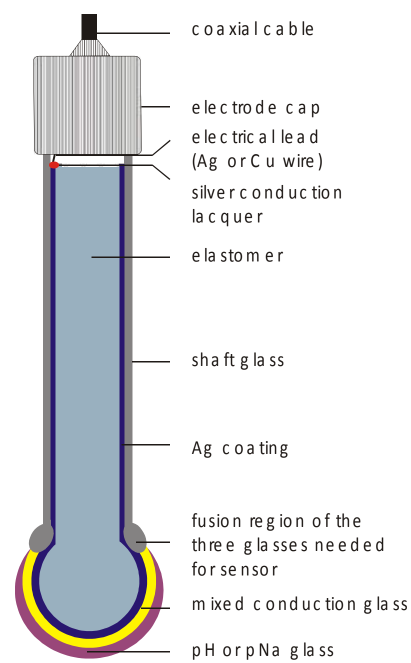
Glass composition:
e.g. 72% SiO_2, 22% Na_2O; 6% CaO

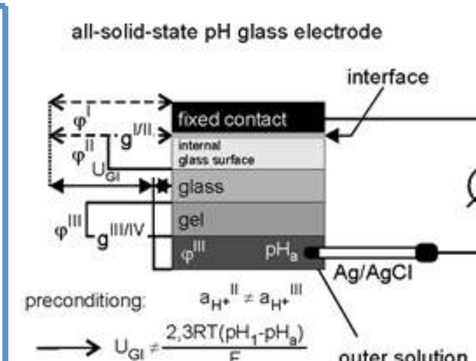


Metallized pressure resistant glass electrode according to LIENEWG and NAUMANN

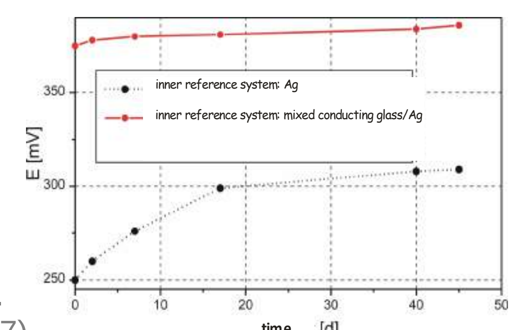


Jenaer flask electrode with metal coating and elastically supported membrane according to KRATZ

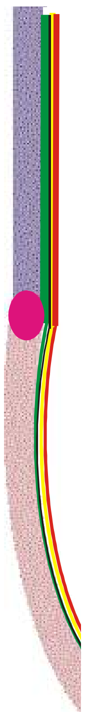


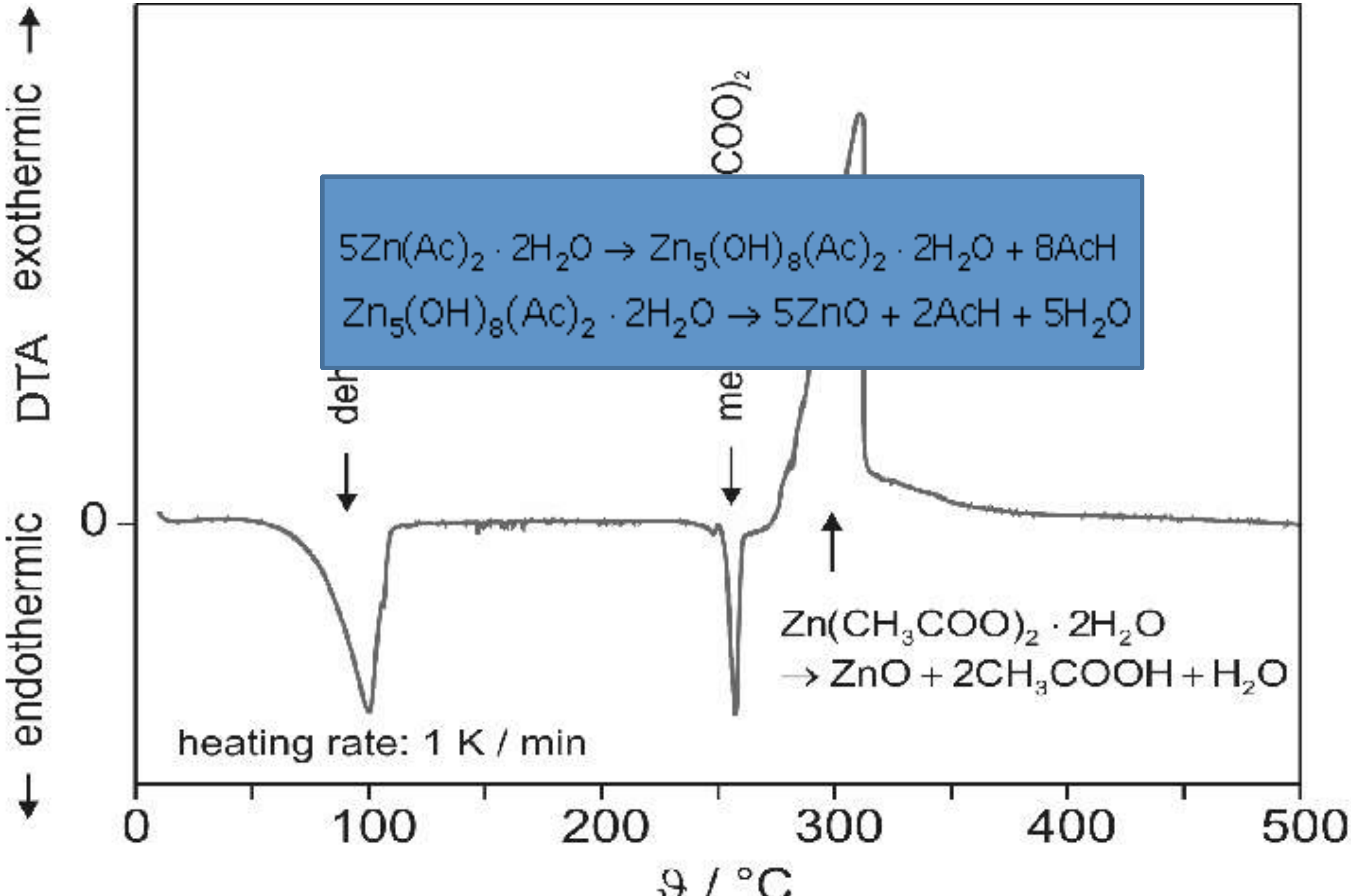


Vonau, W.; Kaden, H.: Glastech. Ber. Glass Sci. Technol. **70** (1997) 5, 155-160



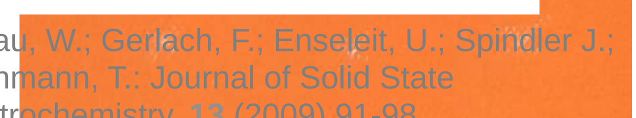
MEINSBERG KSI





$$5Zn(Ac)_2 \cdot 2H_2O \rightarrow Zn_5(OH)_8(Ac)_2 \cdot 2H_2O + 8AcH$$

$$Zn_5(OH)_8(Ac)_2 \cdot 2H_2O \rightarrow 5ZnO + 2AcH + 5H_2O$$

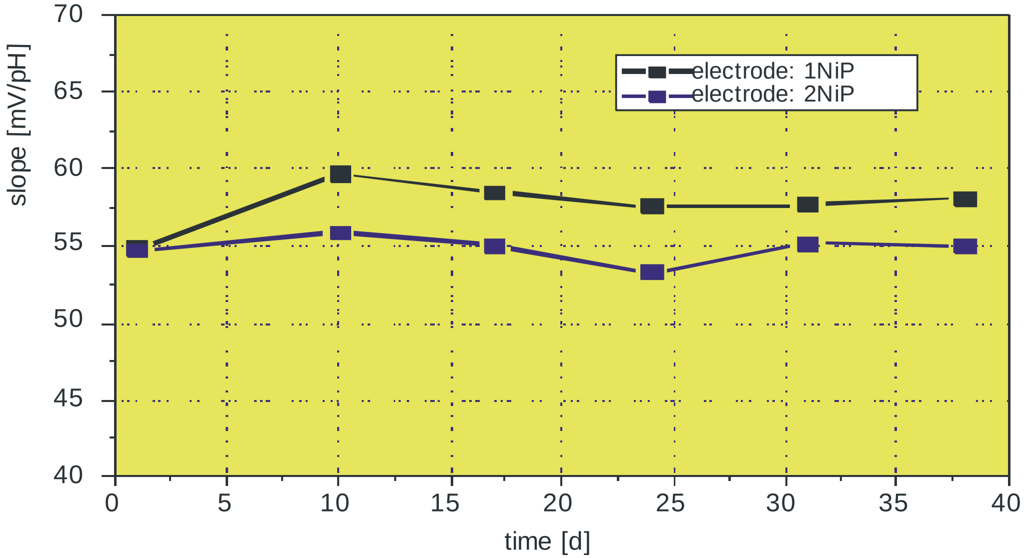


Bachı Spind W.; G 1020(

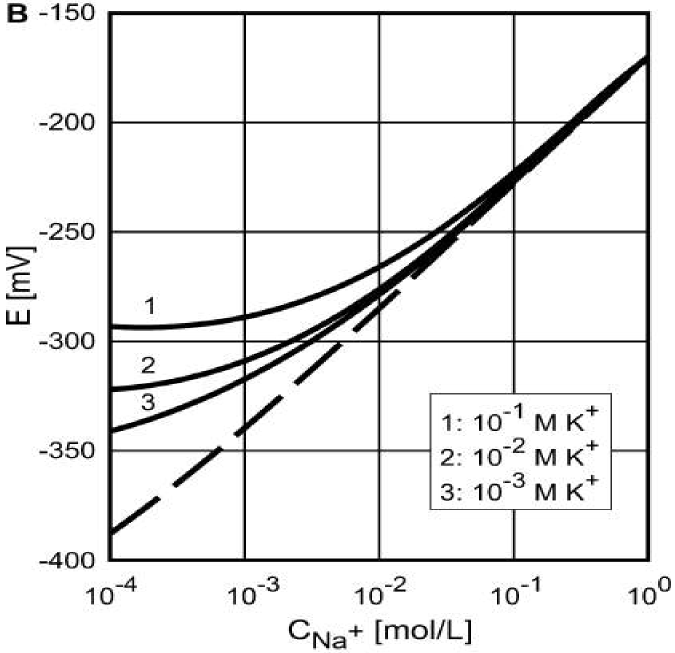
Reinecke, M., Spindler, J.; Berthold, F.; Vonau, W.: MO **56** 3 (2002) 20-24

layer on top of the Corning 015 glass membrane
(4 µm x4 µm x 57 nm)

Vonau, W.; Gerlach, F.; Enseleit, U.; Spindler J.; Bachmann, T.: Journal of Solid State Electrochemistry. **13** (2009) 91-98



solid state pH flow-through electrodes

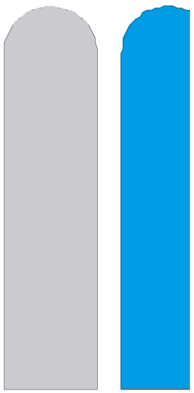


Vonau, W.; Enseleit, U.; Gerlach, F.; Bachmann, T.; Spindler, J.: Durchflussmessfühler zur Bestimmung von Ionenaktivitäten und Verfahren zu dessen Anwendung. german patent 10 2007 042 476.2

Vonau, W.; Gerlach, F.; Enseleit, U.; Bachmann, T.: Mehrparameter-Elektrode. german patent 10 2008 016 985.4

Vonau, W.; Enseleit, U.; Gerlach, F.: Electrochemistry Communications **10** (2008) 1355-135

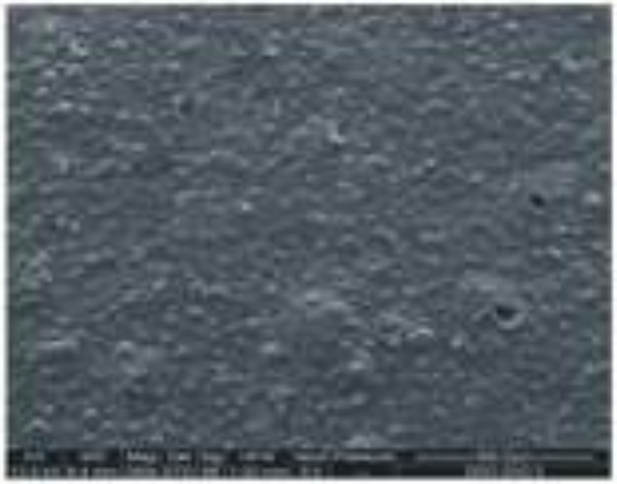
sensor ass

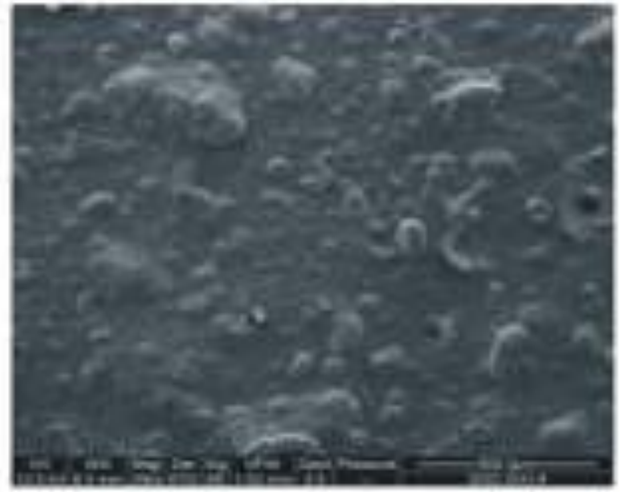


ous $Zn(NO_3)_2$ solution

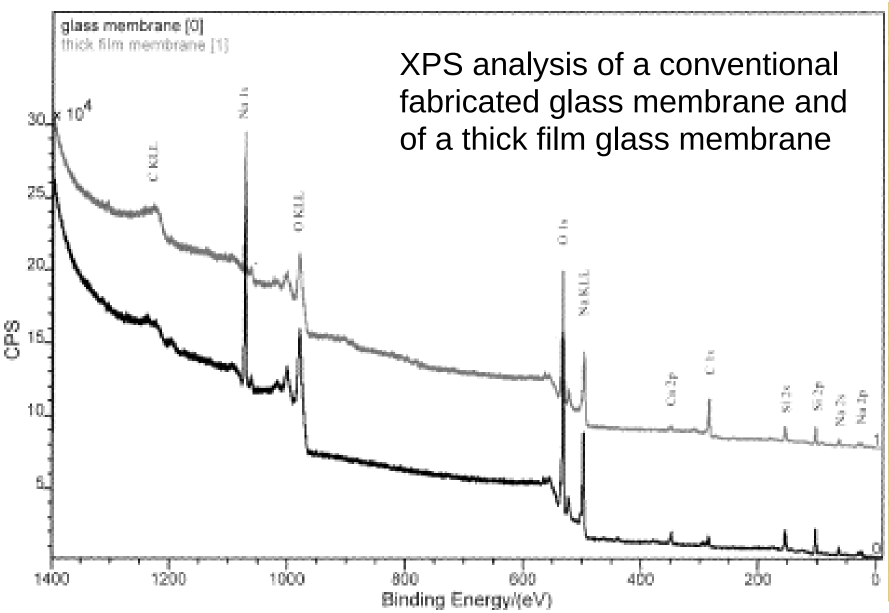
ulated steel substrates

at.
e to air
a drying oven
a muffle furnace

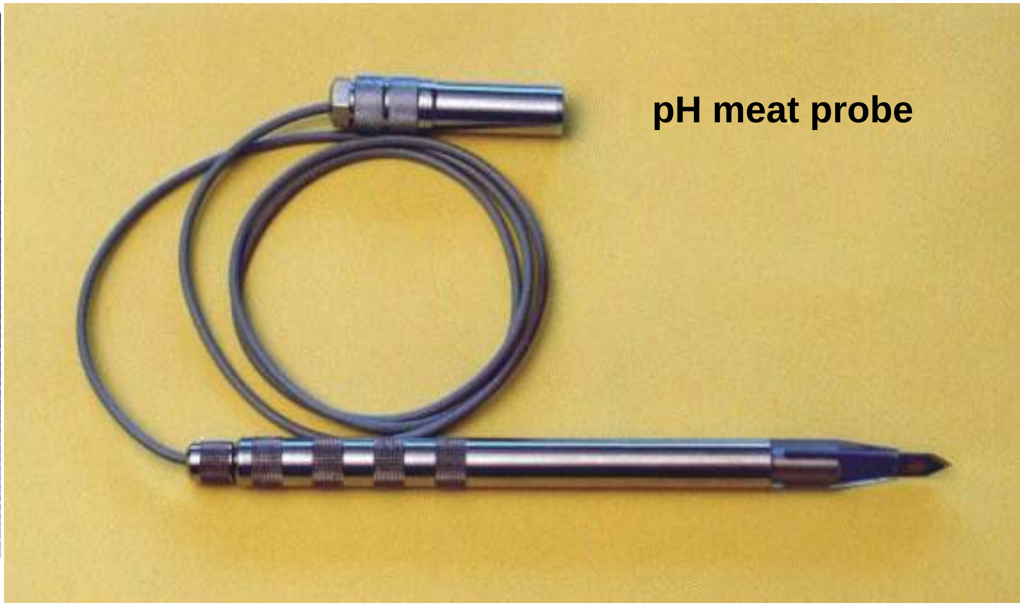




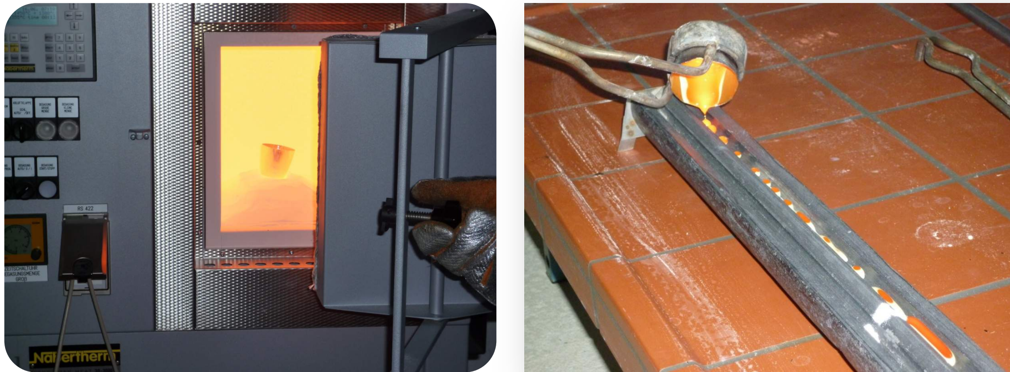
SEM shootings of the ZnO covered gold electrodes



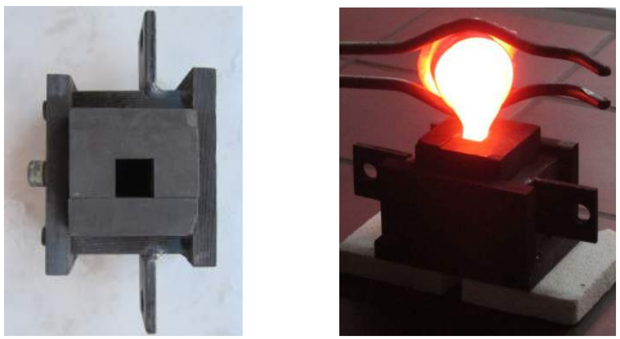
XPS analysis of a conventional fabricated glass membrane and of a thick film glass membrane



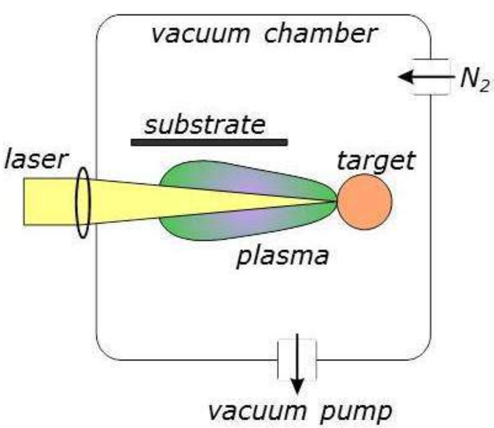
PLD pH sensor



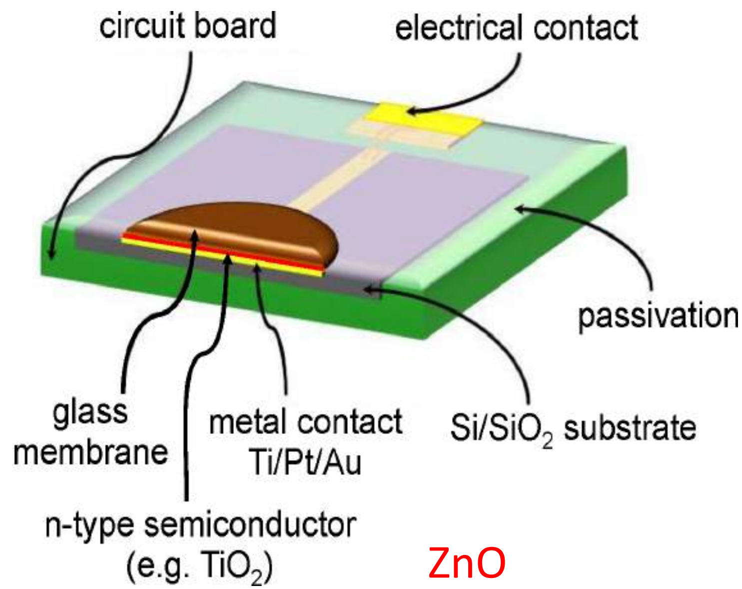
Glass melting process



Two-piece graphite mold and of the glass pouring process



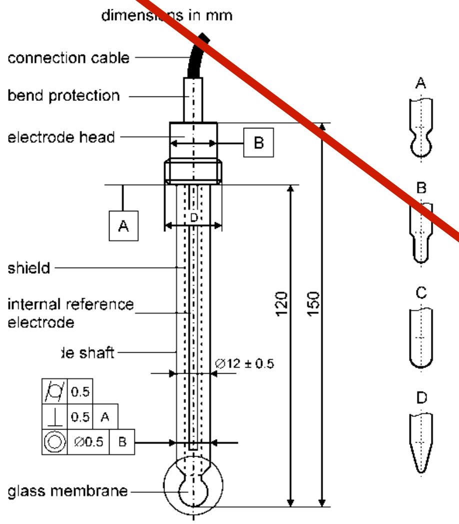
Pulsed laser deposition (PLD)	
Power	1.2 J/cm²
Wavelength	248 nm
Repetition rate	10 Hz
Ablation time	5 min
Pressure	2×10^{-2} mbar N_2
Temperature	RT



Cross-sectional schematic of the pH glass thin-film sensor attached to a printed circuit board, electrically contacted and encapsulated

W. Vonau, K. Ahlborn, F. Gerlach, H. Iken, W. Zander, J. Schubert, M.J. Schöning: PLD-Based Planar pH Sensor. The Fourth International Conference on Sensor Device Technologies and Applications SENSORDEVICES 2013, 25 – 31. August 2013 - Barcelona, Spain

Ion conducting glasses



pH glass electrode according to GERMAN STANDARD DIN 19 263

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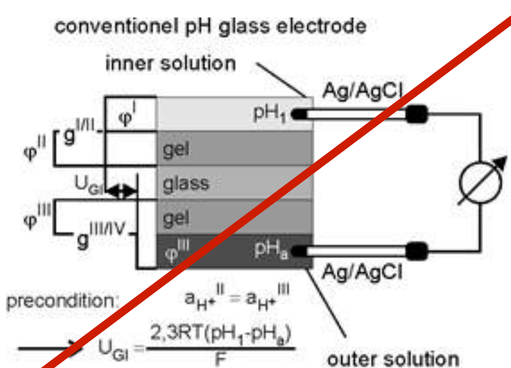
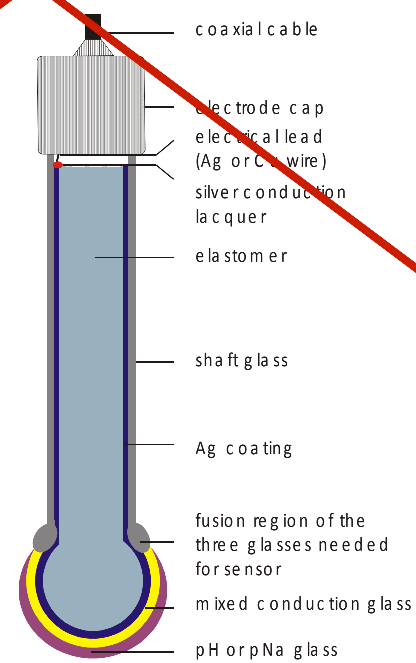
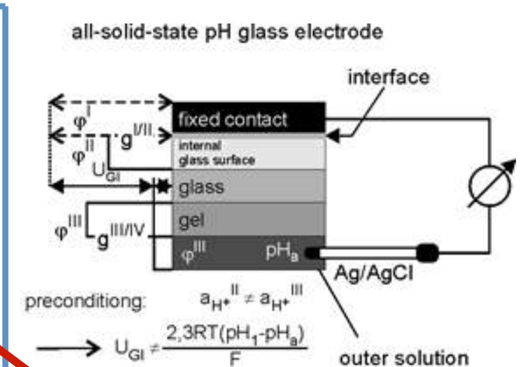
e.g. 72% SiO_2, 22% Na_2O; 6% CaO

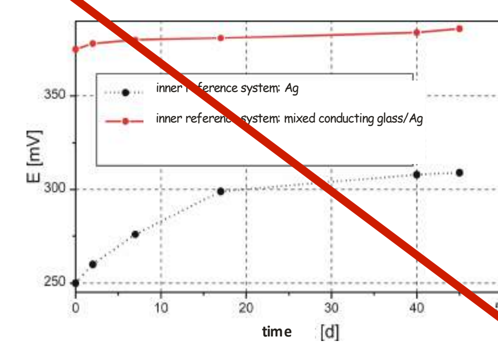


Metallized pressure resistant glass electrode according to LIENEWG and NAUMANN

Jenaer flask electrode with metal coating and elastically supported membrane according to KRATZ







~~Ion conducting glasses~~ **Electron conducting glasses**

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oxidic glasses

siliceous glasses:
quartz glass
sodium lime glass (pH, pNa, pK)
semiconducting glass (redox potential)

mixtures of several basic glasses:
borosilicate glass

non-siliceous glasses:
borate glass
phosphate glass

non-oxidic glasses

saline glasses:
nitrate glass
fluoride glass

chalcogenide glasses
(mono and polyvalent metal ions)

metallic glasses

Polymer glasses:
PS
PMMA

GLASS-FORMING SYSTEMS

An **amorphous solid** is a solid in which there is no long-range order of the positions of the atoms.

electrodes with amorphous membranes (e.g. pH-glass, chalcogenide glass or redox glass)

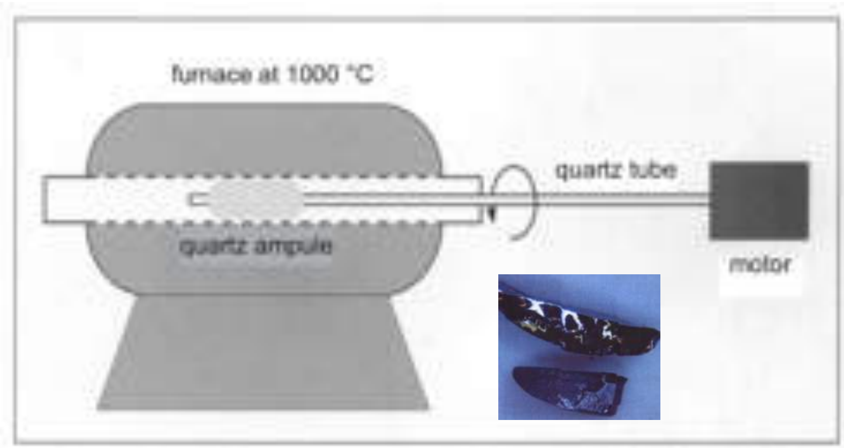
Table 1. Main stages of work in the field of developement of chemical sensors for solution analysis

Year	Author	Content of work	References
1906	Cremer	Influence of pH on emf in galvanic cell with glass membrane	[3]
1909	Haber, Klemensiewicz	Development of glass electrodes	[4]
1936	Beckman	Production of pH-meters	[5]
1937	Nikolsky	Nikolsky equation and principles of ion-exchange theory of the glass electrodes	[6, 7]
1961	Pungor	Development of solid-state heterogeneous crystalline ISE	[8]
1966	Frant, Ross	Single crystalline lanthanum fluoride ISE	[9]
1968	Simon	Liquid ISEs with neutral carriers in membrane	[10]
1967	Ross	Liquid ISE with ion-exchange membrane	[11]
1969	Guilbault, Montalvo	Potentiometric molecular-sensitive electrode (biosensor)	[12]
1970	Bergveld	Development of ion-selective field effect transistor (ISFET)	[13]
1971	Baker, Trachtenberg	Chalcogenide glasses as membrane materials for ISEs	[14]
1986	Thorn EMI Microsensors	First commercial production of ISFETs	[15]
1976	Emmerich	Enamel pH electrodes	
1983	Läppävouri	pH glass electrodes in thick film technology	
…			

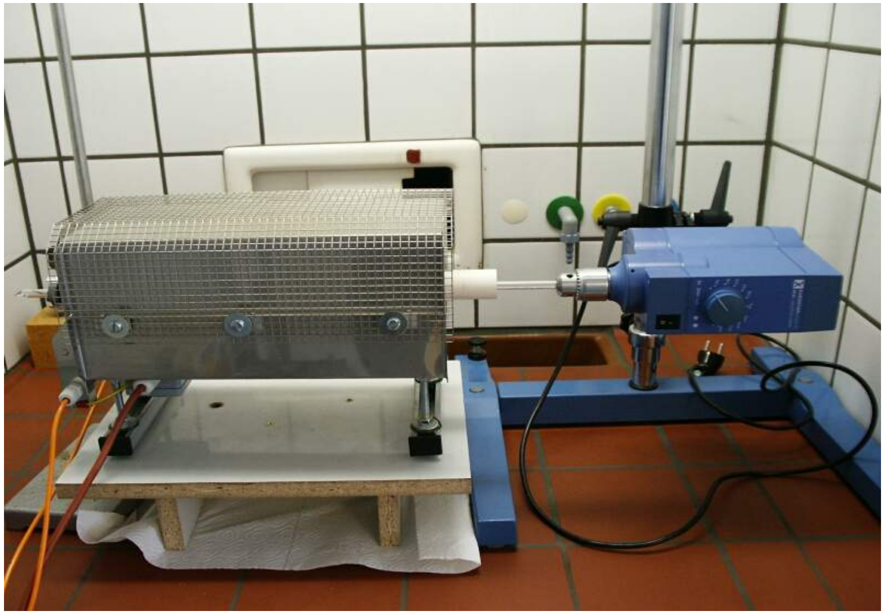
From: Vlasov YG, Fresenius Z Anal Chem (1989) 355:92-99

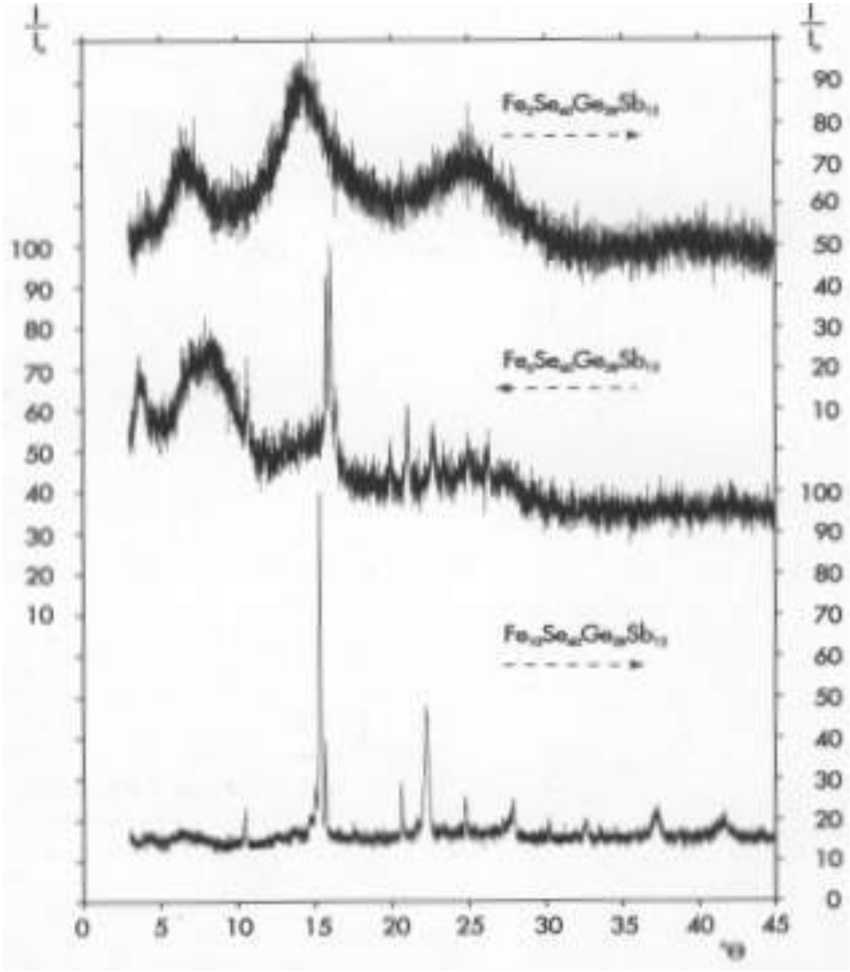
Table 2. Chalcogenide glass ion-selective sensors

Determined ion, X	Membrane composition	S, mV/pX	Detection limit, (mol/l)	pH	References: Analytical properties	References: Solid-state study
Ag^+	Ag–As–S	59	1×10^{-7}	up to 6 mol/l HNO_3	[24]	[25, 26]
	Ag–As–Se					
Cu^{2+}	Cu–Ag–As–Se	29	1×10^{-7}	up to 1 mol/l HNO_3	[27, 28]	[29, 30]
Pb^{2+}	$PbI_2-Ag_2S-As_2S_3$	29	1×10^{-7}	2–6	[31, 32, 35]	[33, 34, 36]
	$PbS-Ag_2S-As_2S_3$					
	$PbS-AgI-As_2S_3$					
Cd^{2+}	$CdS-Ag_2S-As_2S_3$	28	1×10^{-7}	1–7	[37–38]	[37–39]
	$CdI_2-Ag_2S-As_2S_3$					
Fe^{3+}	$Ge_{28}Sb_{12}Se_{60}(Fe)$	58	5×10^{-5}	1–2	[42]	[40–44]
Br^-	$AgBr-Ag_2S-As_2S_3$ [a]	59.5	5×10^{-7}	2–10	[45, 46, 49]	[46–48]



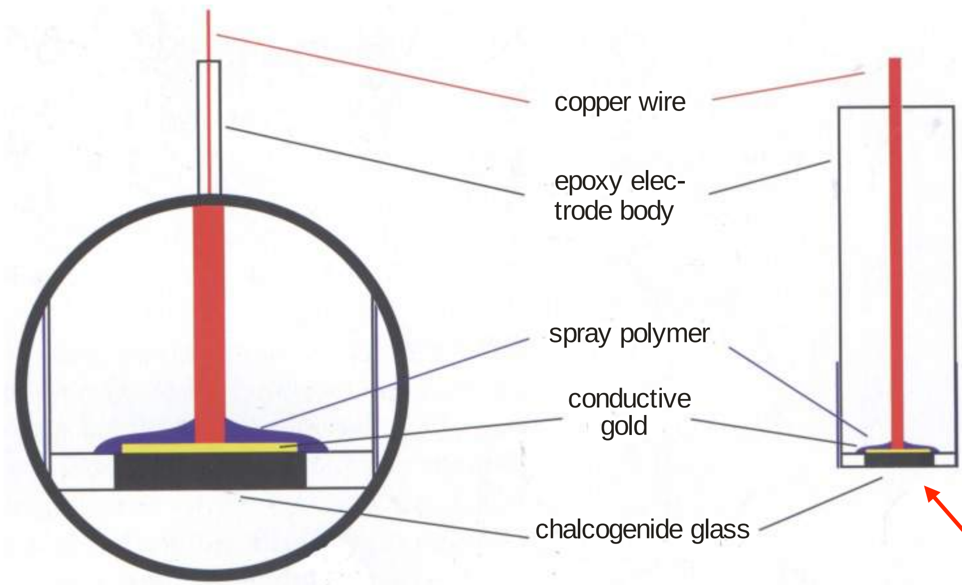
tube furnace to prepare chalcogenide glasses





X-ray diffraction diagram

Pollrich, S.: Diploma Thesis, Mittweida, 2004



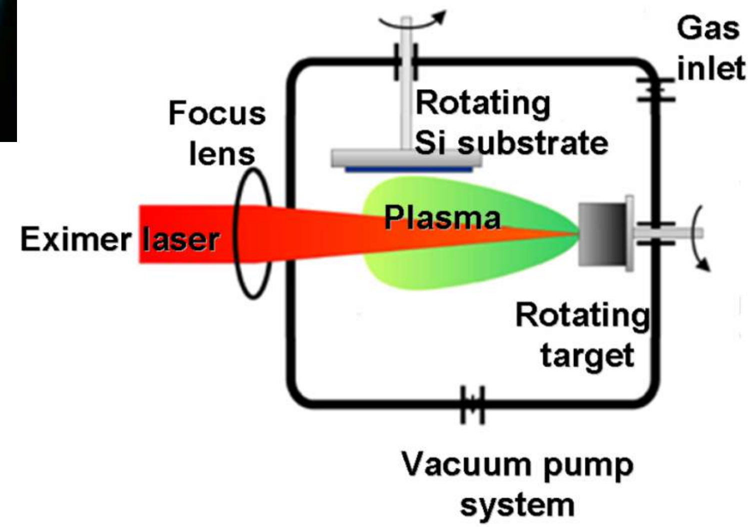
schematic drawing of a chalcogenide glass electrode according to the state of the art

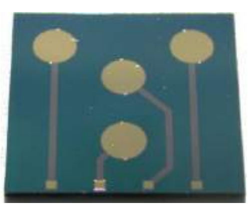
photograph of a chalcogenide glass electrode

PLD – pulsed laser deposition

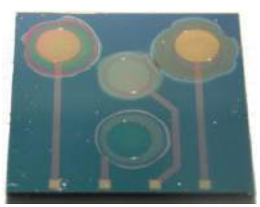
Chalcogenide glass membrane

- used glasses
  - $CdSAgIAs_2S_3$
  - $PbSAgIAs_2S_3$
  - CuAgAsSe
  - $AgIAs_2S_3$
- Deposition by laser ablation





Si substrate wit 4 electrodes



PLD-process

Si- substrate after PLD of the chalcogenide glass thin films and encapsulation

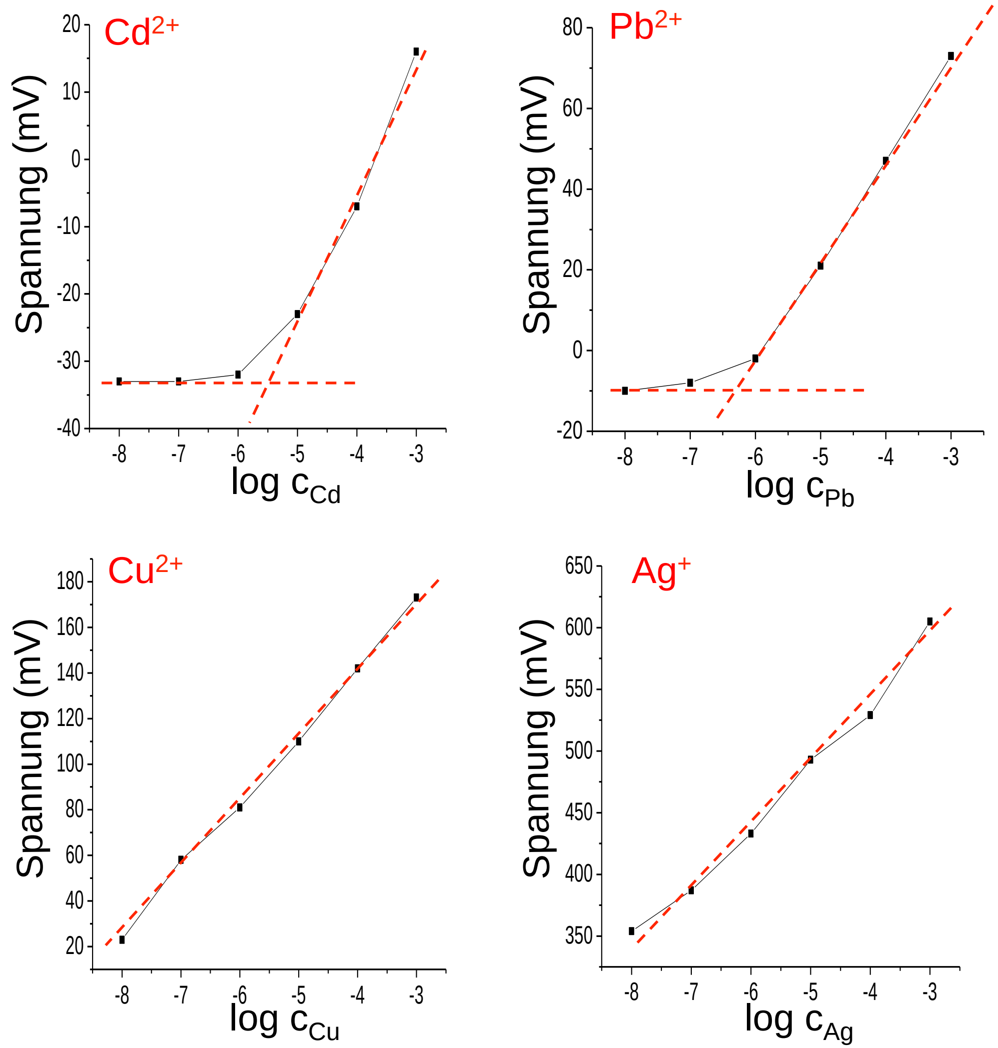
Spelthahn, H.; Kirsanov, D.; Legin, A.; Osterrath, T.; Schubert, J.; Zander, W.; Schöning, M.J., Development of a thin-film sensor array for analytical monitoring of heavy metals in aqueous solutions, *Phys. Status Solidi A* 209(5) (2012) 885-891

Chalcogenide glass

Chalcogenide -glass	Sensitivity [mV/dec]
$CdSAgIAs_2S_3$	25,5 - 0,9
$PbSAgIAs_2S_3$	23,9 - 2,1
$AgIAs_2S_3$	46,1 - 4,5
CuAgAsSe	31,9 - 0,4

Chalcogenide -glass	Detection limit [mol/L]
$CdSAgIAs_2S_3$	4×10^{-7}
$PbSAgIAs_2S_3$	5×10^{-8}
$AgIAs_2S_3$	2×10^{-7}
CuAgAsSe	4×10^{-8}

Schöning, M.J.; Kloock, J.P.: Electroanalysis 19(19-20) (2007) 2029-2038.



Electrode functions of chalcogenide glass electrodes

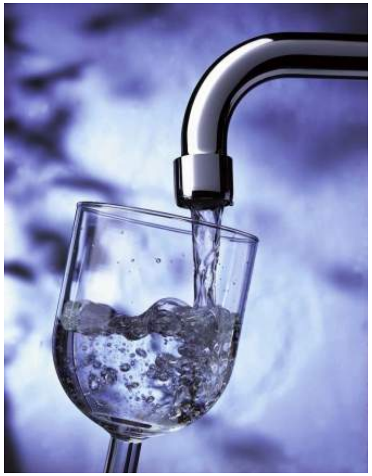
oxidic glasses

<u>siliceous glasses:</u>
quartz glass
sodium lime glass (pH, pNa, pK)
semiconducting glass (redox potential)

<u>mixtures of several basic glasses:</u>
borosilicate glass

<u>non-siliceous glasses:</u>
borate glass
phosphate glass

Important applications for redox potential measurements



Drinking water

Swimming-pool water

Waste water

- Introduction
- New approach for redox potential measurement
- Fabrication of redox electrode glass and glass paste incl. characterisation
- Fabrication of the electrodes
- Electrode test (laboratory)
- Field operation (Control of Process and Waste Waters)
- Outlook
- Conclusion
- Acknowledgement

glass	Na	K	Li	Fe	Ca	Si	addition
2	x	-	x	x (Fe_2O_3)	-	x	-
3	x	-	-	x (Fe_2O_3)	-	x	Al
4	x	-	x	x (Fe_2O_3)	-	x	-
7 (7x)	x		x	x (Fe_2O_3)	-	x	-
11	x	x	-	x (Fe_2O_3)	-	x	-
12	x	x	-	x (Fe_2O_3)x	-	x	-
14 (2x)	-	-	x	x (Fe_2O_3)x	-	x	-
15	-	-	x	x (Fe_2O_3)	-	x	-
16	x	-	x	x (Fe_2O_3)		x	U
17 (3x)	-	-	x	x (Fe_2O_3)	x	x	-
18	x	-	x	x (Fe_2O_3/Fe_3O_4)	-	x	-
20	x	-	-	x (Fe_2O_3)	x	x	-
21	x	-	-	x (Fe_3O_4)	x	x	-
22	x	-	x	x (Fe_3O_4)	-	x	-
23	x	-	x	x (Fe_2O_3)	x	x	-
24	x	-	x	x (Fe_2O_3)	x	x	-
25	x	-	x	x (Fe_2O_3)	x	x	-

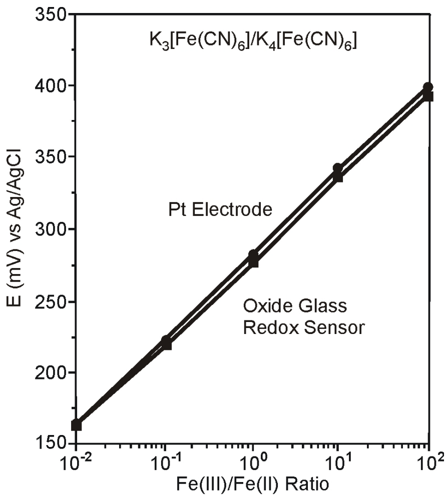
	Na	K	Li	Ti	Nb	Ta	Si
glass 1	x	-	x	x(TiO_2)	x	x	x
glass 5	x	x	-	x(TiO_2/Ti_2O_3)	x	-	x
glass 6	x	x	x	x(TiO_2/Ti_2O_3)	x	x	x
glass 8 (2x)	x	-	x	x(TiO_2/Ti_2O_3)	x	x	x
glass 9 (2x)	x	x	-	x(TiO_2/Ti_2O_3)	x	-	x
glass 10 (3x)	x	x	-	x(TiO_2/Ti_2O_3)	x	-	x
glass 13 (2x)	x	x	-	x(TiO_2/Ti_2O_3)	x	-	x
glass 19	-	x	x	x(TiO_2/Ti_2O_3)	x	x	x
glass 19 (Argon)	-	x	-	x(TiO_2/Ti_2O_3)	x	x	x
glass 26	x	x	-	x(Ti_2O_3)	x	-	x

MEINSBERG KSI

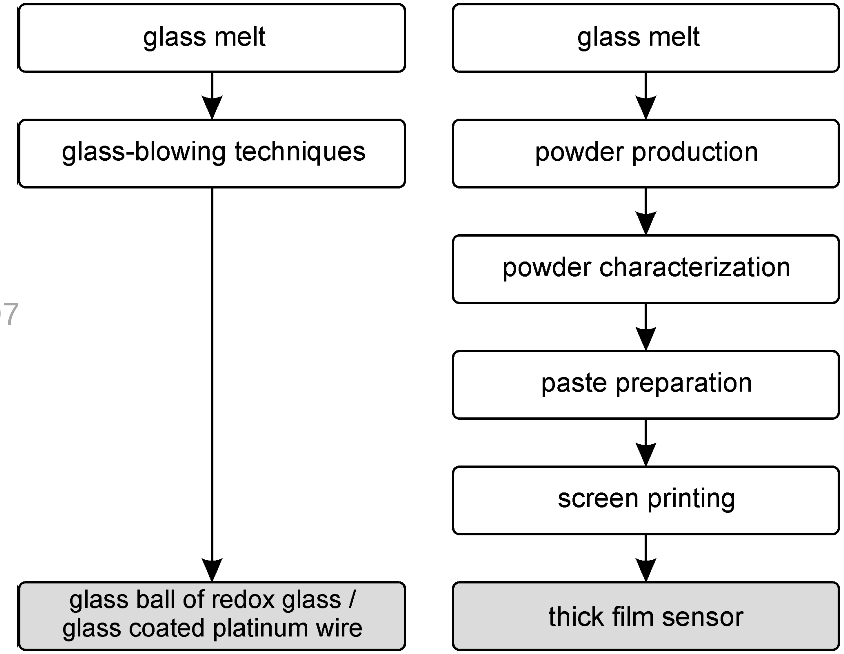
Glass compositions

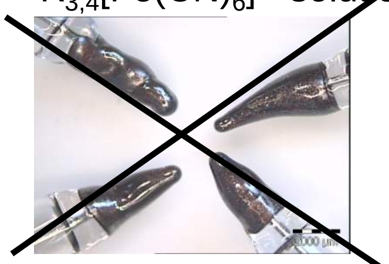
Melting of redox glass

B.P. Nikolskij, M.M. Schulz: US 3 773 642 (197

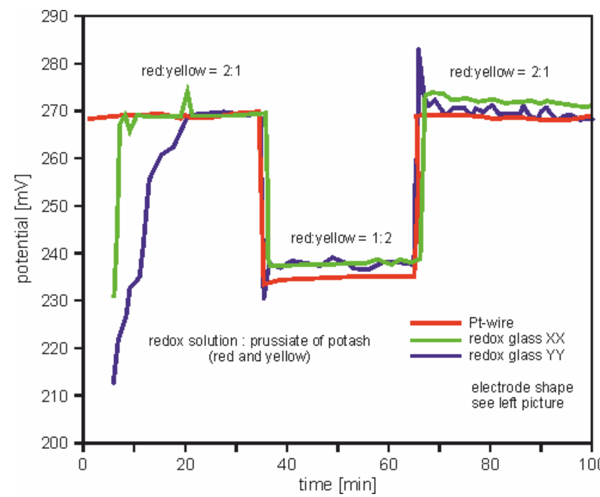


electrode function of a redox sensor from oxide glass and a platinum electrode in $K_{3,4}[Fe(CN)_6]$ - solutions

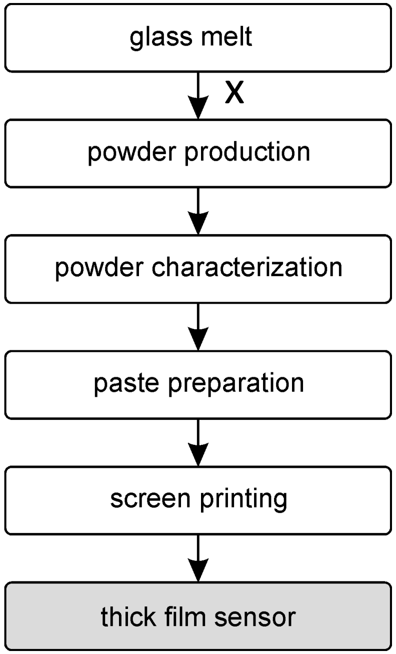




W. Vonau, E. Pöhler, F. Gerlach, K. Ahlborn: Glass based redox sensor. 14th International Meeting on Chemical Sensors (IMCS 2012). Proceedings, pp. 600-603, ISBN 978-3-9813484-2-2



Electrode function of several redox electrodes

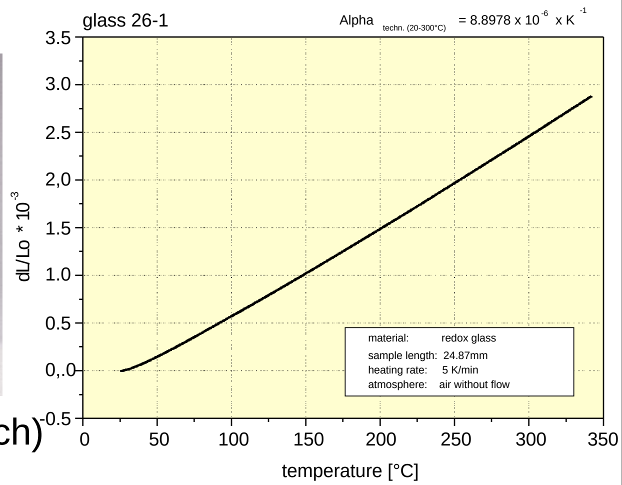


- glass was mechanically processed
- milled in a planetary ball mill for one hour
- glass powder was sieved through a mesh

X

Determination of the linear thermal coefficient of expansion

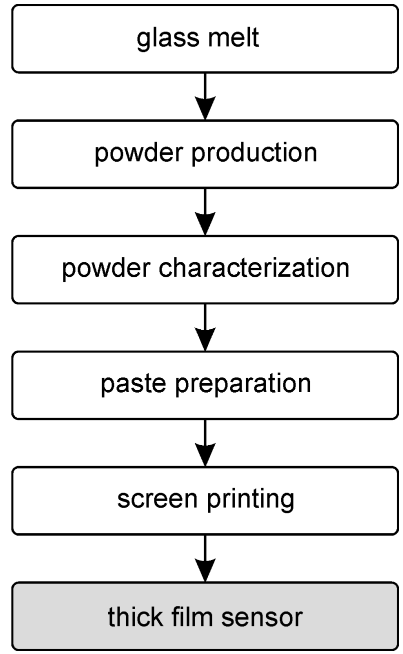
Dilatometer DIL 402C/4/G (Fa.Netzsch)



Thermographic investigations (Setsys TG-DTA 12 of SETERAM)

- low mass loss of the glasses
- even at 1200 °C still 99.5 % of the initial mass remained
- By means of DTA investigations several crystallisation peaks were identified, indicating that beside an amorphous phase redox glasses also possess crystal structures

Microscopic characterisation of Ti-containing glass powder



Determination of the liquidus temperature
(no crystalline devitrification above that temperature)

Ti-glass	liquidus temperature [°C]	crystal phase
8	1295	unknown
9	1000	rutil
10	1210	rutil
13	1255	rutil
26	1260	rutil

Granulometric analysis of glass powder

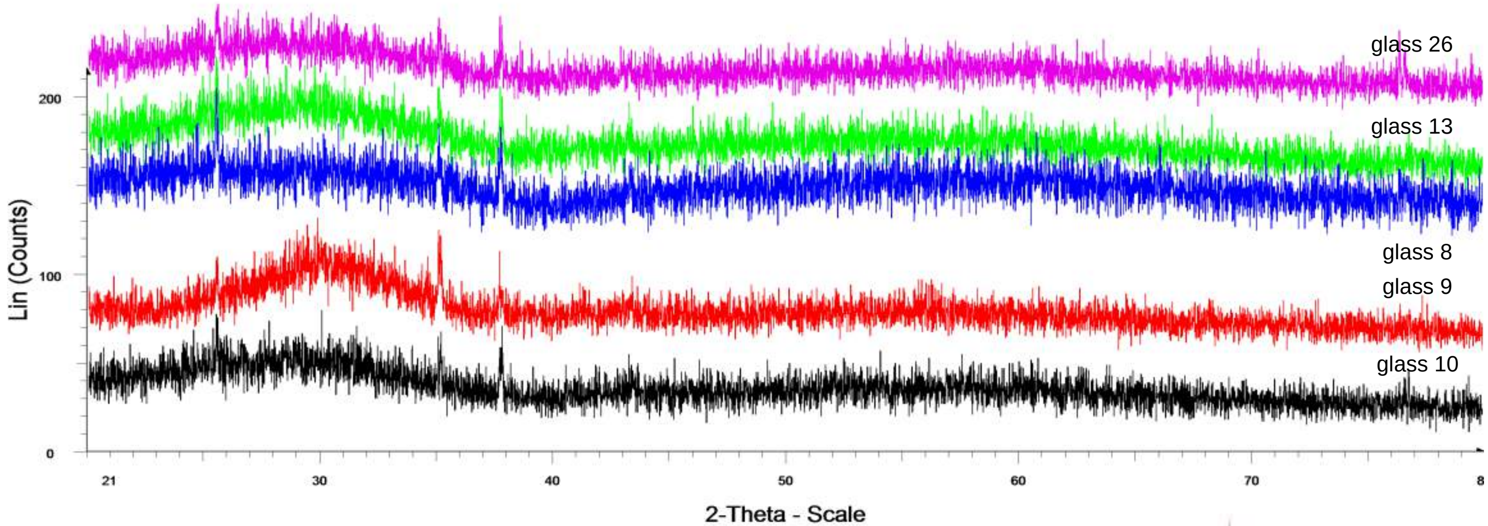
Brunauer-Emmet-Teller (BET) surface area by analysis of gas adsorbtion

Particle size by laser diffraction methods

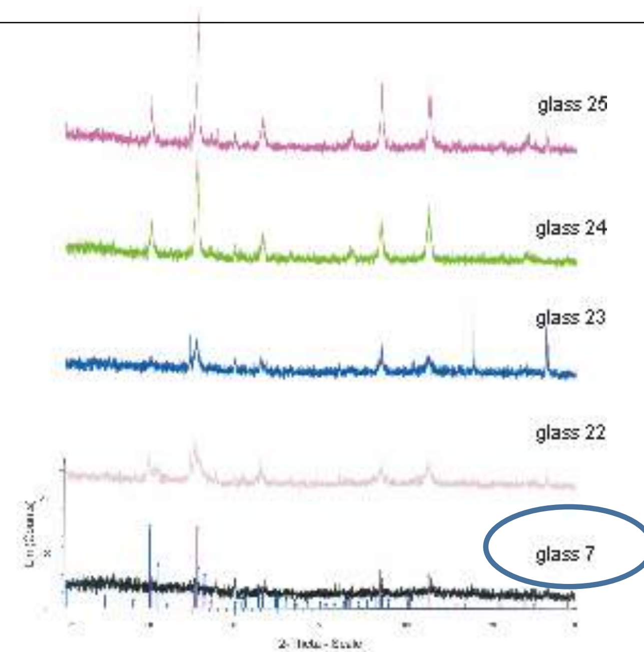
Glas-Nr.	BET surface [m^2/g)]	particle size [µm]
7	0.12	1.5
8	0.30	1.7
9	0.38	1.5
10	0.13	1.7
11	0.17	4.0
13	0.14	1.1
14	0.13	1.4
17	0.18	1.0
19	0.18	1.5
22	0.13	0.4
23	0.21	1.4
24	0.13	1.1
25	0.14	0.8
26	0.13	1.7

X-ray characterisation

XRD-diffractograms at Ti-containing redox glass powder



XRD-diffractograms at Fe-containing redox glass powder

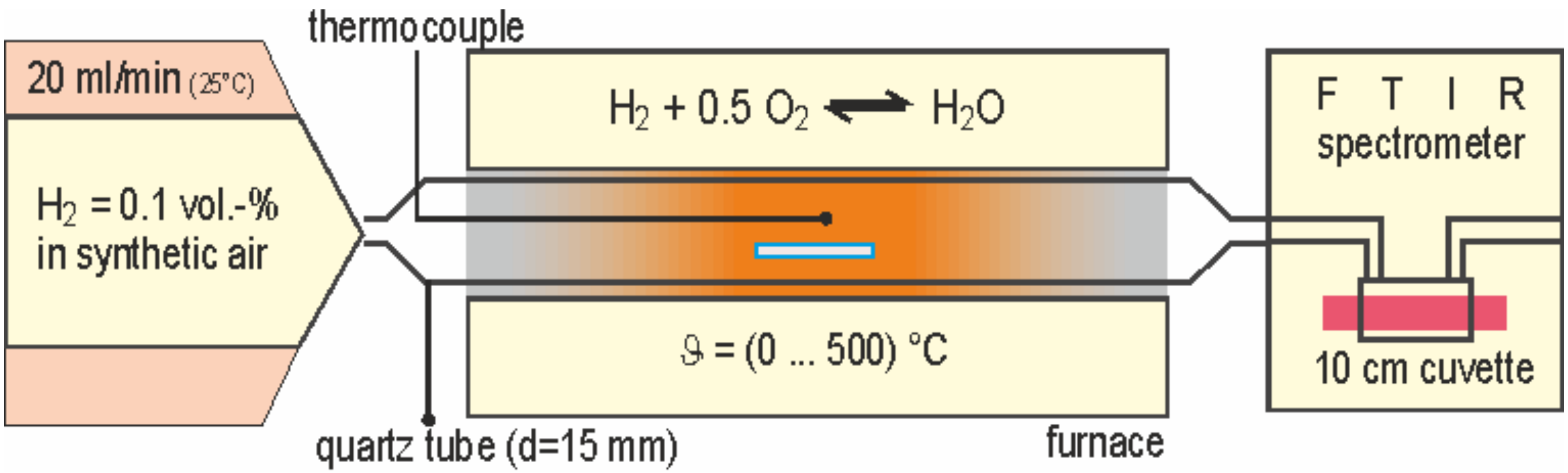


A

Powder diffractometer XRD 7 from SEIFERT (GE Inspection) with a CuKα radiation of a wave length of 1.5418 Å was used. The X-ray tube was operated with 40 kV and 40 mA. The measurements were performed with a counting period between 8 and 30 seconds per test point and a step size of 0.03°.

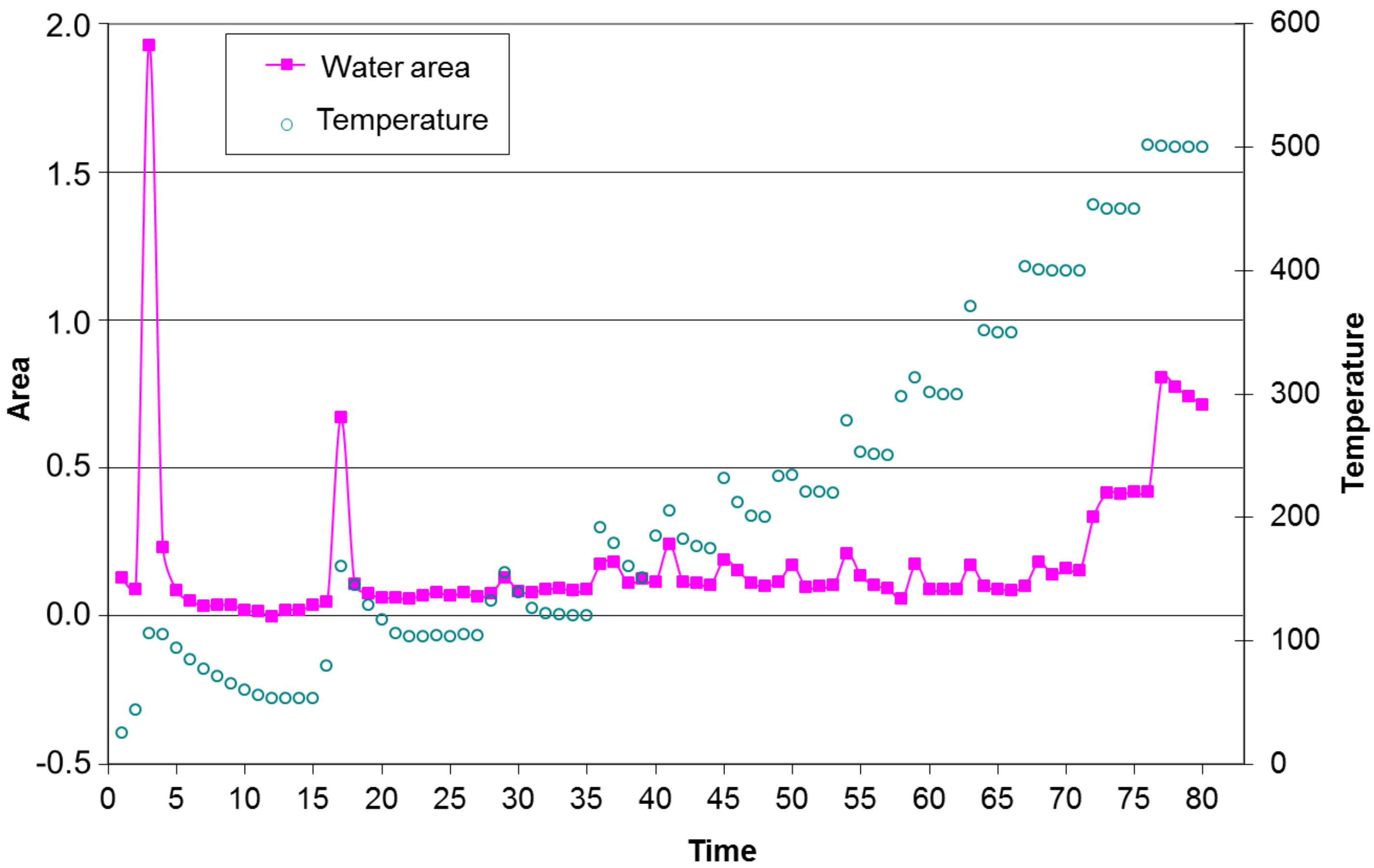
Measurements of the catalytic activity

- Carried out in a controllable, temperature programmable tube furnace of HTM REETZ
- Within the oven a quartz vessel (∅ 15 mm) was located.
- Gas: synthetic air with 1000 ppm hydrogen
- Reaction product water is investigated with FTIR spectroscopy (NICOLET 8700 of THERMO SCIENTIFIC)



Results

Measurements of the catalytic activity (glass A)



E. Pöhler: Master Thesis, Univ. Leipzig, 2012 glass melt

↓

powder production

↓

powder characterization

↓

paste preparation

↓

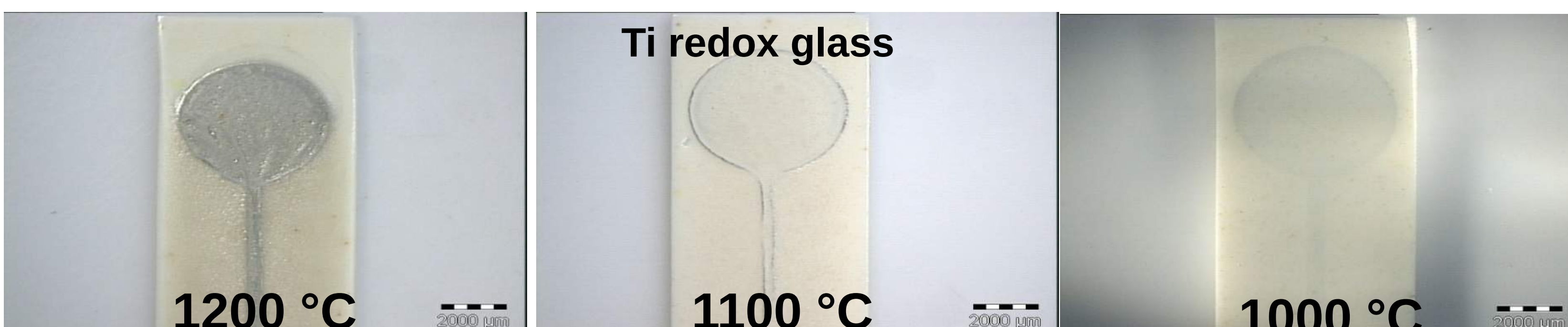
screen printing

↓

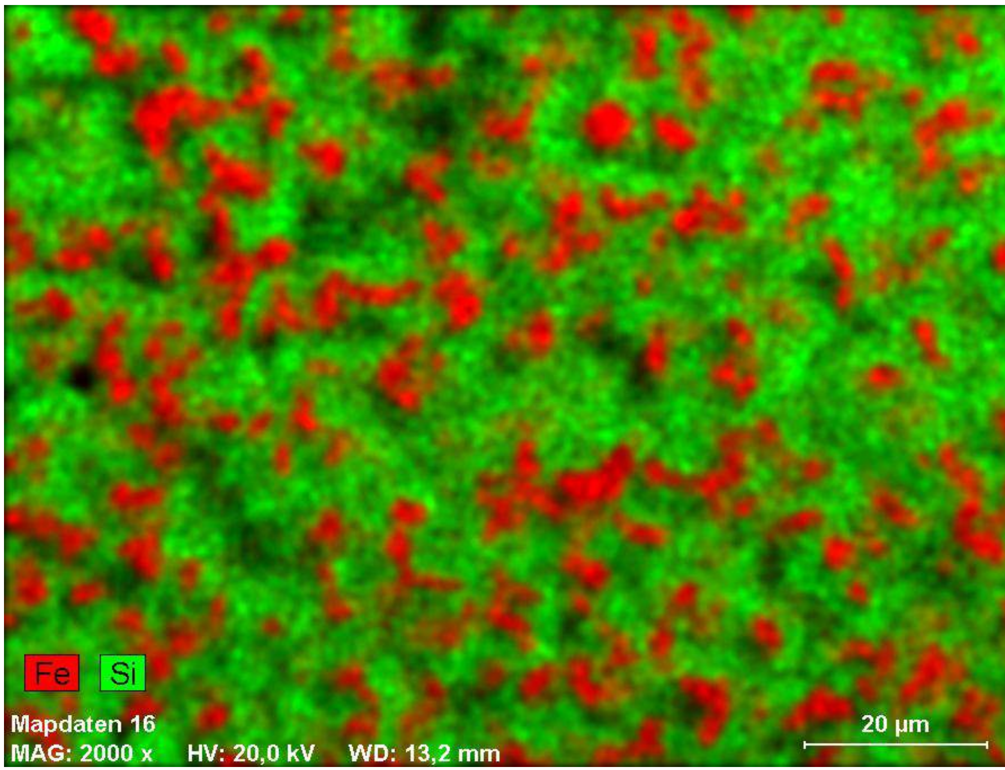
thick film sensor

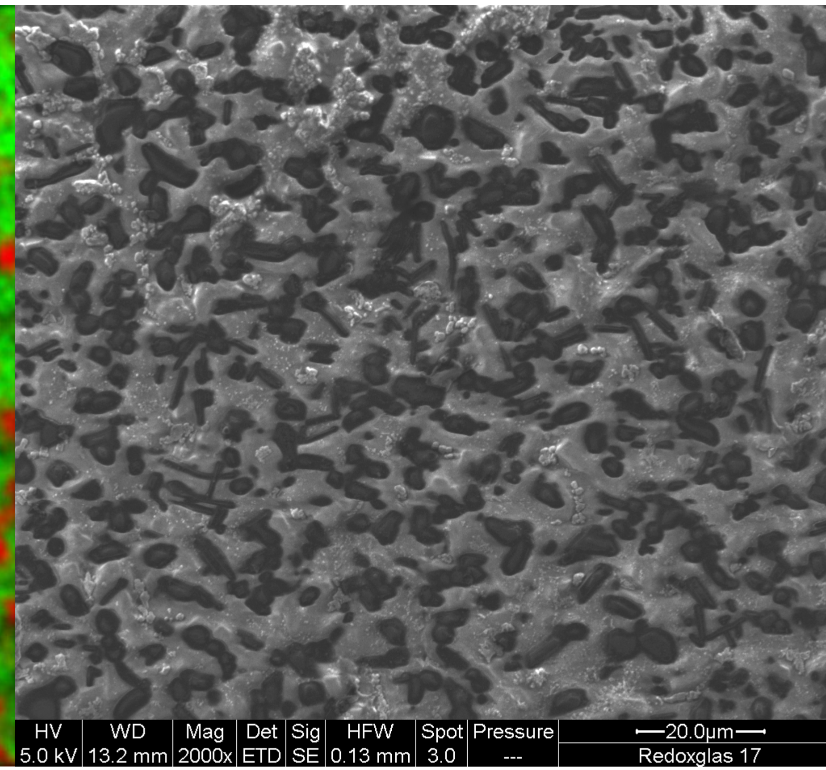
- powder was weighted, blended with the identical amount of a terpineol containing binder
- mixed again in the planetary ball mill for further 16 hours

Optimised sintering temperature

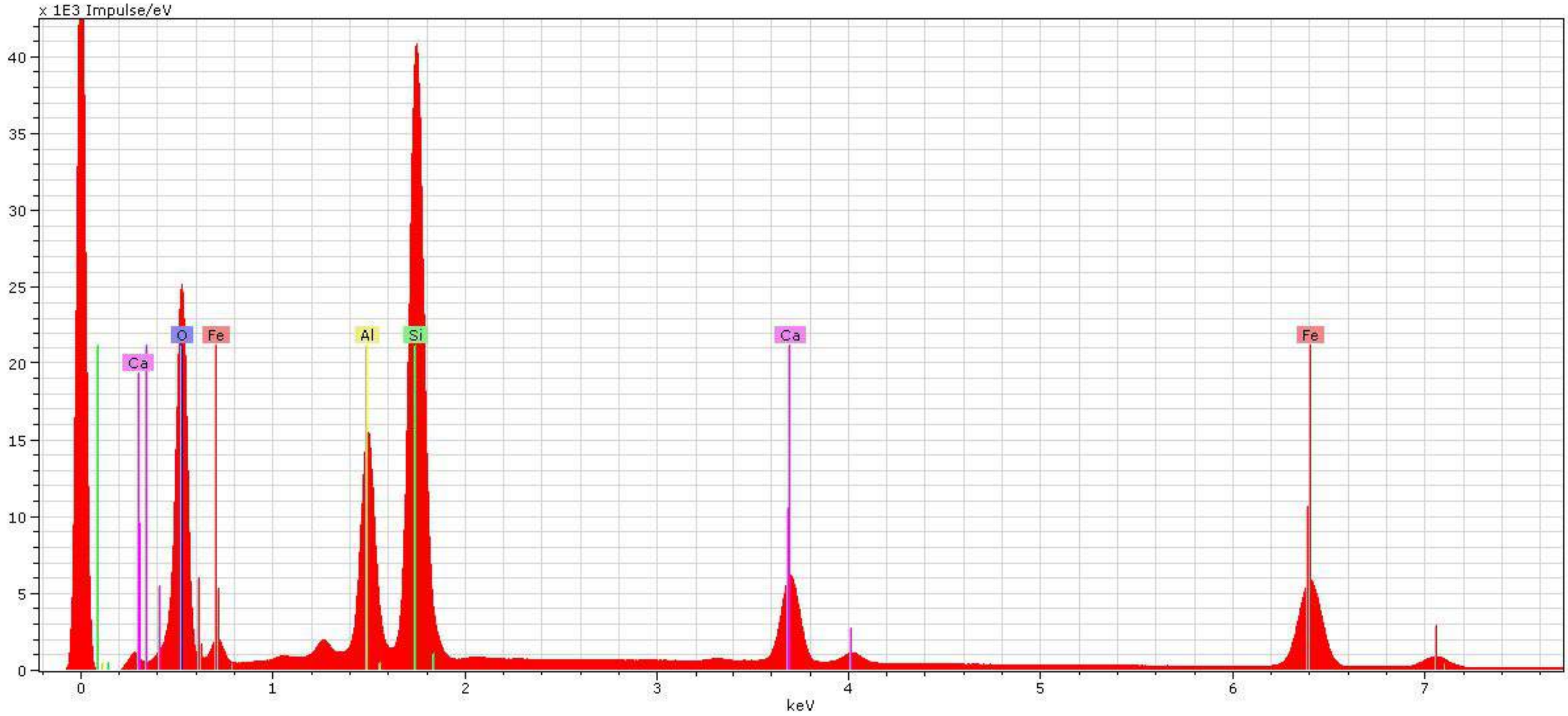


SEM shooting of a thick film of glass A

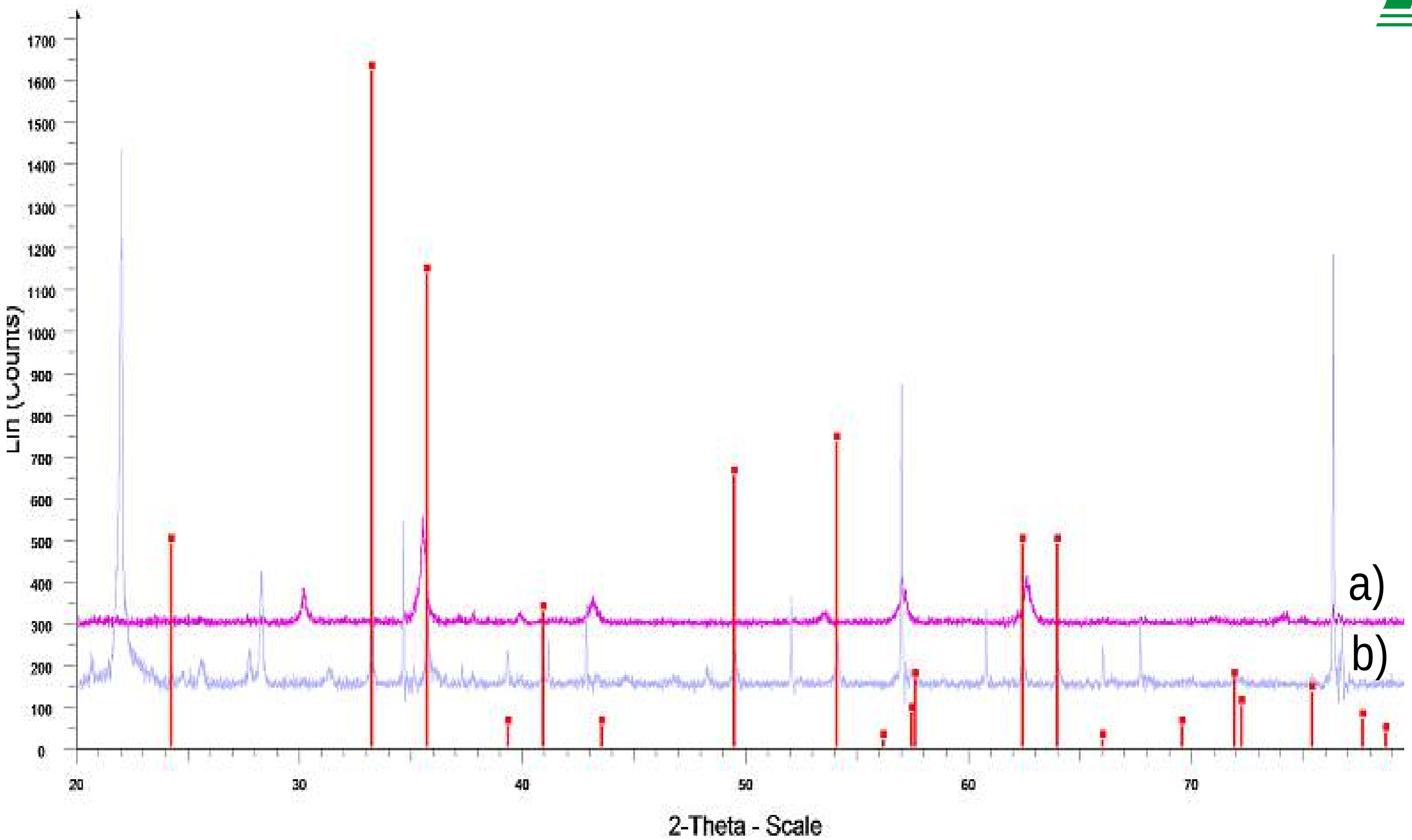




EDX spectrum of a thick film of glass A



Comparision of X-ray diffractograms on powder and thick film paste of redox glass



a) glass powder A
b) glass thick film A

red:
expected peak positions for Fe_2O_3

The degree of recrystallisation increased in the order initial glass - glass powder - thick film glass electrode membrane!

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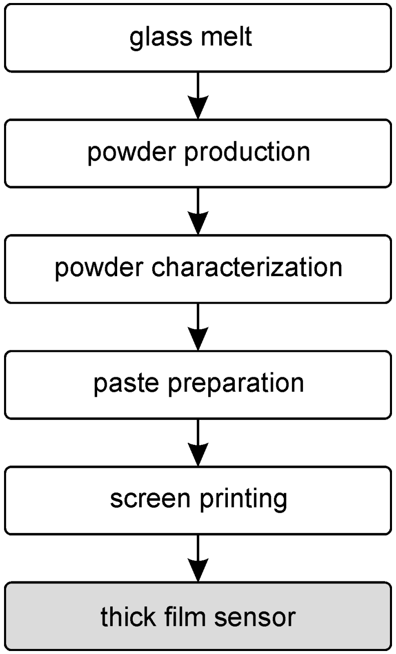
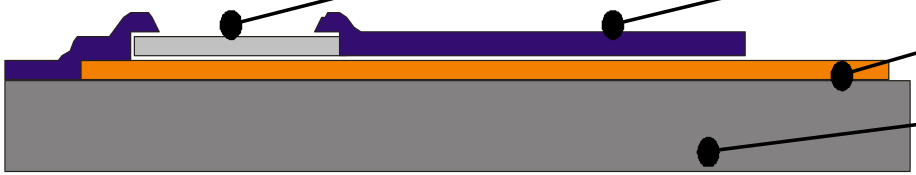
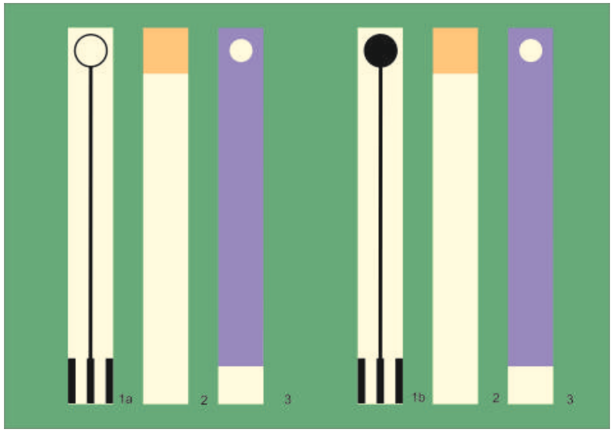


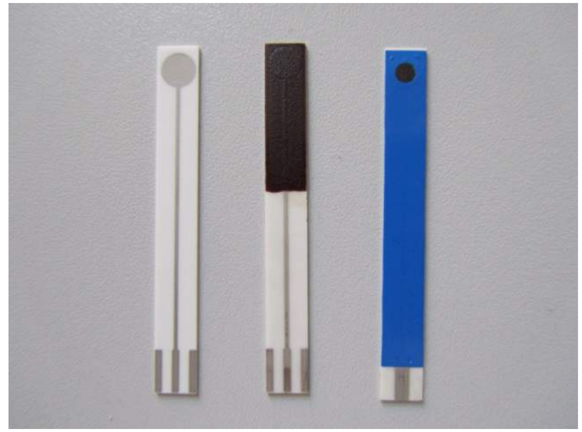


glass Nr.	**α [10^{-6}/K]**	**glass Nr.**	**α [10^{-6}/K]**	**glass Nr.**	**α [10^{-6}/K]**	**glass Nr.**	**α [10^{-6}/K]**
5	7.02	11	7.02	16	8.59	21	7.08
6	7.48	12	9.44	17 - Fe	7.42	22 - Fe	8.80
7- Fe	8.73	13 -Ti	8.77	18	8.87	23 - Fe	8.23
8 - Ti	7.73	14	10.05	19	8.11	24 - Fe	6.95
9 – Ti	n.b.	15	9.48	20	6.87	25 - Fe	7.50
10 - Ti	8.98					26 - Ti	8.89

Al_2O_3 α [10^{-6}/K]: 8.5

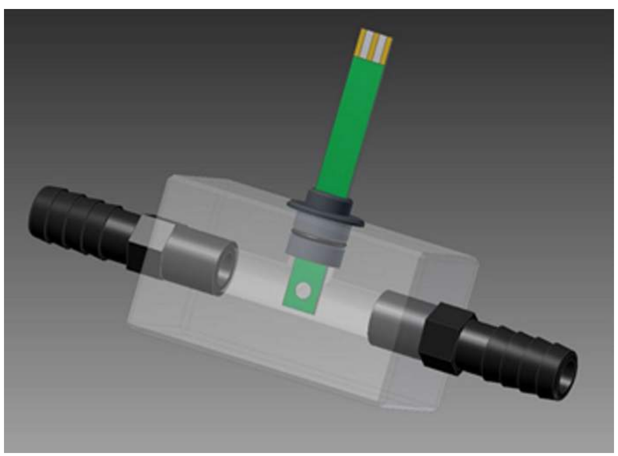
Layout development/ sensor confectioning



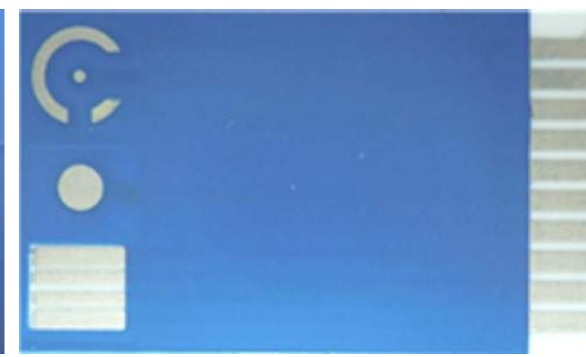


single electrode in a flow-through probe

multisensor



front view



back view

W. Vonau, K. Ahlborn, F. Gerlach, B. Hahnebach, E. Pöhler: DE 10 2011 118 409

- Introduction
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  incl. characterisation
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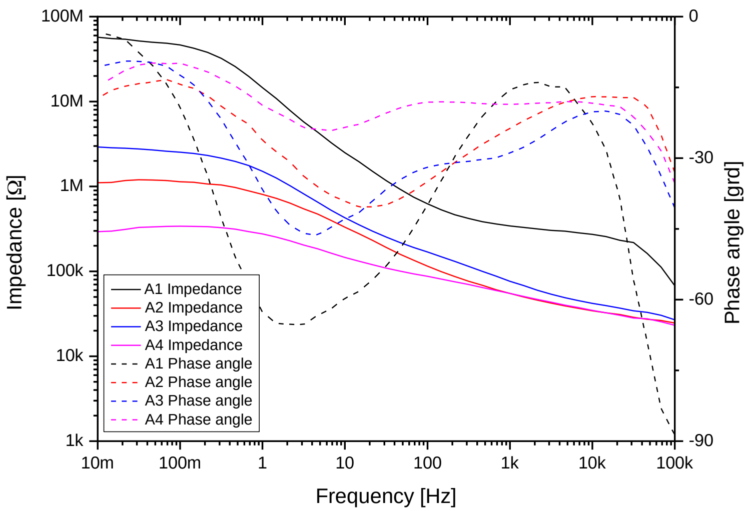
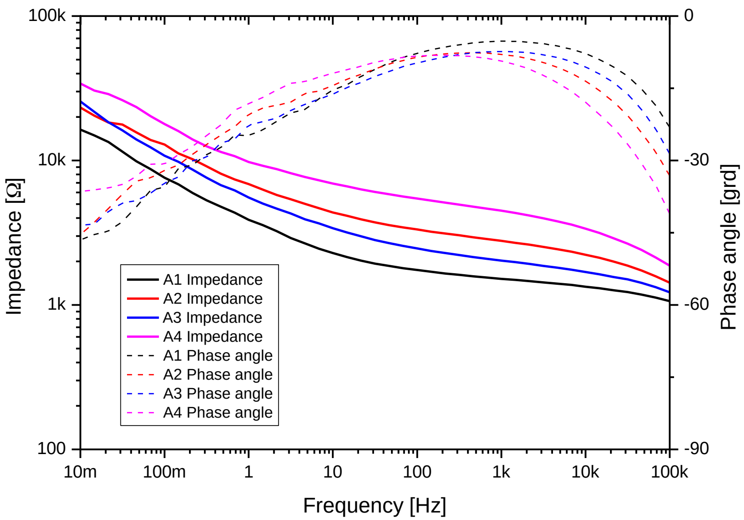
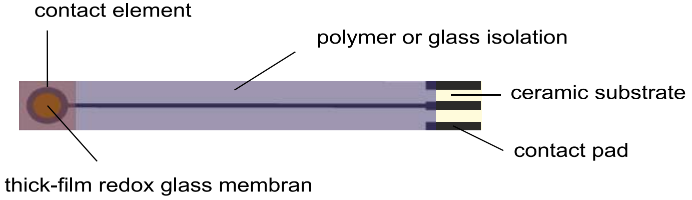
Impedance measurement

- To compare the internal resistances of the different redox glass electrodes
- Ag/AgCl reference electrode, platinum counter electrode and the redox glass electrode as working electrode were inserted in a mixture of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ (ratio of ingredients: 2:1) in a measuring chamber acting as Faraday cage
- Voltage amplitude: 20 mV; measuring range 10 kHz – 100 mHz.
- VersaSTAT 3; software VersaStudio of PRINCETON APPLIED Research







coated Pt wire (glass A)

thick film electrode (glass A)

Redox potential measurement with different conventional electrodes compared to a redox glass electrode (glass A)

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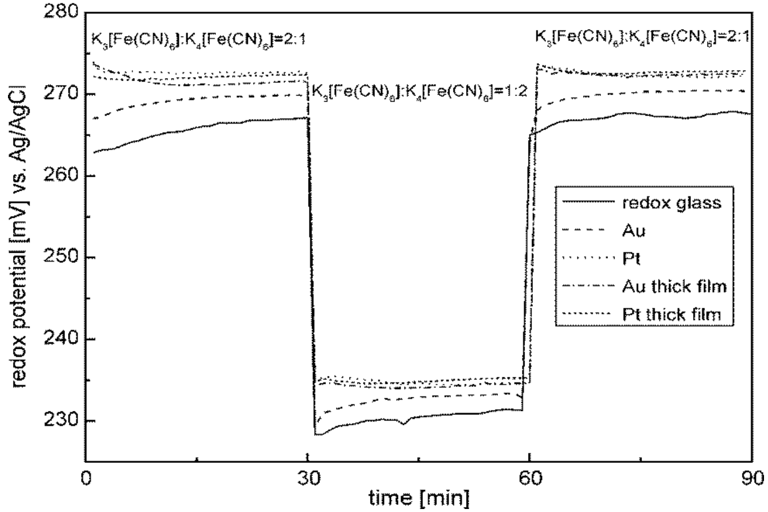
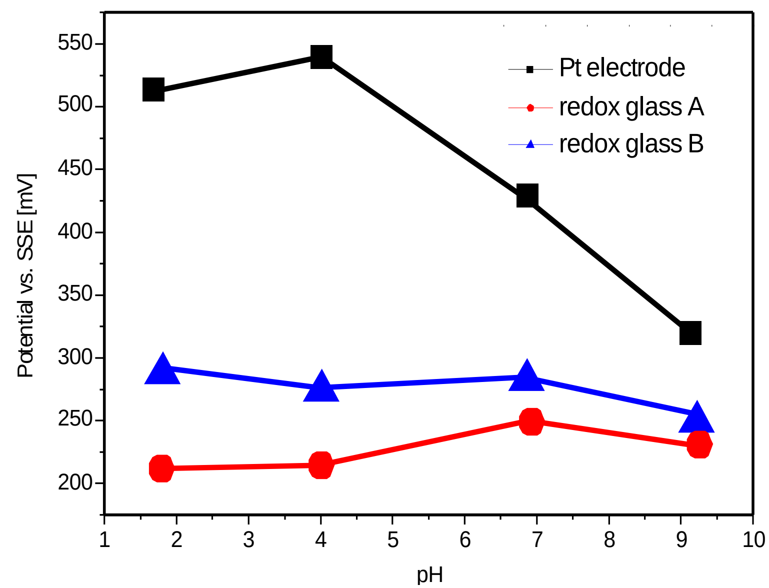
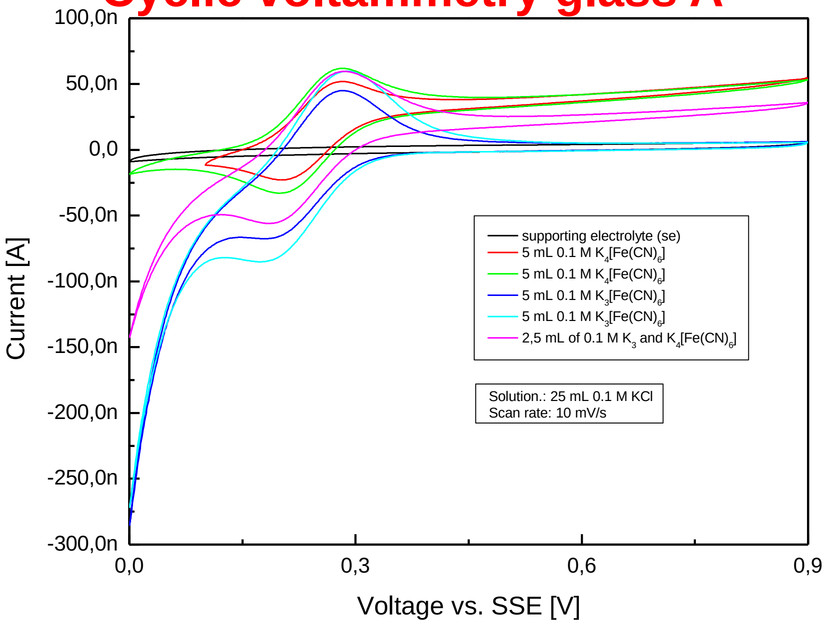


pH dependency of redox potential



Cyclic voltammetry glass A



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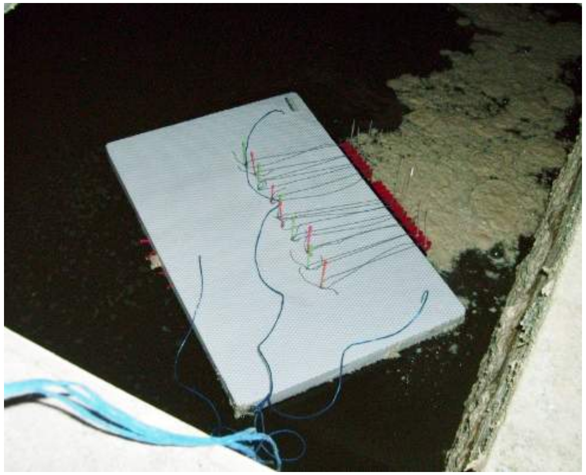
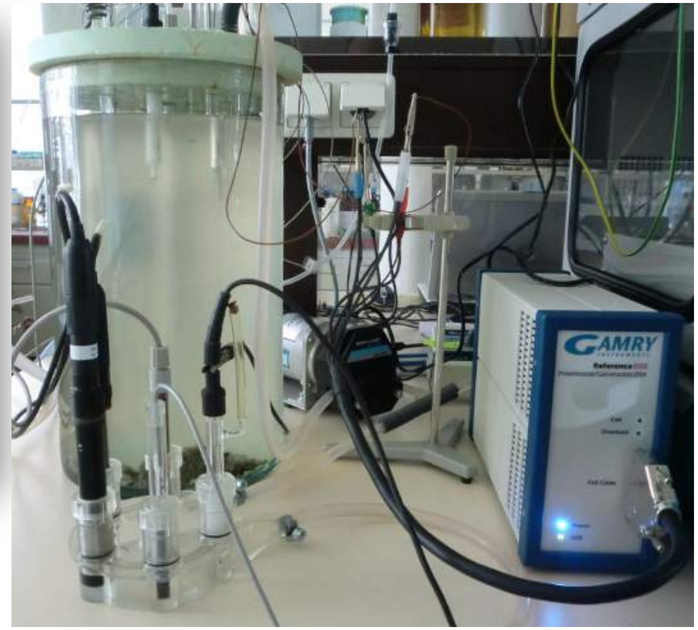
Situation and problems

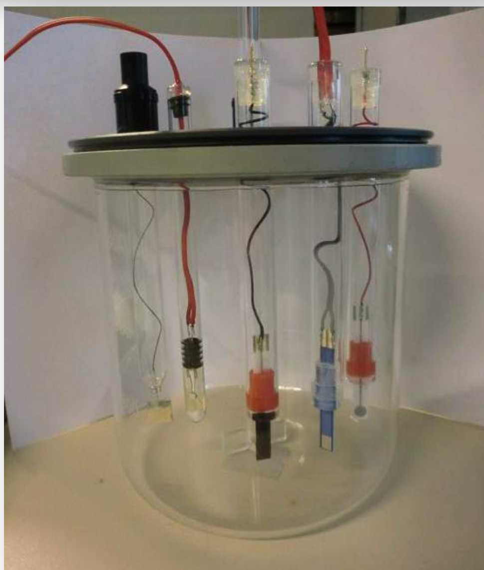
- In the production of paper, water is required for auxiliary and cleaning purposes and it is often used several times.
- In reducing the volume of waste water the proportion of soluble substances increases, creating an undesirable nutrient-rich habitat for micro-organisms (slime + biofilm growth).
- The problem is treated effectively by an optimised application of biocide active substances.
- For the controlled addition of peroxide based biocides to suppress the slime growth in the process water, redox potential determination can make an essential contribution, whereby the complicated composition of the medium does not require the use of precious metal electrodes.
- For the assessment of the determined redox potentials it has to be taken in account that beside the concentration of the biocides the position-dependent amount of oxygen and/or the pH values have a significant influence on the sensor signal. These parameters should additionally be determined and considered for the evaluation of the redox potentials.



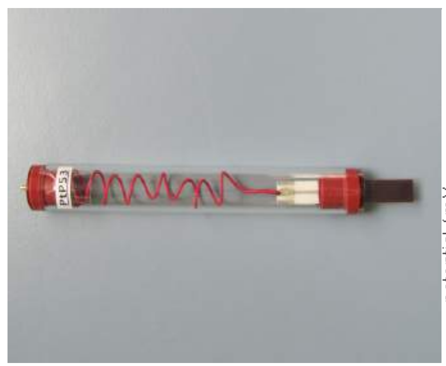


Laboratory setup (circuit water)

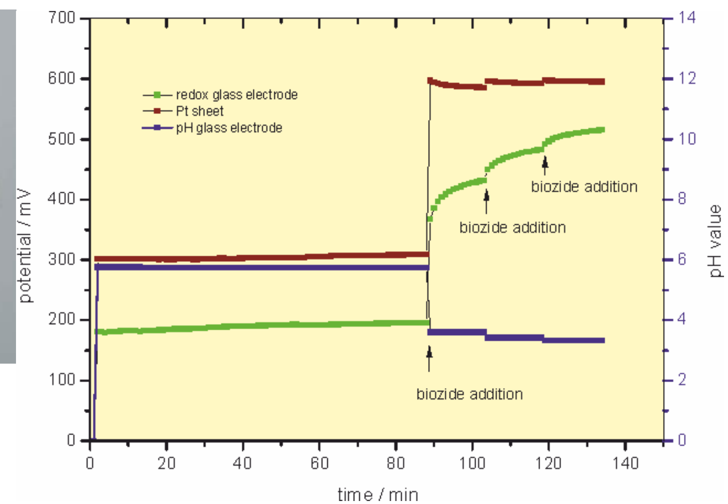
model solution:
$CaCl_2*6\ H_2O$, $Na_2SO_4*10\ H_2O$, starch and NaCl



2x redox potential
- chlorine
- oxygen
- conductivity
- pH value



Redox glass electrode



Redox potential depending on biozide (peracedic acid) addition in process water of the paper industry

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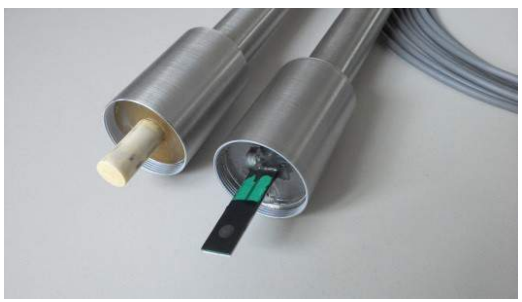
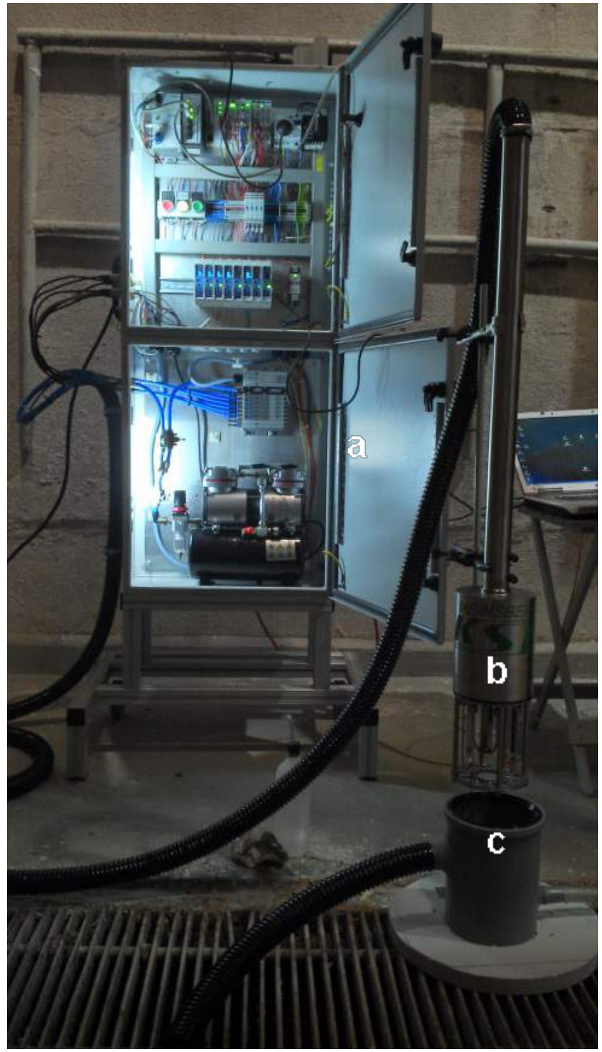
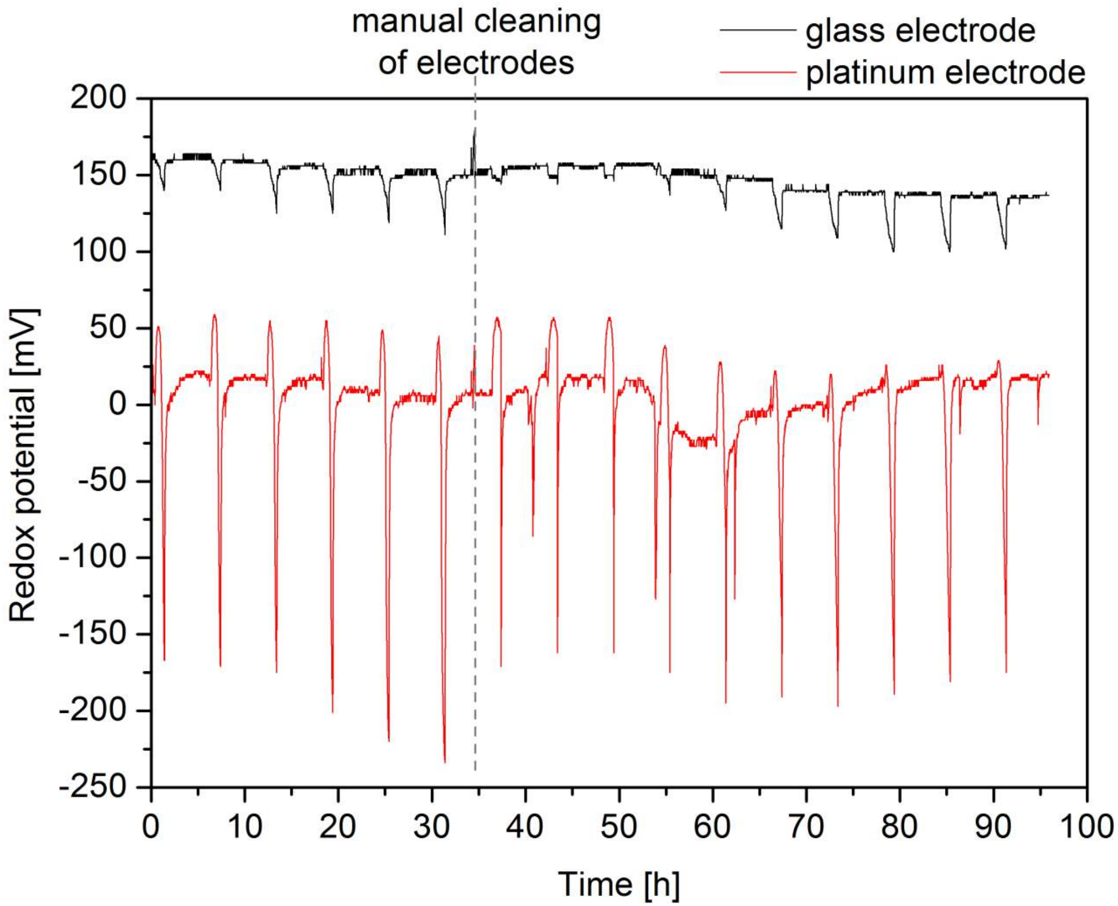


Glass based redox potential probe (right) and polymer based reference electrode (left) for the industrial application



Measuring system for the monitoring of process water, consisting of control box (a), measuring lance (b) and measuring barrel (c)

Multi sensor system to control process water of the paper industry left contaminated; right after cleaning with compressed air



Use in practice

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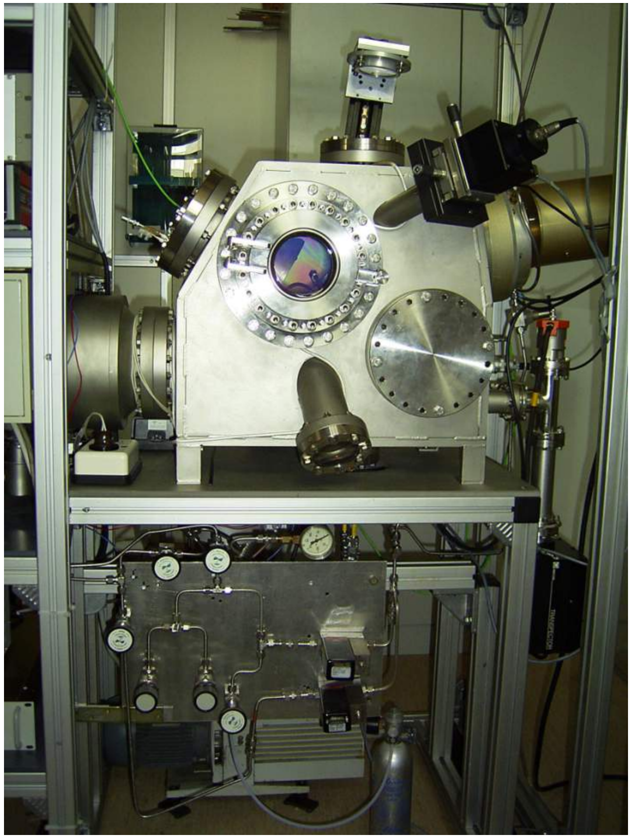
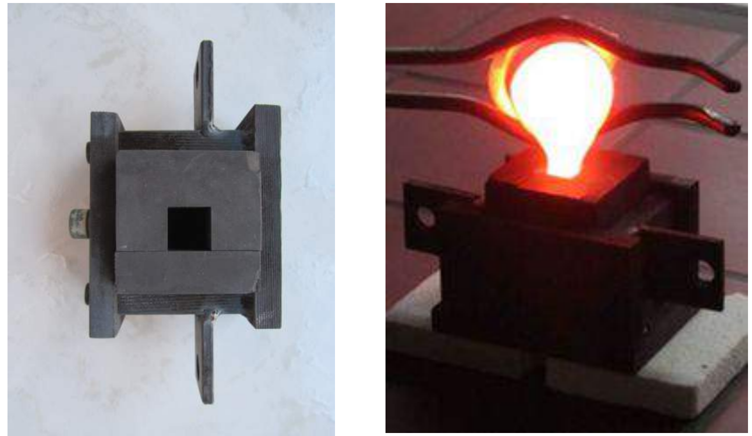
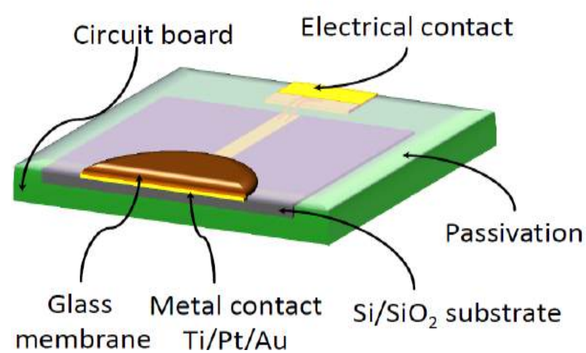


PLD equipment



Casting mould target preparation

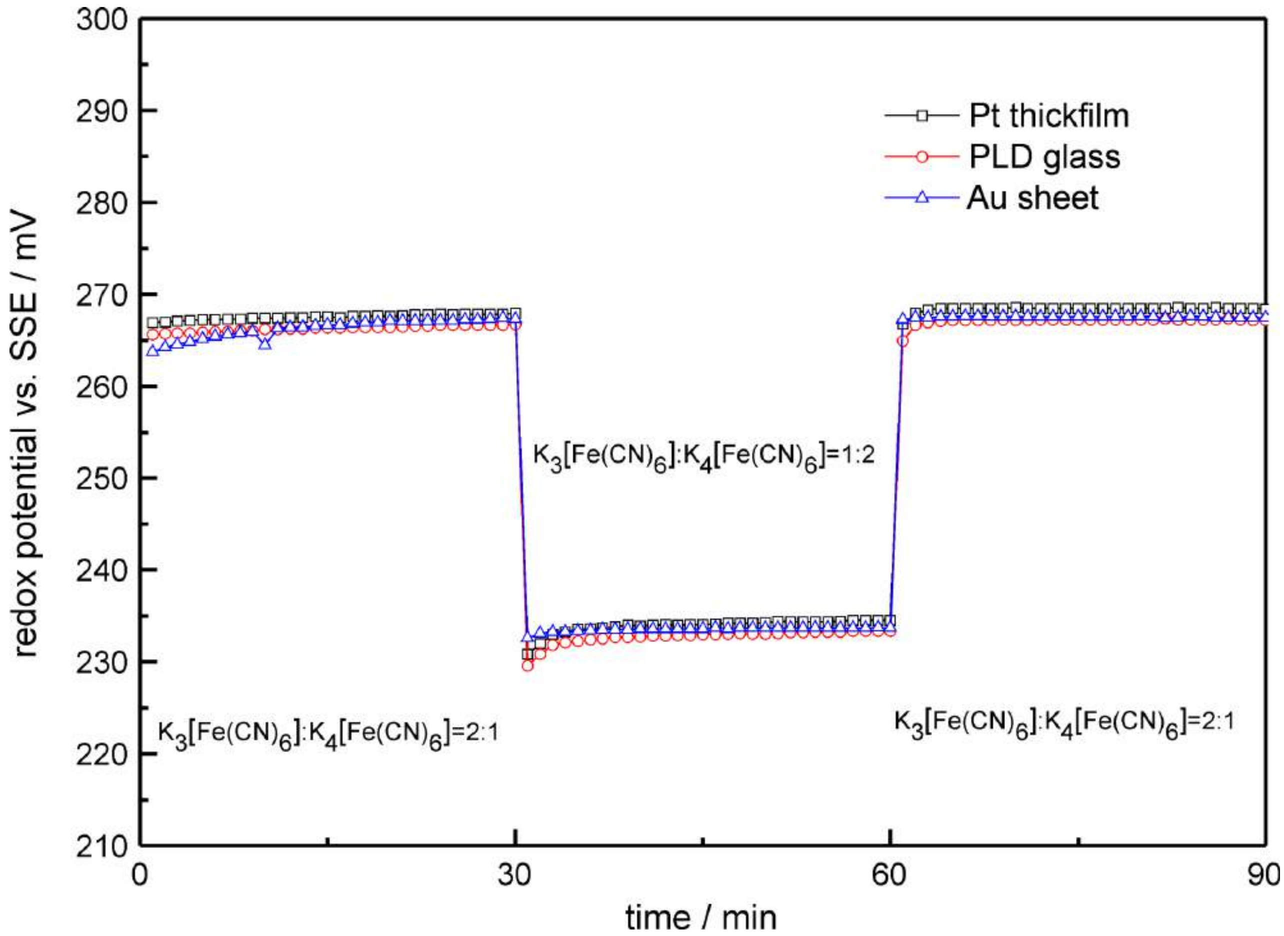
Redox glass target



PLD based sensor

W. Vonau, F. Gerlach, K. Ahlborn, M.J. Schöning, H. Iken: **DE** 10 2012 014 861

Comparison of electrode functions



H. Iken, K. Ahlborn, F. Gerlach, W. Vonau, W. Zander, J. Schubert, M.J. Schöning: Electrochimica Acta 113 (2013) 762–767

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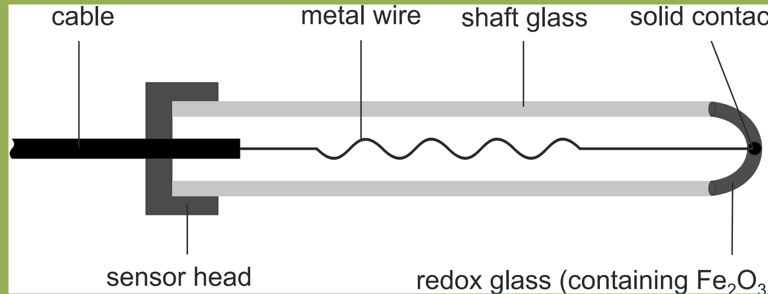
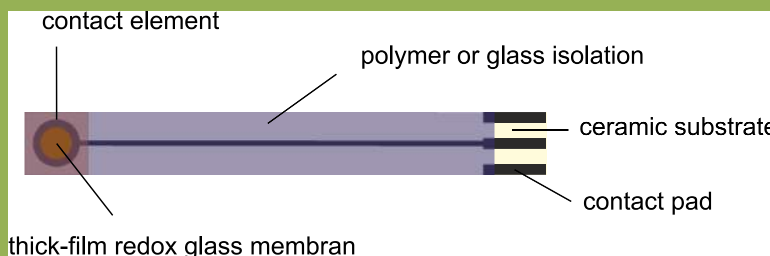
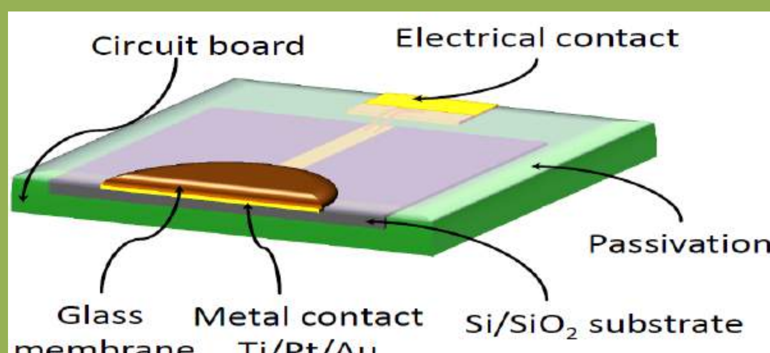
Glass blower

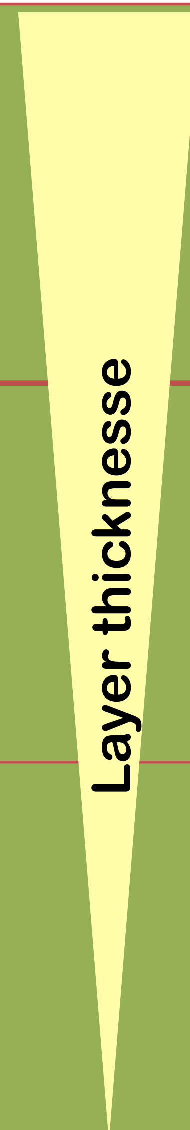


Thick film technology



Laser ablation





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The financial supports of this work by the German Federal Ministry of Economics and Technology (BMWi) in the context of two AiF projects (grant numbers 16274 BR/1 and KF2218311RH1) are gratefully acknowledged.

Thank you for your attention.