Ion-selective electrodes & ion-sensors - engineering analytical tools

...electrochemical sensors in routine clinical chemistry

Andrzej Lewenstam

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Pro Sens

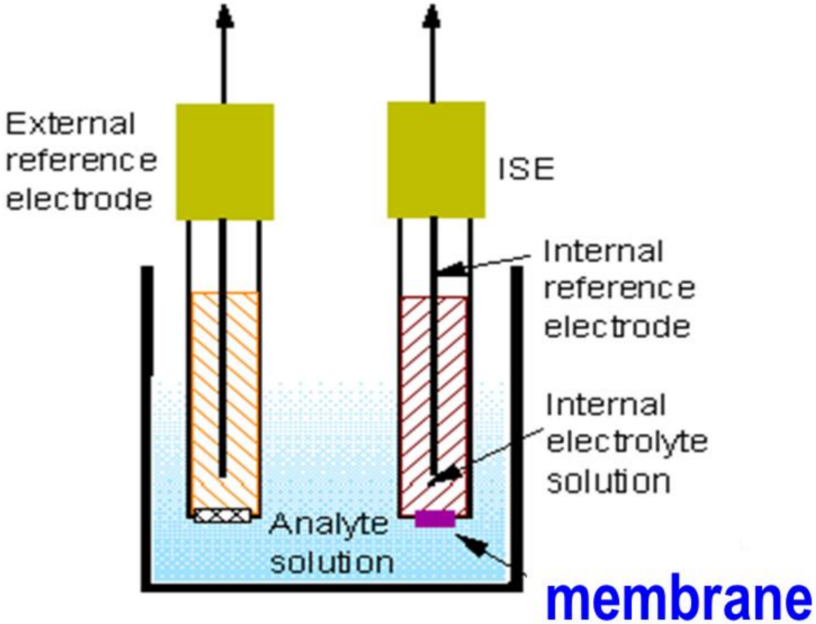
Åbo Akademi University Åbo -Turku, Finland

KONE

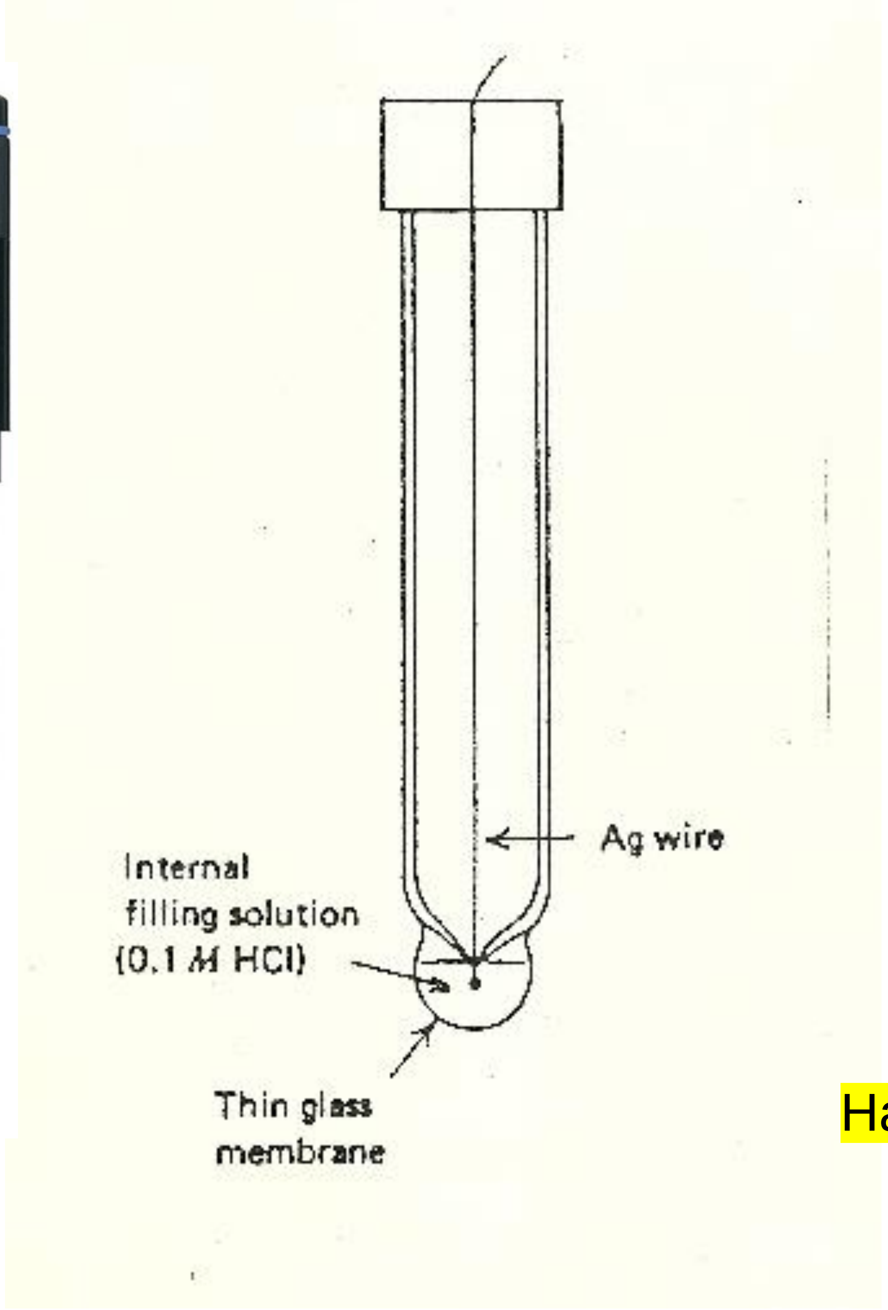
ThermoFisher SCIENTIFIC

Helsinki, Finland / Boston, USA

GALVANIC CELL

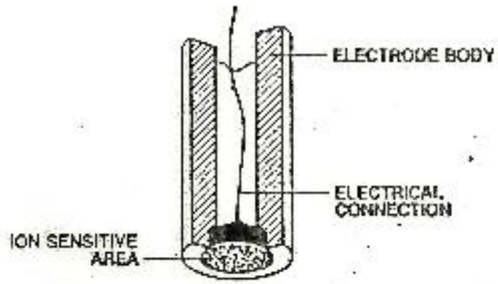


Ion selective electrodes (ISEs): WITH A GLASS MEMBRANE

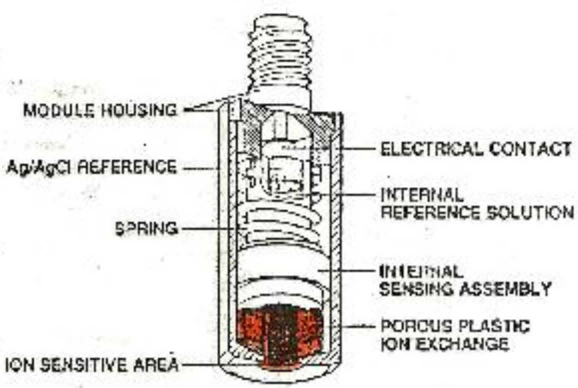


Haber Klemensiewicz 1909

ISEs with SOLID-STATE and PLASTIC MEMBRANES



Solid State Electrode (Ca^{2+})



Liquid Membrane Electrode (Module) (Ca^{2+})

Active materials of electrode membranes

Primary ion	Orion electrode	Other homogeneous membranes	Heterogeneous membranes
F^-	LaF_3		—
Cl^-	$AgCl/Ag_2S$	Hg_2Cl_2/HgS, $AgCl$	$AgCl$
Br^-	$AgBr/Ag_2S$	Hg_2Br_2/HgS, $AgBr$	$AgBr$
I^-, CN^-, Hg^{2+}	AgI/Ag_2S	AgI	AgI
SCN^-	$AgSCN/Ag_2S$	$Hg(SCN)_2/HgS$, $AgSCN$	$AgSCN$
S^{2-}	Ag_2S	Ag_2S	Ag_2S
Cu^{2+}	Cu_xS/Ag_2S	$CuSe$	Cu_xS, Cu_xS/Ag_2S
Pb^{2+}	PbS/Ag_2S		PbS/Ag_2S
Cd^{2+}	CdS/Ag_2S		CdS/Ag_2S

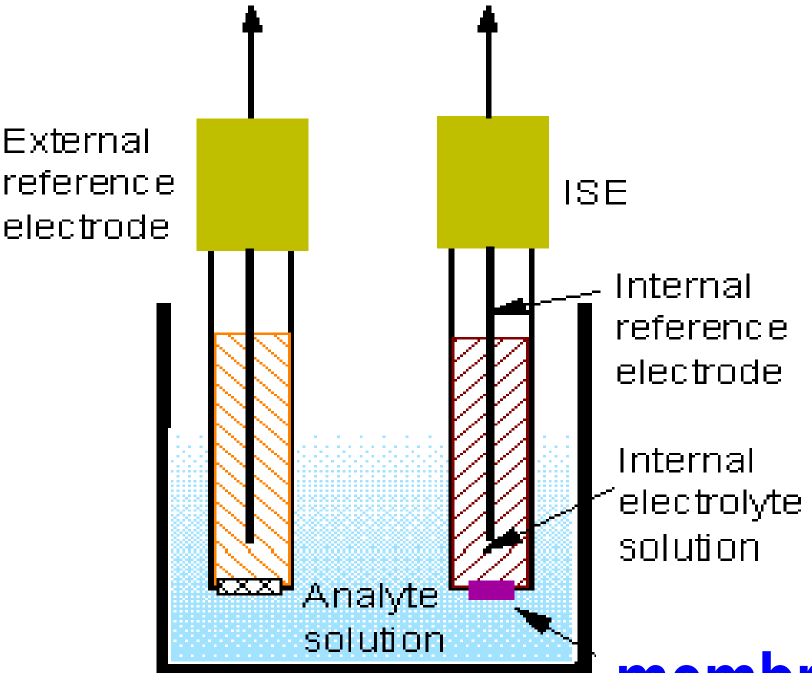
Electrodes based on ion exchangers

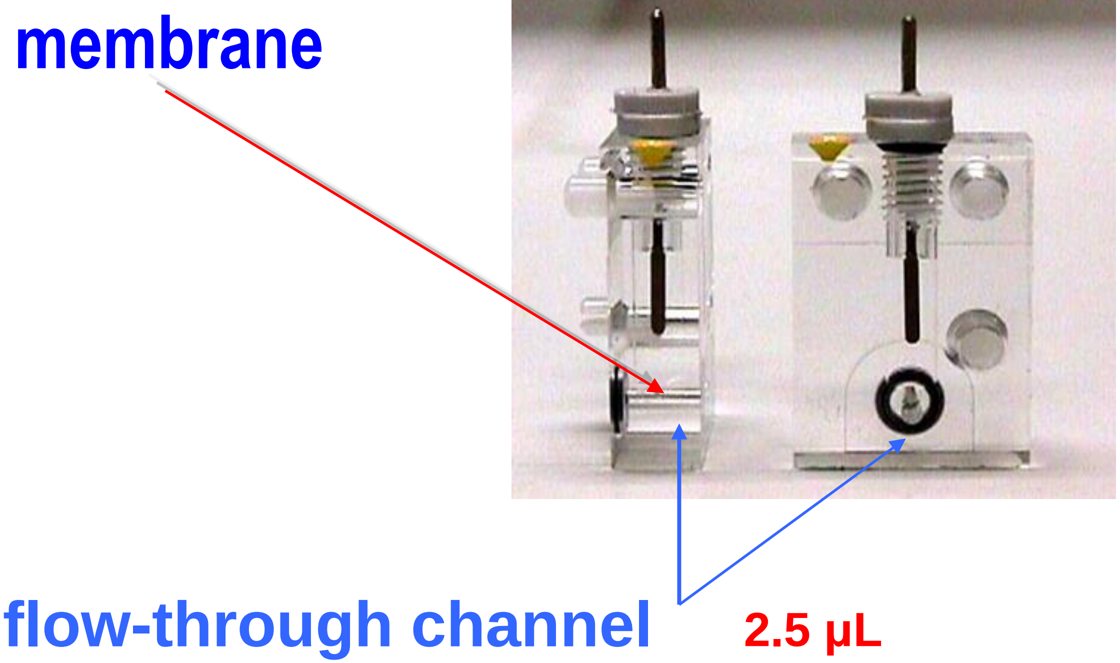
Determinand	Form of membrane	Active material	Solvent or plasticizer
Ca^{2+}	(a) liquid	calcium di-(n-decyl) phosphate	di-(n-octylphenyl) phosphonate
	(b) solid (PVC)	calcium di-(n-decyl) phosphate	di-(n-octylphenyl) phosphonate
	(c) solid (PVC) 'Selectrode'	calcium di-(n-octylphenyl) phosphate	di-(n-octylphenyl) phosphonate
NO_3^-	(a) liquid	tridodecylhexadecylammonium nitrate	n-octyl-2-nitrophenyl ether
	(b) solid (PVC)	tridodecylhexadecylammonium nitrate	n-octyl-2-nitrophenyl ether
	(c) liquid	tris(substituted 1,10-phenanthroline) nickel(II) nitrate	p-nitrocymene
	(d) solid PVC	tris(substituted 1,10-phenanthroline) nickel(II) nitrate	p-nitrocymene
	(e) liquid	tris(substituted-1,10-phenanthroline) nickel(II) nitrate	p-nitrocymene
ClO_4^-	liquid	tris(substituted 1,10-phenanthroline) iron(II) perchlorate	p-nitrocymene
BF_4^-	liquid	tris(substituted 1,10-phenanthroline) nickel(II) tetrafluoroborate	p-nitrocymene
Divalent cations ('water hardness')	liquid	calcium di-(n-decyl) phosphate	decanol
CO_3^{2-}	liquid	tri(n-octyl)methylammonium chloride	trifluoroacetyl-p-butylbenzene
U (VI)	(a) liquid	methylene blue-uranyl tribenzoate	o-dichlorobenzene
	(b) solid (PVC)	di(2-ethylhexyl) phosphoric acid	diamylamyl phosphonate
Cl^-	liquid	dimethyl-dioctadecylammonium chloride	?

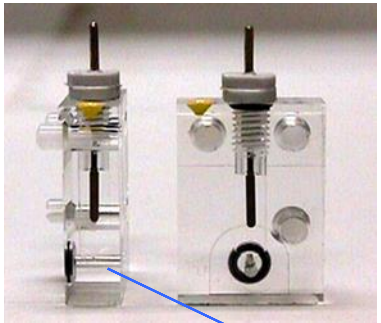
Electrodes based on neutral carriers

Determinand	Form of membrane	Active material	Solvent or plasticizer
K^+	(a) liquid	valinomycin	diphenyl ether
	(b) solid (PVC)	valinomycin	dioctyladipate
	(c) solid (silicone rubber)	valinomycin	—
NH_4^+	liquid	nonactin/monactin	tris(2-ethylhexyl) phosphate
Ca^{2+}	solid (PVC)	see Ref. 18	o-nitrophenyl octyl ether
Ba^{2+}	liquid	nonylphenoxy poly (ethylene oxy) ethanol Ba^{2+} (tetraphenylborate)$_2$	p-nitroethylbenzene

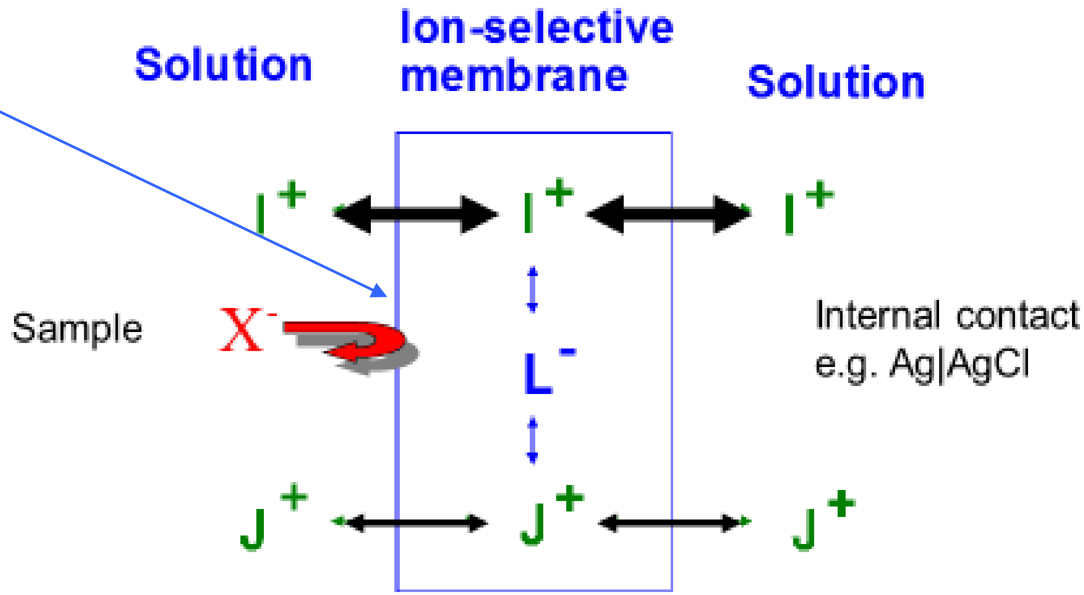
ISE electrodes







Membrane potential formation process



(1) charge separation at the membrane-solution interface is the prerequisite of a membrane potential

…ion-sensor response
(under equilibrium)

$$E = E^0 + \frac{RT}{z_i F} \ln(a_i)$$

W. H. **NERNST**
1864-1941

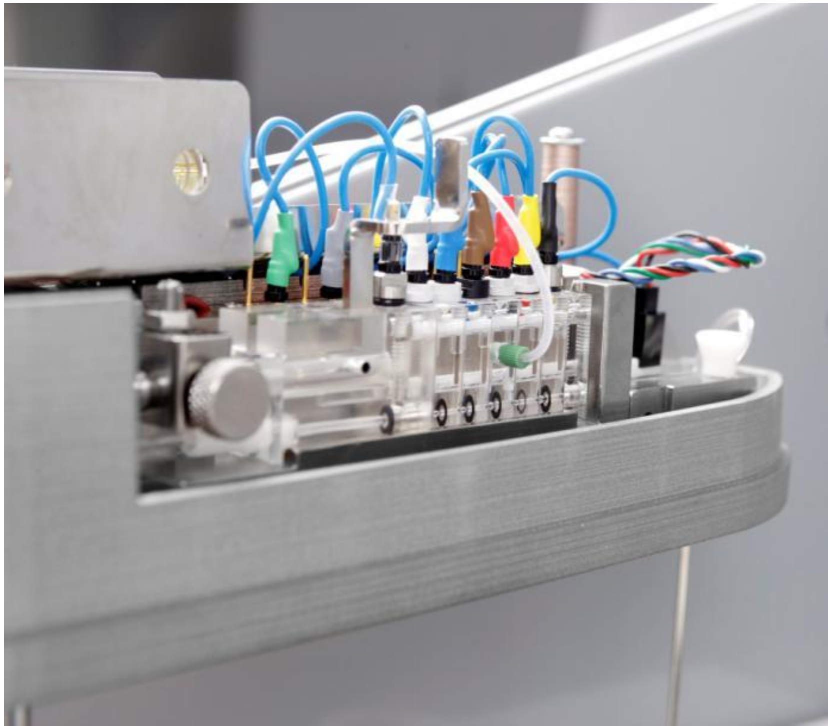
$$E = const + \frac{RT}{z_i F} \ln\left[a_i + \sum_{j \neq i} K_{ij}^{Pot} (a_j)^{z_i / z_j} + L \right]$$

Ion-Selective Electrodes (ISEs) unit in clinical analyzer

- Direct measurements
  Na^+, K^+, Cl^- (pH, Ca^{2+}, Mg^{2+}, Li^+, TCO_2)

- **Maintenance-free electrodes**, delivered as ready-to-use
- **Response time: 2.5 sec**
- **Reproducibility: +/- 0.1 mV**

- **Life-time 10000 samples**
- **Shelf life-time 1 year**



Electroanalysis 2014, 26, 1171 – 1181

Review Wiley Online Library ELECTROANALYSIS

DOI: 10.1002/elan.201400061

Routines and Challenges in Clinical Application of Electrochemical Ion-Sensors

Andrzej Lewenstam *[a, b]

Abstract: This review provides information on application of potentiometric ion-sensors in routine clinical analysis. The text comprises sensor design, way-of-use, conventions and practical recommendations, and elements of IS response theory. An instrument producer point of view, based on direct industrial involvement of the author, is emphasized.

Keywords: Clinical analysis · Electrolytes in blood · Ionized magnesium · Ion-sensors · Solid-contact

CHALLANGES
…ion-sensor response
(under equilibrium)

W. H. **NERNST**
1864-1941

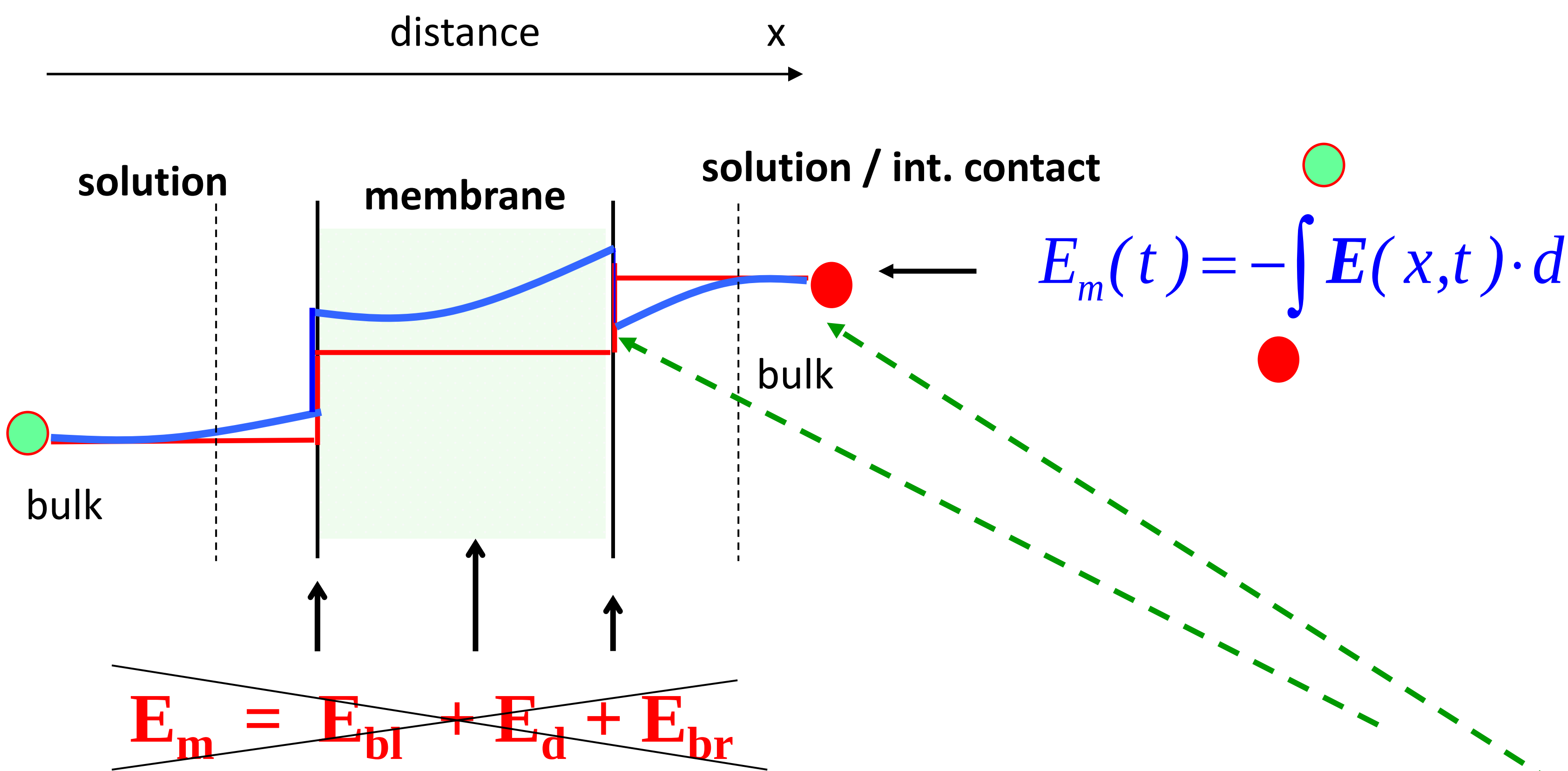
$$E = E^0 + \frac{RT}{z_i F} \ln(a_i)$$

But….

$$E = const + \frac{RT}{z_i F} \ln\left[a_i + \sum_{j \neq i} K_{ij}^{Pot} (a_j)^{z_i / z_j} + L \right]$$

time-dependant

Equilibrium vs. advanced modelling of membrane potential



$$E_m(t) = -\int \boldsymbol{E}(x,t) \cdot dx$$

$$E_m = E_{bl} + E_d + E_{br}$$

Electroneutrality is not assumed

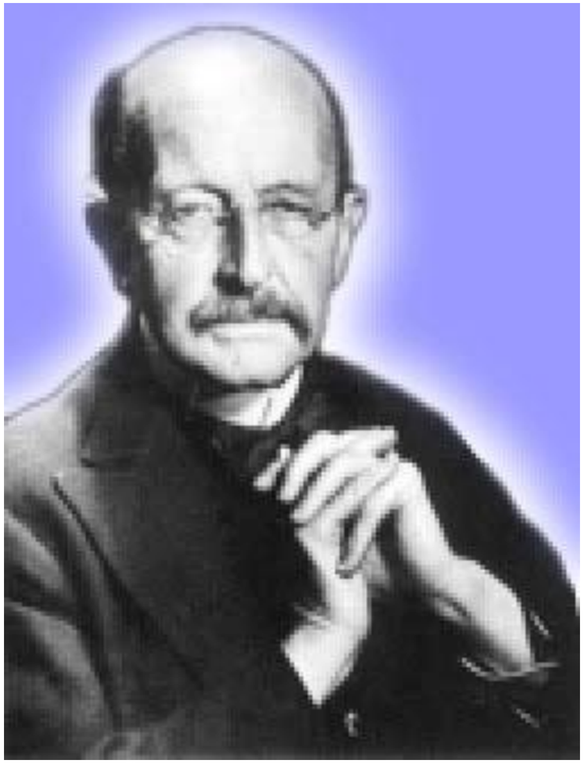
Equilibrium is not assumed ($c_{surface} \neq c_{bulk}$)

T.Sokalski and A.Lewenstam, *Electrochemical Communications*, 2001,**3**, 107

NPP Model

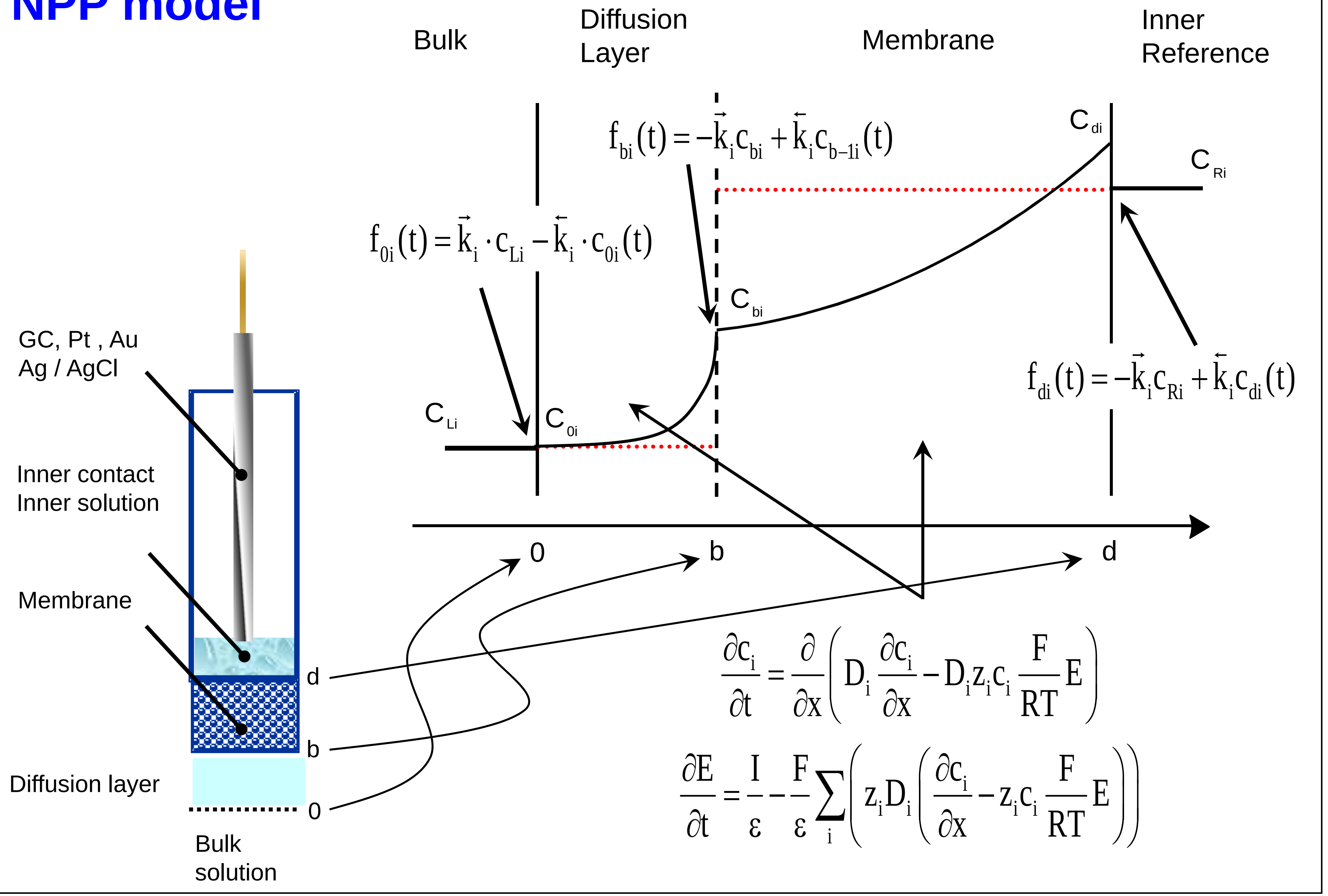
Siméon Denis **POISSON**
1781 -1840

Walther Hermann **NERNST**
1864-1941



Max **PLANCK**
1858-1947

NPP model



P.Lingenfelter, T.Sokalski,, A.Lewenstam, J.Phys.Chem.B (2003)

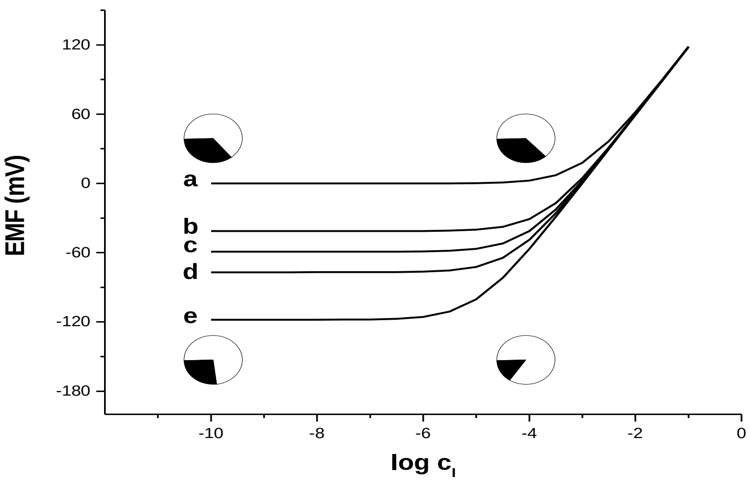
J Solid State Electrochem (2011) 15:15–22
DOI 10.1007/s10008-010-1199-1

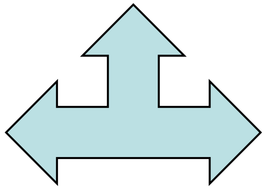
REVIEW

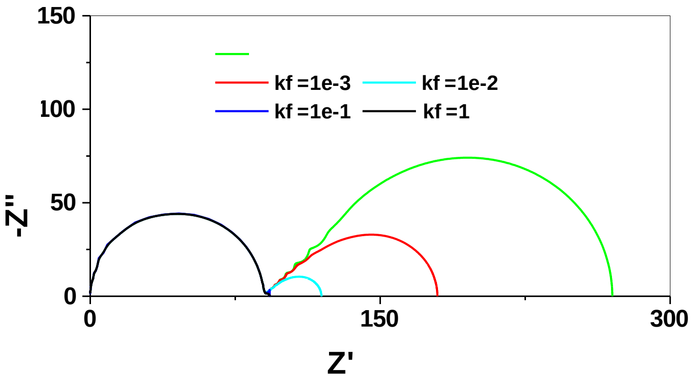
Non-equilibrium potentiometry—the very essence

Andrzej Lewenstam

Non equilibrium potentiometry: NPP ’general’ power







$E_m = \mathrm{f}\,(a_i, a_j, a_r, d, \varepsilon, \delta, D_i, D_j, D_r, k_i, k_j, k_r, x, t)$

I or Z = f (…) **AND INVERSE**

Journal of The Electrochemical Society, **164** (11) E3559-E3568 (2017)

JES Focus Issue on Mathematical Modeling of Electrochemical Systems at Multiple Scales in Honor of John Newman

Modeling of Electrodiffusion Processes from Nano to Macro Scale

K. Szyszkiewicz, J. J. Jasielec, M. Danielewski, A. Lewenstam, and R. Filipek[z]

Faculty of Materials Science and Ceramics, AGH University of Science and Technology, 30-059 Kraków, Poland

Mass and charge transport processes play an important role in different areas of science. The membrane processes involving charge transport are of vital importance in cell biology since they support homeostasis of living organisms. In the field of ion-selective electrodes transport of ions determines generation of electrochemical signals. The process of ionic diffusion remains of primary importance in many civil engineering problems since the long-term durability of building materials, such as concrete, is directly affected by the transport of chemical species. Length scale of the above processes range from nanometers for biological membranes through micrometers for ion selective electrodes up to centimeters for ions transport in concrete.
 [DOI: 10.1149/2.0571711jes]

Manuscript submitted April 3, 2017; revised manuscript received June 23, 2017. Published July 13, 2017. *This paper is part of the JES Focus Issue on Mathematical Modeling of Electrochemical Systems at Multiple Scales in Honor of John Newman.*

CHALLANGES…cont.

Membranes glass, crystal (solid-state), liquid (plastic), gas sensors, biosensors (metabolites, enzyme)

New parameters...new membranes

…ionized Mg^{2+} (1992)

…bicarbonates HCO_3^- (2019)

A historical success: the measurement of ionized magnesium

Andrzej Lewenstam, Head of Sensor Technology Group at Kone Instruments, announced the possibility of fully automatic determination of ionized magnesium during the 11th Meeting of International Federation of Clinical Chemistry on "Methology and clinical application of ion-selective electrodes" held in Monterey, California, this summer.

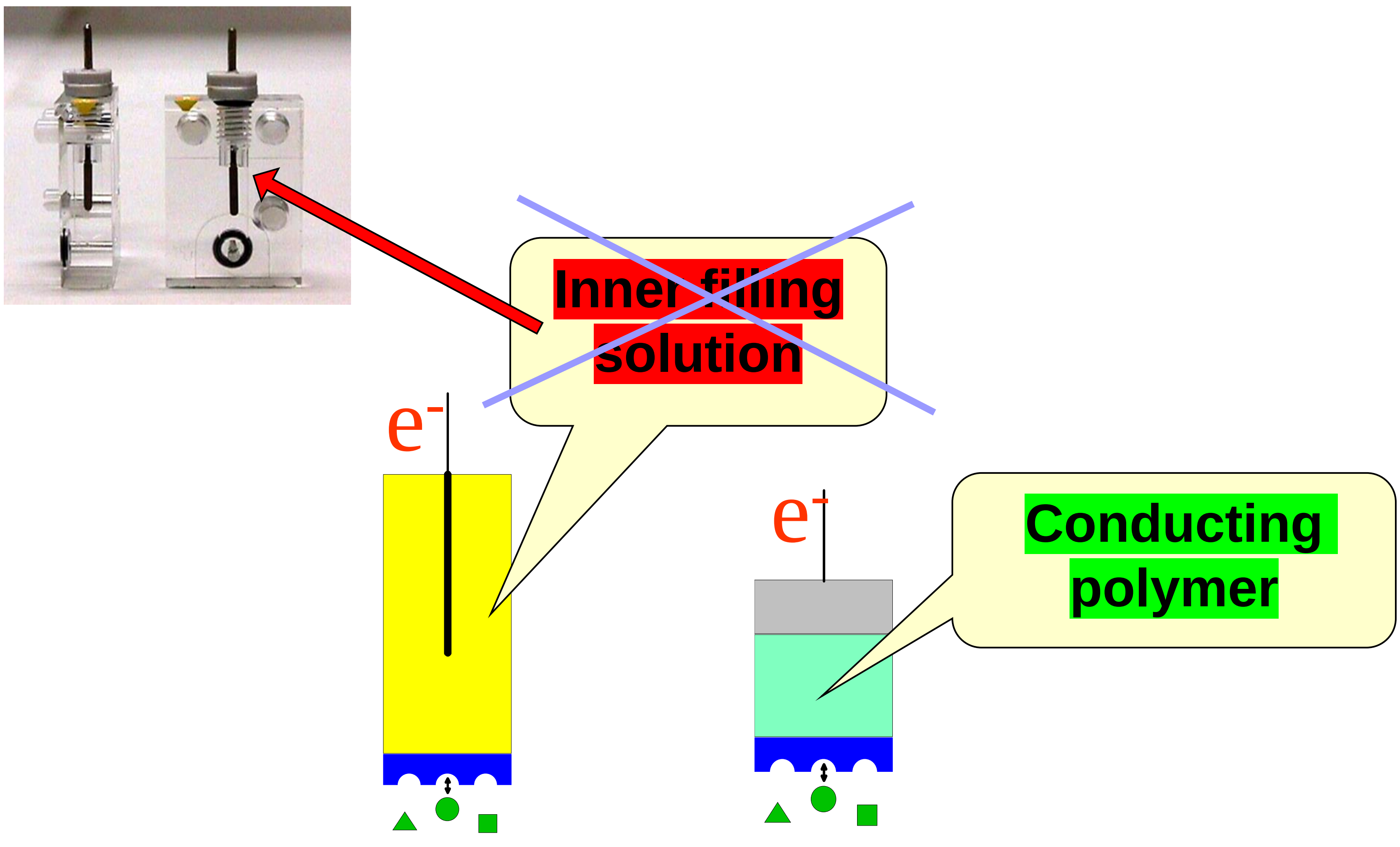
Andrzej Lewenstam for once not photographed in laboratory surroundings.

A Breakthrough Application of a Cross-Linked Polystyrene Anion-Exchange Membrane for a Hydrogencarbonate Ion-Selective Electrode

S. Dabrowska, J. Migdalski, A. Lewenstam

Sensors, **2019**, *19*(6), 1268

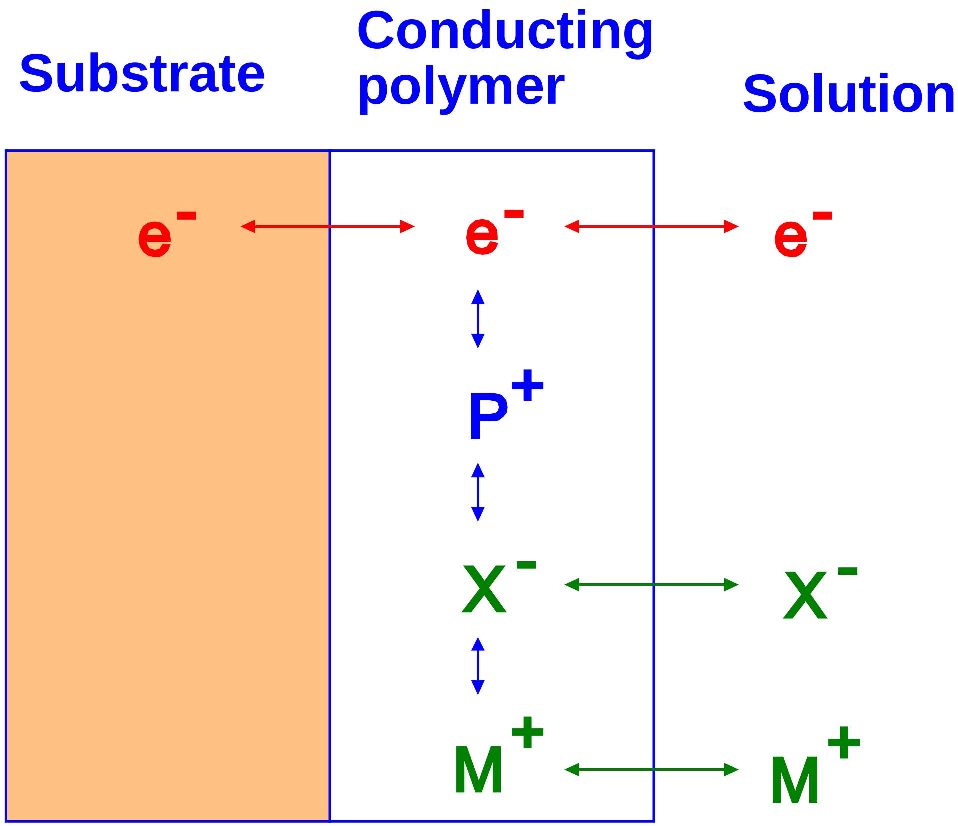
Solid-contact ion-sensors



A. Lewenstam et al, Analytical Chemistry **1992** *64* 2496

Ion-to-electron transduction by conducting polymer

Generalized interpretation of a potentiometric (open-circuit) response of conducting polymer



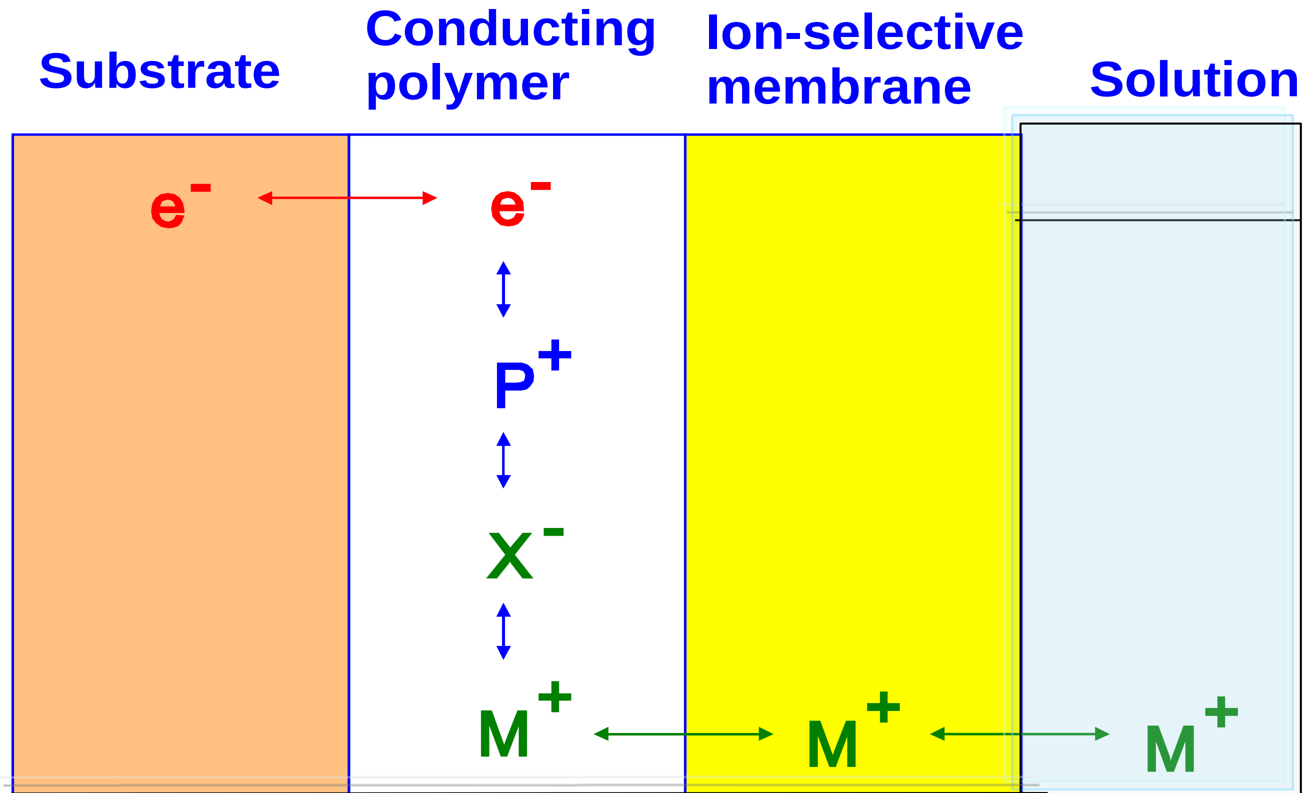
$$E = const' + \frac{RT}{F}\ln\frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

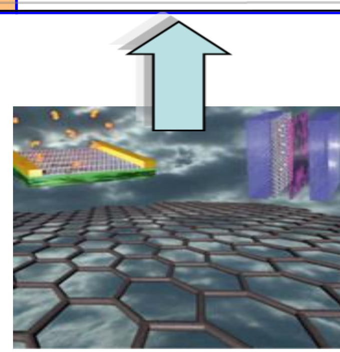
$$E = const'' - \frac{RT}{F}\ln\left[X^{-}\right]$$

$$E = const''' + \frac{RT}{F}\ln\left[M^{+}\right]$$

A. Lewenstam et al. J. Electroanal. Chem., ***368*** *(1994) 23-31*.

Solid contact all-solid-state ion-sensor

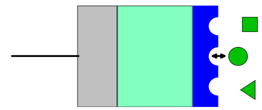


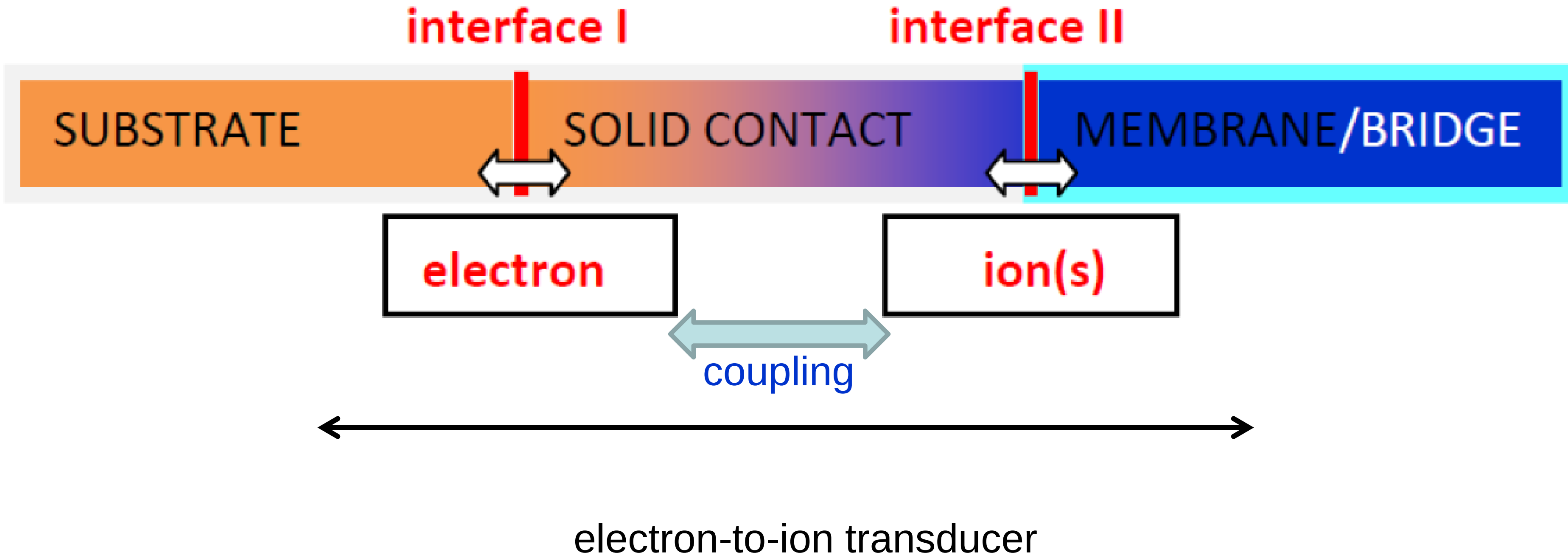


Graphene

Graphene: Nobel 2010
Conducting polymer: Nobel 2000

B. Paczosa-Bator el al, AGH
A. Michalska et al, UW





Solid contact as ion-to-electron transducer. Ion-to-electron coupling scheme.

…toward fully integrated galvanic probes…

György Inzelt · Andrzej Lewenstam · Fritz Scholz *Editors*

Handbook of Reference Electrodes

Reference Electrodes are a crucial part of any electrochemical system, yet an up-to-date and comprehensive handbook is long overdue. Here, an experienced team of electrochemists provides an in-depth source of information and data for the proper choice and construction of reference electrodes. This includes all kinds of applications such as aqueous and non-aqueous solutions, ionic liquids, glass melts, solid electrolyte systems, and membrane electrodes. Advanced technologies such as miniaturized, conducting-polymer-based, screen-printed or disposable reference electrodes are also covered. Essential know-how is clearly presented and illustrated with almost 200 figures.

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Inzelt · Lewenstam
Scholz *Eds.*

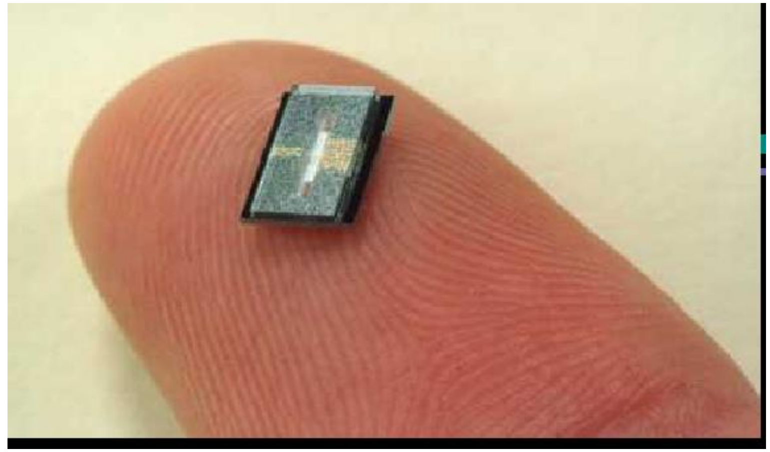
Handbook of Reference Electrodes

György Inzelt
Andrzej Lewenstam
Fritz Scholz *Editors*

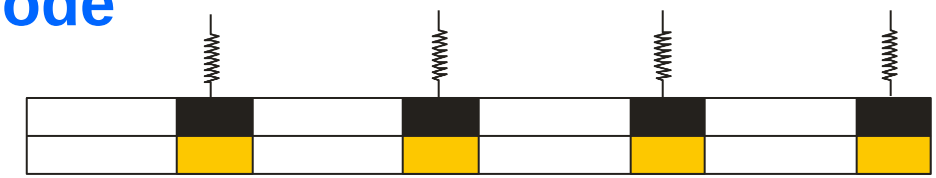
Handbook of Reference Electrodes

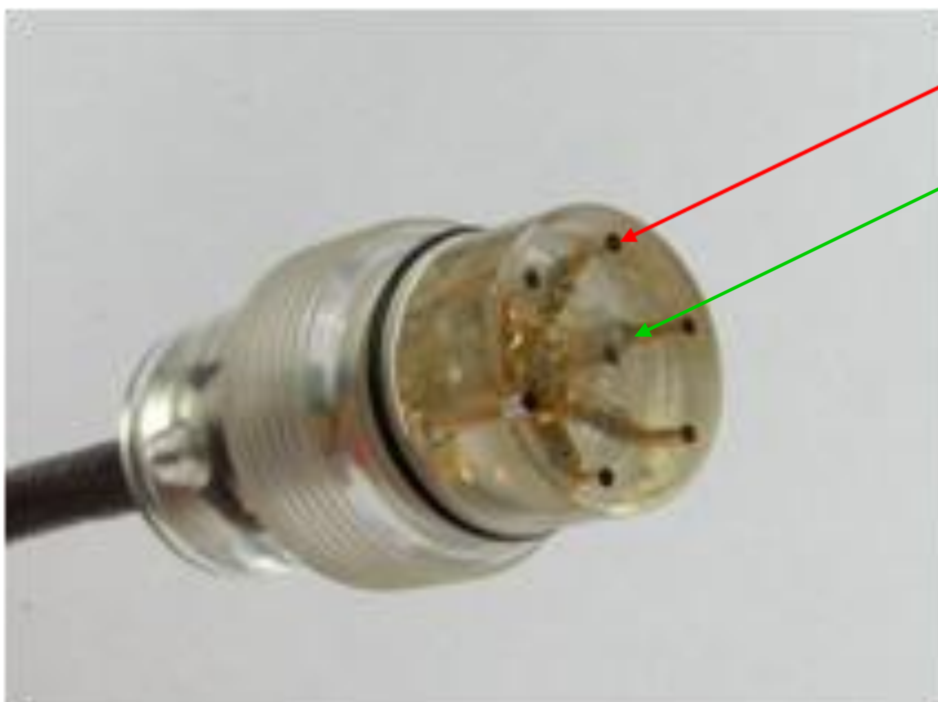
Springer

Solid contact ISE
All-solid-state ISE
& REF electrode



…multielectrode platform





J. Migdalski, B. Bas, T. Blaz, J. Golimowski, A. Lewenstam
J. Solid State Electrochem., 2009, **13**, 149

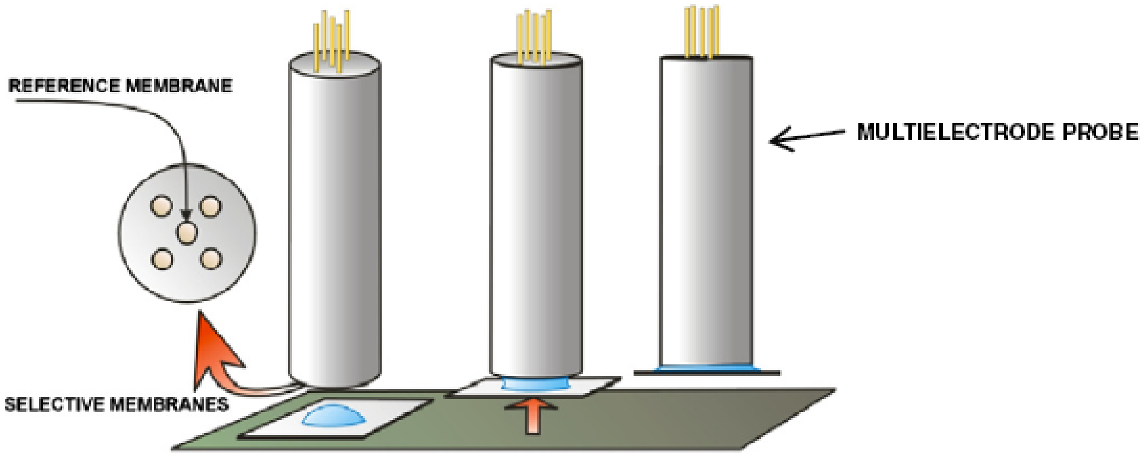
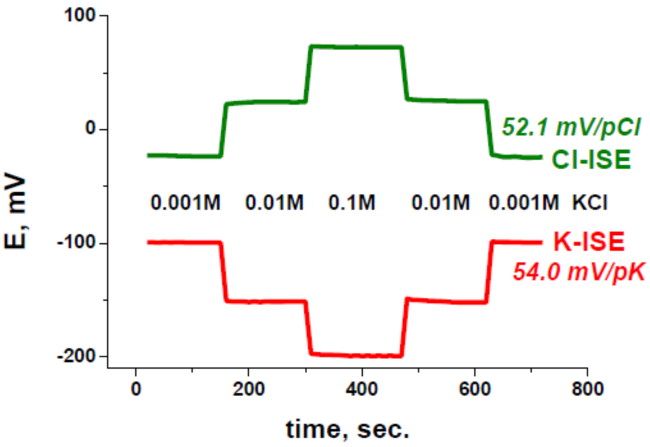


Fig. 1. Principle of “contact-type” one-drop measurement.



Multielectrode potentiometry in a one-drop sample

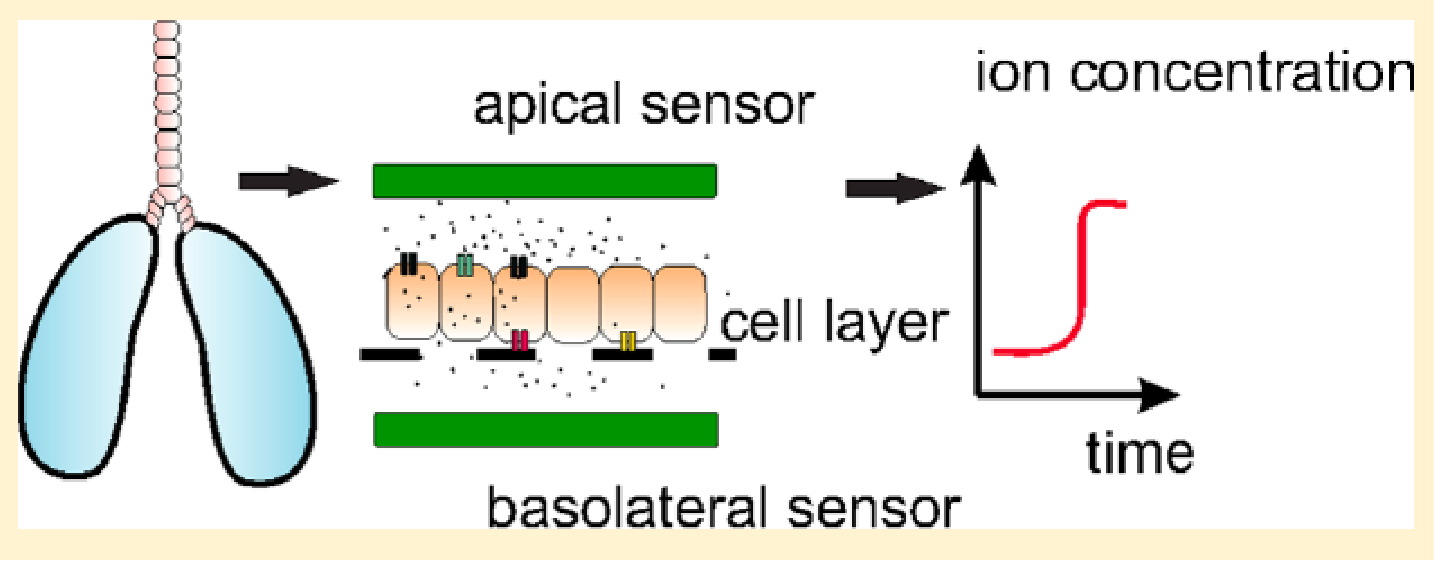
T. Blaz, B. Baś, J. Kupis, J. Migdalski, A. Lewenstam *

Electrochemistry Communications 34 (2013) 181–184

Multielectrode Bisensor System for Time-Resolved Monitoring of Ion Transport Across an Epithelial Cell Layer

Renata Toczyłowska-Mamińska,[†] Andrzej Lewenstam,[*,‡] and Krzysztof Dołowy[†]

Anal. Chem. 2014, 86, 390–394



….a human bronchial epithelium cell line 16HBE14σ- was used

Fabrication of Electrodes
by 3D Printing

Solid contact reference electrode with a PVC-based composite electroactive element fabricated by 3D printing

A. Lewenstam, B. Bartoszewicz, J. Migdalski, A. Kochan

Electrochemistry Communications 109 (2019) 106613

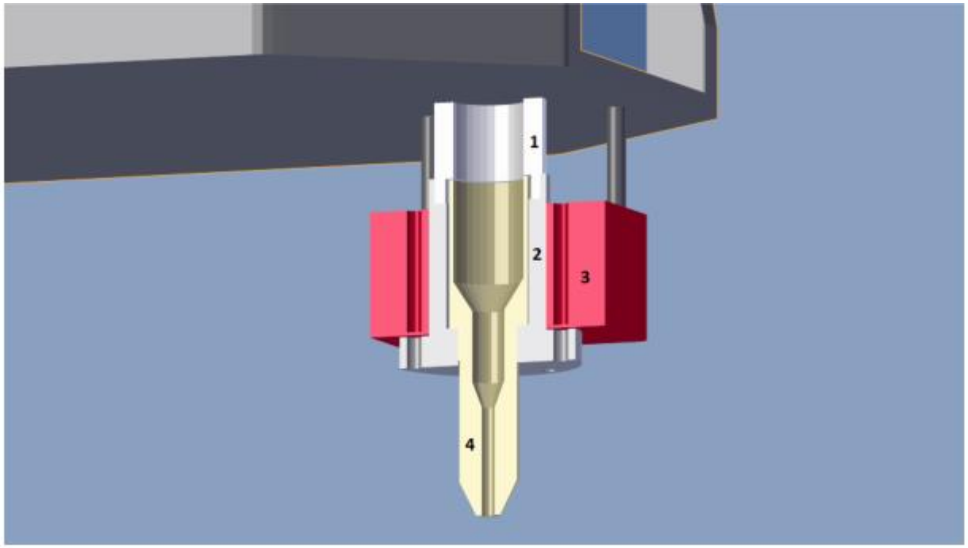


Fig. 1. Cross-section of the nozzle area of a composite printing module. 1 – PTFE heat break, 2 – aluminum heat link, 3 – aluminum heat block, 4 – brass nozzle additional intermediate compression zone.

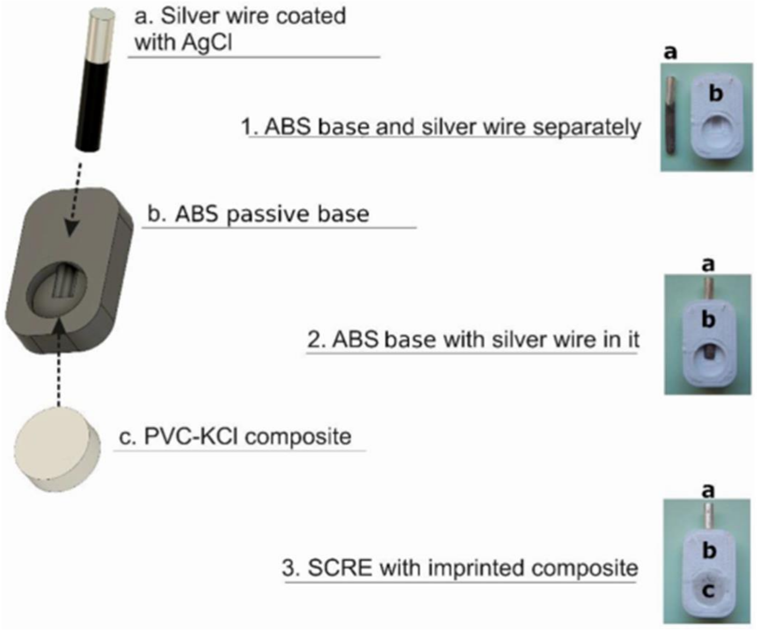
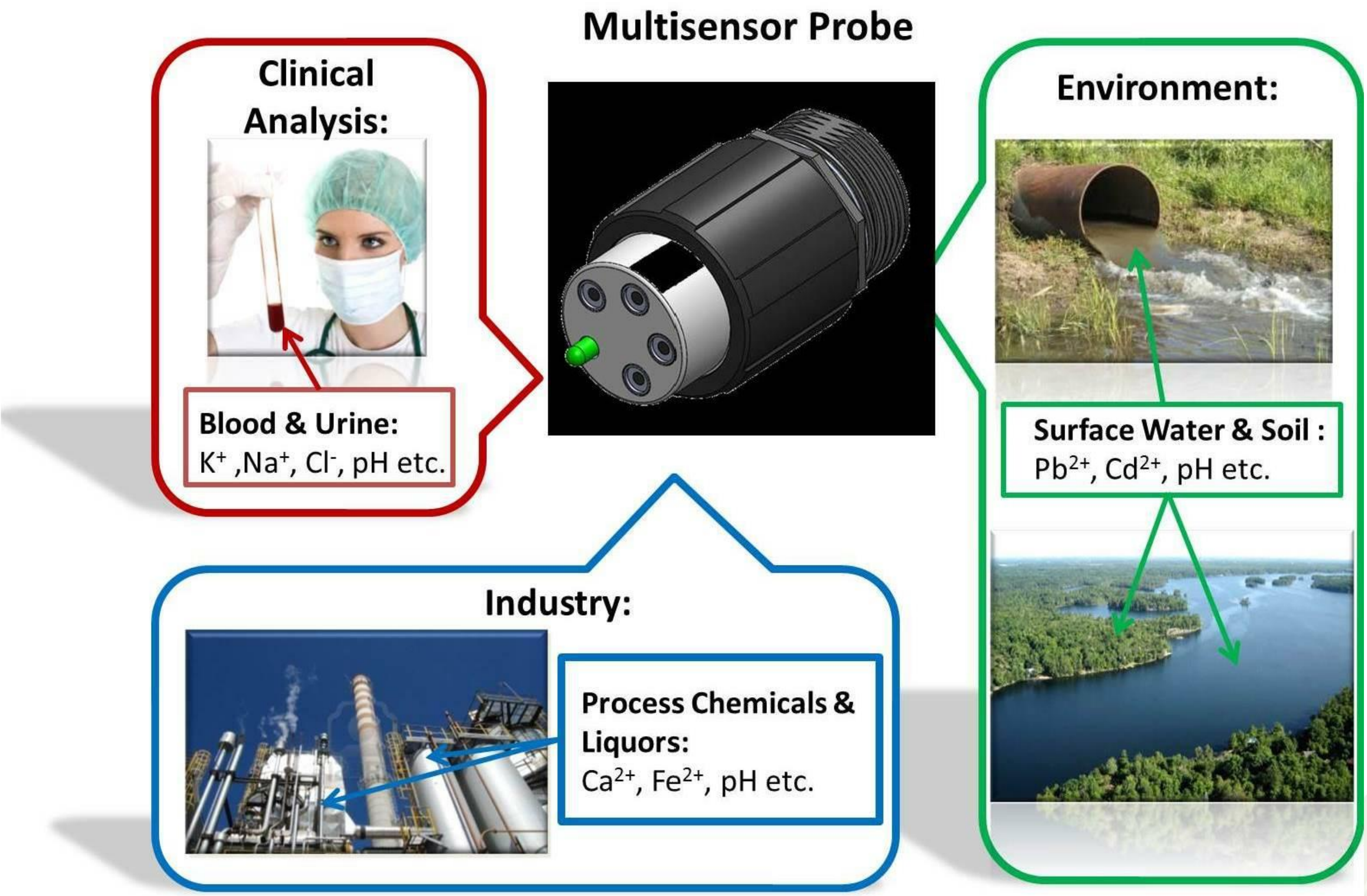


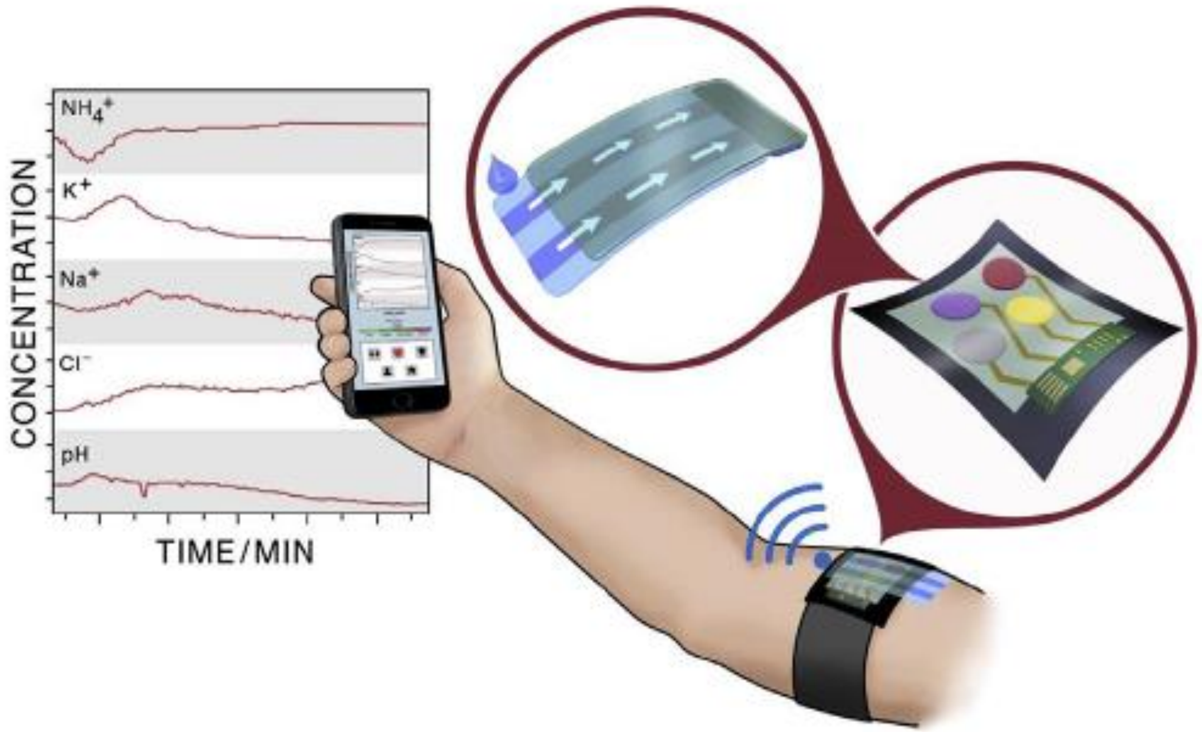
Fig. 2. Solid state 3D printed reference electrode. On the left-side a scheme with electrode parts; on the right-side fabrication steps and photos of a real product (dimensions of the base: 30 mm × 20 mm and cavity diameter 11 mm).

Applications...

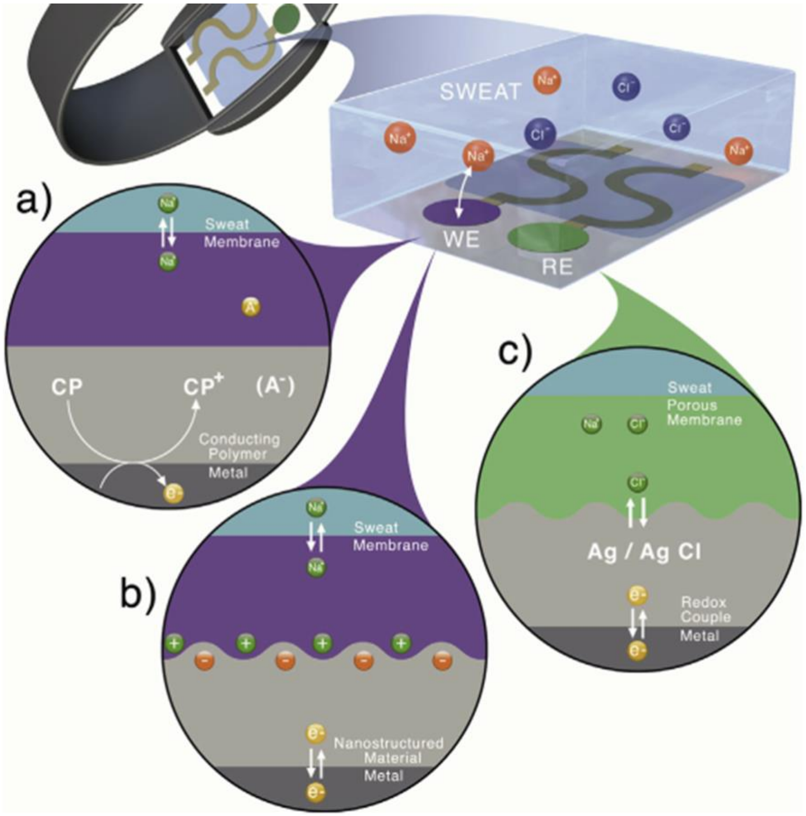
…environmental analysis
…process control
…point-of-care measurements
…wearable sensors



Sokalski et al AAU



….potentiometric ion-sensors as health quality controllers.



…solid contact wearable ion-sensors

M. Parrilla et al, *Trends in Analytical Chemistry* 110 (**2019**) 303-320

membranes

Advances in Artificial and Biological Membranes

Mechanisms of Ionic Sensitivity, Ion-Sensor Designs and Applications for Ions Measurement

Edited by
Andrzej Lewenstam and Krzysztof Dołowy

Printed Edition of the Special Issue Published in *Membranes*

www.mdpi.com/journal/membranes

MDPI

2021

SUMMARY

From pH measurements to automated clinical analysis …