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Advances in Sensor-based Applications and Systems: Next Challenge's

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Challenges for Smart Wearable Systems I

- **Complex data monitoring and integrated analysis of various parameters**

- **Lack of any unified, modularised Mobile Platform or Application Programming Interface (API) for biofeedback monitoring**

- **Extensive and often platform targeted implementation**

- **Lack of "on-the-go" intelligent data processing**

- **Requires highly skilled IT specialists in:** Electronics, Advanced Low Level Programming, Signal Processing, Control Theory, Networking, Mobile Application Development, Artificial Intelligence, Mobile GUI programming

Coventry University

Challenges for Smart Wearable Systems II

- Lack of systems' efficiency, reliability, and unobtrusiveness
- Long life cycle of system development and validation
- Lack of unified multi-platform telemedicine solution for the mobile and desktop operating systems
- Not clear requirements from health care professionals and end-users
- Cost
- Services availability and interoperability issues

Coventry University

All solid state reference electrodes for electrochemical measurements

Motivation

Importance of electrochemical reference electrodes:

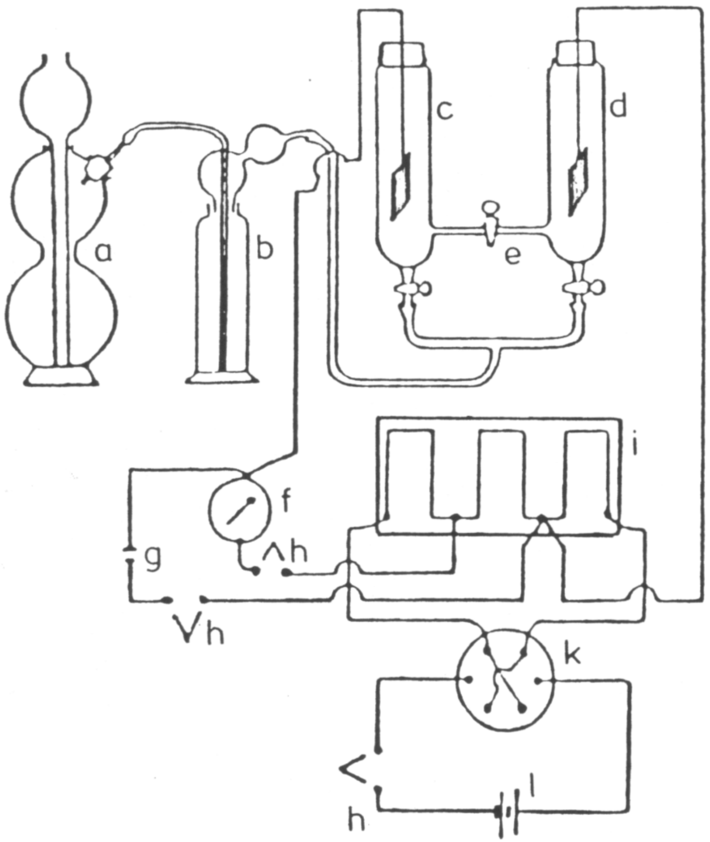
- The reference electrode is an essential component of electrochemical systems.
- In particular, it must maintain a defined and stable reference potential for potentiometric sensors.

Need for all-solid-state reference electrodes:

- Miniaturised all-solid electrochemical sensors need adequate reference electrodes in planar design.
- For process monitoring electrochemical sensors must be very robust, pressure- and heat resistant and steam sterilisable.

Therefore, already for a long time considerable efforts have been made to develop all-solid-state reference electrodes.

Hydrogen reference electrodes



Measuring Equipment with Pt/H_2 electrodes (c, d) [W. Salessky: Über Indikatoren der Azidimetrie und Alkalimetrie, Z. Elektrochem. 10 (1904) 204-208]

Hydrogen reference electrode HydroFlex (Gaskatel) according to US Patent 5 407 555 (1995)

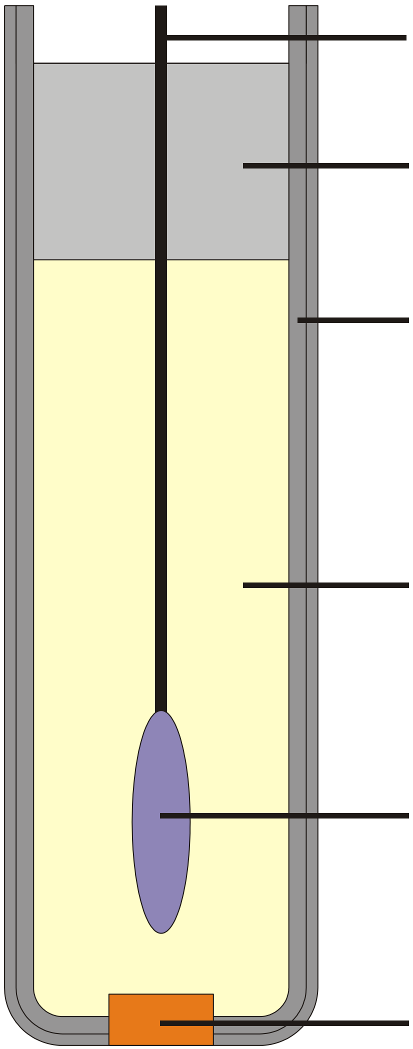
Some conventional reference electrodes

Reference System	pros and cons	Potential vs. SHE [mV]
Silver/silver chloride Ag/AgCl, Cl^-	Stable potential, Environment-friendly Applicable at temperatures up to 100 °C Temperature dependent (– 0,73 mV/K)	+ 222 (sat.)
Mercury/calomel Hg/Hg_2Cl_2, Cl^-	Very stable and reliable potential Maximum temperature 40 °C Toxic (Hg)	+ 241 (sat.)
Mercury/mercury sulphate Hg/Hg_2SO_4, SO_4^{2-}	Cl^--free Toxic (Hg)	+ 651 (sat.)
Thalamid Tl,Hg/TlCl, Cl^-	Temperature-resistant up to 135 °C Stable and reliable potential Toxic (Hg)	- 577 (sat.)
Jod/Jodit (Ross) $Pt/3I^-/I_3^-$ (redox system)	Faster response to temperature changes Low long-term potential stability	+ 420 ($[J_3^-]/[J^-]^3 = 2x10^{-4}$)

Criteria:

- Potential stable, reproducible and temperature-independent
- Electrode not polarisable, easily constructed and convenient for use

Main components of reference electrodes of second kind



Reference electrolyte:

Defined anion activity provides for a stable potential

Liquid, gel-like, pasty or solid

Reference element:

Metal, covered with a sparingly soluble metal salt or metal oxide

Junction:

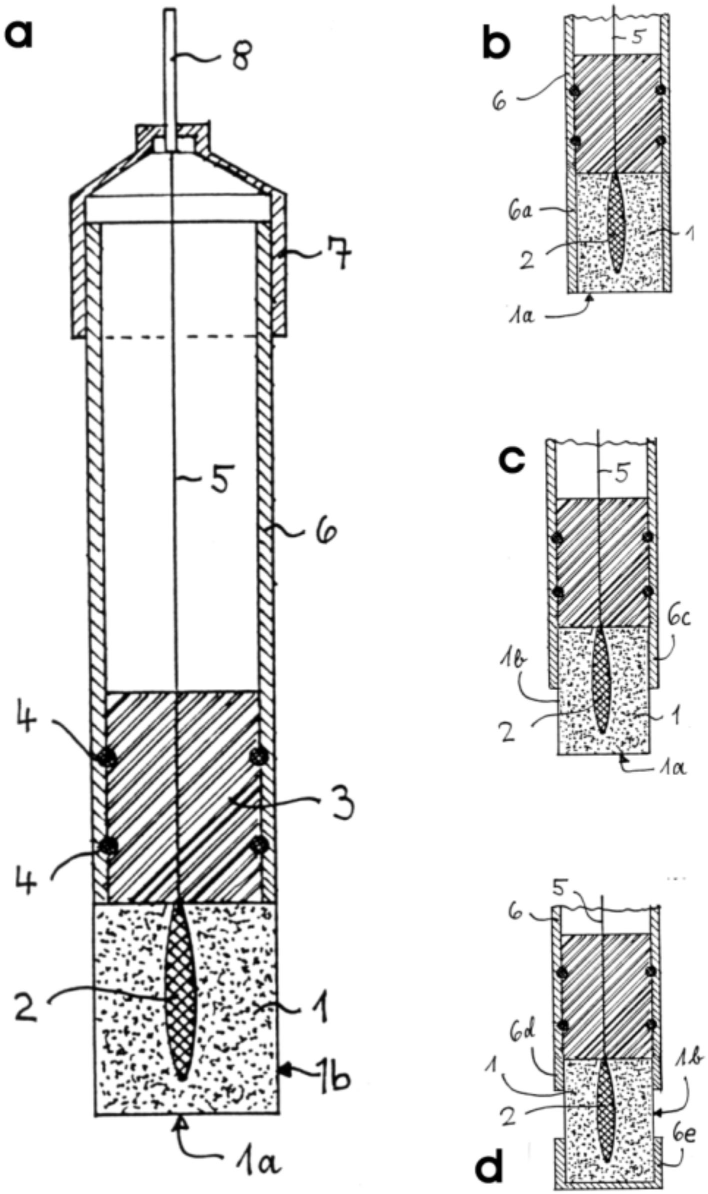
Makes the electrical contact between the analyte and the reference system.

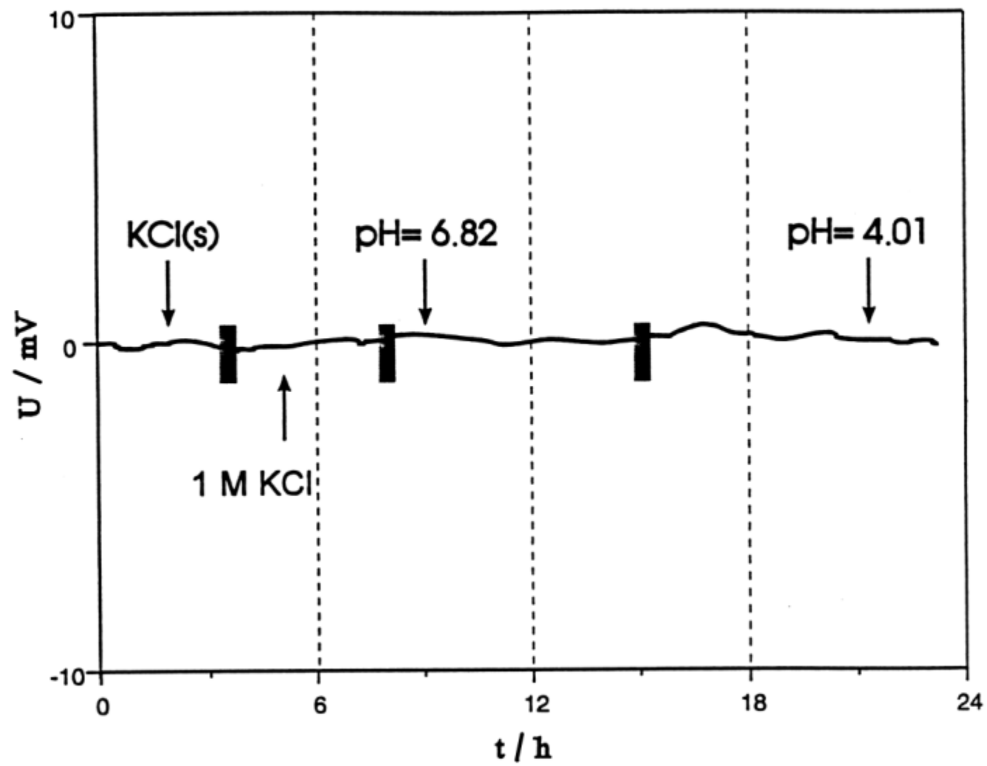
Sleeve, hole, diaphragm from ceramic, wood, teflon platinum fibres etc.

Reference electrodes with gel electrolyte

pros	cons
✓ Potentials comparable to those of electrodes with liquid electrolyte	- Increased diffusion potentials
✓ Applicable at higher temperatures up to 140 °C	- Irreversible bleeding
✓ Pressure resistant up to 16 bar	- Biofouling (for several gels)
✓ Steam sterilisable	- Electrolyte not renewable
✓ Position independent usage	- Gel ageing
✓ Hole diaphragm possible	- Discolouration
✓ Decelerated diffusion of solution into the electrolyte	- Extensive preparation
	- Some gels contain toxic/carciogenic substances

Reference electrode with polymer electrolyte



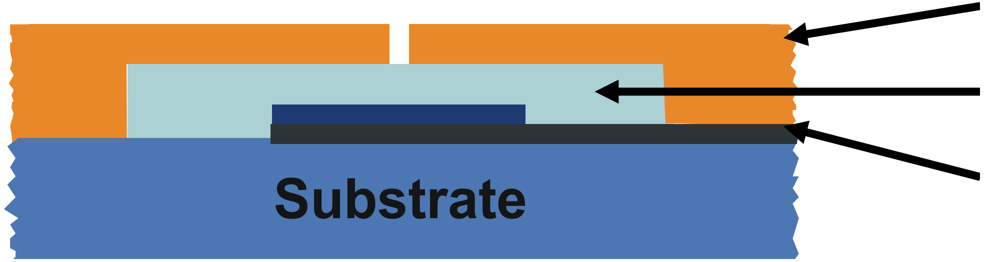


1: filled polymer
2: reference body
3: unfilled polymer
4: O-ring
5: silver wire
6: shaft segments
7: electrode cap
8: cable

W. Vonau et al.: DE 195 33 059 C 2 (1999)

Approaches for solid planar reference electrodes

Miniaturised planar Ag/AgCl reference electrode

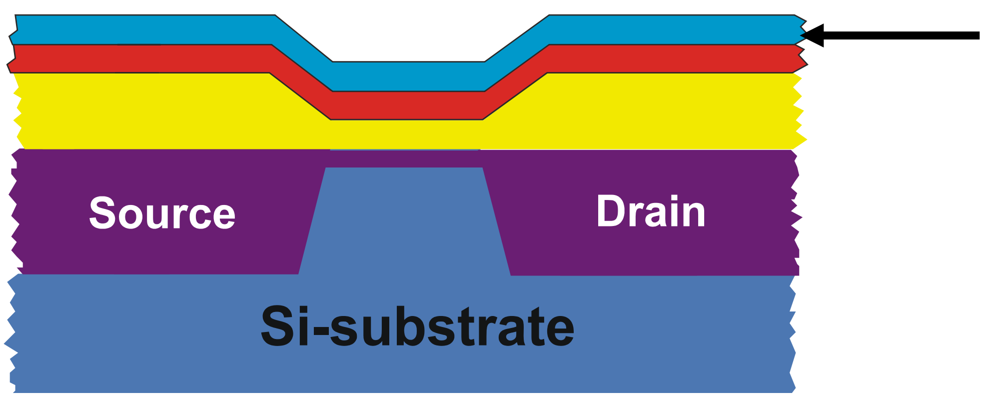


Cover with some kind of junction

KCl containing solidified material

Ag/AgCl reference element

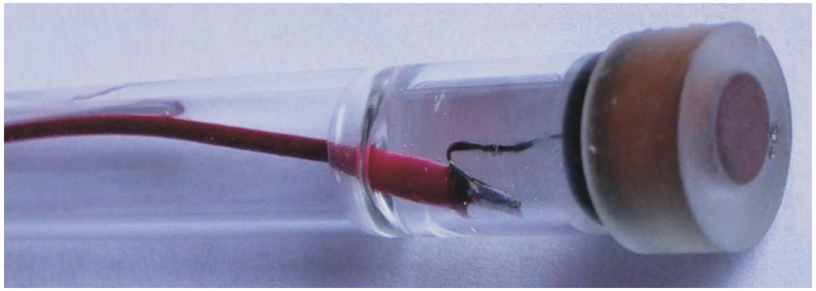
ISFET based planar reference electrode (REFET)



Chemically modified surface layer on the chemically sensitive gate material of the ISFET

Reference electrodes based on tungsten-substituted molybdenum bronzes

Bronze	pH	pO_2	redox	cation
$Na_{0.9}Mo_6O_{17}$	+	+	+	+
H_xMoO_3	+/-	-	+	+
$Ba_{0.12}WO_3$	-	-	+	+
$Li_{0.4}Mo_{0.95}W_{0.05}O_3$ (powder)	-	-	-	+
$Li_{0.4}Mo_{0.95}W_{0.05}O_3$ (mono crystal)	+	+	?	+

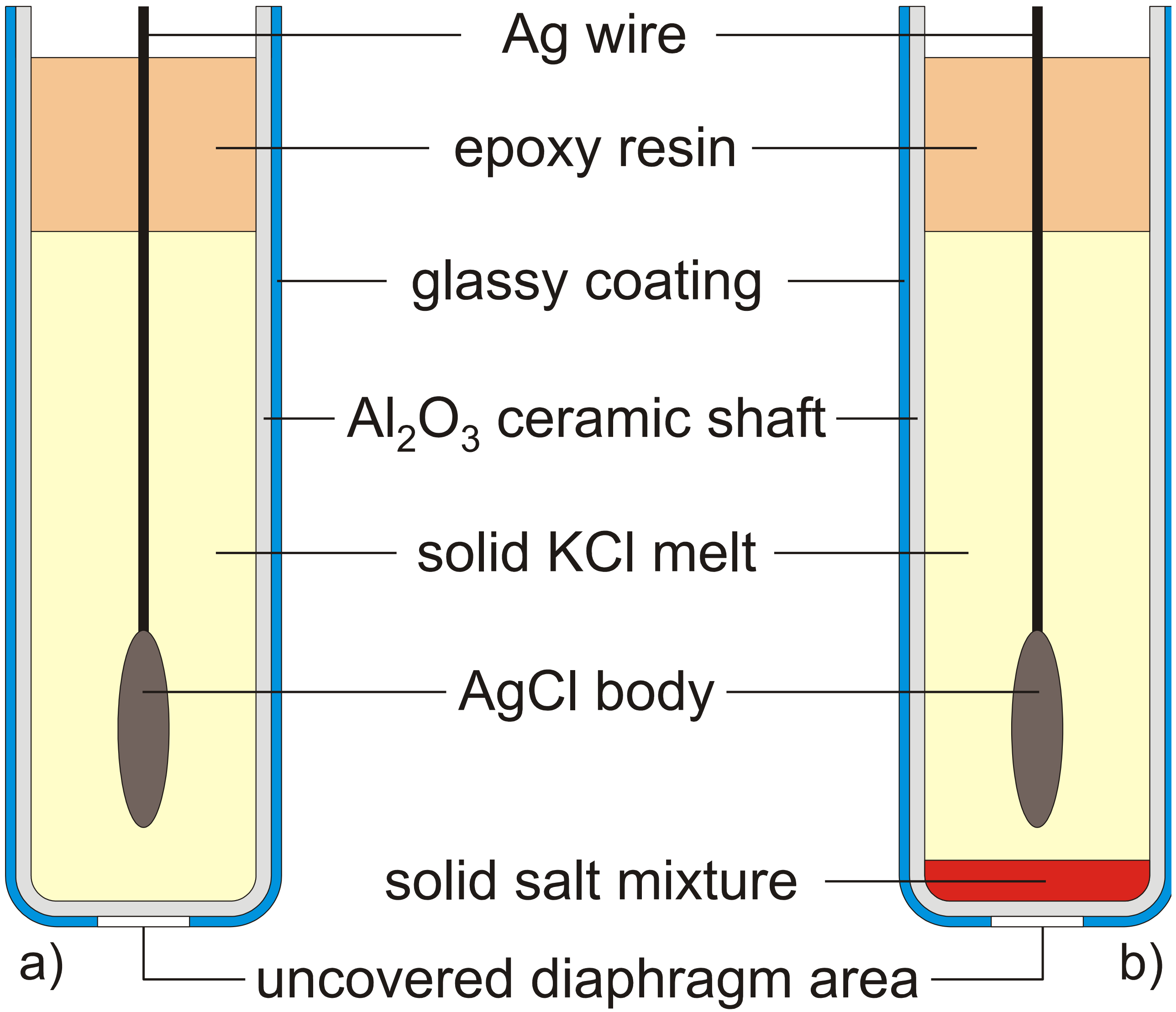


Resin pellet electrode made from $Li_{0.4}Mo_{0.95}W_{0.05}O_3$ bronze powder

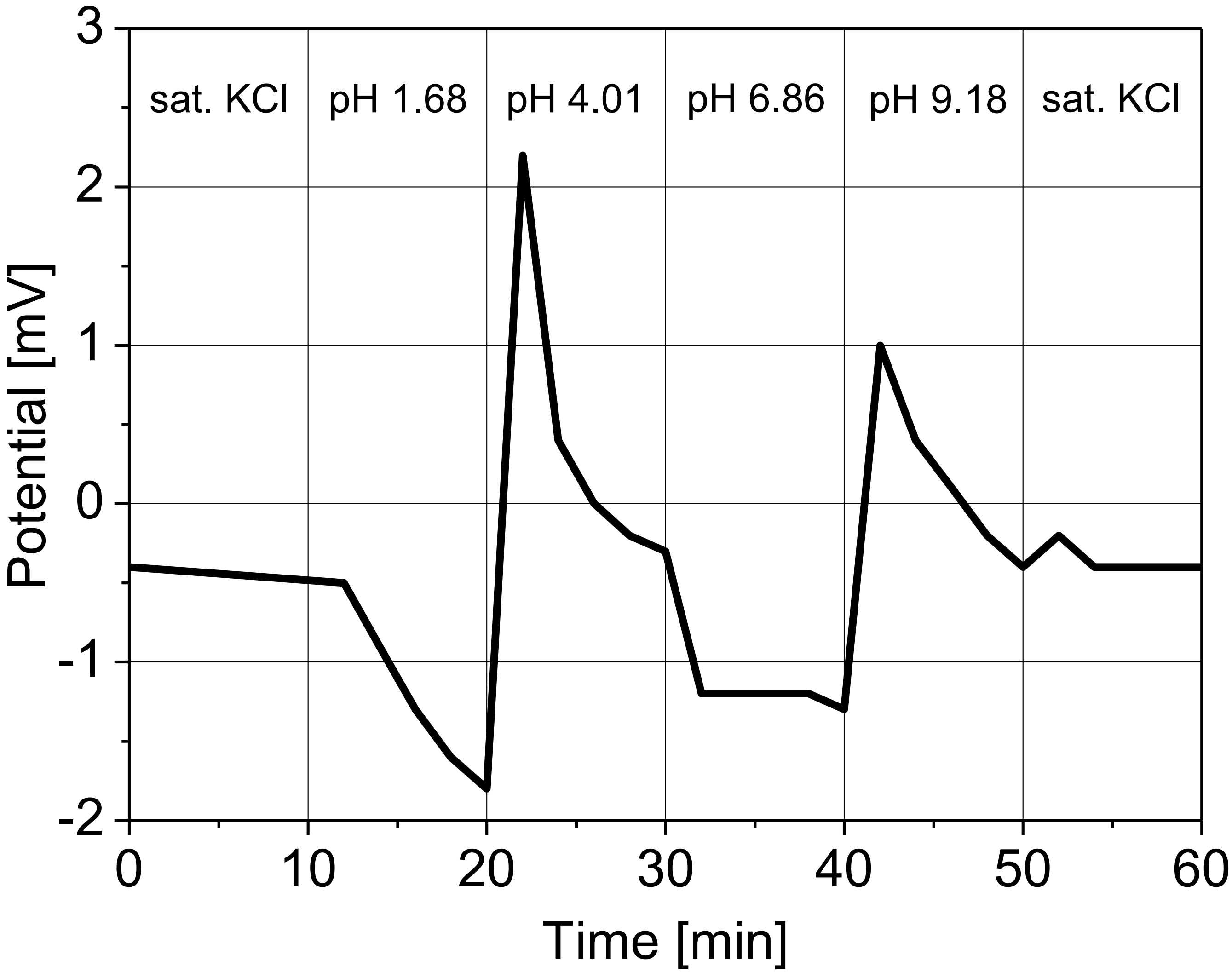
Sensitivities of transition metal bronze electrodes to dissolved species

+	response
?	no information up to now
-	no sensitivity

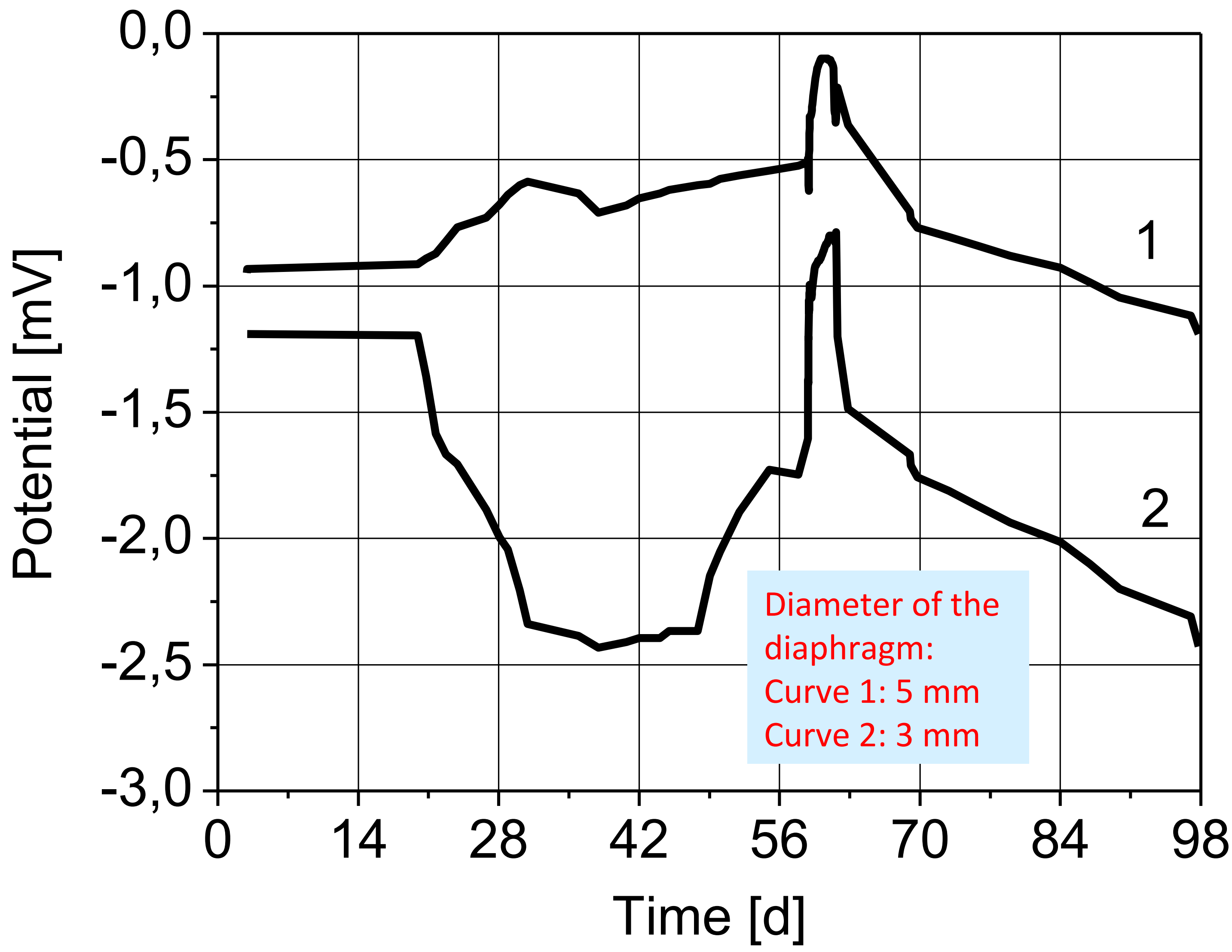
Reference electrodes with solidified electrolyte



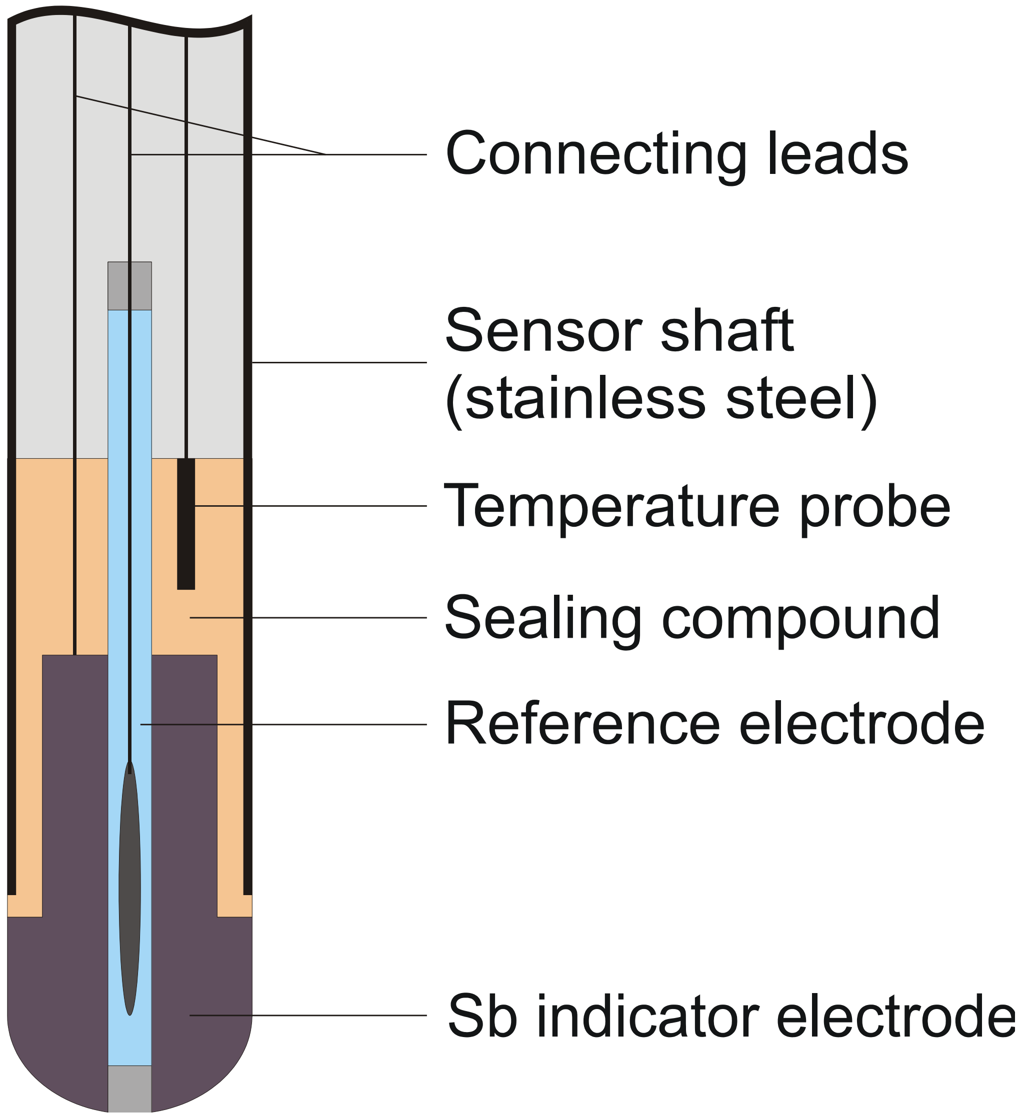
Potential of an all-solid reference electrode in different test solutions



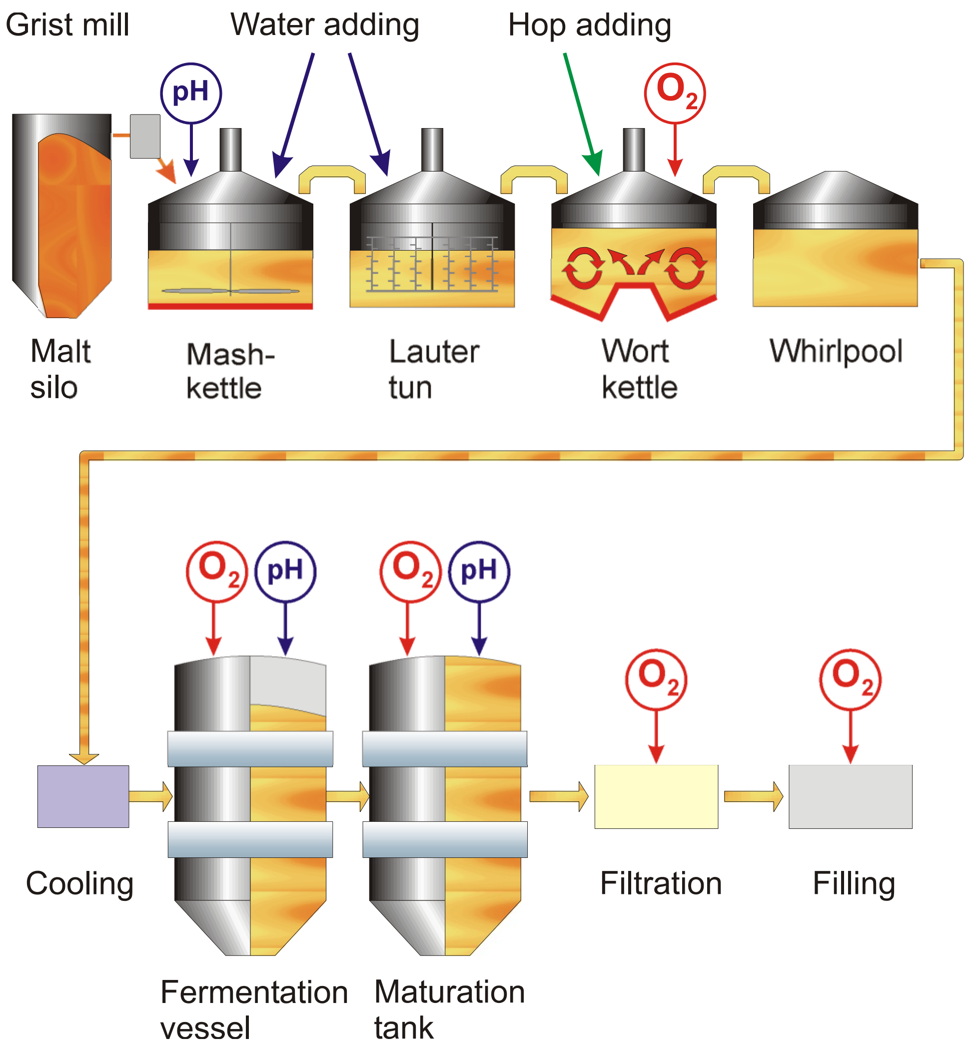
Long-term drift of two all-solid reference electrodes in sat. KCl solution at room temperature

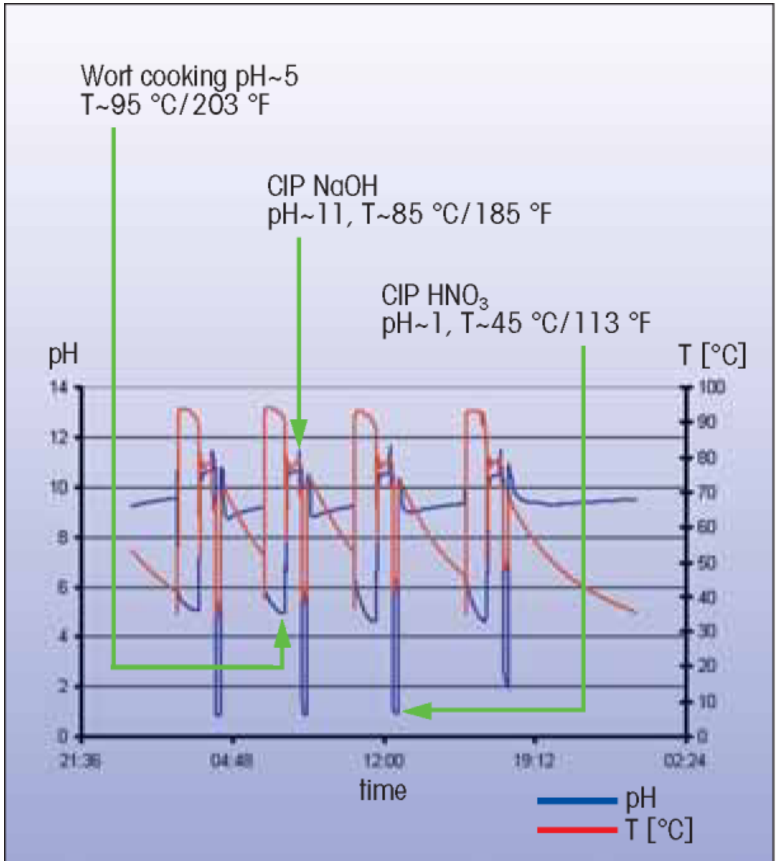


All-solid pH combination electrode with antimony indicator electrode and solid reference electrode



Examples for the application of electrochemical sensors in a brewery





pH measurement in Wort cooking (from METTLER TOLEDO Brewery News 9, p. 5)

Conclusions and outlook

- The reference electrode is an essential component of electrochemical systems. It must maintain a defined and stable reference potential for potentiometric sensors.
- Reference Electrodes with liquid or gel-like electrolyte are commercially available in a wide variety of embodiments for different practical applications.
- Miniaturised all-solid electrochemical sensors need adequate reference electrodes. Despite intensive development activities suitable long-term stable planar reference electrodes are not available so far.
- For process monitoring all-solid state electrochemical sensors are needed. They must be very robust, pressure- and heat resistant as well as steam sterilisable.
- By now the problem of solid-state reference electrodes is not satisfactorily solved. It remains a challenge to innovation.

I thank you for your attention

Underwater sensor networks

Need for reduced costs of hardware

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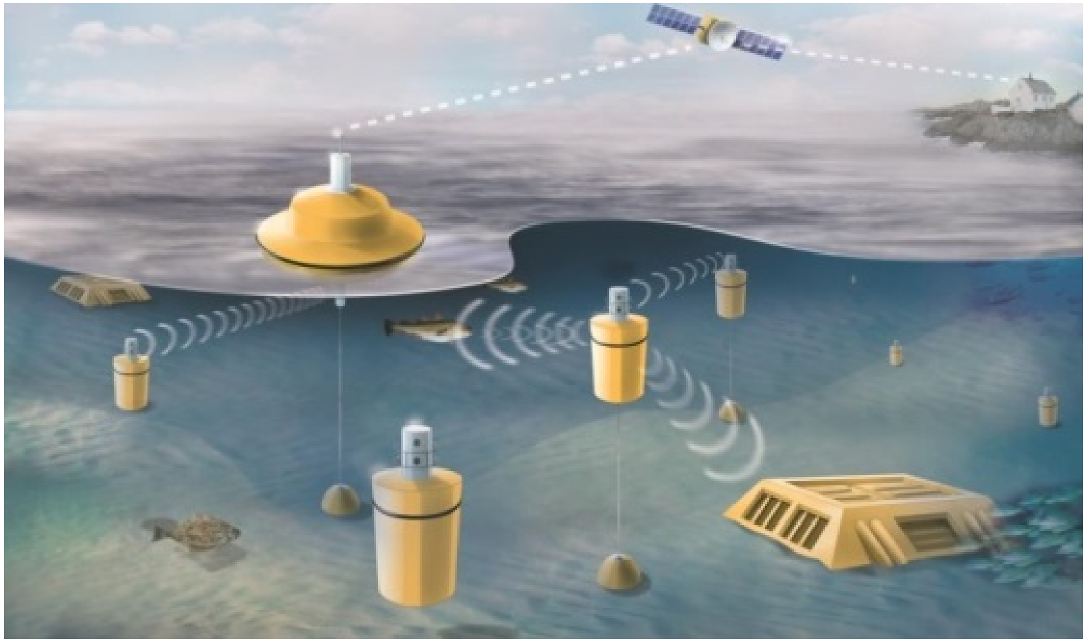


An important example

Marine operations and management based on ocean models

Sea currents: A main driving force → **Hydrodynamic modelling**

e.g. in

Aquaculture

Environmental monitoring Water quality, infections

Offshore oil and gas

Minimize environmental impact, discharges

Critical operations

Comparison	Model 1	Model 2	Model 3	Model 4	Model 5	Model 6
Semi-diurnal tidal current amplitude	Too large near bottom	Stronger currents under-estimated	Slight under-estimation	Greatly over-estimated	Good agreement	Slight under-estimation
Semi-diurnal tidal current orientation and phase	Good agreement	Good agreement	Poor agreement	Poor agreement	Good agreement	Poor agreement
Diurnal tidal current amplitude	Large scatter	Slight over-estimation	Greatly under-estimated	Greatly under-estimated	Slight under-estimation	Under estimated
Diurnal tidal current orientation and phase	Good agreement	Good agreement	Poor agreement	Good agreement	Slight phase error	Poor agreement
Residual current time series	No skill	No skill	No skill	No skill	No skill	No Skill
Current speed probability distribution	Large over-estimation	Slight over-estimation at 99%. Good agreement at 99.9%	Slight under-estimation	Large under-estimation	Un-biased, but larger scatter than Model 2	Too small near the surface and too large near the bottom
Current roses	Too narrowly concentrated around mean direction	Good agreement	Good agreement	Small errors in mean direction	Slightly narrower directional spread than measurements	Mean directions do not agree with measurements
Temperature	Biased low	Good agreement	Biased low	Biased low	Biased slightly high	Drifts to higher temperatures
Salinity	Slight high bias	Biased low	Biased low	Biased low	Slight low bias	Large low bias

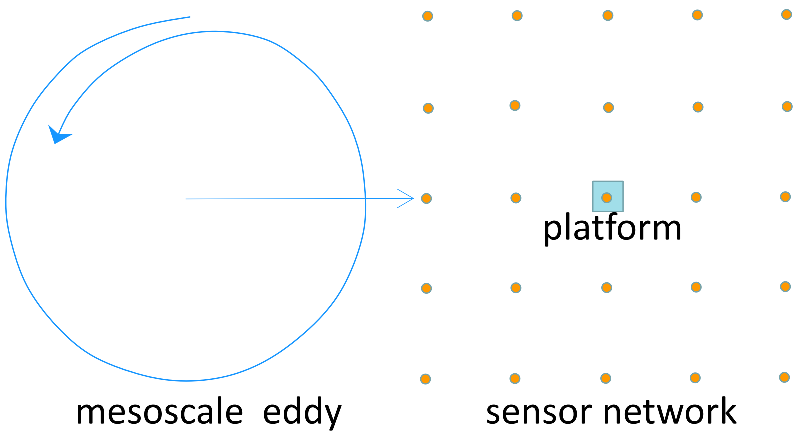
For detailed situation awareness

Modelling not sufficient.
Measurement too difficult alone

Combination needed

Data assimilation into models like in meteorology
But flow-dynamic lengths scales are much smaller in water → denser networks

O&G critical operation:
Predict sea currents



1 Doppler profiling sensor
+ acoustic modem 50 k€

x 25 nodes 1250 k€ ☹

+ additional sensors
and equipment
+ significant deployment
and maintenance costs

EU FP7 formulation

From the call for proposals Ocean 2013.2 (2012):

Innovative multifunctional sensors for in-situ monitoring of marine environment and related maritime activities

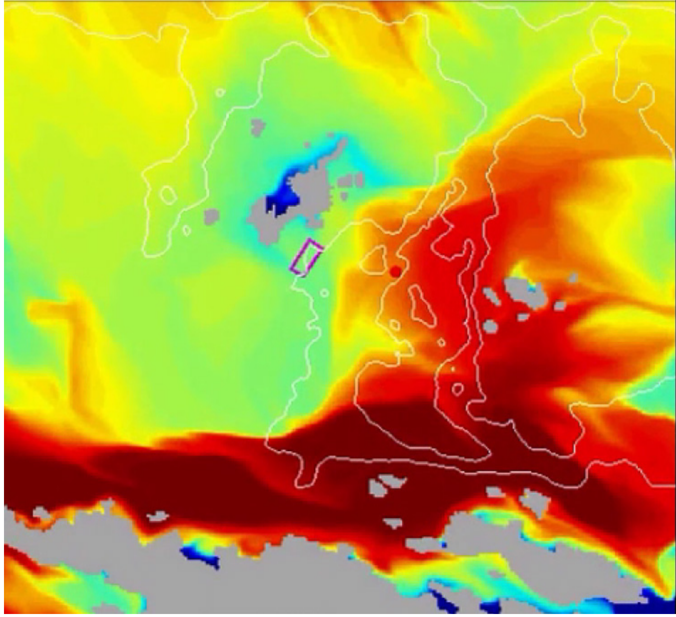
"**… urgent need to improve the in-situ component of the ocean observing systems** to achieve an appropriate understanding of the functioning of the marine environment … and the monitoring of marine and maritime activities …"

" **As commercially available sensors tend to be too large, expensive, and power-hungry for widespread use, reducing the cost for acquisition of data is a key priority** in order to implement EU legislations …….seeks to develop robust, easily usable across multiples platforms, cost effective multifunctional sensors and their packages that provide reliable in-situ measurements of key parameters."

Expected impact

- Provide a **large increase in the temporal and geographic coverage** from in-situ marine sensors to enhance the European **contribution to Global Monitoring of the Oceans**
- Increase availability of **standardised in-situ data** that is suitable for integration within key **marine observation, modelling and monitoring** systems and reduce ocean modelling uncertainty
- Reduce cost of data collection system in **support of fisheries management**
- **….**
- **Support implementation of European Maritime Policies** (MSFD, CFP, IMP, etc.);
- **Promote new discoveries** leading to better understanding of the seas.

How to proceed?



Research and development needed to increase efficiency in manufacturing and use

Some topics

- Manufacturing technology – large scale integration
- Sensors – new principles?
  + Antifouling & robustness
  + Energy efficiency & harvesting
- Low cost communication technology
- How to make use of the technology
  - mobile platforms
  - smart sampling
- ….

Advances in Sensor-based Applications and Systems: Next Challenge

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SENSORCOMM 2013August 25 - 31, 2013 - Barcelona, Spain

DCU

MESTECH
Marine & Environmental Sensing Technology Hub

NCSR
National Centre for Sensor Research

Challenges?

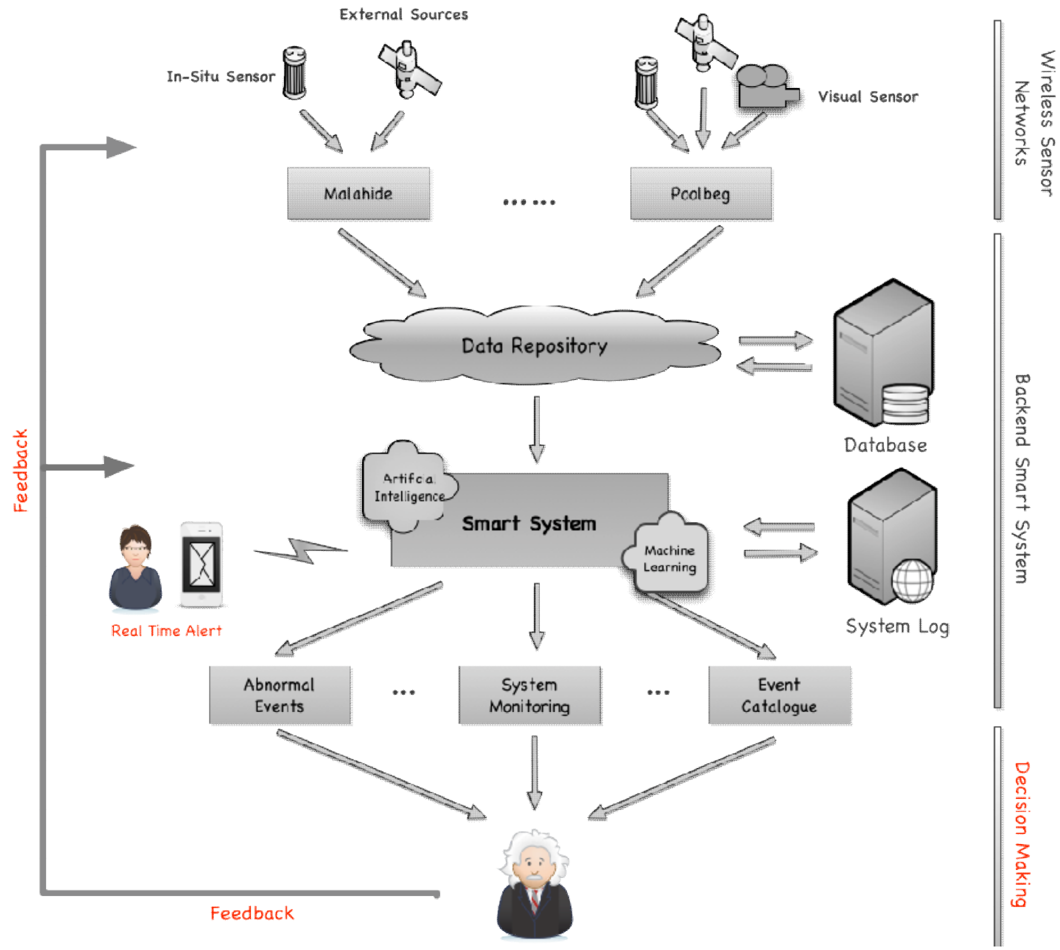
We can now collect lots of data (sometimes easily!) – however challenges:

- Sensor integration
- Data Management/Access flow – scalable networks
- Individual nodes:

Higher sensor accuracy /resolution

e.g. pH – ocean acidification

- New sensors?



Data Access and signal Processing

- Data depository – standard methods, how are data stored once a project finishes (locked away in a drawer /hard drive)? How do we automate / design the system for smooth data access?
- Different data types and modalities – connecting these vital for decision making
- However, system integration does not mean just putting everything in the same box! - true integration necessary – smart systems, how can we design future sensor systems to address this?

Future

- Better data management / ease of accessibility?
- Better use of modeling to inform positioning of sensor systems and suitability of sensor applications?
- Can we design modular, integrated and scalable sensor systems – that can be tailored to applications (perhaps deployed by non-specialists)? Would this expand and /or improve use of sensor networks?
- Open access?