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
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
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/H₂ electrodes (c, d) [W. Salessky: Über Indikatoren der Azidimetrie und Alkalimetrie, Z. Elektrochem. 10 (1904) 204-208]

HydroFlex (Gaskatel) according to US Patent 5 407 555 (1995)
## Some conventional reference electrodes

<table>
<thead>
<tr>
<th>Reference System</th>
<th>pros and cons</th>
<th>Potential vs. SHE [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver/silver chloride Ag/AgCl, Cl⁻</td>
<td>Stable potential, Environment-friendly Applicable at temperatures up to 100 °C Temperature dependent (− 0,73 mV/K)</td>
<td>+ 222 (sat.)</td>
</tr>
<tr>
<td>Mercury/calomel Hg/Hg₂Cl₂, Cl⁻</td>
<td>Very stable and reliable potential Maximum temperature 40 °C Toxic (Hg)</td>
<td>+ 241 (sat.)</td>
</tr>
<tr>
<td>Mercury/mercury sulphate Hg/Hg₂SO₄, SO₄²⁻</td>
<td>Cl⁻-free Toxic (Hg)</td>
<td>+ 651 (sat.)</td>
</tr>
<tr>
<td>Thalamid Tl,Hg/TICl, Cl⁻</td>
<td>Temperature-resistant up to 135 °C Stable and reliable potential Toxic (Hg)</td>
<td>- 577 (sat.)</td>
</tr>
<tr>
<td>Jod/Jodit (Ross) Pt/3I⁻/I₃⁻ (redox system)</td>
<td>Faster response to temperature changes Low long-term potential stability</td>
<td>+ 420</td>
</tr>
</tbody>
</table>

([J₃⁻]/ [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

- Connecting lead
- Sealing cap
- Sensor shaft
- Electrolyte
- Reference element
- Junction

**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

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

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

<table>
<thead>
<tr>
<th>Bronze</th>
<th>pH</th>
<th>pO₂</th>
<th>redox</th>
<th>cation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₀.₉Mo₆O₁₇</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>HₓMoO₃</td>
<td>+/-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ba₀.₁₂WO₃</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Li₀.₄Mo₀.₉₅W₀.₀₅O₃ (powder)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Li₀.₄Mo₀.₉₅W₀.₀₅O₃ (mono crystal)</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>+</td>
</tr>
</tbody>
</table>

Sensitivities of transition metal bronze electrodes to dissolved species

<table>
<thead>
<tr>
<th></th>
<th>response</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td></td>
</tr>
<tr>
<td>?</td>
<td>no information up to now</td>
</tr>
<tr>
<td>-</td>
<td>no sensitivity</td>
</tr>
</tbody>
</table>

Resin pellet electrode made from Li₀.₄Mo₀.₉₅W₀.₀₅O₃ bronze powder
Reference electrodes with solidified electrolyte

- Ag wire
- epoxy resin
- glassy coating
- $\text{Al}_2\text{O}_3$ ceramic shaft
- solid KCl melt
- AgCl body
- solid salt mixture
- uncovered diaphragm area

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

![Graph showing potential changes over time in different pH solutions](image)
Long-term drift of two all-solid reference electrodes in sat. KCl solution at room temperature

<table>
<thead>
<tr>
<th>Potential [mV]</th>
<th>Time [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.0</td>
<td>0</td>
</tr>
<tr>
<td>-2.5</td>
<td>14</td>
</tr>
<tr>
<td>-2.0</td>
<td>28</td>
</tr>
<tr>
<td>-1.5</td>
<td>42</td>
</tr>
<tr>
<td>-1.0</td>
<td>56</td>
</tr>
<tr>
<td>-0.5</td>
<td>70</td>
</tr>
<tr>
<td>0.0</td>
<td>84</td>
</tr>
<tr>
<td>2.0</td>
<td>98</td>
</tr>
</tbody>
</table>

Curve 1: 5 mm
Curve 2: 3 mm

Diameter of the diaphragm:
All-solid pH combination electrode with antimony indicator electrode and solid reference electrode

Diagram labels:
- Connecting leads
- Sensor shaft (stainless steel)
- Temperature probe
- Sealing compound
- Reference electrode
- Sb indicator 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**

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e.g. in

**Aquaculture**

Environmental monitoring *Water quality, infections*

**Offshore oil and gas**

Minimize environmental impact, *discharges*

Critical operations

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

Modelling not sufficient. Measurement too difficult alone

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

Combination needed

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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The Seventh International Conference on Sensor Technologies and Applications
SENSORCOMM 2013
August 25 - 31, 2013 - Barcelona, Spain
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?