20.04.04 Tuesday: 915 - 1100 (Classroom 300, Main Building)

"A comparison of electrode materials used in potentiometry, what they are and how they act. A look into "electrolytics".

Various electrode materials are used in potentiometry. Is there a common working principle? These electrode materials are ionically conductive electrolytes. What are the differences with electronically conductive materials. How do both types of materials behave in combination?
a look at a glass membrane:
covalent lattice, amorphous, rigid, slight ionic conductivity due to H⁺ on silanol groups
Single crystal ionic lattices are used in electrodes for simple ions such as F$^-$ selective electrodes. It must be doped with Eu(II) to make it more ionically conductive. The conductivity is due to F$^-$ jumping into nearby vacancies.
vacancy, substitutional impurity, interstitial impurity, self interstitial
In this type of potentiometry, potential development is driven by the “tendency to mix”.

\[ xM F^- \quad \leftrightarrow \quad 1M F^- \]
let’s try the chemical potential concept to calculate it

\[ \mu_{F \text{ in inner soln}} = \mu_{F}^{0} + RT \ln c_{F,\text{inner}} + z_{F} F E_{\text{inner soln}} \]

\[ \mu_{F \text{ in analyte soln}} = \mu_{F}^{0} + RT \ln c_{F,1} + z_{F} F E_{\text{analyte soln}} \]
\[ \mu_{F \text{ in inner soln}} = \mu_{F}^0 + RT \ln c_{F \text{ inner}} + z_F F E_{\text{inner soln}} \]

\[ \mu_{F \text{ in analyte soln}} = \mu_{F}^0 + RT \ln c_{F \text{ anal. soln.}} + z_F F E_{\text{anal. soln.}} \]

Only the F⁻ ion gets through the membrane: permselectivity. This creates a potential, until

\[ \mu_{F \text{ in inner soln}} = \mu_{F \text{ in analyte soln}} \]

So, at that point:

\[ E_{\text{inner}} - E_{\text{anal. soln.}} = \frac{RT}{nF} \ln c_{F,\text{inner soln}} / c_{F \text{ anal. soln.}} \]
Charge transfer in solid AgBr. Conductivity due to Ag$^+$ and interstitial holes. Example of cation movement in ionic lattice. Ag$^+$ sensor.
let's move to polymer films!
composition of a typical "liquid" membrane

PVC

plasticizer

analyte
cation, eg RNH$_3^+$

tetra (p-chlorophenyl)borate
“inner solution” format. Even in this case, potentials develop at the interfaces only. The potential development is driven by the tendency of the cation to be extracted in the membrane. Intermolecular interactions are important!
substrate electrode

coating

analyte solution

“coated wire” format
Interface A gives interfacial tensions depending on eluent composition. Little is known on substrate/membrane adhesion chemistry.
The “rubber” state

PVC polymer

wiggling PVC polymer

liquid: segmental motion

rubber: polymer “wiggling”
studying plastics and the rubber state: Differential Scanning Calorimetry (DSC)

phase (1st kind) transition

2nd kind transition ($C_m$ change)
<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (LDPE)</td>
<td>-125</td>
</tr>
<tr>
<td>Polypropylene (atactic)</td>
<td>-20</td>
</tr>
<tr>
<td>Poly(vinyl acetate) (PVAc)</td>
<td>+28</td>
</tr>
<tr>
<td>Poly(ethyleneterephtalate) (PET)</td>
<td>+69</td>
</tr>
<tr>
<td>Poly(vinyl alcohol) (PVA)</td>
<td>+85</td>
</tr>
<tr>
<td>Poly(vinylchloride) (PVC)</td>
<td>+81</td>
</tr>
<tr>
<td>Polypropylene (isotactic)</td>
<td>+100</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>+100</td>
</tr>
<tr>
<td>Poly(methylmethacrylate) (atactic)</td>
<td>+105</td>
</tr>
</tbody>
</table>
The ionic conductivity of a polymer electrolyte is dependent on its glass transition temperature. The relation is known as the Vogel-Tamman-Fulcher equation:

\[ \sigma = A T^{1/2} e^{-\frac{E}{T-T_0}} \]

E is an activation energy, dependent on the polymer electrolyte, \( T_0 \) is the glass transition temperature (actually \( T_g \)).

Mechanical properties of membrane electrodes:

relative force needed to pull off membrane from substrate:

PVC                   1
silicone               30
polyurethane       5

Biocompatibility of plastic membranes is less good than eg glass:

Total protein adsorption (the first biocompatibility indicator)
The ratio of adsorbed albumin to fibrinogen (the second biocompatibility indicator)

polyurethanes and silicones somewhat better than PVC

Microfabricated potentiometric electrodes and their in vivo applications, E. Lindner, RP Buck, Anal. Chem., may 1, 2000, 336A.
For simple chemical analytes such as sodium, potassium, chloride, ion-selective electrodes can be made, even for in vivo measurement.

Can highly selective potentiometric (ion-selective) electrodes be made for organic ionics?

Probably yes, if the right macrocyclic receptor molecules (ionophores) can be synthesized:


Polymer coatings for amperometric sensors:
“Loaded ionomers” and “Redox hydrogels” (redox polymers).

These materials can at their best improve the heterogeneous rate constant for slowly reacting redox active substances.

Metal oxides can do better: see PAD.
From "Polymer (bio)materials design for amperometric detection in LC and FIA",
LJ Nagels, E Staes, TrAc 20(4) 2001

What is there to be expected?
Amelioration for already redox active substances. Nothing more!
Dimethylferrocene, tetrathiafulvene, tetracyanoquinodimethane, Meldola blue.

Redox mediators can be covalently coupled to redox polymers, used as counterions in loaded ionomers, mixed with carbon paste...

Carbon paste: paraffin $C_nH_{2n+2}$ + graphite composite.
Co-phtalocyanine is a known mediator. Compare it to nature's mediators, the porphyrins in cytochromes.
one example of a redox polymer: polyvinylferrocene

The ultimate mediators for non redox active substances are redox enzymes: see next dia
use of these materials in amperometric biosensors

2nd generation: redox polymer or loaded ionomer plus linked enzyme

Polymer (bio) materials design for amperometric detection in LC and FIA TrAc 20(4) 2001, Nagels and Staes
Amperometric devices have been successful only for glucose and urea. These compounds are present in high concentrations.

One other example: a 3rd generation enzyme electrode for fish and meat freshness: hypoxanthine

Xanthine oxidase and horseradish peroxidase (HRP) are co-immobilized in electropolymerized films utilizing conducting and non-conducting polymers

Why electropolymerized films? Film thickness.

Why hypoxanthine → H₂O₂ (oxidase) → H₂O (HRP)

Possible to reduce peroxide at 0-200mV. Interferences in biomatrices start at +400mV!

HRP is a good enzyme for third generation biosensors: see L. Gorton
Protein-receptor-based electrodes

Bio-receptor molecules are mighty molecules for electrochemistry-based sensors!

from: Joe Wang, Analytical Electrochemistry, Wiley, 2000
Monolayers, with attached redox mediators or enzymes

Making sensors with all the above amperometric technology is OK, but making fuel cells is better!
$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
Two kinds of machines...

chemical energy $\rightarrow$ work

- low T
  - muscle,
  - battery+electromotor

chemical energy $\rightarrow$ warmth $\rightarrow$ work
(2x less efficient)

- high T
  - combustion engines