Chemical Sensors

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The earliest chemical sensor in human history:

Canary in a Coal Mine
Modern Competitions

Mine-sniffing rats head to Asia

This African Giant Pouched Rat is a hero. Belgian innovator Bart Weetjens has trained rats, which have a powerful sense of smell, to detect lethal buried landmines in Mozambique. He calls them HeroRATs.

Their next frontier is the Thai-Cambodia border, where hidden landmines have caused immense loss of human life and limbs.

Mr. Weetjens is a winner of Singapore’s inaugural Hero of the Year Challenge, a global contest to encourage innovative non-profit ideas for the good of Asia.

SEE SATURDAY SPECIAL REPORT, PAGE 33

Singapore Strait
Times, Oct 24, 2009
What is Biosensor / Chemical Sensor

- Research (medical, biochemical, biotechnological)
- Monitoring
- Pharmaceutics & Drug Discovery
- Environment
- Food control
- Biodefense
- Forensics
- Diagnostics

Diagram:
- Sensing platform
- Transducer
- Signal
- NO signal
Chemical sensors

1 Under dry condition: Gas sensor
   1.1 Hydrogen chemical field effect transistor (ChemFET)

2 Solution based chemical sensor
   2.1 Basic concepts of electrochemistry
   2.2 Electrochemical double layer
   2.3 Example – Ion Sensitive Field Effect Transistor (ISFET)
Gas sensors are sensing devices that interact with various gases and then provide the output to an instrument for displaying the measurements. Their applications are in toxic and combustible gas detection.

Global market for gas sensor reached $1.24 billion for 2008, and is projected to reach $1.4 billion by 2012.

The major gas sensor types are:

- Electrochemical
- Semiconductor
- Catalytic
- Infrared
Gas sensor – conventional vs. solid state

**Conventional gas sensor:**
- Catalytic bead sensors, explosimeter, infrared point sensor, etc.

**Semiconductor gas sensor:**
- Sensitive, ultra-small in size, low cost, easily integratable, mass manufacturing...

<table>
<thead>
<tr>
<th>Type of solid state devices</th>
<th>Physical changes</th>
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<tbody>
<tr>
<td>1</td>
<td>Field effect gas sensor: Diode, transistors, capacitors</td>
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<tr>
<td>2</td>
<td>Piezoelectric sensors: Quartz crystal microbalances (QCM), surface acoustic wave (SAW), microcantilevers</td>
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<tr>
<td>3</td>
<td>Optical sensors: fibre optic or thin film</td>
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Fig. 9 (a) Energy band diagram of an isolated metal and an isolated semiconductor with an oxide layer between them. (b) Energy band diagram of an MOS diode in thermal equilibrium.

\[ V_{FB} = \frac{\phi_m - \phi_s}{q} \]

\[ V_T = V_{FB} + 2\psi_B + \frac{d}{\varepsilon_i} \left[ 2\varepsilon_s q N_A (2\psi_B) \right]^{\frac{1}{2}} \]
A Hydrogen ChemFET is made by using Palladium (Pd) as a metal gate.

H$_2$ diffuses through the Pd gate changing the metal work function.

$V_T$ changes and the $I_D-V_{GS}$ characteristic shifts.

Palladium is the functional material which provides specificity!
Hydrogen adsorb on palladium surface to form palladium hydride and generate positive charge at the metal – gas interface.

A dipole layer is formed

\[ V_{FB} = -\psi_{int} \]
\[ V_{FB} = \frac{\phi_m - \phi_s}{q} - \psi_{int} \]

Alternative explanation:
Remember:
\[ \phi_m = \text{work done to extract an electron from the metal} \]
This work is done against the surface dipole
Other gases can be detected by this principle: $\text{H}_2\text{S}$, $\text{NH}_3$, $\text{CO}$ etc.
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2  Solution based chemical sensor
   2.1  Basic concepts of electrochemistry
   2.2  Metal-electrolyte interface
       - Helmholtz model
       - Gouy-Chapman model
       - Gouy-Chapman-Stern model
   2.3  Example - ISFET
Solid state sensor device in contact with a solution, which contains the chemical to measure. Properties of liquid solution, and liquid-solid interface have to be considered in this type of sensors.

Example:
Ion-Sensitive-Field-Effect Transistor (ISFET)
• $4 billion annual US market including biosensors
• Annual growth rate between 7-8%
• Including optical, electrochemical, semiconductor and others
• Medical diagnostic remains the largest sector
Definitions:

• **Solution**: a liquid, normally water, referred to as the solvent, containing other species, normally a salt, like sodium chloride, \( \text{NaCl} \), referred to as the solute.

• **Mole** of a monoatomic substance: *the atomic weight expressed in grams* \((g=10^{-3} \text{ Kg})\)

  Example:  
  - Al (atomic weight = 27) \( \quad 1 \text{ mole} = 27 \text{ g} \)
  - Au (atomic weight = 197) \( \quad 1 \text{ mole} = 197 \text{ g} \)

• **Mole** of a molecular substance: *the molecular weight expressed in grams*

  Example:  
  - \( \text{H}_2\text{O} \) (molecular weight 2+16=18) \( \quad 1 \text{ mole} = 18 \text{ g} \)
Important property: whatever the substance, 1 mole contains the same number $N_A$ of “particles”:

$$N_A = 6 \times 10^{23} \quad \text{Avogadro’s number}$$

- **Concentration of a solution**:
  
  $\frac{\text{moles of solute}}{\text{moles of solvent}}$  
  
  Abbrev. : $\text{mol/l} = \text{Molar}$

- **pH of a solution**:
  
  $$\text{pH} = -\log_{10} [H^+]$$

  $[H^+] = \text{concentration of hydrogen ions in mol/l}$

  - $\text{pH} < 7$  
    - *acidic* solution
  - $\text{pH} > 7$  
    - *basic* solution
• **Electrolyte**: a solution which is also an ionic conductor. For NaCl in water, for instance, due to the high relative permittivity of water ($\varepsilon_r = 80$), the electrostatic force keeping the Na$^+$ and Cl$^-$ together is much lower than in air. The two ions separate and can move under the action of an electric field. Like in a semiconductor there are positive and negative charge carriers, but in this case they are ions, not electrons and holes!

• **Redox**: reduction-oxidation reaction, describes all chemical reactions in which atoms have their oxidation state changed. Oxidation is the loss of electron or increase in oxidation state by a molecule, atom or ion. Reduction is the gain of an electron.

**Discussion**: what is ionic conductor and what’s the difference between ionic conductor and electronic conductor?
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Electrochemistry is the study of structures and processes at the interface between an electronic conductor (the electrode) and an ionic conductor (the electrolyte).

We start from an ideal case: a planar metal electrode in contact with an electrolyte with no chemical reactions occurring between the electrolyte and the metal.

Like in the case of a metal-semiconductor junction, charge neutrality requires:

\[ Q_M = -Q_S \]

\( Q_M \) charge on metal, all the surface
\( Q_S \) charge in electrolyte; distributed in a volume next to the interface

The resulting charge distribution – two regions of equal and opposite charge – is known as the electrical double layer. It can also be viewed as a capacitor.
The double layer capacitance depends on:

- applied potential
- electrolyte ionic strength

Three models frequently used to describe the metal/electrolyte interface:

- Helmholtz model
- Gouy-Chapman model
- Gouy-Chapman-Stern model

$E_z$: potential of zero charge
The earliest model presented for the double layer:

- Opposite charge in solution resides at the surface of the charged electrode;
- Two sheets of charge, having opposite polarity, separated by a distance of molecular order, \( d \).

=> The double layer was first considered as a parallel plate capacitor:

\[
C_D = \frac{\varepsilon \varepsilon_0}{d}
\]

Like an ordinary capacitor where its capacitance is independent of the potential.

**Problem:** In practice, the double layer capacitance is NOT independent of the potential applied, and it is also a function of the electrolyte concentration!
A simple but surprisingly accurate theory was proposed independently by Gouy and Chapman in 1910. The basic ideas are the following:

• The solution is modeled as point ions embedded in a dielectric continuum representing the solvent;

• The metal electrode is considered as a perfect conductor;

• The distribution of the ions near the interface is calculated from electrostatics and statistical mechanics.
We consider a planar electrode in contact with a solution of a $z - z$ electrolyte, i.e. cations of positive charge $+zq$ and anions of negative charge number $-zq$, $q = 1.6 \times 10^{-19}$ coulomb, the electronic charge.

The electrode surface is situated in the plane at $x = 0$.

The treatment is similar to that of the depletion region of a Schottky barrier in semiconductors. The electrostatic potential $\psi(x)$ obeys Poisson's equation:

$$\frac{d^2 \psi}{dx^2} = -\frac{\rho(x)}{\varepsilon \varepsilon_0}$$  \hspace{1cm} (1)

\begin{align*}
\rho(x) & \quad \text{charge density in the electrolyte} \\
\varepsilon & \quad \text{dielectric constant of the solvent} \\
\varepsilon_0 & \quad \text{permittivity of the vacuum}
\end{align*}
Assign \( n_+(x) \) and \( n_-(x) \) as densities of cations and anions in the solution in the bulk:

\[
\text{near the interface there is a net charge:}
\]

\[
\begin{align*}
\psi(\infty) &= 0 \quad \text{(2)} \\
\end{align*}
\]

The ionic densities depend on the potential. We choose \( \psi(\infty) = 0 \) as our reference, and apply Boltzmann statistics:

\[
\begin{align*}
\rho(x) &= n(x) = \left( \frac{2\pi m kT}{\hbar^2} \right)^{\frac{1}{2}} e^{-\frac{zq(x)\psi(x)}{kT}} \\
\end{align*}
\]
Substituting Eqn. (3) and (4) into Eqn. (1):

**Poisson-Boltzmann Equation**

\[
\frac{d^2 \psi}{dx^2} = -\frac{zq n_0}{\varepsilon \varepsilon_0} \left[ \exp\left(-\frac{zq \psi(x)}{kT}\right) - \exp\left(\frac{zq \psi(x)}{kT}\right) \right]
\]

Simple case: \( \frac{zq \psi(x)}{kT} \ll 1 \)

\[
\frac{d^2 \psi}{dx^2} = k_D^2 \psi(x)
\]

where:

\[
L_D = 1 / k_D \text{ is the Debye length}
\]
Solution: \( \psi(x) = \psi(0) \exp(-k_D x) \)

To find \( \psi(0) \): Charge neutrality:

\[
\int_0^\infty \rho(x) dx = -Q_M
\]

(9)

\( Q_M \) charge /unit surface on electrode surface

From Eqn. (1) and (6):

\[
\psi(x) = -\frac{\rho(x)}{\varepsilon \varepsilon_0 k_D^2} \Rightarrow \rho(x) = -\varepsilon \varepsilon_0 k_D^2 \psi(x)
\]

From Eqn. (8) and (9):

\[
\psi(0) = \frac{Q_M}{\varepsilon \varepsilon_0 k_D^2}
\]

(10)

Therefore:

\[
\psi(x) = \frac{Q_M}{\varepsilon \varepsilon_0 k_D^2} \exp(-k_D x)
\]

(11)
What determines the charge and therefore the potential of the electrode?

Answer: The chemistry at the electrode-solution interface.

That’s how a battery works: place two different metals in a solution and you can measure a potential difference between the two metals.

If the potential of one electrode is fixed (reference electrode) and the potential of the other is varied through an external voltage source, for a certain voltage $V_{pzc}$ we shall have:

$$\psi(0) = 0 \quad Q_M = 0$$

$V_z$ potential of zero charge
Double layer potential profile:

\[ \psi(x) = \psi(0) \exp(-k_D x) \]

where

\[ \psi(0) = \frac{Q_M}{\varepsilon_0 \varepsilon k_D} \]

Note: \( \psi(0) \) is related monotonically to \( Q_M \)

\[ k_D = \left( \frac{2(zq)^2 n_0}{\varepsilon \varepsilon_0 kT} \right)^{1/2} \]

**Concentration**

\( n_0 \) mol / l

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<tr>
<th></th>
<th>10^{-4}</th>
<th>10^{-3}</th>
<th>10^{-2}</th>
<th>10^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye length=1/k_D Å</td>
<td>304</td>
<td>96</td>
<td>30.4</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Potential exponentially decays through the diffuse layer from the interface, in Gouy-Chapman model.
The assumption made between Eqn. (5) and (6),

\[
\frac{zq\psi(x)}{kT} << 1
\]

oversimplified the model.

Remove this simplification results Grahame equation:

\[
Q_M = (8kT \varepsilon \varepsilon_0 n_0)^{\frac{1}{2}} \sinh\left(\frac{zq\psi(0)}{2kT}\right)
\]

(12)

Note the potential is still related monotonically to the state of charge on the electrode.
The differential capacitance is defined as

\[ C_D = \frac{d\sigma}{d\psi(0)} \]  

(13)

Substitute \( \sigma \) with \( Q_M \) from Eqn. (12), hence

\[ C_D = \frac{dQ_M}{d\psi(0)} = \left( \frac{2z^2q^2\varepsilon_0n_0}{kT} \right)^{1/2} \cosh \left( \frac{zq\psi(0)}{2kT} \right) \]

(14)

For dilute aqueous solution at room temperature, (14) can be written

\[ C_D = 228qC^*^{1/2} \cosh[19.5q\psi(0)] \]

(15)

where \( C^* \) is the concentration of the electrolyte
Double layer capacitance calculated from Eqn. (15) for the indicated concentrations of a 1:1 electrolyte in water at 25°C
• The double layer capacitance calculated from Gouy-Chapman model increase unlimitedly with potential.

• Ions have a finite size and cannot approach the surface any closer than its only radius.

• Define a plane of closest approach for the centre of the ions at distance $x_2$

• The plan at $x_2$ is called outer Helmholtz plan (OHP)

• Total capacitance is serial connection of diffuse layer capacitance and OHP capacitance.
The total double layer capacitance now is

$$C_d = \frac{1}{C_a} = \frac{1}{\frac{2z^2 q^2 \varepsilon \varepsilon_0 n_0}{kT}} \left( \cosh \left[ \frac{zq\psi(0)}{2kT} \right] \right) + \frac{x_2}{\varepsilon \varepsilon_0}$$

Gouy-Chapman-Stern Model
From Eqn. (18), the expected behaviour of double layer capacitance is...
Helmholtz Layer: $x_H \sim 1\text{nm}$

Diffuse Layer

Helmholtz Layer: $x_H$
dielectric with constant capacitance $C_H$

$C_H = \frac{\varepsilon \varepsilon_0}{x_H}$

For $\frac{zq\psi(x)}{kT}$ not $<< 1$

$$\psi(0) = \frac{Q_M}{C_H} + \frac{2kT}{ze} \sinh^{-1} \left[ \frac{Q_M}{(8kT\varepsilon\varepsilon_0 n_0)^{1/2}} \right]$$
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Helmholtz Layer: \( x_H \)  
Diffuse Layer

FREE ELECTRON CHARGE

Fixed interface charge due to surface reactions
Ion-Sensitive-Field-Effect Transistor (ISFET)

MOS

- electrolyte
- dielectric
- Si

Electrolyte

MOSFET

- electrolyte

Fixed interface charge due to surface reactions
\[ \psi_L = \frac{Q_{\text{int}}}{C_{\text{dl}}} \]

where: \( Q_{\text{int}} = \) charge on insulator surface

\( C_{\text{dl}} = \) capacitance of the electrochemical double layer

\[ V_{\text{FB}} = \phi_E - \phi_S - \psi_L \]
What is $Q_{\text{int}}$ due to? - Surface Adsorption / Desorption for SiO$_2$

1. Surface Dangling Bonds on SiO$_2$

\[
\begin{array}{c}
\text{Si} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{Si} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{Si} \\
\text{O} \\
\end{array}
\]

2. Ions in aqueous solution form bonds at surface.

eg. Water: $\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$
Ion-Sensitive-Field-Effect Transistor (ISFET)

3. Acidic / Basic Reactions at Surface:

\[ \text{SiOH} + \text{H}_s^+ \rightarrow \text{SiOH}_2^+ \]

\[ \text{SiOH} \rightarrow \text{SiO}^- + \text{H}_s^+ \]
** Ion-Sensitive-Field-Effect Transistor (ISFET) **

\[
\text{SiOH} + H_S^+ \rightarrow \text{SiOH}_2^+ \\
\text{BASE} \quad K_b = \frac{[\text{SiOH}_2^+]}{[H_S^+] [\text{SiOH}]} \\
\]

\[
\frac{K_a}{K_b} = \frac{[H_S^+]^2 [\text{SiO}^-]}{[\text{SiOH}_2^+]} \\
\]

\[
[H_S^+] = \sqrt{\frac{K_a}{K_b} \frac{[\text{SiOH}_2^+]}{[\text{SiO}^-]}} \\
\]

\[
\begin{align*}
[\text{SiOH}^-] & \quad \text{Concentration of } \text{SiO}^- \text{ on the insulator surface} \\
[\text{SiOH}_2^+] & \quad \text{Concentration of } \text{SiOH}_2^+ \text{ on the insulator surface} \\
\end{align*}
\]
Ion-Sensitive-Field-Effect Transistor (ISFET)

To find the double layer potential $\psi_L$:

Boltzmann relationship

$$\left[ H^+_S \right] = \left[ H^+_b \right] \exp \left( -\frac{q\psi_L}{kT} \right)$$

where

$\left[ H^+_b \right]$ Concentration of H$^+$ in the solution bulk

$$-\ln \left[ H^+_b \right] + \ln \left( \frac{K_a}{K_b} \right)^{\frac{1}{2}} = -\frac{q\psi_L}{kT} + \ln \left( \frac{[\text{SiO}^-]}{[\text{SiOH}_2^+]} \right)^{\frac{1}{2}}$$

$$-\ln \left[ H^+_b \right] + \ln \left( \frac{K_a}{K_b} \right)^{\frac{1}{2}} \approx -\frac{q\psi_L}{kT}$$

$pH = -\log_{10} \left[ H^+_b \right]$  and  $pH_{pzc} = -\log_{10} \left( \frac{K_a}{K_b} \right)^{\frac{1}{2}} = \text{constant}$

$$\psi_L = 2.303 \frac{kT}{q} (pH_{pzc} - pH)$$

$\Delta\psi_L = 59 \text{mV/(pH unit)}$  at  $300^\circ \text{K}$
pH Sensor – Poly-Si TFT with Si₃N₄ gate

$V_{GS} = -(V_S \text{ vs } V_{Ag/AgCl})$

$V_{DS} = 0.1 \text{ V}$

54 mV/pH-unit

W/L = 10 µm / 6 µm
Si₃N₄ pad: 990 x 990 µm²

An ISFET senses and amplifies the change in Double layer potential due to the change in pH.

pH measurements are important (blood pH).

By functionalising the gate insulator organic/bio/inorganic compounds can be detected.