Electrochemical Sensors and Their Impedances: a Tutorial

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ABSTRACT: Electrochemical sensors are the largest group of chemical sensors. It is shown that electrical impedances play crucial role in design, construction, and interpretation of the results obtained with these sensors. It is also shown that impedances are implicated not only in the transduction mechanism but also in interpretation of selectivity of these sensors.

I. INTRODUCTION

Electrical impedances play an important role in electrochemical sensors. In this tutorial a generalized approach to operating principles of electrochemical sensors is offered from a somewhat nonconventional perspective. It casts them in terms of equivalent circuit elements. It does not introduce any new concepts but offers a different explanation of most important governing electrochemical phenomena of this largest group of chemical sensors. There are three important points in equivalent circuit analysis: (1) description of individual physical processes by realistic equivalent circuit elements; (2) arrangement of these elements in rationally constructed equivalent circuit; (3) optimization of values of the elements in the equivalent circuit such that the overall transfer function (response) matches the response of the real cell. This approach may be particularly appealing to students who are more familiar with electrical circuits than with fundamentals of physical chemistry.

Every electrochemical sensor is an electrochemical cell that consists of minimum two electrodes, A and B, serving as contacts to the electrolyte (Figure 1). The cell current, I_{cell}, is governed by the cell voltage, E_{cell}, and by the cell impedance, Z_{cell}, according to the generalized, frequency (ω) dependent Ohm's Law

$$I_{cell}(\omega) = \frac{E_{cell}(\omega)}{Z_{cell}(\omega)} \tag{1}$$

Individual electrochemical processes are represented by simple circuit elements. Thus for example, transformation of electronic to ionic current (i.e., Faradaic electrolysis) is represented by equivalent voltage dependent resistor (i.e., diode), transport of ions in the electrolyte is represented by impedance of the transmission line, separation of charge at the interface by a capacitor, etc. One circuit element that has not yet appeared on the sensor scene is the inductance. The overall cell impedance is then the sum of impedances in the path of the cell current.

$$Z_{cell} = Z_A + Z_B + Z_{EL} \tag{2}$$

The simplest form of impedance is the parallel combination of capacitor C and resistor R.

In this simple circuit the flow of electrons (i.e., the current I) is divided into two branches, one containing the capacitor (i_C) and the other the resistor (i_R). According to the Kirchoff's law $I = i_C + i_R$. The ratio of the two currents is dictated by the respective admittances (i.e., frequency dependent resistances) of the two branches. The overall admittance is their sum

$$\frac{1}{Z} = \frac{1}{R} + j\omega C = \frac{1 + j\omega RC}{R} \tag{3}$$

It is useful to perform the dimensional analysis of Z, at this point. The charge on a capacitor C is related to the voltage E as $Q = CE$ and to the current as $[Q] = [I] [\tau]$. Therefore
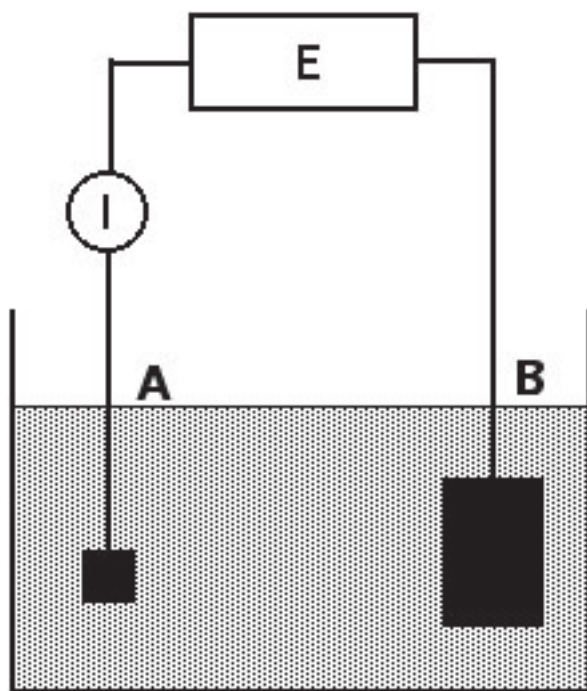
FIGURE 1. General representation of electrochemical sensor.

$$[RC] = \left[\frac{E}{I}\right] \times \left[\frac{Q}{E}\right] = \left[\frac{I \times \tau}{I}\right] = [\tau] \qquad (4)$$

Symbol τ is used to represent the time constant. Therefore, the knowledge of equivalent values of R and C can help to identify the processes reponsible for the response time of chemical sensors.

Frequency ω plays important role in the analysis of equivalent electrical circuits. However, time response of most chemical sensors to the chemical stimulus is usually limited by the relatively slow mass transport. In other words, its frequency approaches zero and it is possible to replace the impedances by resistors $(Z)_{w=0} = R$. Thus,

$$R_{cell} = R_A + R_B + R_{EL} \qquad (5)$$

Unfortunately, this is where the simplifications end. The resistances representing the electrochemical processes are complex and usually unknown functions of concentration, potential, and time

$$R's = f(C, E, t) \qquad (6)$$

In the following sections, the behavior and the meaning of these resistances will be related to the underlaying electrochemical processes.

II. CHEMIRESISTORS

Chemiresistors are the simplest electrochemical sensors. They consist of the sensing layer positioned between two contacts (electrodes). The sensing layer can be ionic liquid and ionic or electronic solid. Because they are relatively easy to fabricate they are inexpensive and very popular. However, interpretation of their response can be quite tricky.

In the simplest realization of a chemiresistor the resistance of the selective layer is much higher than that of the contacts

$$R_{EL} >> R_A, R_B \qquad (7)$$

If the sensing layer is ionic (i.e., an electrolyte) transformation of electronic to ionic charge (electrolysis) takes place at the electrode/sensing layer interface:

$$O + ne \Leftrightarrow R \qquad (8)$$

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where the oxidized species O is reduced by n number of electrons to R. The two-way arrow in Eq. 8 implies that this transformation is reversible.This process is governed by the Faraday's law which is one of the fundamental relationships of electrochemistry

$$m = \frac{Q}{nF} \qquad (9)$$

In this equation, Q is the total charge passing through the interface and F is the Faraday constant (96,493 Coulombs), which is the amount of electrical charge required to transform one mole of oxidized species to its corresponding reduced form or *vice versa*. It is obvious that passage of DC **electronic** current through the contact/ionic electrolyte interface results in **chemical** changes according to Eq. 8. This phenomenon is known as *chemical polarization*. If it takes place in chemiresistors it is invariably the cause of changing contact resistances R_A and R_B. It is invariably a source of drift in chemiresistors using **ionic** selective layer This problem does not exist in selective layers that are electronic conductors.

The schematic representation of a chemiresistor is shown in Figure 3a and its equivalent circuit in Figure 3b. The most successful chemiresistors are semiconducting oxides, such as SnO_2 sensors that depend on the chemical modulation of the surface resistance R_{surf}. Another common group of chemiresistors uses measurement of bulk resistance (R_b) of electronically conducting polymers. In both cases the charge transport is entirely electronic. The parasitic par-

allel resistances due to the interface resistance R_{int}, and the lack of understanding of the explicit relationship between concentration of the analyte and the conductivity are the most common problems in interpretation of chemiresistor data. The measurements are usually performed under constant applied voltage and the measured variable is the DC current.

There is a special class of sensors that relies on the changes of capacitances. In the context of this tutorial they are grouped with chemiresistors because the sensing parameter is the impedance. An important distinguishing feature of these sensors is the fact that they **may contain ionic sensing layer**. Their excitation is usually done by sinusoidal voltage of low amplitude (~10 mV) and frequency from tens of Hz to hundreds of kHz. The AC current is the observed variable. In an ideally reversible system there is no net chemical change because the electrochemical reactions in the "positive" and "negative" half-periods of the cycle cancel out. The phase relationship between the applied voltage and the observed current, and its frequency dependence play an important role in the impedance analysis of the signal. The starting point for such analysis of these sensors are Eqs. 2 and 3. Capacitive humidity sensors, water quality monitors and various capacitive biosensors belong to this group. They often use so-called "interdigitated electrodes" layout (Figure 4).

IN CHEMIRESISTORS, THE CHEMICAL SENSING INFORMATION IS CONTAINED IN THE **LARGEST** RESISTOR IN THE **SERIES** CONFIGURATION OR IN THE **SMALLEST** RESISTOR IN THE **PARALLEL** CONFIGURATION.
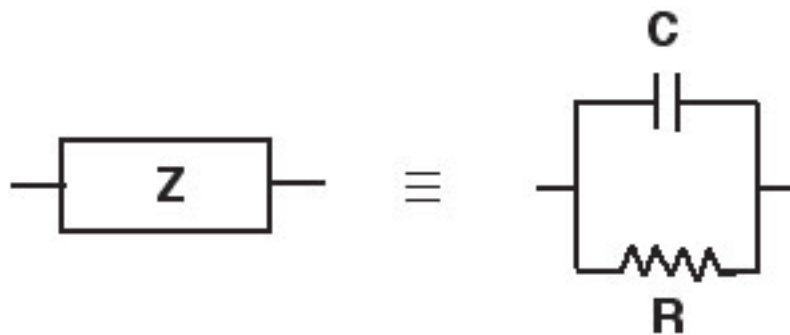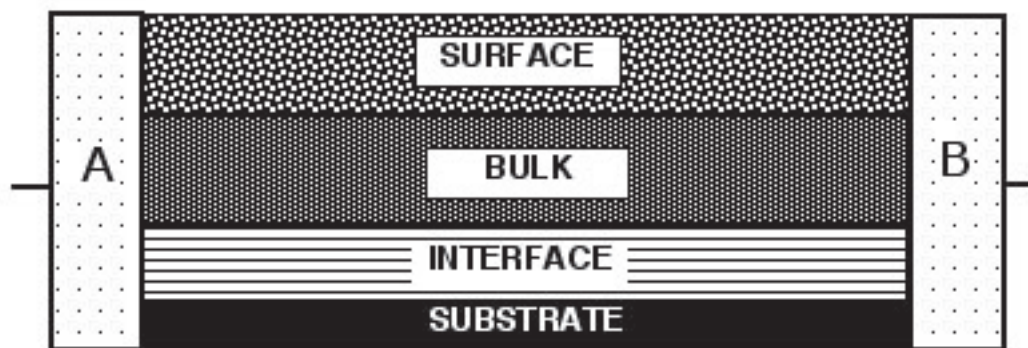

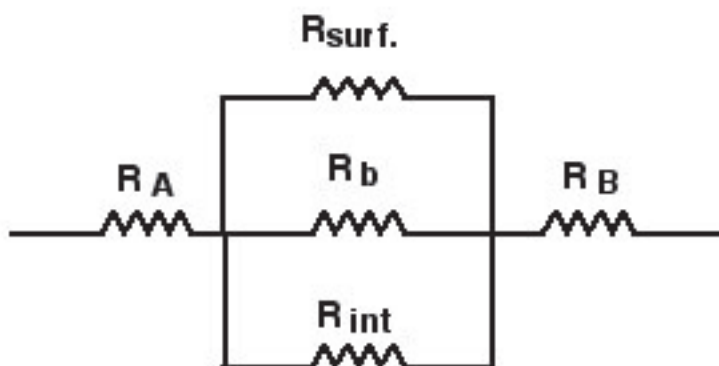**FIGURE 2.** Simplest electrical impedance found in electrochemical sensors.

(a)

(b)

FIGURE 3. Types of resistances and found in chemiresistors. (a) general chemiresistor; (b) equivalent circuit.

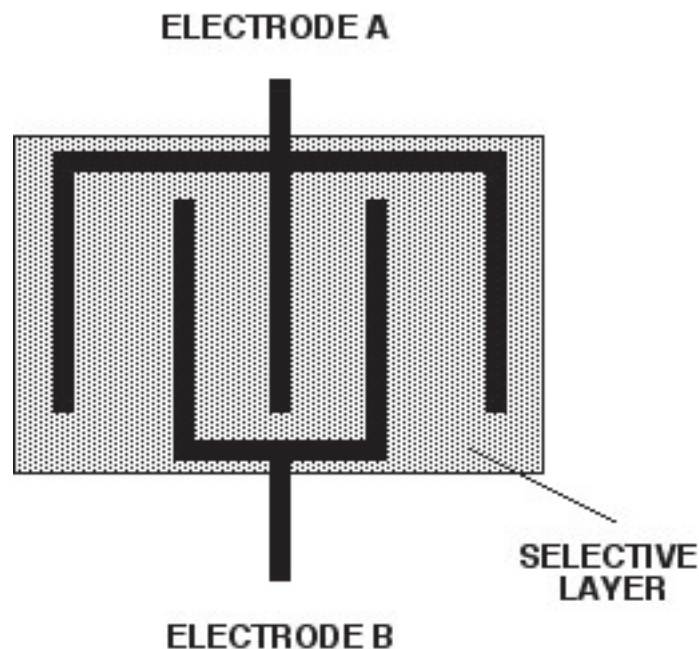**112**

ELECTRODE A

FIGURE 4. Interdigitated electrode layout commonly used in chemiresistors.

III. AMPEROMETRIC SENSORS

As the name implies, the experimental variable in amperometric sensors is current. Impedances again play major role in amperometric sensors. The equivalent electrical circuit corresponding to the electrochemical cell in Figure 1 is shown in Figure 5. Each interface at electrodes A and B can be represented by parallel combination of capacitor C_d and resistor $R_{A,B}$. These elements have an important electrochemical meaning and are crucial for understanding of responses of amperometric sensors. The interpretation can be greatly simplified by a judicious design of the electrochemical cell. It is customary to make the surface area of the **auxiliary** electrode much larger than that of the **working** electrode. In that case the interfacial capacity of the auxiliary electrode becomes correspondingly larger than that of the working electrode and the interfacial resistance of the auxiliary electrode becomes much smaller. Therefore, in the equivalent circuit the impedance associated with the auxiliary electrode becomes negligible when compared with the impedance of the working electrode. Furthermore, there is no separation of charge in the bulk of the electrolyte at low frequencies, and therefore the bulk impedance can be represented by a resistor R_s placed in series

with the electrode resistance. There is another added bonus to making the working electrode smaller: It defines the **polarity** of the applied voltage. Thus, the phrase "positive applied voltage" means that the working electrode is positive with respect to the reference (or auxiliary) electrode. Obviously, such a statement would be meaningless if the two electrodes were identical. In most amperometric sensing applications the conductivity of the electrolyte is high, therefore

$$R_A \gg R_B; R_S \tag{10}$$

We now examine this statement in detail. The electrode resistance can be formally represented as the sum of charge transfer resistance, R_{ct}, and the mass transport resistance, R_{mt}.

$$R_A = R_{ct} + R_{mt} \tag{11}$$

If an increasing voltage is applied to the electrodes shown in Figure 1 the current response is highly nonlinear (Figure 6). This is due to the complex nature of the polarization of the working electrode. The current-voltage curve A in Figure 5 defines so-called "electrochemical window", that is, the operating range of potentials of the amperometric sensor. Outside this window (i.e.,
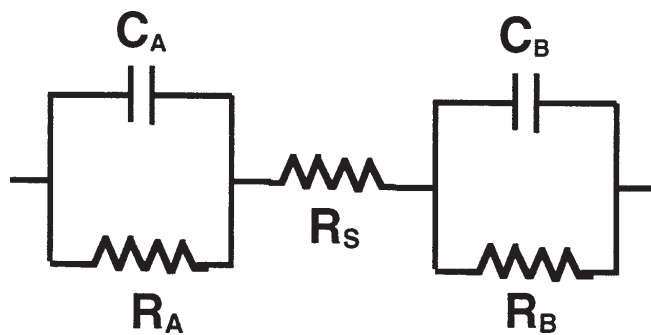
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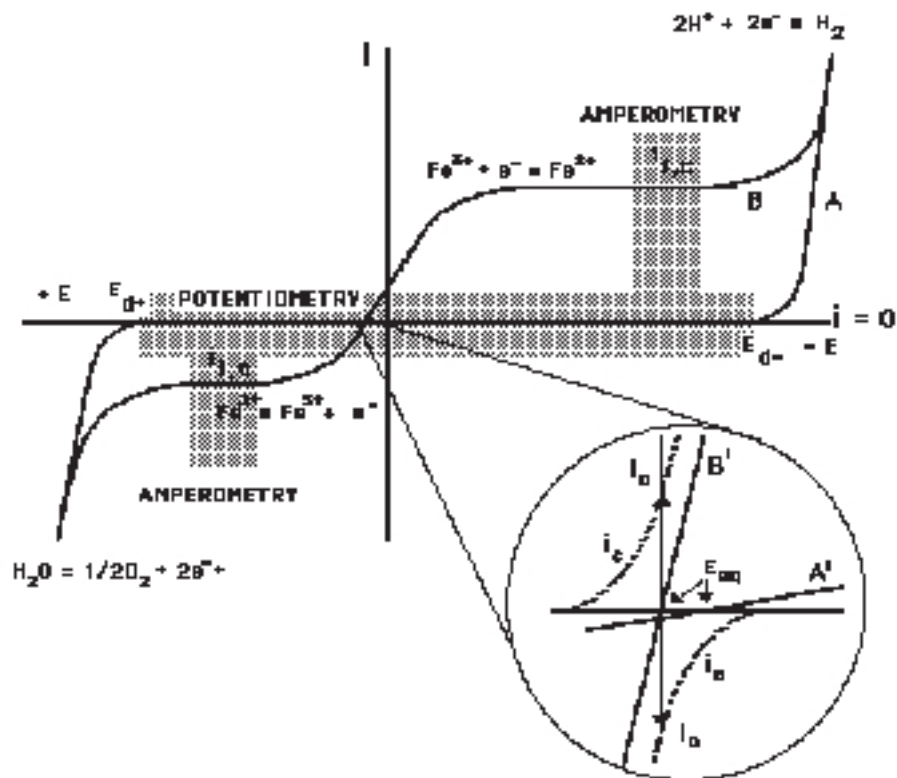**FIGURE 5.** Equivalent electrical circuit corresponding to cell in Figure 1.

FIGURE 6. Current-voltage curve in electrochemical cell.

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at $E_{d+} < E < E_{d-}$) the electrolysis of the supporting electrolyte takes place. The span of this window depends on the electrode material and on the composition of the electrolyte. This window is shown for aqueous electrolyte where the limiting (i.e., decomposition) potentials are given by the reduction and oxidation of water, respectively (Figure 6).

In the ideal case there is virtually no current in the potential region between E_{d+} and E_{d-}. Therefore, the electrode can be represented by a simple double layer capacitor C_{dl} (Figure 5). Its value can be determined by *impedance spectroscopy*. In this *ideal* situation the R_A is infinitely large (i.e., there is no Faradayic reaction). The addition of electrochemically active (i.e., Eq. 8) compounds such as redox couple Fe^{III}/Fe^{II} shown in Figure 5 results in current-voltage curve B. This remarkable change of response pattern is due to the fact that the equivalent electrode resistor R_A now has a finite value and the DC current can flow through the resistive branch of the equivalent circuit (Figure 2)

A. Charge-Transfer Region

The potential at which curve B crosses the zero current line has a special meaning in chemical sensing. It is this potential that governs the response of *potentiometric sensors*. Therefore, electrochemical cell at zero current is the **domain of equilibrium potentiometric sensors**. We discuss potentiometric sensors later.

The *nonideality* in all electrode reactions is highlighted in the circle in Figure 6. In real electrode reactions the current curve "A" has a non-zero value at all potentials other than E_{eq}. In this case the electrode reaction is said to be "**charge-transfer limited**" and $R_A = R_{ct}$. The double-sided arrows in Eq. 8 imply that even at the equilibrium potential the reaction proceeds in both directions, but **at the same rate.** This, in turn, means that there are two currents, equal but opposite in sign passing through the electrode. They are called **exchange currents**[1] i_a (anodic) and i_c (cathodic), and are shown as dashed curves in the circular inset in Figure 6. The exchange currents for curve A' are much smaller than those for curve B and

are not shown for the sake of clarity. The concept of exchange reactions is common in physical chamistry. It is very important in chemical sensors. First, because the magnitude of those two currents is the same there is **no net electrochemical transformation**. Second, the magnitude of these currents determines how fast will the equilibrium be reached, following an external perturbation. Thus, we talk about "fast equilibrium" (i.e., large exchange current) or "slow equilibrium" (low exchange current) reactions. The curves B' and A' correspond to such "fast" and "slow" equilibria, respectively. Third, at $i = 0$ the slope of the current B' and A' has dimensions of conductance

$$\left(\frac{di}{dE}\right)_{i=0} = \frac{1}{R_{ct}} \tag{12}$$

Thus, R_{ct} is intrinsically linked to the shape of the current-voltage curve. The rates of electrochemical conversions due to the exchange currents are

$$j_c = k_c nFAC_O(0) = k_a nFAC_R(0) = -j_a \tag{13}$$

Naturally, there is no net conversion since the two processes are equal and opposite in magnitude. The equilibrium constant for Eq. 8 is

$$\frac{k_c}{k_a} = K = \frac{C_R(0)}{C_O(0)} \tag{14}$$

The rate constants k_c and k_a increase exponentially with the applied potential.

$$k_c = k_0 \exp[-\frac{\alpha nF}{\Re T}(E - E_{eq})] \tag{15a}$$

and

$$k_a = k_0 \exp[\frac{(1-\alpha)nF}{\Re T}(E - E_{eq})] \tag{15b}$$

Consequently, the current increases as the applied potential E departs from the equilibrium

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[1]   Strictly speaking, the exchange current is defined only for the condition when the activities of oxidized and reduced species in Eq. 8 are equal. In that case the symbol used for exchange current is j_0 (see Bard and Faulkner).

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potential E_{eq} (Figure 6). Exponential dependence of current on applied voltage is characteristic for diode that could be used as equivalent circuit element in the modeling of amperometric sensors.

The magnitude of the exchange current, j_0, is directly related to the charge transfer resistance, R_{ct}. This relationship can be obtained by linearizing this exponential function (Eq. 15) (Bard and Faulkner). It can be shown that the exchange current is inversely proportional to the charge transfer resistance.

$$j_0 = \frac{nF}{\Re T R_{ct}} \qquad (16)$$

FAST, REVERSIBLE CHARGE TRANSFER MEANS LOW CHARGE TRANSFER RESISTANCE

The rates of interfacial reactions are always normalized to the unit area. Thus, exchange current j_0 becomes exchange current **density** i_0. This is another reason why the working electrode A must be **smaller** than auxiliary electrode B, if we wish to neglect electrochemical processes taking place at the auxiliary electrode. This point is frequently missed when, for convenience of fabrication, electrodes of equal area are used in some amperometric sensors.

B. Mass Transfer Region

At potentials other than the equilibrium potential, the net current through the electrode interface is finite. However, it is linear (i.e., follows the Ohm's law) only in the vicinity of E_{eq}. As the potential increases it becomes highly nonlinear and eventually reaches some limiting value given by the rate of mass transport of the species involved in Eq. 8 to/from the electrode surface. This is said to be "**mass transport limited** region" . It defines the **domain of *amperometric sensors***. In this region the electrode resistance equals the mass transport resistance.

The second term in the electrode resistance (Eq. 11) is the mass transport resistance. As the applied potential increases the R_{ct} decreases and can be neglected against R_{mt}. In that case the electrolytic current depends on the rate of mass transport of the electroactive species from the bulk of the solution to the surface of the electrode according to

$$I = nFAm_0(C_O^* - C_O(0,t)) \qquad (17)$$

Where $C_O(0,t)$ is the time-dependent surface concentration of reducible species, O. When electronic current passes through the electrode surface $C_O(0,t) < C_O^*$. As the rate of charge transfer becomes high surface concentration reaches zero and the current becomes limited by the mass transport. Under those conditions

$$I = nFAm_0 C_O^* \qquad (18)$$

The mass transport coefficient m_O depends on the conditions of the experiment and on the diffusion coefficient. In the simplest case, where there is **no motion of the sensor with respect to the sample** the mass transport coefficient depends only on the diffusion coeffient, D_O, and on the thickness of the diffusion layer δ_O

$$m_0 = \frac{D_o}{\delta_o} \qquad (19)$$

The thickness of the diffusion layer grows in time according to the Einstein-Smoluchovski equation

$$\delta_O = (2D_O t)^{1/2} \qquad (20)$$

Substitution of Eqs. 17 and 18 yields[*]

$$i_L = \frac{nFAD_O^{1/2}C_o}{1.4t^{1/2}} {}_½ \qquad (21a)$$

From the sensing point of view this is an undesirable situation because the amperometric signal changes both with time and with concentration of the analyte C_O (Figure 7).

[*] The exact solution of this problem is the Cottrell equation in which the coefficient 1.4 in Eq. 18 is replaced by factor $\pi^{1/2}$.
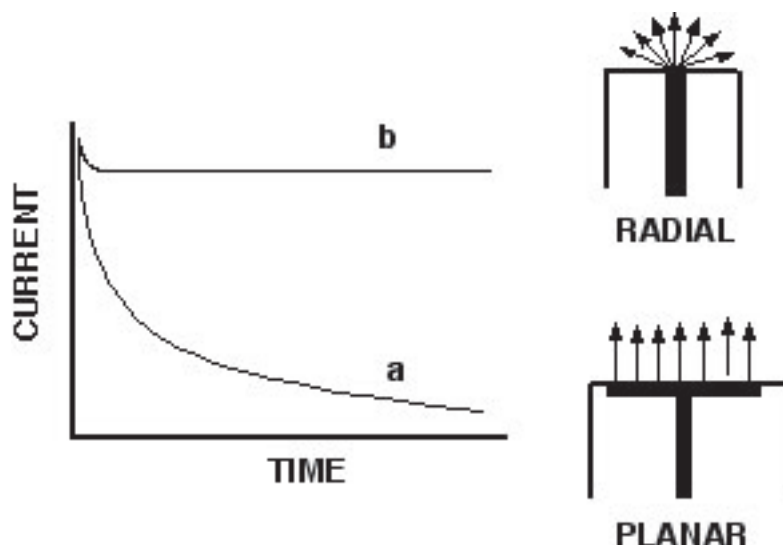
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FIGURE 7. Dependence of current on time for (a) planar diffucion to a macroelectrode and (b) radial diffusion to a microelectrode.

When the dimensions of the working electrode are comparable to the diffusion length of the analyte the **planar** mode of diffusion changes into **radial** mode of diffusion and the equation for the current at such **microelectrode** is (Figure 7, curve a)

$$I(t) = \frac{nFAD_o^{1/2}}{\pi^{1/2}} \frac{C_o}{t^{1/2\ 1/2}} + \frac{nFAD_O^{1/2}C_o}{r_o}$$

(21b)

A short time after the beginning of electrolysis the first term in Eq. 21 can be neglected and the mass transport limited current becomes constant (Figure 7, curve b)

$$I(t) = \frac{nFAD_o^{1/2}\ C_o}{r_o}$$

(22)

The largest characteristic dimension in modern amperometric sensors is on the order of a few microns. Their response obeys Eq. 22.

The discussion of temporal behavior of the amperometric sensors has been done in terms of the limiting current. However, because the applied voltage is constant it is obvious that the parameter responsible for the current variation is actually the mass transport resistance, $R_{mt.}$ For a given voltage range $<E>$, that is, in the mass

transport limited region, the mass transport resistance of a macroelectrode increases with time as

$$R_{mt} = \frac{1.4t^{1/2} <E>}{nFAD_o^{1/2} C_o^{1/2}}$$

(23)

for macroelectrodes, or becomes constant for the microelectrodes

$$R_{mt} = \frac{r_o <E>}{nFAD_o^{1/2}C_o}$$

(24)

1. Selectivity of Amperometric Sensors in Terms of Resistances

Selectivity is defined as the fraction of the overall response of a sensor to the species of interest in the presence of interfering species. For multiple electroactive species detectable by amperometric sensor we can write

$$i_{cell} = i_1 + i_2 + \ldots\ldots i_R$$

(25)

where i's are the partial currents contributing to the overall cell current i_{cell}. From the Ohm's law each of these partial currents can be expressed as the ratio of one common applied voltage $<E>$ and

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partial electrode resistance R_n. Because the electrode resistance is the sum of charge transfer and mass transport resistances (Eq. 11), we can write for each species

$$i_{cell} = \langle E \rangle \left(\frac{1}{R_{ct,1} + R_{mt,1}} + \frac{1}{R_{ct,2} + R_{mt,2}} + ... + \frac{1}{R_{ct,n} + R_{mt,n}} \right)$$

(26)

The equivalent circuit corresponding to this resistive network is shown in Figure 8. This seemingly trivial circuit can help us to design the best strategy for selectivity of amperometric sensors. The current carrying information about the analyte will flow through the path of the lowest resistance. It has been stated before that charge transfer resistances decrease exponentially with applied voltage. Obviously, because the applied voltage is **common** to all partial resistances this is not the best way to achieve selectivity. The same can be said about increasing the temperature because, again, all rate constants are affected in a similar way.

Much more fruitful approach to selectivity is to increase the rate constant of the desired reaction. This can be done by catalysis. Thus, for example, incorporation of highly selective oxidation catalyst such as glucose dehydrogenase (or

glucose oxidase) in the electrode proper increases the rate of charge transfer between the electrode and glucose. Thus, the enzyme effectively and selectively lowers the charge transfer resistance. Both inorganic and organic catalysts have been used to selectively lower the charge transfer resistance of selected substrates.

Manipulation of mass transfer resistances is another possibility. Let us assume that the analyte is an electrically neutral species, but the major interferant is negatively charged. By placing a cation-exchange membrane[*] in front of the electrode the access of the negatively charged species is blocked by the coulombic repulsion. This is precisely the mode of rejection of ascorbic acid (interferant) in amperometric sensing of various uncharged neurotransmitters. These selectivity design strategies can be summarized by the statement

IN AMPEROMETRIC SENSORS THE ANALYTICAL INFORMATION IS CARRIED BY THE LARGEST PARTIAL CURRENT

IV. POTENTIOMETRIC SENSORS

There is no cell current in conventionally operated potentiometric sensors, such as ion-se-

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[*] Cation exchange membrane has fixed negatively charged groups in its pore structure.
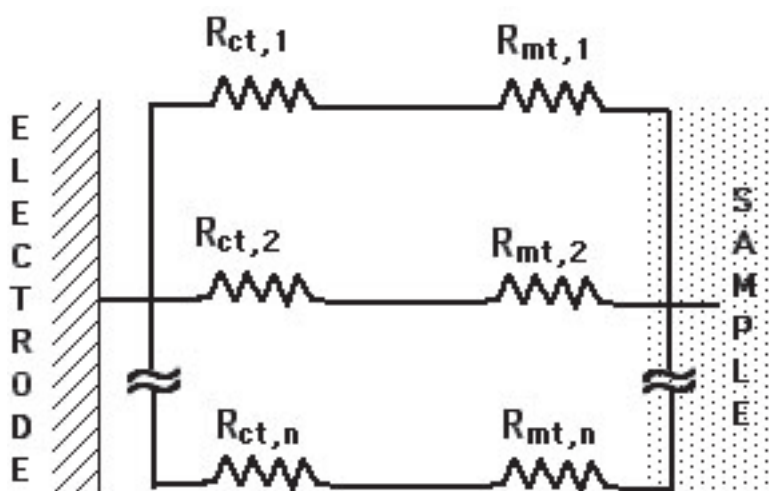

FIGURE 8. Selectivity of amperometric sensors in terms of equivalent resistances.

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lective electrodes or ISFETs. The discussion of resistances therefore seem to be a mute point. Indeed, the mass transport resistances are not an issue. However, the **exchange currents** (Eq. 13) and related charge transfer resistances are extremely important for this type of sensors because they determine their selectivity.

Let us consider an ion-exchange membrane immersed in a solution containing mixture of ions. For an **ideally selective membrane** only one kind of ion would be able to enter and leave the membrane. Therefore, the total exchange current corresponding to this ion exchange could be described by Eq. 13, and the potential of the membrane would be the equilibrium potential corresponding to this dominating exchange process. In a real situation other ions present in the solution will be able to cross the membrane/solution interface, each having its own exchange current. The magnitudes of these exchange currents can vary widely and their sum can be written as

$$J_0 = j_{0,1} + j_{0,2} + ... + j_{0,n} \qquad (27)$$

However, there is a problem: If they were separately treated these exchange currents would each have one unique equilibrium potential. However, there can be **only one** potential at the membrane/electrolyte interface, common to all exchange currents. However, such potential cannot be called "equilibrium" by definition. Another boundary condition characteristic for a multiple ion exchange is that the sum of all exchange currents has to be zero. Thus, the final potential is a kind of "compromise potential" known as **mixed potential**, E_m. Where this potential lies depends on the relative contributions of the partial exchange currents (or relative magnitude of the charge transfer resistances) to the total exchange current.

If the total **exchange current is high and the partial exchange currents are approximately equal** the interface is called **liquid junction**. It is nonselective and has low resistance. Such interface can be found in good reference electrodes. If all exchange currents are low (i.e., all charge transfer resistances are high) the total exchange current is also low and any small variation in any one charge transfer resistance will cause large

change in the mixed potential. This is the case of a **bad ion-selective electrode** or a bad liquid junction. If one exchange current is significantly higher than the rest of the exchange currents the membrane is selective to that ion and the potential of such electrode is expressed by the Eisenman-Nikolski equation

$$E = \frac{\Re T}{z_x F} \ln(a_x + \sum_0^i K_{x,i} a_i^{\frac{z_x}{z_i}}) \qquad (28)$$

where $K_{x,i}$ is the potentiometric selectivity coefficient of the membrane for ion x in preference to ion i, z's are the charges in the ions, and **a**'s are the activities. In a good ion selective electrode the dominating exchange current is so high that other exchange currents can be neglected. The design of good ion selective electrode requires that the charge transfer resistance for the dominating ion is very low and for the interfering ions it is very high.

It follows from the previous discussion that the selectivity coefficient depends on the magnitudes of the individual exchange currents. Unfortunately, this relationship is not explicit and only a general statement

$$K_{x,i} = f(a_i, R_{ct,i}) \qquad (29)$$

can be made. In other words, the concept of expressing selectivity of ion-selective membranes in terms of the exchange currents (or charge transfer resistances) is correct and very powerful; unfortunately, it is mathematically untractable for all but the simplest ion combinations. It also follows from the above discussion that the **Eisenman-Nikolski equation is not an equilibrium relationship** despite the fact that it describes measurements performed at zero net current.

One positive aspect of exchange current approach to selectivity is that the values of charge transfer resistances can be obtained experimentally by performing impedance spectroscopy.

V. CONCLUSIONS

Nonlinear dependence of current passing through the electrochemical sensing cell on ap-

plied voltage can be explained in terms of impedances that depend both on voltage and time. They can be associated with individual components of the cell. This equivalent circuit approach may aid the correct design of electrochemical sensors. It also allows experimental verification of the function (or malfunction) of the individual cell components by constructing and analyzing the equivalent electrical circuit. Impedance spectroscopy is a powerful diagnostic technique that is directly related to this approach. Almost all electrochemical sensors, including zero-current potentiometric electrodes, can be analyzed in terms of their effective impedances. The notable exception are potentiometric gas sensors based on chemical modulation of work function.

FURTHER READING

A. General electrochemistry: Bard, A.J. and Faulkner, L. "*Electrochemical Methods*", 2nd Ed., J. Wiley, New York, 2001.

B. Impedance analysis: Koryta, J., Dvorak, J.Kavan, L., "*Principles of Electrochemistry*", 2nd Ed., Wiley, New York, 1993

Macdonald, J. R. ."*Impedance spectroscopy*" , Wiley, New York, 1987.

Buck, R. P.. "Impedance diagrams applied to the investigation of ion-selective electrodes." Hung. Sci. Instrum. (1980), 49 7-23.**7.**