# Chapter 2
Irreversible and Reversible Redox Reactions: Water Window

As mentioned above, capacitive charging cannot deliver enough current if current density exceeds certain limits. The potential difference between the active (working) and the counter electrodes (used to close the electrical circuit) must remain low enough so that (almost) no redox reactions occur, if only capacitive charge injection is to follow.

Although absence of any redox reactions is ideal for electrode lifetime, these reactions are very hard to avoid. As soon as the electrode materials come in contact with an ionic solution, lots of different reactions may occur, even if no current flows into the electrode. Consider a piece of iron immersed in saline solution. After enough time, rust appears on the iron surface. Corrosion occurs following simultaneous reduction and oxidation reactions on the surface. While the metal is oxidized, oxygen (O_2) or H^+ ions are reduced at the same time to complete the redox reaction.
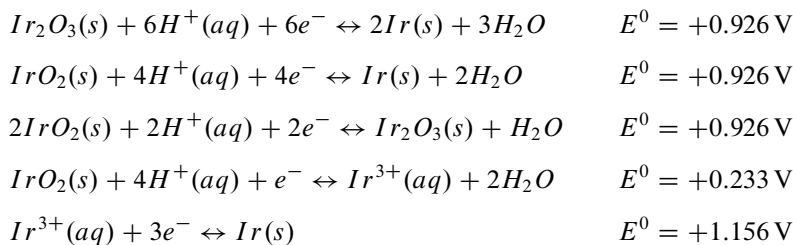
Corrosion is not limited to relatively reactive materials like iron. In TiN, in spite of the rather capacitive nature of the metal-electrode interface for charge injection, corrosion occurs at zero electrode potential in distilled water. However, the reaction is very slow and practically does not result in considerable damage even after long periods of time [6]. Titanyl (TiO_2^{2+}) ions are produced:

$$2TiN + 4H_2O \rightarrow 2TiO_2^{2+} + N_2 + 8H^+ + 12e^- \qquad (2.1)$$
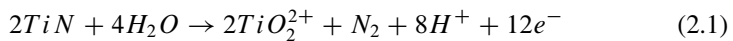
When no current flows into the electrode, the anodic current due to all the oxidation reactions and the cathodic current due to all the reduction reactions are equal. The value of this current is called the corrosion current. It is difficult but possible to experimentally measure this current indirectly for a special material in contact with some electrolyte.[1]

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[1]For details on this please refer to the corresponding application notes on www.gamry.com.

Other redox reactions become thermodynamically favorable at higher electrode potentials. It is practically impossible to find a limit where no redox reaction occurs at all. For example if iridium or iridium oxide comes in contact with water with acidic environment, the following half reactions are possible.

$$Ir_2O_3(s) + 6H^+(aq) + 6e^- \leftrightarrow 2Ir(s) + 3H_2O \qquad E^0 = +0.926\,V$$

$$IrO_2(s) + 4H^+(aq) + 4e^- \leftrightarrow Ir(s) + 2H_2O \qquad E^0 = +0.926\,V$$

$$2IrO_2(s) + 2H^+(aq) + 2e^- \leftrightarrow Ir_2O_3(s) + H_2O \qquad E^0 = +0.926\,V$$

$$IrO_2(s) + 4H^+(aq) + e^- \leftrightarrow Ir^{3+}(aq) + 2H_2O \qquad E^0 = +0.233\,V$$

$$Ir^{3+}(aq) + 3e^- \leftrightarrow Ir(s) \qquad E^0 = +1.156\,V$$

The corresponding standard reduction potentials (E^0) are given. The potentials were measured with a standard hydrogen electrode (SHE) as reference. Reduction potential is a measure of the tendency of a material to acquire electrons and be thereby reduced. Standard conditions are the conditions in which the solutes are at an effective concentration (activity) of 1 mol/dm^3 and gases are at a partial pressure of 1 bar. Temperature is 25 °C and pH = 7.[2] The standard reduction potentials of the above half-reactions are different. Therefore, avoiding every half-reaction requires obeying a different voltage limit. The above potential values cannot be used directly in practice (for neural electrode stimulation studies) as the reference electrode is not SHE here. However, the differences are helpful. Every redox reaction is composed of a simultaneous reduction and oxidation. These two have distinct E^0 values. The difference between these two determines whether the reaction is theoretically spontaneous if a certain working versus counter electrode potential difference exists. In practice, effects called collectively as overpotential affect this spontaneity. Overpotential means that a higher potential is necessary to ignite the redox reaction than anticipated from the reduction potential values. It has different reasons like the activation energy of the redox reactions occurring at the electrode surface.

As avoiding all the redox reactions is not possible, other limits for reliable electrode operation are necessary. This can be settled knowing that not all reactions damage the electrodes. The reactions in which the products are immobilized on the electrode surface may be reversed if the electrode current direction is reversed. These are called reversible reactions [8]. Two examples are:

$$Pt + H_2O \leftrightarrow PtO + 2H^+ + 2e^-$$

$$Ir + 2H_2O \leftrightarrow Ir(OH)_2 + 2H^+ + 2e^-$$

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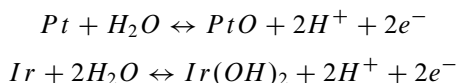
[2]In contrast to electrochemistry where pH = 0 at standard conditions, in biochemistry pH = 7 holds.

These processes do not damage the electrodes if charge injection balance into the electrode is guaranteed. Charge balance roughly means that the total amount of charge injected into the electrode remains zero. This will be explained in detail in the next chapter.

Another group of reactions are the irreversible reactions. These are reactions for which the products are not immobilized on the metal surface. This is the case when gases are produced or when the products spread into the solution by diffusion processes. Irreversible reactions cause corrosion of electrode materials [8]. An example is:

$$Pt + 4Cl^- \rightarrow [PtCl_4]^{2-} + 2e^-$$
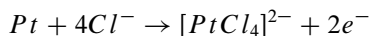
As platinum and gold have similar chemical properties (neighbors in the periodic table of elements and both belonging to the group of transition metals) and the complexes $[PtCl_4]^{2-}$ and $[AuCl_4]^{2-}$ have similar chemical structures, gold dissolution in a medium containing chloride ions (like phosphate buffered saline[3] and body environment) is also irreversible:

$$Au + 4Cl^- \rightarrow [AuCl_4]^- + 3e^-$$
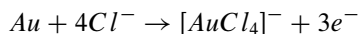
This is probably the reason why gold electrodes suffer dissolution into the tissue environment. Alan Chow et al. [3] have shown that the use of gold as electrode material in visual prosthetics is inappropriate due to gold electrode dissolution into the body environment. Furthermore it was shown that a lack of electrical activity avoids gold dissolution. In the current study gold dissolution on the structures containing gold was observed after symmetric voltages of ± 2 V was applied for 24 h.

Another important irreversible reaction is the hydrolysis of water [8]. The two half reactions occurring on separate electrodes (cathode and anode) are:

$$2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^-$$
$$2H_2O \rightarrow O_2 \uparrow + 4H^+ + 4e^-$$
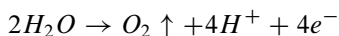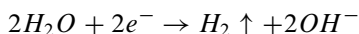
These reactions cannot be reversed once they occur, because the product escapes the surface immediately. In order to prevent electrolysis, the voltage waveform on the electrode interface capacitance is required to never exceed the so called water window limits [4]. Water window is different for different electrode materials [4]. Measured with silver-silver chloride as the reference electrode, water window is between -0.6 and $+0.8$ V for iridium oxide electrodes [10] and ± 0.9 V for TiN [4].

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[3]One liter of phosphate buffered saline (PBS) contains 8 g NaCl, 0.2 g KCl, 1.44 g Na_2HPO_4, 0.24 g KH_2PO_4. HCl is used to adjust the pH to 7.4 [1].

Fig. 2.1 (**a**) Working versus counter electrode model. (**b**) Working electrode model
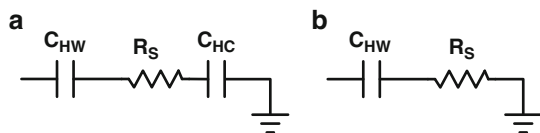
For electrochemical safety, the transients of the electrode-electrolyte interface voltage must stay inside the water window even for pulse widths as short as 0.1–0.5 ms [5, 7, 9–11]. For shorter pulse widths this is even more critical, because with shorter pulses, the reversible reactions cannot be fully utilized, as the reactions don't have an unlimited speed. Therefore, for shorter pulses, the charge available from reversible processes is smaller [7].

The reversibility of the reactions supports the electrode lifetime only if they are fast enough. The relatively low safe charge injection limit of iridium oxide electrodes used in [5] was due to either slow redox kinetics of that type of iridium oxide or diffusion limitations. The pulses used were 0.5 ms long. To find out the charge injection, the electrode voltages were kept inside the safe potential range. Cyclic voltammograms with scan rates as high as 200 mV/s showed that the reactions on the TiN electrodes are not wholly reversible [2].

Both the working and the counter electrodes have a double layer capacitance and the solution in between exhibits a resistance called spreading resistance R_S. The working versus counter electrode pair have a model illustrated in Fig. 2.1a. C_{HW} and C_{HC} are the double layer capacitors of the working and the counter electrodes, respectively. In monopolar stimulation structure in which the counter electrode is much larger than the working microelectrode and is far away, the voltage drop on the counter electrode phase boundary is usually negligible and the large double layer capacitance C_{HC} of the counter electrode can be neglected in the model. The resulting model for the working electrode is the one in Fig. 2.1b. From here on, the impedance of the counter electrode is neglected in the discussions.

In theory, as explained above, in order to determine the charge injection capacity of an electrode the voltage on the Helmholtz capacitance must be monitored. Therefore, in literature the voltage drop on the spreading resistance is usually subtracted from the electrode potential to achieve the voltage drop on the Helmholtz capacitance [7, 9]. However, as is discussed in Chap. 4, this may sometimes lead to too liberal charge injection boundaries.

The voltage drop on the electrolyte is equal to $= I \times R_S$, and is called access voltage. Here I is the injected current into the solution and R_S is the electrolyte's spreading resistance. Figure 2.2 illustrates an example for phase boundary voltage extraction. In the figure, i.p.p. is the interpulse potential, E_c is the maximum cathodic potential, and E_a is the maximum anodic potential both after access voltage correction. The electrode was a smooth disk with a diameter of 1.1 mm (macroelectrode) cut from a platinum foil and mounted in a silicone rubber support.
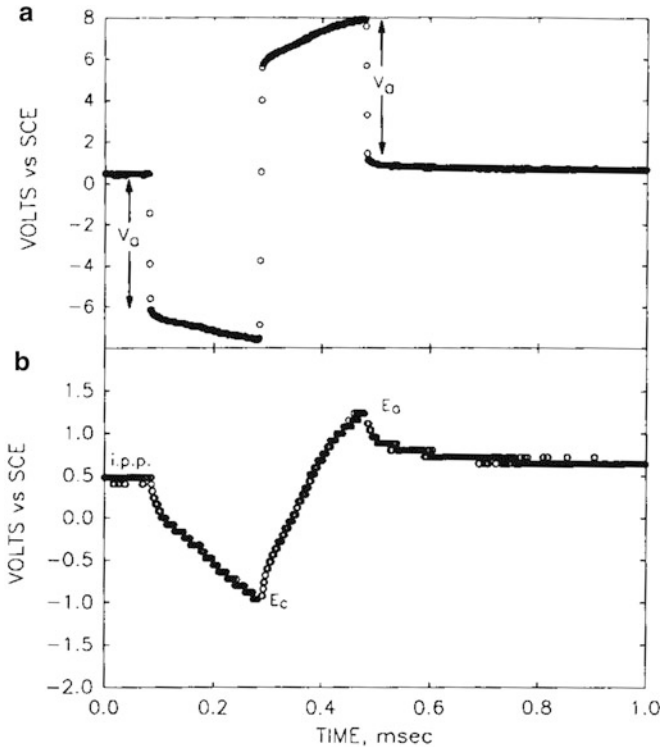
Fig. 2.2 (**a**) Directly measured electrode potential. (**b**) Same waveform plotted on expanded scale after correction for access voltage V_a (by subtracting V_a), this waveform should be kept inside the water window (-0.6 to $+0.9$ V for platinum) for safe operation. The pulse length and the charge injection density were 0.2 ms and $400\,\mu C/cm^2$, respectively. Biphasic cathodic first symmetrical current pulses were used. A saturated calomel electrode (SCE) was used as the reference electrode. From [7], with permission ©1990 IEEE

References

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