B. Reference and Auxiliary Electrodes

1. Reference Electrodes. Voltammetric methods are those in which current passing in an electrochemical cell is measured as a function of the potential applied to the working electrode. Potential, by definition, is not something that can be directly measured. Rather, the measurement of applied potential requires that a reference point first be established, and individual potentials be measured relative to that reference point. This is accomplished by placing a second electrode, called the reference electrode, in the cell and measuring potential as the energy difference between the two electrodes. As Kissinger and Bott have perfectly expressed, “electrochemistry with a single electrode is like the sound of one hand clapping”.

Reference electrodes should be constructed using half-cell components that are stable over time and with changing temperature, present at well-defined values of activity. They should possess fixed, reproducible electrode potentials. The reference half-cell with which most of us are familiar is the standard hydrogen electrode (SHE), composed of an inert solid like platinum on which hydrogen gas is adsorbed, immersed in a solution containing hydrogen ions at unit activity. The half-cell reaction for the SHE is given by

$$2H^+ (aq) + 2 e^- \rightleftharpoons H_2 (g)$$

with a half-cell potential arbitrarily assigned a value of zero ($E^0 = 0.000 \text{ V}$). Tables of electrode potential values for many redox couples relative to the SHE are commonly available.

Practical application of the SHE is limited by the difficulties in preparing solutions containing $H^+$ at unit activity and maintaining unit activity for $H_2$ ($g$) in the half-cell. Most experiments carried out in aqueous solutions utilize one of two other common reference half-cells – the saturated calomel electrode (SCE) or the silver-silver chloride electrode (Ag/AgCl).

a) Saturated Calomel Electrode (SCE). The SCE is a half cell composed of mercurous chloride ($Hg_2Cl_2$, calomel) in contact with mercury metal, either as a pool or as a paste with calomel. These components are either layered under a saturated solution of potassium chloride (KCl), or within a fritted compartment surrounded by the saturated KCl solution (called a double-junction arrangement). A platinum wire is generally used to allow contact to the external circuit. The half reaction is described by

$$Hg_2Cl_2 (s) + 2 e^- \rightleftharpoons 2 Hg (l) + 2 Cl^- (sat’d)$$

with a potential of 0.241 V with respect to the SHE at 25 °C. The double-junction arrangement of the SCE is illustrated in Figure 34, at left. Contact to the electrochemical cell is made through a porous glass frit or fiber, which allows ions to cross but not bulk mixing of the electrolytes.
b) Silver/Silver Chloride Electrode (Ag/AgCl). The silver/silver chloride reference electrode is composed of a silver wire (Ag) that has been coated with a layer of solid silver chloride (AgCl), immersed in a solution that is saturated with KCl and AgCl. The pertinent half reaction is

\[ \text{AgCl (s)} + e^- \leftrightarrow \text{Ag (s)} + \text{Cl}^- \text{(sat'd)} \]

with a potential of 0.197 V with respect to the SHE at 25 °C. This value differs slightly from the \( E^0 \) for the couple (0.222 V) because both KCl and AgCl contribute to the chloride activity, which is not exactly unity. A schematic of the Ag/AgCl reference electrode is shown in Figure 34, at right.

![Schematic of Ag/AgCl Reference Electrode](image)

Both the SCE and the Ag/AgCl reference electrodes offer stable half-cell potentials that do not change over time. Only a slight temperature dependence of the potential is observed in these electrodes, changing by approximately 0.5 – 1.0 mV/°C.\(^{22}\) In addition, the loss of electrolyte to evaporation does not change the saturated nature of the solution, nor the potential.

One must be aware that the contact junctions of the half cells by nature slowly leak fill solution into the external solution in which they are found. For example, a small amount of soluble AgCl\(^{2-}\) ion in the internal KCl solution of the Ag/AgCl reference can find its way into the analyte solution over time, where it can lead to silver deposition on the working electrode at relatively low applied potentials. Silver deposited in this way can contaminate the surface and change the properties of the working electrode. Additionally, there are instances where certain measurements can be affected by the ions, like chloride ion, introduced to the measurement solution by leakage. A double-junction design can reduce the problem of contamination by placing a second solution between the reference half cell and the measurement solution.

c) Non-aqueous reference electrodes. In many applications, even a small amount of electrolyte solution leaking from the reference electrode can immediately compromise the electrochemical
reactions occurring in the analyte solution. Primary among these applications is non-aqueous electrochemistry. In these applications, it may be possible to use what is called a pseudo-reference electrode. The simplest pseudo-reference electrode is a metal wire, like platinum, inserted directly into the analyte solution. A reference potential will develop that is strictly due to the composition of that solution. Though this half-cell will supply a constant reference potential during a single experiment, any changes in the cell solution will result in a change in the reference potential. It is accepted practice when employing such a reference that an internal reference redox compound with well-defined potentials, like ferrocene, be added (generally at the end of an experiment), and observed experimental potentials adjusted to the known potential of the standard.

A slightly better approach is to use a reference half-cell that includes the solvent system employed in the analyte solution. One such half-cell that can be used with most organic solvents is the silver/silver ion (Ag/Ag⁺) pseudo-reference electrode. In this electrode, a silver wire is immersed in a fill solution of the desired organic solvent that is saturated with a silver salt and which contains the same supporting electrolyte contained in the analyte solution. A porous glass or Vycor frit is used to separate the inner solution from that containing the working electrode. The half reaction for this electrode is given by

\[ \text{Ag}^+ + e^- \leftrightarrow \text{Ag}^0 \]

with the reference potential being a function of the given electrolyte solution.

Lastly, there are commercially available reference electrodes that advertise themselves as “no-leak” which are suitable for many non-aqueous applications. Users should test these under their particular cell conditions before accepting them for routine use. They should also be aware that many of the materials which constitute the body of the reference electrode may not hold up well in the solvent of choice.

2. Auxiliary electrodes. The purpose of the auxiliary electrode (AE) is to provide a pathway for current to flow in the electrochemical cell without passing significant current through the reference electrode. There are no specific material requirements for the electrode beyond it not adversely influencing reactions occurring at the working electrode (WE). Remember that if a reduction occurs at the WE, there must be an oxidation that takes place at the AE. Care should be taken that electrode products formed at the AE do not interfere with the WE reaction. The AE can be physically separated from the WE compartment using a fritted tube, but one should be aware that under certain circumstances this can have a deleterious effect.

The most commonly used material for the auxiliary electrode is platinum, due to its inertness and the speed with which most electrode reactions occur at its surface. Other, less expensive materials may also be used as auxiliary electrodes. Choices include carbon, copper, or stainless steel if corrosion is not an issue for a particular electrolyte solution or reaction.

As discussed in the previous section on electrochemical cells, the AE should supply current density and potential that is constant across the length of the WE. Many times this means fashioning the AE such that it “mirrors” the shape of the WE, as is the case for a rectangular WE being located near a rectangular AE of similar area. Wire is convenient in that it can be coiled in a symmetrical arrangement around the WE. In some instances, the electrochemical cell can be fashioned from the material chosen for the AE, and the cell itself can serve that purpose.