

# Practical Problems in Voltammetry 3: Reference Electrodes for Voltammetry

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*Reference electrodes can give rise to a number of problems in electrochemical experiments. However, a basic understanding of the construction and operation of these electrodes can prevent such problems and can improve their reliability.*

In all electrochemical experiments, the reactions of interest occur at the surface of the working electrode. Therefore, we are interested in controlling the potential drop across the interface between the surface of the working electrode and the solution (i.e., the interfacial potential). However, it is impossible to control or measure this interfacial potential without placing another electrode in the solution. Thus, two interfacial potentials must be considered, neither of which can be measured independently. Hence, one requirement for this counter electrode is that its interfacial potential remains constant, so that any changes in the cell potential produce identical changes in the working electrode interfacial potential.

An electrode whose potential does not vary with the current is referred to as an ideal non-polarizable electrode, and is characterized by a vertical region on a current vs. potential plot (**F1**). However, there is no electrode that behaves in this way (although some approach ideal non-polarizable be-

havior at low currents). Consequently, the interfacial potential of the counter electrode in the two-electrode system discussed above varies as the current is passed through the cell. This problem is overcome by using a three-electrode system, in which the functions of the counter electrode are divided between the reference and auxiliary electrodes. This ensures that the potential between the working and reference electrodes is controlled and the current passes between the working and auxiliary electrodes. The current passing through the reference electrode is further diminished by using a high-input-impedance operational amplifier for the reference electrode input.

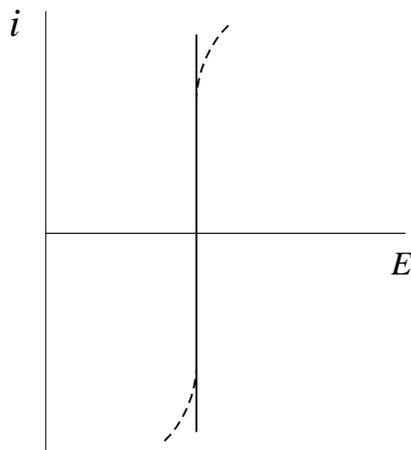
The requirements for the counter electrode of the two-electrode system include a high exchange current (fast electron transfer kinetics), a very large surface area (to lower the current density) and a high concentration of the species involved in the redox reaction, such that the concentrations are not significantly changed by the pas-

sage of a current. One previously widely used reference electrode that fulfills these criteria is the saturated calomel electrode (with a large surface area mercury pool). However, since the current passing through the reference electrode in the three-electrode system is many orders of magnitude lower than the current that passes through the two-electrode system, the requirements for the reference electrode are less demanding; hence, smaller, more polarizable electrodes can be used.

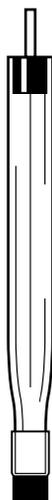
One aspect that is often overlooked is the variation of the reference electrode potential with temperature. Ideally, the potential should be temperature independent; however, it typically changes by 0.5 - 1 mV per degree Celsius. Consequently, precise potential measurements require the use of a constant temperature apparatus. In addition, the temperature at which the measurements were made should always be reported. The absence of any temperature control limits the accuracy of the measurements to about 5 - 10 mV (although this level of

**F1**

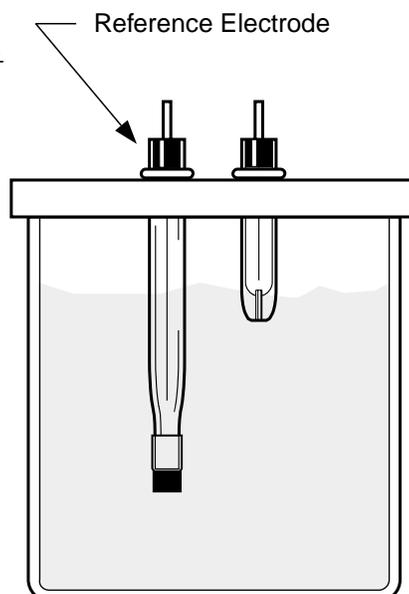
Current-potential curves for an ideal non-polarizable electrode (dashed lines show the behavior of electrodes that approach the ideal).

**F2**

BAS silver/silver chloride reference electrode.

**F3**

Storage of the silver/silver chloride reference electrode.

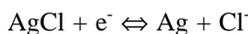


precision may be acceptable for some experiments).

Two widely used aqueous reference electrodes are the silver/silver chloride electrode and the saturated calomel electrode (1). These are now discussed in more detail.

### Silver/Silver Chloride Reference Electrode

The redox process for this electrode is:



This electrode consists of a silver wire, coated with silver chloride, which is immersed in a solution containing chloride ions. The BAS RE-5 electrode (**F2**) uses an aqueous solution containing 3M sodium chloride (the use of sodium as the cation rather than potassium is discussed below). A porous Vycor frit is used for the junction between the reference electrode solution and the sample solution.

The potential  $E$  for any electrode is determined by the Nernst equation, which relates  $E$  to the standard potential  $E^0$  and the activities of the redox components (2) (the standard potential is the potential of the electrode at unit activity under standard conditions). The Nernst equation for the silver/silver chloride electrode is

$$E = E^0 + \frac{RT}{nF} \ln \frac{1}{a_{\text{Cl}^-}}$$

(the activities of the solid silver and silver chloride under standard conditions are unity).

It is generally more convenient to consider concentrations rather than activities ( $a_{\text{Cl}^-} = \gamma_{\text{Cl}^-} [\text{Cl}^-]$ ), and the Nernst equation can be rewritten as follows:

$$E = E^0 + \frac{RT}{nF} \ln \frac{1}{[\text{Cl}^-]}$$

where  $E^0$  is the formal potential and is related to the standard potential by the equation:

$$E^0 = E^0 + \frac{RT}{nF} \ln \frac{1}{\gamma_{\text{Cl}^-}}$$

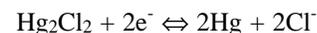
When quoting a redox potential, it is important to be specific. For example, the standard redox potential ( $E^0$ ) for the silver/silver chloride redox reaction at 25 °C is +0.222 V (vs. NHE), whereas the redox potential ( $E$ ) for the BAS silver/silver chloride reference electrode at this temperature is +0.196 V (vs. NHE).

The above equations show that variations in the chloride ion concentration in the electrode change the redox potential. Since there is generally a large chloride concentration gradient across the reference electrode frit, there is slow diffusion of chloride ions from the reference electrode solution into the sample solution; that is, the reference potential will gradually change when used.

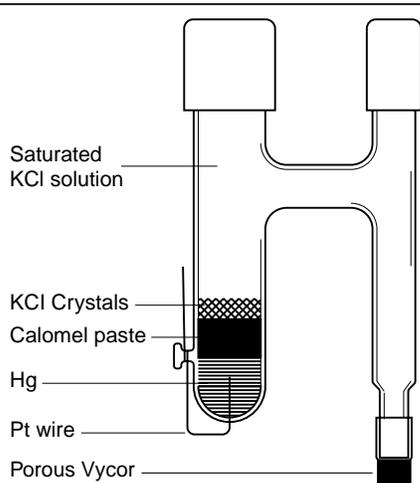
There are some precautions that can be taken to minimize the reference potential drift. When the electrodes are made, the Vycor frit is covered in plastic to prevent leakage. This plastic should be carefully removed immediately upon receipt, and the Vycor frit should be immersed in a 3M aqueous sodium chloride solution (**F3**). The reference electrode should also be removed from the electrochemical cell and stored in this solution between experiments (this is particularly important when using non-aqueous solvent systems, for reasons discussed below). Occasionally, air bubbles will form in the solution next to the Vycor frit; these should be removed by gently flicking the end of the electrode.

### Calomel Reference Electrode

The redox process for this electrode is:



The BAS RE-2 saturated calomel electrode (SCE) is shown in **F4**. One arm of the H-cell contains



mercury covered by a layer of mercury(II) chloride (calomel). This is in contact with a saturated solution of potassium chloride. A porous Vycor frit is again used for the junction between the reference electrode solution and the sample solution.

The RE-2 electrode is provided as a kit requiring user assembly (N.B. the kit does NOT include any mercury). Once assembled, the electrode should be stored with the Vycor frit immersed in a saturated solution of potassium chloride to maintain the chloride concentration in the reference electrode (*vide supra*).

As noted above, the composition of the reference electrode solution (i.e., high chloride ion concentration) is generally different from the composition of the sample solution. This leads to a potential difference across the interface of the two solutions (i.e., the Vycor frit), due to unequal rates of diffusion of the constituent ions (1,2). This liquid junction potential cannot be measured (although it can be estimated), and can cause problems with voltammetric measurements. For example, the redox potentials of a given analyte measured in different solvent systems cannot be directly compared, since the liquid junction potential will be different for each solvent system. However, the junction potential can generally be ignored for a given solvent system

provided it is constant and reproducible. If there is any doubt that this is so, an internal reference (e.g., ferrocene) can be used; that is, the reference compound is added to the sample solution at the end of the experiment, and its redox potential is recorded. This approach can also be used to compare redox potentials measured in different solvent systems

There has been much debate over the use of aqueous reference electrodes such as the silver/silver chloride electrode and saturated calomel electrode with non-aqueous solvent systems. One area of concern is the junction potentials across the salt bridge, which can range from tens to hundreds of millivolts; however, as discussed above, such problems can be compensated by the use of an internal reference. There are two more serious problems; the precipitation of electrolyte and the contamination of the sample solution.

The electrolytes commonly used in reference electrodes (sodium and potassium chloride) are not very soluble in organic solvents, and prolonged immersion of aqueous reference electrodes in organic solvents can lead to precipitation of these electrolytes in the Vycor frit. Salts that are combinations of the ions of the two electrolytes can also be precipitated; for example, potassium perchlorate is insoluble in acetonitrile and can be deposited in the frit of an aqueous potassium chloride reference electrode in an acetonitrile solution of tetraethyl ammonium perchlorate. Such precipitation can be avoided by judicious choice of electrolytes. For example, sodium perchlorate is much more soluble than potassium perchlorate, so sodium chloride is used in BAS silver/silver chloride reference electrodes rather than potassium chloride. Tetraethylammonium chloride has also been used as the reference electrode electrolyte, since it is soluble in both aqueous and non-aqueous media (these reference electrodes are not

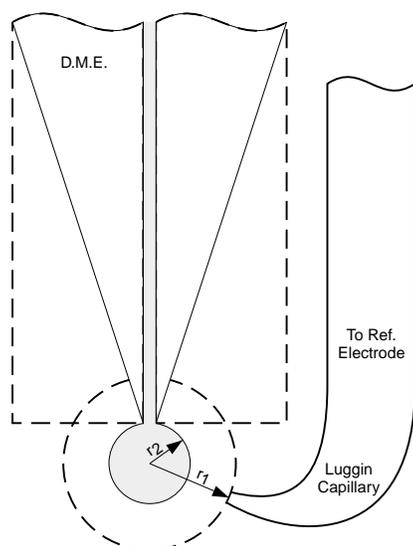
available commercially). The precipitation of electrolyte salts increases the reference electrode impedance (*vide infra*) and changes the liquid junction potential, which causes the reference potential to change with time. Therefore, prolonged exposure to organic solvents should typically be avoided, and the stability of the reference potential should be regularly checked (by using an internal reference or by comparing with another reference electrode). However, aqueous reference electrodes can be used for bulk electrolysis experiments in non-aqueous solvents, since a large overpotential is typically used and the small potential drift that occurs during the experiment should therefore have little effect (although the magnitude of the potential change should be checked after the experiment).

Another potentially serious problem that can occur is contamination of the sample solution by components of the reference electrode solution (e.g., water and chloride ions). In fact, many organometallic compounds are highly reactive to water and cannot be exposed to the small amounts of water that diffuse from the reference electrode during the experiment. One approach that has been used to overcome this has been the use of 'double-junction' reference electrodes, in which the aqueous reference electrode is isolated from the sample solution using a salt bridge containing a non-aqueous solvent/electrolyte system. However, this approach does not rigorously exclude water, so it is not appropriate for highly-water sensitive systems. In addition, there are disadvantages to this approach, as the introduction of the second junction not only alters the reference potential by the addition of another junction potential, it also increases the impedance of the reference electrode (*vide infra*).

Another reference electrode modification that can be particularly appropriate for non-aqueous systems is the use of a Luggin cap-

**F5**

A Luggin capillary and its placement relative to a mercury drop electrode.



illary (**F5**). This allows the tip of the reference electrode to be placed very close to the working electrode surface, thereby decreasing the uncompensated solution resistance ( $R_u$ ) between the reference and working electrodes. However, exact placement of the Luggin probe is required in order to obtain reproducible resistance compensation; in addition, if the tip is too close, part of the electrode surface is blocked, which leads to non-uniform current distribution. The Luggin capillary also increases the reference electrode impedance (*vide infra*).

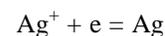
There are two reference electrode systems that do not require water, and hence are suitable for non-aqueous electrochemistry of water-sensitive systems. These are pseudo-reference electrodes and the silver/silver ion electrode.

### Pseudo-Reference Electrodes

Pseudo-reference electrodes are simply metal wires (e.g., platinum or silver) immersed in the sample solution. Although such electrodes do provide a constant potential, the reference potential is unknown, and is dependent on the composition of the sample solution. Consequently, redox potentials measured using a pseudo-reference electrode should be quoted relative to redox potential of the internal reference compound. One advantage of pseudo-reference electrodes is their low impedance (*vide infra*).

### Silver/Silver Ion Electrode

The redox process for this electrode is



This electrode is less stable than the aqueous electrodes discussed above (due to diffusion of silver ions out of the electrode and the photoreactivity of these ions), and must be prepared frequently. BAS provides a non-aqueous reference electrode, which requires assembly by the user. The BAS non-aqueous reference electrode consists of a silver wire immersed in a solution of silver nitrate or perchlorate (0.001M to 0.01M) and electrolyte (e.g., 0.1M TBAP) in the desired organic solvent. Suitable organic solvents include acetonitrile, dimethylsulfoxide, methanol, ethanol and tetrahydrofuran. Silver ions are reduced by dimethylformamide and are insoluble in methylene chloride. Therefore, these solvents are not suitable for this reference electrode (acetonitrile can be used as the reference electrode solvent when one of these

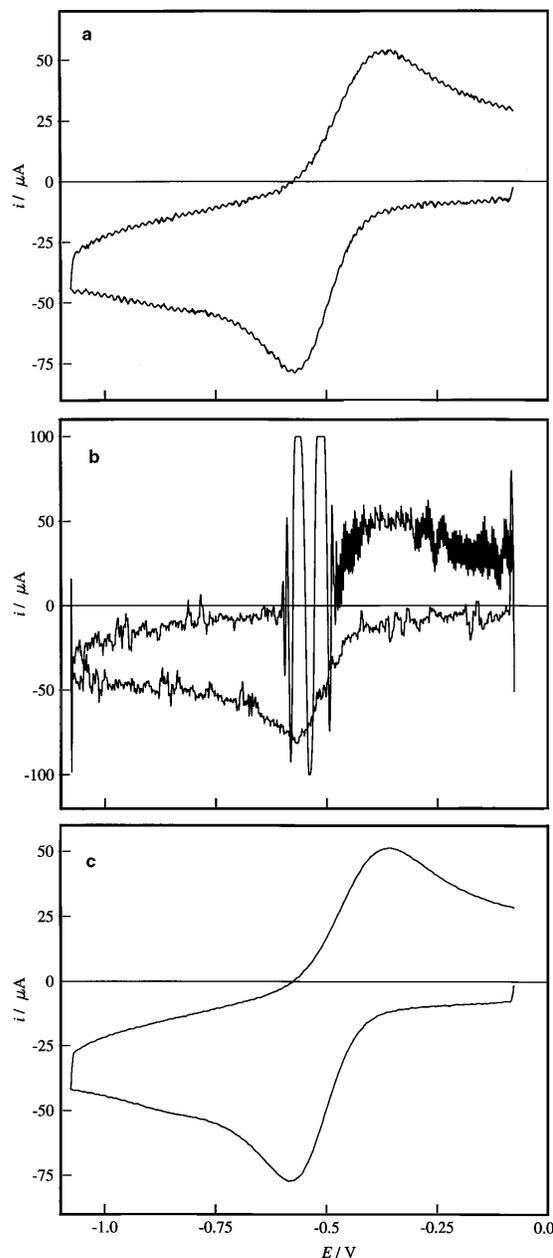
**F6**

Cyclic voltammograms of a 0.59 mM solution of  $\text{Co(III)(Salen)}^+$  in DMF/0.1 M  $\text{NBu}_4\text{PF}_6$ , scan rate =  $10.24 \text{ Vs}^{-1}$ .

a) Single reference electrode system, sensitivity =  $10^4 \text{ A/V}$ .

b) Single reference electrode system, sensitivity =  $10^5 \text{ A/V}$ .

c) Dual reference electrode system, sensitivity =  $10^4 \text{ A/V}$  (reproduced from ref. 3).

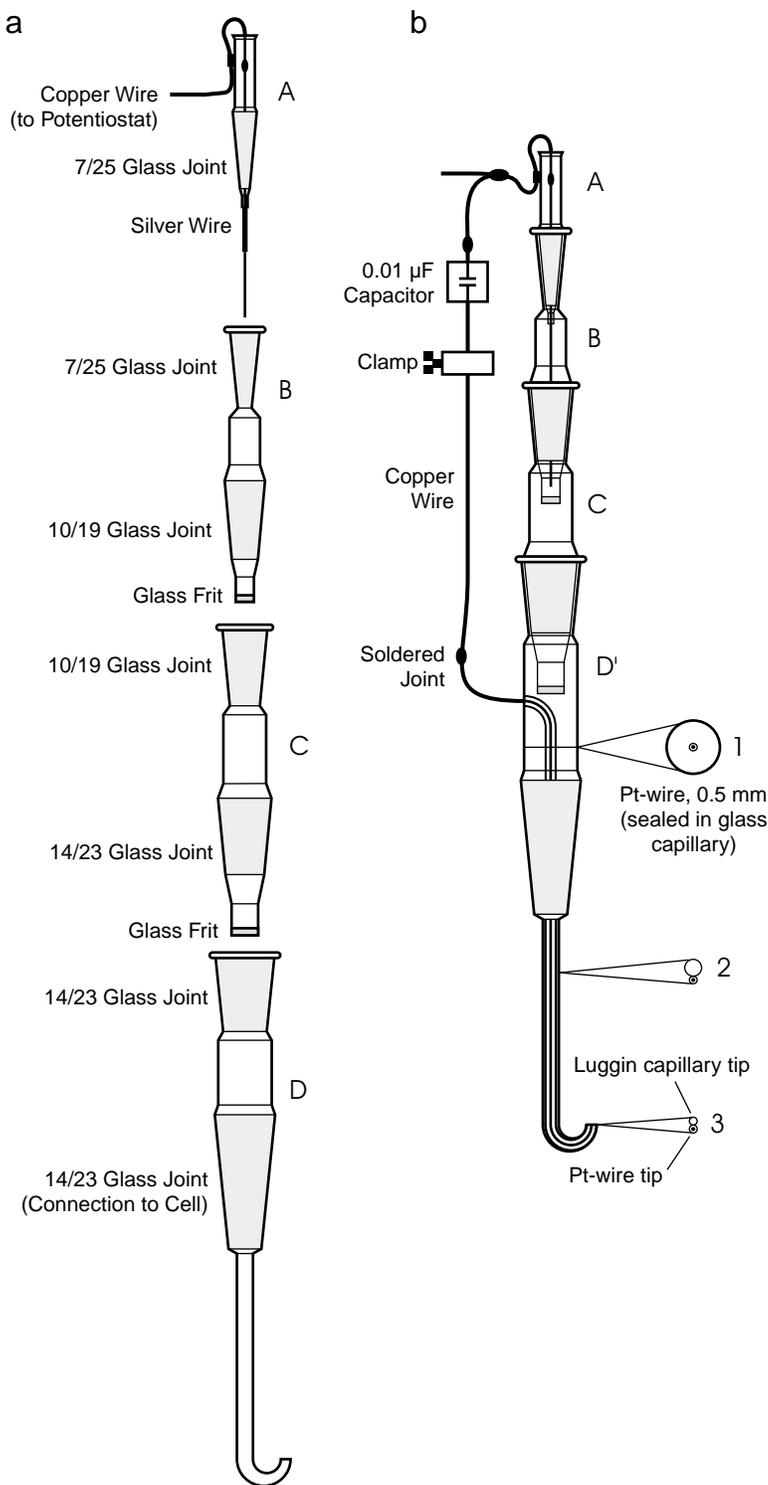


**F7**

Schematic view of reference-electrode constructions from Ref. (3).

a) Parts are Haber-Luggin capillary/**single** reference electrode system (A: Ag wire and lead to potentiostat, B: reference compartment, containing 0.01 M AgClO<sub>4</sub> in CH<sub>3</sub>CN/0.1 M NBu<sub>4</sub>PF<sub>6</sub>, C: intermediate compartment, filled with solvent/supporting electrolyte, D: Haber-Luggin capillary, filled with solvent/supporting electrolyte).

b) Assembled single-unit Haber-Luggin capillary/**dual** reference-electrode system with parts A, B, C, and the improved Haber-Luggin part D'. The drawing includes cross sections above and below the glass joint for insertion into the cell body, as well as close to the tip of the capillary.



other two solvents is used for the sample solution).

The potential for the silver/silver ion reference electrode depends on the solvent, the silver ion concentration, as well as the nature and concentration of the electrolyte. It is also changed by the introduction of salt bridges, which are used to

decrease contamination of the sample solution by silver ions.

**Reference Electrode Impedance**

The impedance of the reference can have a significant effect

on the current response of the cell. A high impedance reference electrode can not only slow the response of the potentiostat (slow rise time), it also increases the susceptibility of the system to environmental noise (particularly power line noise) (3). There are a number of factors that can increase the impedance (*vide supra*), and the construction of the reference electrode can require careful consideration. An example of the effect of high reference electrode impedance is shown in **F6a** and **b**, and the reference electrode used in this example is shown in **F7a** (3). This is a non-aqueous silver/silver ion electrode containing two frits and a Luggin capillary. The noise was removed (**F6c**) through the use of a dual reference electrode, which consists of a platinum wire in parallel with the silver/silver ion electrode (**F7b**). The platinum wire reference also decreases the rise time of the potentiostat.

**Conclusion**

The aqueous silver/silver chloride reference electrode is used for a wide range of applications, and with appropriate care, it can provide a stable potential in both aqueous and non-aqueous solvent systems. However, there are applications for which water must be strictly excluded from the sample solution; pseudo-reference and non-aqueous reference electrodes should be used for such applications.

*Vycor is a registered trademark of Corning Glass.*

**References**

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- 2) A.J. Bard and L. R. Faulkner, "Electrochemical Methods", Wiley, New York, 1980, Chapter 2.
- 3) B. Gollas, B. Krauss, B. Speiser and H. Stahl, *Curr. Sep.* 13 (1994) 42-44.