

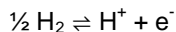
Reference electrodes and their usage

Introduction

A reference electrode has a stable and well defined electrochemical potential (at constant temperature) against which the applied or measured potentials in an electrochemical cell are referred. A good reference electrode is therefore non-polarizable, in other words, the potential of such an electrode will remain stable upon passage of a small current. One could also say that the impedance of an ideal reference electrode is zero. In practice the non-polarizability only holds at small currents, and therefore the input impedance of the reference electrode input on a potentiostat should be as high as possible.

Types of reference electrodes

An absolute standard for the measurement of electrochemical potentials is not available. It is therefore that the equilibrium potential of the so-called Standard Hydrogen Electrode (SHE) is defined as being 0 Volt at $a_{\text{H}^+}=1$ and $P_{\text{H}_2}=10^5$ Pa. In practice this means that the following reaction:



taking place on a Platinum electrode in 1.19 M HCl (H^+ activity = 1) has an equilibrium potential of 0 Volt.

The SHE is difficult to use in practice as it involves bubbling H_2 gas through solution, therefore a number of other reference electrodes are

available, the most important of which are shortly discussed below:

Silver/Silver Chloride (Ag/AgCl in saturated KCl)

This is probably the most widely used reference electrode, since the use of mercury became less popular. This electrode consists of a Ag wire in contact with AgCl in a saturated KCl solution. This results in an electrode potential of +0.197 Volt vs SHE at 25°C.



Although most electrodes of this type use saturated KCl as electrolyte, 3 M and 1 M solutions are used as well. The electrode potential then also changes. The main disadvantage of this reference electrode is the use of chloride, which is unwanted in some cases. Electrodes of this type can be used up to fairly high temperatures (80-100°C). The reference solution is separated from the electrochemical cell by a ceramic frit, or by a glass sleeve (as shown above). Slow leakage of electrolyte takes care of electrical contact.

Saturated Calomel Electrode (SCE) (Hg/Hg₂Cl₂ in saturated KCl)

Traditionally this was the most widely used electrode (publications in the 1960-1970's almost

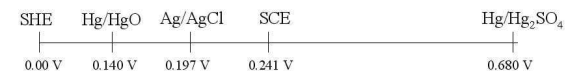
exclusively refer to this electrode) until the use of mercury was banned from more and more laboratories. The electrode potential is +0.241 V vs. SHE at 25°C. Compared to the Ag/AgCl electrode, this electrode has the disadvantage that it cannot be used above 50°C due to instability of the Hg_2Cl_2 .

Mercury/mercury sulphate (Hg/Hg₂SO₄ in 0.5 M H₂SO₄)

This reference electrode is used in some cases where the use of chloride ions is not desirable. The electrode potential of this system is +0.680 Volt vs SHE

Mercury/mercury oxide (Hg/HgO in 1 M NaOH)

Used in alkaline solutions only. The electrode potential of this electrode is +0.140 Volt vs. SHE



Reference electrode scale with potentials vs SHE at T=25°C

Non aqueous reference electrodes

In order to avoid contact between organic solvents and water from the reference electrode, in non-aqueous solutions usually a Ag wire in contact with AgNO_3 is used as a reference electrode. When using a 0.1 M AgNO_3 solution, the electrode potential in Acetonitrile is around +0.36 V vs. SHE. Another alternative is the use of a so-called double junction Ag/AgCl electrode in which the outer compartment is filled with LiCl in ethanol. Many other variations on this can be found in the literature. As the electrode potentials of non-aqueous reference electrodes are less well defined, it is good practice to also use an internal

reference when measuring in organic solvents. The ferrocene-ferricinium redox couple for example can be used for this purpose. The redox potential measured for this couple can then be used as an extra reference point.

Influence of the reference electrode on potentiostat stability

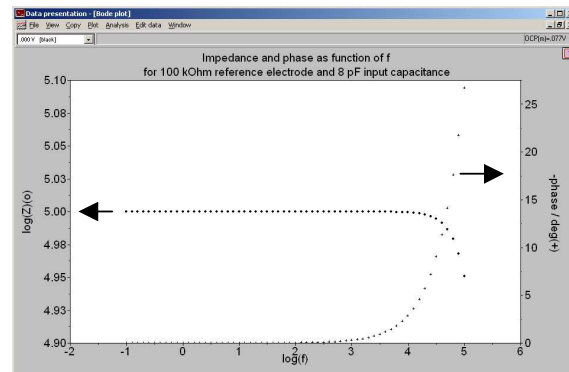
Although the interest of the user usually lies in the behaviour of the working electrode, the reference electrode can have considerable influence on the stability of a potentiostat.

As stated above an ideal reference electrode has zero impedance. In practice however, due to the use of ceramic (or Vycor) frits or salt bridges, the impedance maybe considerably higher (up to 20 kOhm or more). In order to avoid stability problems it is thus advisable to take good care of the reference electrode:

1. Make sure that the reference electrode compartments are filled with electrolyte solution (i.e. KCl in case of a Ag/AgCl electrode)
2. Avoid Luggin capillaries that are very narrow at the end
3. Avoid the use of extra (high impedance) frits between the cell and the reference electrode when possible
4. Only use the High Speed setting of the Autolab when needed (i.e. when signals with frequencies higher than 12.5 kHz are involved).

Consequences for AC measurements

In the Autolab instruments the reference electrode input typically has a capacitance of 8 pF. The impedance of the reference electrode in combination with the input capacitance, results in a RC low pass filter. A typical value for a Metrohm Ag/AgCl reference electrode is 1 kOhm, but when using the double junction electrode with LiCl in Ethanol as the outer electrolyte, the impedance of the reference electrode may be as high as 100 kOhm. The latter case in combination with a 8 pF input capacitance results in an RC filter with a 800 ns time constant. This filter will result in a phase shift of -27° at 100 kHz. (see figure below) As the effect is especially noticeable at higher frequencies, for impedance measurements it is recommended to use a platinum wire coupled to the reference electrode through a capacitor (typically 0.1 μ F- 1 μ F). The high frequency signal will bypass the reference electrode, whereas the dc component will still pass through the reference electrode.



Bode plot of the impedance and phase angle change, due to the presence of a reference electrode with 100 kOhm impedance.

Stability issues on capacitive cells

Potentiostats use a so-called negative feedback system to keep the desired potential between WE and RE stable. As soon as there is a change in the desired potential in the positive direction, the feedback system ensures a change in the negative direction, hence the term negative feedback. Positive feedback however may arise as soon as the phase shift becomes 180° , for example due to a phase shift contribution of the feedback system itself. If positive feedback occurs, the potentiostat will go into oscillation. Under normal circumstances this will not happen, but the presence of a reference electrode with high impedance will result in an additional phase shift (added to the one of the feedback system), which can in turn lead to instability.

The Autolab potentiostats have been tested on capacitances ranging from 10 pF to 3000 F, both on the High Stability and High Speed settings, this poses no stability problems. However, as soon as the reference electrode impedance reaches values higher than 30 kOhm the system becomes unstable in the High Speed mode.

It is therefore recommended to use low impedance reference electrodes in combination with the High Stability setting when possible.