Metrohm
Autolab

Application Area: Fundamental

Reference Electrodes and Their Usage

Keywords

Reference electrode; Potential scale; Pseudo reference electrode; Reference electrode for organic environments

Summary

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 stable and non-polarizable. In other words, the potential of such an electrode will remain stable in the used environment and also upon the passage of a small current. Also, the impedance of an ideal reference electrode should be zero. In practice the non-polarizability only holds at small currents, and therefore the input impedance of the reference electrode on a potentiostat should be as high as possible.

Types of reference electrodes

Standard Hydrogen Electrode (SHE)

An absolute standard for the measurement of electrochemical potentials is not available. Therefore, equilibrium potential of the so-called Standard Hydrogen Electrode (SHE) is defined as being $0\,V$ at proton activity $a_{H^+} = 1$ and hydrogen pressure $p_{H_2} = 105\ Pa$.

In practice, this means that the following reaction:

$$\frac{1}{2} H_2 \rightarrow H^+ + e^- \qquad 1$$

Which takes place on a Pt electrode in 1.19 M HCl (proton activity $a_{H^+} = 1$) has an equilibrium potential of 0 V.

The SHE is difficult to use as it involves bubbling H_2 gas through solution. A number of other reference electrodes are available, the most important ones being shortly discussed in this application note.

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 V vs. SHE at 25 °C. Although most electrodes of this type use saturated KCl as electrolyte, 3 M KCl and 1 M KCl 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 assures the electrical contact.

Saturated Calomel Electrode (SCE) (Hg/Hg_2Cl_2 in saturated KCl)

Traditionally this was the most widely used electrode (publications in the decade 1960-1970 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 sulfate (Hg/Hg_2SO_4 in 0.5 M H_2SO_4)

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 V 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 V vs. SHE.

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 alternatives 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. For example, the ferrocene-ferricinium redox couple can be used for this purpose. The redox potential measured for this couple can be used as an extra reference point.

In Figure 1, the potential scale of reference electrodes versus SHE is shown.

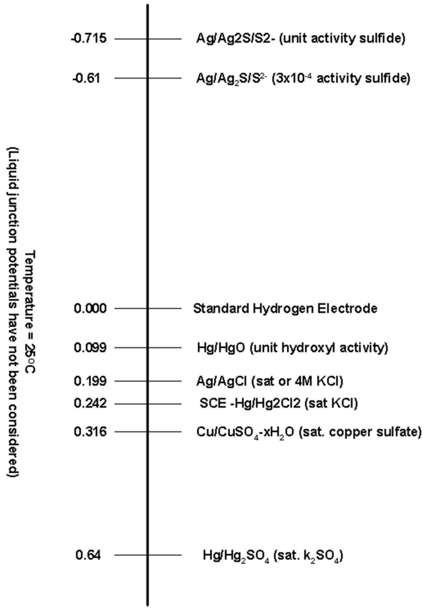

Figure 1- Reference electrode scale with potentials vs. SHE at T= 25 °C

Influence of the reference electrode on potentiostat stability

Although the interest of the user usually lies in the behavior 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 kΩ or more). In order to avoid stability problems due to the reference electrodes it is recommended to consider the following:

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. If possible, avoid the use of extra (high impedance) frits between the cell and the reference electrode
4. Use the High Speed setting of the Autolab only when needed (i.e., when signals with frequencies higher than 12.5 kHz are involved)

Consequences for AC measurements

In the Metrohm Autolab potentiostats/galvanostats, 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 kΩ 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 kΩ which, 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 2).

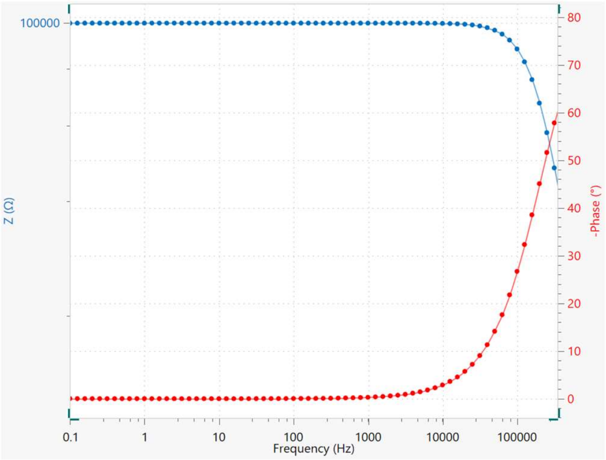

Figure 2– Simulated Bode plot of the impedance (blue) and phase angle change (red), due to the presence of a reference electrode with 100 kΩ impedance in combination with 8 pF input capacitance.

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 $0.1\ \mu F - 1\ \mu F$). The high frequency AC signal will bypass the reference electrode, whereas the DC component will pass through the reference electrode.

Stability issues on capacitive cells

Potentiostats use a so-called negative feedback system to keep stable the desired potential between WE and RE. As soon as the 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 kΩ, 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.

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **www.metrohm.com/en/products/electrochemistry.**