

Understanding the Differences between a Quasi-Reference Electrode and a Reference Electrode

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Editorial

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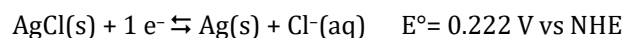
The terms “pseudo-reference electrode” and “quasi-reference electrode” are widely mentioned in the literature and used interchangeably or as synonyms. However, it is not clear about its meaning or the characteristics a system should have to be considered as a quasi-reference electrode. For example, if we search the Internet for a meaning we can find the following definition of quasi-reference electrode at the Royal Society of Chemistry web page: “An electrode based on a ferrocene or cobaltocene redox couple internal standard through which no appreciable current is allowed to flow and is used to observe or control the potential at a working electrode” [1]. Meanwhile, Bard and Faulkner define in their book a quasi-reference electrode as “just a metal wire, Ag or Pt, used with the expectation that in experiments where there is essentially no change in the bulk solution, the potential of this wire, although unknown, will not change during a series of measurements” [2]. Finally, a reference electrode designed for its use in non-aqueous solvents (e.g., an Ag metal wire immersed in an AgNO₃ acetonitrile solution) is also named in some literature as a pseudo-reference electrode. All these definitions are describing completely different systems under the same name. Therefore, new researchers initiating in the electrochemistry field, in particular, and those initiating in the chemistry field, in general, may not understand the difference between these definitions, and more importantly, the differences between a pseudo-reference electrode (or a quasi-reference electrode) and an actual reference electrode.

What is a Reference Electrode?

A reference electrode is a hemi-reaction in a galvanic cell of known potential value, which does not change with

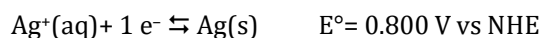
the passage of small current, approaching an ideal non-polarizable electrode behaviour. Non-polarizability is experimentally observed as a nearly vertical region on a current vs. potential plot. Deviation from this non-polarizable condition is only observed when large current flows throughout the reference electrode.

Commercially available reference electrodes are of the metal/insoluble metal salt type, which normally consists of a metal electrode [e.g., silver (solid) or mercury (liquid)] cover with a layer of an insoluble salt of that metal (for example, silver metal wire coated with insoluble silver chloride). This is then placed in contact with a solution of the anion part of the insoluble salt at a well-known concentration (e.g., a 3 M solution of sodium or potassium chloride in the example above). Electron transfer occurs between the metal atoms of the electrode and the metal ions in the insoluble salt following the equation:



Due to the reversibility of this equation (thermodynamic equilibrium), a small current flowing through the electrode will not affect the equilibrium. Then, the potential of the reference electrode will be maintained constant during the experiment. It is worth notice that this will not be the case if a large current is flowing in the system. In such a case, a three-electrode system should be used. Metal/insoluble metal salt is not the only type of reference electrode we can use. The reference electrodes based on i) redox (e.g., ferrocene and ferrocenium); ii) gas [e.g., Pt(s)|H₂(g)|H⁺(aq)]; and iii) metal/metal ion (soluble salt) electrode types can also be used. The first two types of reference electrodes (i and ii)

require an inert metal wire (e.g., Pt) immersed into a solution containing a compound in two different oxidation states and at well-known concentration. This last point is very important as the potential of this reference system will depend on the concentration of both redox-active species. The last type of reference electrode (iii) is commonly used in non-aqueous solvents. Electron transfer occurs between the metal atoms of the electrode and the metal ions in solution, for example:



The potential of this reference system depends on the silver ion concentration ($E = E^\circ = 0.8 \text{ V vs NHE}$ at 1 M concentration and 25°C), which is always used at the millimolar level (10-100mM AgNO_3) for electrochemical studies in organic solvents. It is important to mention here that these three kinds of reference electrode will behave as a non-polarizable electrode if small current flows throughout the system. Besides, evaporation of the organic solvent in case of reference electrode iii should be prevented. If this is impossible, then constant calibration against an internal reference redox system is required [3]. If we carefully analyse the definition mentioned at the Royal Society of Chemistry web page (see above), we would immediately notice they are describing a particular kind of reference electrode (type i mentioned above) and not a quasi-reference electrode. The same situation can be observed for the third definition, which is just describing the reference electrode iii mentioned above.

Therefore, what is a “Quasi-Reference Electrode”?

The appropriated definition for a pseudo reference electrode is that provide by Bard and Faulkner. It is just a metal wire immersed in the working solution system, which is not under thermodynamic equilibrium with its oxidised ion (soluble or insoluble). The prefix of quasi- or pseudo-, meaning “incomplete” or “false” reference electrode, is then introduced to differentiate them from true reference electrodes.

The potential obtained with the use of silver or platinum wire as a quasi-reference electrode is based on the presence of various compounds (most commonly Ag_2O or Pt_2O , respectively) on the metal surface, where the exact concentration of the metal oxide molecules are never known with any confidence [4]. Therefore, the potential of the quasi-reference electrode is likely to change greatly in the event of (a) reaction with impurities

present in the media; (b) dissolution of the oxide compounds (present onto the metal surface) in the solvent system; (c) polarization, due to lack of potentiostatic control, or (d) its recently history. These changes can occur dynamically throughout the period when the wire is immersed in the solvent system during, or even as a consequence of, the electrochemical experiment. Therefore, the assumption that the potential(s) of the electrochemical processes of interest recorded against a quasi-reference electrode can be calibrated, at some stage (or before and after the experiment), against a suitable reference electrode or an internal reference redox system, cannot always be relied upon to provide an accurate potential value over the entire range of potentials measured.

Despite this, quasi-reference electrodes are commonly used in electrochemical studies in non-aqueous solvents, where, as is the case with ionic liquid investigations, well-defined reference electrodes are difficult to prepare and stabilize. Furthermore, they are usually found forming part of disposable screen-printed electrodes; generally used in biosensor and low-volume work in aqueous solvent systems. In most ionic liquids, volatility is not an issue compared to the situation prevailing in some organic solvents in which evaporation can vary the composition of the reference electrode half-cell. However, the small volume of ionic liquid typically used (in general, several tenths or hundreds of microliters) to perform simple and cost-efficient research, justifies the use of this kind of reference system. The majority of reports that employ quasi-reference electrode are based on silver or platinum wire immersed directly into the working solution. However, lithium, zinc, cadmium, and magnesium metal are also used.

Very Important to Consider:

The use of quasi-reference electrodes should be avoided, except for the collection of qualitative data. If impossible, the redox potential of the analyte under investigation must be calibrated against an internal reference redox system. The key requirement under this situation is that the voltammetric response for the analyte under study must be independent of the internal reference redox system response [3]. Errors associated with the quasi-reference electrode drift during the voltammetric experiments must be considered.

In situations where a large number of experiments are to be performed in a single organic solvent or IL, it is recommended to prepare an Ag/Ag^+ reference electrode

using the same solvent. If an organic solvent is used, the potential of this reference electrode may change with time, as solvent evaporation is difficult to be prevented. Therefore, it must be calibrated against an internal reference redox system before and after the experiment, to evaluate possible drifts of the reference system during the electrochemical experiment.

References

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