



Reference Electrodes for electrochemical measurements in high-temperature high-pressure aqueous environments—Review of potential corrections for ‘external’ reference systems[☆]



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ARTICLE INFO

Article history:

Received 28 August 2015

Received in revised form 19 April 2016

Accepted 22 April 2016

Available online 27 June 2016

Keywords:

reference electrodes

sensors

calibration

correction factors

ABSTRACT

Corrosion studies in high-temperature high-pressure aqueous environments, and in particular electrochemical corrosion measurements in these environments, are again becoming more important for a number of industrial applications. Reliable and accurate electrochemical measurements in high-temperature high-pressure aqueous systems (i.e. up to ca. 300 °C) are, however, not straightforward. Especially the stability of so-called ‘internal’ reference electrode systems or the accuracy of ‘external’ reference systems continues to pose major measurement problems.

In this paper we will present a brief state-of-the-art, and we will demonstrate the possibility of transforming the huge amount of correction data for external reference electrode systems into one simple analytical expression, at least for neutral and alkaline solutions. For acidic solutions, there is a small deviation. Precisions of the order of ± 5 to 15 mV (depending on the temperature) can generally be obtained, which should be sufficient for applications like corrosion monitoring, redox potential measurements, etc.

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1. INTRODUCTION

1.1. General

Corrosion studies in high-temperature high-pressure aqueous environments are gaining renewed interest. Not only continuing problems in various traditional power plants (both fossil and nuclear), but also new interest in geothermal systems, seawater desalination, etc. are asking for new corrosion studies or (electrochemical) tools for continuous corrosion monitoring.

There is, however, still an immanent need for better electrochemical corrosion sensors for these high-temperature aqueous environments, despite a lot of previous research. Reliable and accurate electrochemical measurement in high-temperature high-pressure aqueous systems (i.e. up to ca. 300 °C) are still not straightforward, definitely not above 200 °C; the bottleneck being the availability of suitable reference electrodes [1].

In general, the experimental difficulties are related to the combined presence of high temperature and high pressure, which produces significant problems associated with bringing electrochemical information across the pressure boundaries, while additional difficulties include safety and pressure leaks. More fundamentally important, however, are the uncertainties regarding reference electrodes and related thermodynamic constants. The latter have greatly hampered the wide application of electrochemical techniques to corrosion studies in high temperature aqueous environments.

1.2. Internal versus External Reference Electrodes

It is common practice to classify the available high-temperature reference electrodes into “internal” and “external” types [2–4]. In the case of *internal reference electrodes* the potential sensing or electroactive element is maintained at the system temperature and pressure, so that ideally these electrodes exist in a state of thermodynamic equilibrium. On the other hand, *external reference electrodes* have their electroactive elements kept outside the high temperature system and they are maintained at ambient temperature, with communication to the high temperature zone being made via a non-isothermal (cooled) electrolyte bridge. Accordingly, these systems are essentially non-equilibrium in

[☆] EMCR 2015 – 11th International Symposium on Electrochemical Methods in Corrosion Research – Session: Electrochemical Corrosion Sensors (Troia, Portugal–May, 2015).

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nature, due to the establishment of *thermal diffusion phenomena* along the non-isothermal electrolyte bridge.

Each of these approaches introduces its own specific difficulties and advantages.

The intrinsic advantage offered by *internal reference electrodes* is precision. Provided that the electrode behaves reversibly it is possible to measure potentials with a precision (and accuracy) of better than 1 mV. However, few electroactive elements are capable of withstanding thermal hydrolysis at temperatures exceeding 200 °C, so that irreversible processes become important in determining the potential. These phenomena distort the measurement, such that reliable potentials may not be obtained, particularly not during prolonged exposure periods. A further factor which can diminish the accuracy of a practical system is the occurrence of a so-called 'liquid junction potential' between the reference electrode electrolyte and the test environment.

Therefore, even the more recent internal reference systems mostly still suffer from limited stability and long-term durability, certainly in the higher temperature ranges up to 300 °C. Recent studies and developments on these systems have been reviewed by Bosch and Bogaerts and various co-authors in the framework of an extensive European research project [4,5].

The stability or thermal hydrolysis problem is normally avoided in the case of *external reference electrodes*, because the electroactive element (e.g. Ag/AgCl) is maintained under conditions where thermal hydrolysis does not occur. However, the precision obtainable using a reference electrode of this kind is limited by the reproducibility of the 'thermal liquid junction potential' that is established along the non-isothermal electrolyte bridge due to coupling between heat and diffusional fluxes, and external reference electrode systems therefore require potential corrections for the thermal diffusion of ions across the electrolyte bridge [2–6].

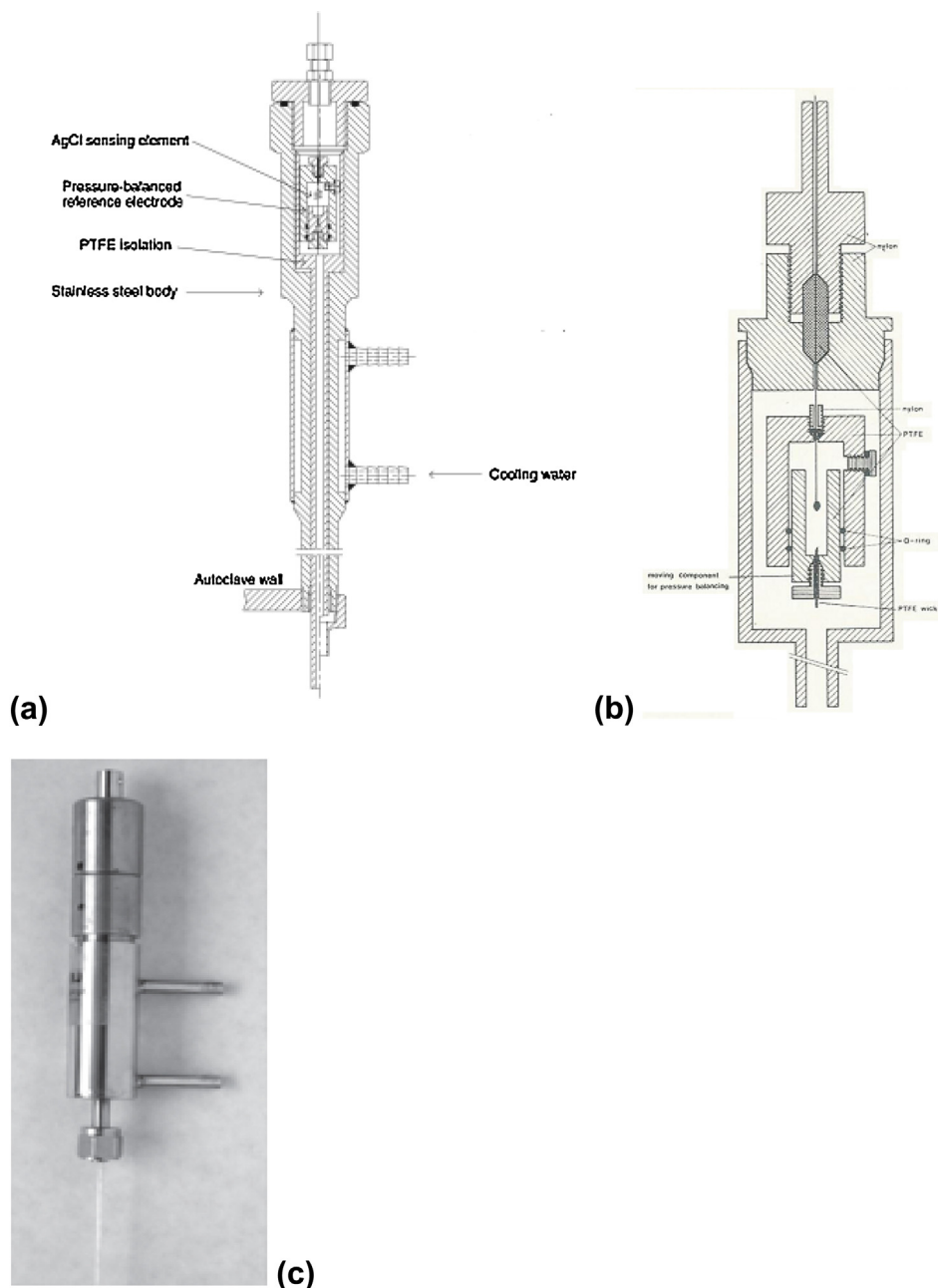


Fig. 1. Construction details and assembly of external pressure balanced external reference electrode (EPBRE) [3].

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