Pd/H_2 REFERENCE ELECTRODE

The palladium hydrogen electrode is a very suitable internal reference electrode for high temperature aqueous work for several reasons. The mechanism of hydrogen evolution reaction has been extensively studied and is now reasonably well understood. In addition, the species (H_2, H^+) are stable over the temperatures of interest and they do not contaminate the environment where the measurements are carried out.

Theory

The electrode reaction for the hydrogen electrode is

$$H^+ + e^- \Leftrightarrow \frac{1}{2} \cdot H2$$

The Nernst equilibrium potential for this reaction can be written as

$$E_T = -\frac{2.303 \cdot RT}{2 \cdot F} \cdot \log f_{H_2,T} - \frac{2.303 \cdot RT}{F} \cdot pH_T$$

where

T = operating temperature
pH_T = thermodynamic pH value at T,
F = Faradays constant,
R = gas constant and
$f_{H2,T}$ = hydrogen fugacity.

An accurately calculated value of E_T requires precise knowledge of the hydrogen fugacity and high temperature pH_T values. If some other electroactive species are present in the solution, the observed potential may be a mixed potential.

The palladium - hydrogen electrode is acting as Reversible Hydrogen Electrode (RHE). When properly calibrated the electrode potential of the palladium electrode follows the equilibrium line H^+/H_2. Increasing the pH decreases the electrode potential with (2.303 RT/F) V/pH unit. Increasing the temperature increases the negative slope of the pH dependence.

Accuracy of the Pd/ H_2 reference electrode is about ± 10 mV when properly calibrated.

Operation in special environments

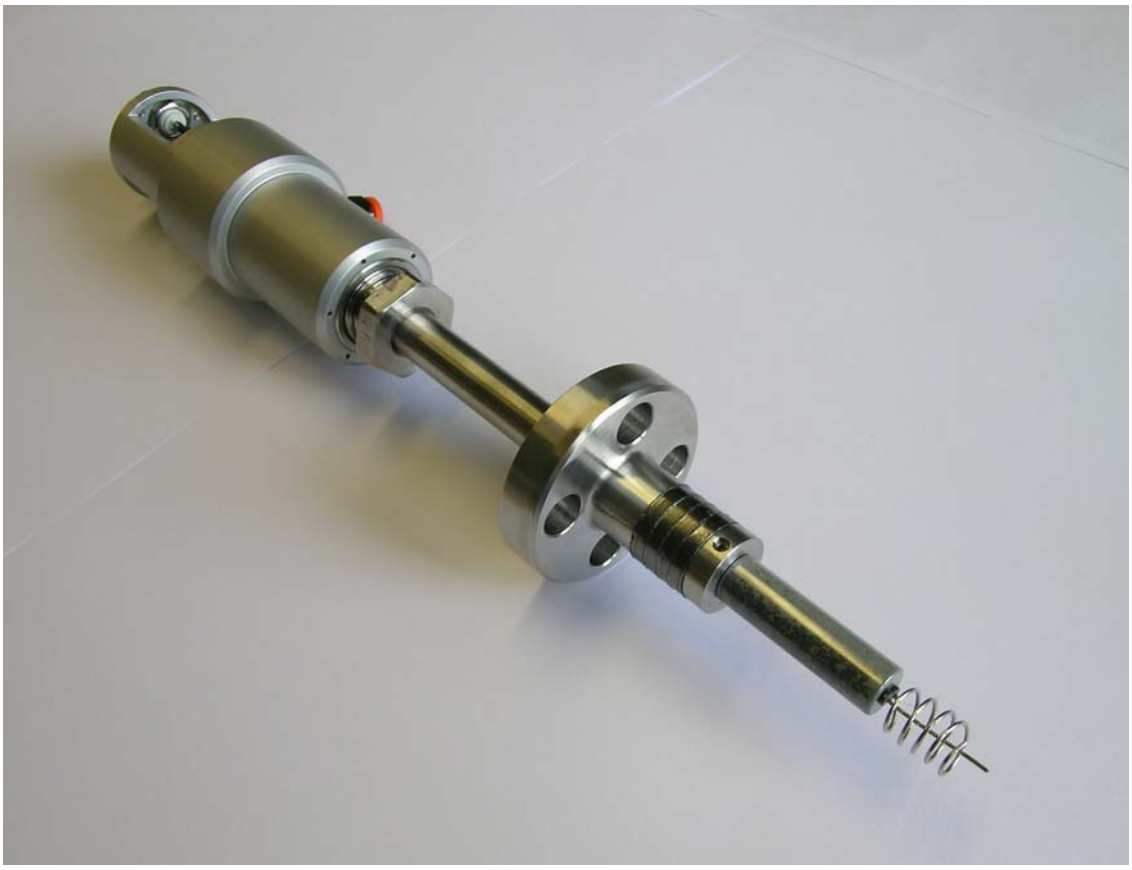
The layer of hydrogen being continuously produced on the Pd-electrode surface has been found to be rather sensitive to the flow rate. If the electrode will be used in flow through cells, check that the flow does not interfere with the potential of the electrode. In extreme conditions, where the flow rate is high and/or where oxygen is present in excess of about 200 ppb, a special shielded electrode construction has to be used.

In very low conductivity solutions such as BWR water, the polarisation current will cause a potential field to be generated around the electrode, which will cause erroneous readings (in a similar way to the so called IR drop). In such a case a special discontinuous polarisation sequence can be used.

Operation of the electrode

The Pd/H_2 electrode can be built in Cormet's specimen holder or in the case there is not enough space available in the autoclave, the electrodes can be mounted in the autoclave. If the temperature exceeds 300°C the wires can be covered with special insulation tubes to provide insulation.

Before the autoclave heating the electrodes can be cleaned using sand paper. The calibration at the operation temperature will give the correct measurement current. After the electrode stabilisation it can be connected to DVM, potentiostat or any other suitable data acquisition unit.



Cormet's Pd/H_2 reference electrode