The PallapHode Electrode System

A ROBUST LONG-LIFE SENSOR FOR MEASURING THE HYDROGEN ION CONCENTRATION IN MANY MEDIA

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The ability to determine accurately the acidity or alkalinity of a solution is an obvious necessity for innumerable purposes, and for much routine work a pH meter which measures the potential difference between a standard electrode and a glass electrode may be employed satisfactorily to give quick and accurate results. There are however, several limitations to such meters some of which can be overcome by using the system described here which incorporates a palladium-hydrogen pH electrode.

Theoretical Concept

Palladium has the power to absorb hydrogen by either gaseous or electrolytic methods, and the alloy formed may be one of three phases (α, $\alpha\beta$, β,) depending on the hydrogen:palladium ratio present. Hydrogen desorbs spontaneously from the alloy, and for specific ranges of hydrogen:palladium composition the resulting vapour pressure is constant at any particular temperature. Thus, for example, from 0.03 to 0.59 hydrogen:palladium concentration (in the $\alpha\beta$ phase) this vapour pressure remains constant at 16 mm of mercury, at 25°C. But at, say, 160°C it is 1520 mm of mercury over a hydrogen:palladium concentration range of 0.12 to 0.48. Thus as the temperature increases, the range of hydrogen:palladium concentration over which vapour pressure is constant decreases, and changes in the alloy composition may be followed by electrical resistance changes. It is believed that, since absorption of hydrogen into the lattice is by either protons or atoms, the thermodynamic relationship

$$\mu_{H\,(alloy)} \neq \mu_{H^{\bullet}\,(surface/solution\ interface)} = \mu_{H^{+}\,(aqueous\ solution)} \quad \text{(i)}$$

holds for a hydrogen-palladium electrode in the $\alpha\beta$ phase. The non-equilibrium condition

$$\mu_{H\,(alloy)} \neq \mu_{H^{+}\,(aqueous\ solution)} \quad \text{(ii)}$$

is considered to be responsible for the origin of an electrode potential. The spontaneous desorption of hydrogen from the alloy arises from this non-equilibrium state when a hydrogen-palladium electrode is immersed in hydrogen-free solutions. Due to restrictive kinetic factors, the slow rate of equilibration of the inequality (ii) allows non-equilibrium to be maintained for a considerable time at room temperature. Therefore, providing the hydrogen:palladium ratio corresponding to the $\alpha\beta$ phase can be maintained within prescribed limits, such a system gives a stable potential which varies with the hydrogen ion activity, in accordance with the Nernst equation.

In the PallapHode system the required hydrogen:palladium ratio is maintained by electrolytic recharging with hydrogen from the solution under examination. The amount of hydrogen involved is minute, and decomposition of the water is insufficient to change the concentration of the electrolyte significantly.

Principal Features

The key component of the PallapHode system consists of a palladium-hydrogen electrode incorporated in a probe that also contains reference and auxiliary electrodes. This is placed in the solution to be measured and is connected to specially developed electronic measurement and control circuits contained in conventional pH type meter format. The potential produced by the electrode, when measured with respect to the reference electrode, indicates the pH of the solution under examination.

The electronic circuits perform three major functions:

(1) Measurement of the electrode potential, and therefore of pH

(2) Control of the composition of the palladium-hydrogen electrode by continuously monitoring its resistance and electrolytically maintaining its hydrogen content.

(3) Periodic cleaning, and maintenance of ideal Nerstian behaviour, is accomplished by electrochemical pulses at the palladium-hydrogen electrode surface, which also allows its use in dirty environments.

Stability and Performance

The plots of electromotive force against time for a range of solutions with quite different pH values show that, even for periods up to 80 days, drift is only a few millivolts in an instrument not subject to recalibration, Figure 1.

As the composition of the palladium-hydrogen electrode is maintained in the $\alpha\beta$ phase, the plot of electromotive force against pH value gives a linear Nerstian response at temperatures up to 250°C, shown in Figure 2.

Advantages and Applications

The PallapHode system is primarily a special-purpose instrument for use in adverse environments. However, a number of advantages over the familiar glass electrode system are apparent and these may warrant its use even under moderate conditions. The main advantages are:

(i) Automatic in situ cleaning permits use in solutions containing solid suspensions.

(ii) Frequent recalibration is not required.

(iii) The probe can be used at up to 250°C in aggressive aqueous and non-aqueous media, and is extremely durable.

(iv) The probe performance is unaffected by previous usage and, in contrast to the metallic ions that may be leached from glass electrodes, can only liberate minute quantities of hydrogen over a long time

(v) It remains accurate at high concentrations of dissolved salts, such as alkali metal ions.

In addition the system may be used in electrolytes containing up to 10^{-2}mol/kg of reducible metal ions, (although the electrode can become plated by some ions).

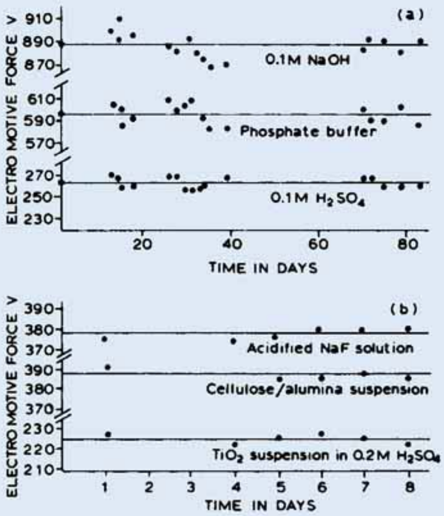

Fig. 1 (a) The stability of the PallapHode is excellent, with low drift over long periods of time. (b) Even in these aggressive media remarkable stability is achieved over considerable periods of time

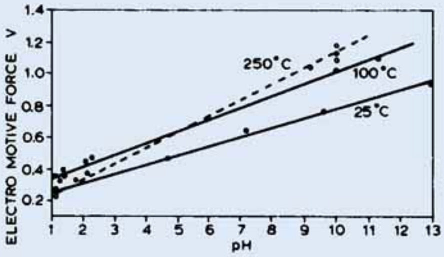

Fig. 2 With the PallapHode, the linear Nerstian response holds at temperatures as high as 250°C. As far as is known, no other pH sensor can operate over such a wide temperature range

Thus, as well as laboratory uses, the PallapHode has important advantages for environmental pollution measurement, oceanographic research, industrial process control, and very small electrodes have found in vivo medical applications.

Acknowledgement

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