EXPIRED

ICRN-12

IAPWS Certified Research Need - ICRN

Kinetics of the Oxygen and Hydrogen Electrode Reactions in Subcritical and Supercritical Aqueous Systems

The IAPWS Working Group - Physical Chemistry of Aqueous Solutions has examined the published work in the area of oxygen and hydrogen electrode reactions.

IAPWS recognizes that there is a requirement for work to be pursued in this field and has prepared this document to assist potential investigators in obtaining sponsorship. Specifically, measurements of the kinetic parameters for the oxygen and hydrogen electrode reactions are needed. These are needed to model the corrosion processes in thermal power plants.

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contacts can provide any further development information and will liaise between research groups.

Issued by the

International Association for the Properties of Water and Steam

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Kinetics of the Oxygen and Hydrogen Electrode Reactions in Subcritical and Supercritical Aqueous Systems

All corrosion processes occurring in aqueous systems involve either hydrogen evolution or oxygen reduction (or both) as the cathodic process. In oxygenated fluids, such as those that exist in supercritical water oxidation systems or in power plants that operate on oxygenated water chemistry, the oxygen electrode reaction (OER) is the process that consumes the electrons released by metal oxidation. In deoxygenated systems, and in those aqueous systems that contain relatively small amounts of oxygen, the electrons are consumed predominantly by hydrogen evolution, so that the hydrogen electrode reaction (HER) is of paramount importance. Indeed, which of these two reactions dominates depends upon the relative values of the corrosion potential and the equilibrium potentials for the HER and OER.

The most exhaustive study of the HER is that reported in HCl solutions on mercury at temperatures as high as 300°C (Tsionsny et al., 1991). Although this is an appropriate substrate for fundamental studies, it is of little use technologically. Kriksunov et al. (1993) studied the anodic OER in acid solutions on platinum at temperatures as high as 325°C. For more practical use, however, data are needed on passive metals (such as stainless steel) that are used to fabricate the coolant circuits of thermal power plants.

In the last two decades, considerable attention has been focused on studying the electrochemical kinetics of Type 304 stainless steel in aqueous solutions at elevated temperatures. A number of experiments have been carried out in high temperature, deaerated or aerated water, in conjunction with stress corrosion tests. Jones (1975) studied the electrochemical behavior of Type 304 stainless steel in high-temperature water containing various concentrations of chloride ions, while using a platinum wire as a reference electrode. Huebner et al. (1974) investigated the polarization behavior of Type 304 stainless steel in an aqueous solution of sodium sulfate, at temperatures up to 300°C. Fugii et al. (1976) also used an external reference electrode for polarization studies on a number of metals, including Type 304 stainless steel, in a sodium sulfate aqueous solution at temperatures up to 290°C. These researchers studied the effect of oxygen concentration on the polarization behavior of metals in high temperature aqueous solutions. Indig and Mellree (1978) carried out measurements of the polarization curves of Type 304 stainless steel in deaerated sodium sulfate solutions at 274°C. Lee (1978) studied the kinetics of reduction of oxygen on austenic stainless steel, including Type 304 stainless steel, in sodium sulfate solutions at temperatures between 100 and 250°C under flowing conditions.

However, the hydrodynamics of the flowing solution was not controlled in these research efforts.

The HER and OER are of such fundamental importance that modeling of corrosion in practical systems, such as thermal power plants, is virtually impossible in the absence of accurate kinetic data covering a wide range of conditions.

From fundamental electrochemical theory, the current density due to a charge transfer reaction of the type

$$R \Leftrightarrow O + ne^- \tag{1}$$

is given by

$$i = \frac{e^{(E-E^{eq})/b_a} - e^{-(E-E^{eq})/b_c}}{\frac{1}{i_o} + \frac{1}{i_{l,f}} e^{(E-E^{eq})/b_a} - \frac{1}{i_{l,r}} e^{-(E-E^{eq})/b_c}} \tag{2}$$

where E is the potential, E^{eq} is the equilibrium potential (calculated from thermodynamic data), $i_{l,f}$ and $i_{l,r}$ are the mass-transfer limited current densities for the reaction in the forward and reverse directions, respectively, i_o is the exchange current density, and b_a and b_c are the anodic and cathodic Tafel constants. The limiting current densities ($i_{l,f}$, $i_{l,r}$) depend upon the hydrodynamics of the system, which can be set experimentally. The kinetic parameters of interest are the exchange current density (equivalent to a rate constant) and the Tafel constants. There are few data of this kind in the literature, and virtually none exist for high temperature subcritical/supercritical aqueous systems, for the substrates of interest (noble metals, carbon steel, stainless steels, high nickel alloys, etc.).

The exchange current density is given in terms of the standard exchange current density (i_o^o) and the species concentrations as

$$i_o = i_o^o \, C_O^{\alpha} \, C_R^{\beta} \tag{3}$$

where α and β are constants that depend on the kinetic orders of the reaction with respect to O and R. Thus, a complete characterization of the kinetics of a reaction requires the measurement of the exchange current density as a function of C_O and C_R.

NEEDED RESEARCH ACTIVITIES

This ICRN is issued to document the need to measure kinetic parameters for the OER and the HER in high temperature aqueous systems. A variety of controlled hydrodynamic techniques, including rotating discs and cylinders, and flow-through ducts (tube, annuli, etc.), have been developed for use at ambient temperature and pressure conditions. However, few of these techniques have been employed at elevated temperatures and pressures. An annular duct geometry (Flarsheim et al., 1986 and 1988, Macdonald et al., 1988, Lvov et al., 1998) can be suggested to carry out electrode-kinetic measurements under well defined hydrodynamic conditions in subcritical and supercritical aqueous systems. An annular duct geometry is recommended for this work because (1) this technique has been subjected to both extensive theoretical and experimental analysis on mass transfer, (2) useful correlations are available for this geometry over a wide range of Reynolds numbers covering both the laminar and turbulent flow regimes, and (3) this hydrodynamic system can be easily used in high temperature aqueous systems.

The measurement of current vs voltage, from which the kinetic parameters are derived, can be carried out in a controlled hydrodynamic cell. Good knowledge of the hydrodynamics is necessary in order to explore the kinetics of the charge transfer processes (OER and HER), which occur in series with mass transfer. The kinetic parameters are then obtained by regression of Equation (2) to the experimental data.

Once the kinetic data have been measured, they can be used in deterministic models for estimating corrosion potential, pit growth rates, and crack growth rates in steels in power plant coolant circuits. The required deterministic models have been developed (Macdonald and Urquidi-Macdonald, 1991), and their utility for predicting the development of damage in BWR primary heat transport circuits and in low pressure steam turbines has been demonstrated, even though the kinetic parameters were "estimates". Extension of these models into the unknown or poorly-defined conditions that exist, for example, in reactor cores, requires experimentally-determined kinetic parameters. The development of deterministic models for predicting damage is vital for plant life extension activities.

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