EXPIRED

IAPWS Certified Research Need - ICRN 8

Development of an Accurate External Reference Electrode for Use in High Temperature and High Pressure Aqueous Solutions

The IAPWS Working Group - Physical Chemistry of Aqueous Solutions has examined the published work in the area of reference electrodes for use in aqueous solutions to temperatures of 374 °C and pressures of 22.1 MPa.

IAPWS recognizes that there is a requirement for work to be pursued in this field and has prepared this document to assist potential investigators obtain sponsorship. Both experimental and theoretical studies are needed for internal and external reference electrodes. In the latter case, both theoretical and experimental studies are required to help define, for appropriate systems, the following properties at high temperatures: the composition of the junction, the transport numbers and entropies of transport. Systems include: NH_3-H_2O, Na_2HPO_4-KH_2PO_4-H_2O, $Na_2B_2O_7$-H_2O, HCl-H_2O, $NaOH$-H_2O, KOH-H_2O, etc.

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

Issued by the

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The Problem

An investigation of the corrosion processes on materials such as iron, nickel, chromium, etc. in high temperature and high pressure aqueous environments has aroused considerable interest in the past few years and has become a well-defined area of concern in the chemistry of power plant cycles. To learn about these phenomena, it is required to develop a detailed understanding of the thermodynamics of the physical-chemistry processes that control the solution chemistry, phase relations, as well as mass and heat transfer. By knowing the equilibrium composition of aqueous solution at high temperature and high pressure and by accessing the thermodynamic properties of the corrosion products, it is possible to predict the initial stage of the corrosion processes and to protect plant equipment against damage.

To make accurate assessments of corrosion rates of the materials used to construct power plant, high quality in situ pH measurements at the prevailing temperatures and pressures should be carried out. These data can only be obtained by using a high-temperature pH sensor together with some external (working at room temperature) or internal (working at high temperature) reference electrode. While the problems of high-temperature yttria-stabilized zirconia (YSZ) pH sensors are well understood (Hettiarachchi et al., 1993), a reliable reference electrode for high temperature environments has not yet been constructed.

A great deal of effort has been expended in recent years to develop a reliable and stable reference electrode to perform high temperature and pressure electrochemical measurements. At the present time there are three feasible approaches for tackling the problem: (1) to use an internal reference electrode operating within the high temperature and pressure aqueous environment (Macdonald, 1978); (2) to employ an all-solid phase reference electrode (Hettiarachchi et al., 1993), which seems to be a valid approach but which has significant problems; (3) to utilize an external reference electrode working at room temperature by solving the problem of thermal liquid junction potential (TLJP) (Macdonald et al., 1979; Perboni and Broglia, 1992).

The external pressure balanced reference electrode (EPBRE) has been extensively employed for power plant pH monitoring, it is currently the most practical option but it has been found that the TLJP has a very significant contribution to the measured potential. However, the available data show that the value of the TLJP varies with the temperature difference across the junction, electrolyte composition, and possibly electrode geometry. The uncertainty in these parameters currently renders the EPBRE no more accurate than 10-20 mV. This uncertainty in the reference potential needs to be reduced by at least a factor of ten if highly accurate pH studies are to be performed using YSZ pH electrodes.

Needed Research Activities

The phenomenological irreversible thermodynamics of the thermal diffusion phenomenon in electrolyte solutions gives an expression (De Groot, 1951; Agar, 1959) for the initial state value of the TLJP E_{TLJ} (T, P, $\bar{n}_{\mathrm{i}}$ at temperature T, pressure P, and composition $\bar{n}_{\mathrm{i}}$ as

$$E_{\mathrm{TLJ}}(T,P,\bar{n}_{\mathrm{i}}) = -\frac{1}{F}\int_{T_1}^{T_2}\left(\sum_{\mathrm{i}}\frac{t_{\mathrm{i}}(T,P,\bar{n}_{\mathrm{i}})S_{\mathrm{i}}^{*}(T,P,\bar{n}_{\mathrm{i}})}{Z_i}\right)dT$$

where Z_i is ionic valence, $t_i(T,P,\bar{n}_{\mathrm{i}})$ and $S_{\mathrm{i}}^{*}(T,P,\bar{n}_{\mathrm{i}})$ are the transport number and the Eastman entropy of transport of i-th charged species, respectively, and F is the Faraday constant.

Therefore, as may be inferred from the above equation, the need to develop methods to derive t_i $(T,P,\bar{n}_{\mathrm{i}})$ and $S_{\mathrm{i}}^{*}(T,P,\bar{n}_{\mathrm{i}})$ over wide ranges of temperature, pressure and composition $\bar{n}_{\mathrm{i}}$ is necessary to obtain accurate values for E_{TLJ} $(T,P,\bar{n}_{\mathrm{i}})$ and hence develop accurate external pressure balanced reference electrodes for use in laboratories and in power plants.

An appropriate strategy of research for developing methods for estimating thermal liquid junction potentials in high temperature and pressure aqueous solutions should consist of devising techniques for obtaining information on the following:

- **The ionic composition** $\bar{n}_{\mathrm{i}}$ of the thermal liquid junction by finding the total composition of the solution at given temperature and pressure

- **The transport numbers** t_i $(T,P,\bar{n}_{\mathrm{i}})$ of all ions in the aqueous solution at given temperature and pressures

- **The Eastman entropies of transport** $S_i^*(T,P,\bar{n}_i)$ of all ions in the aqueous solution at given temperatures and pressures

Brief descriptions of how these problems might be solved are given below:

First, the ionic composition of high temperature and pressure aqueous solutions can be estimated using various computer codes. Solution composition may be estimated with reasonable accuracy at temperatures up to 250 °C. Additional experimental data will be required for higher temperatures and pressures.

Second, some limiting ionic transport numbers are available for temperatures to 100 °C as are some limiting equivalent conductivities for a few dozens of electrolytes at higher temperature. Also a quite reliable extrapolation can be made by using a linear relationship when $\log(t_{anion}/t_{cation})$ is plotted against $1/T$ (Quist and Marshall, 1965). These methods might be used to obtain the needed transport numbers for some systems, but it is probably the case that $t_i\ (T,P,\bar{n}_i)$ values for many ions will have to be measured experimentally by using a high temperature electrochemical cell with and without transport or possibly by developing a moving boundary method.

Finally, it is anticipated that the most significant problem will be to derive ionic entropies of transport $S_i^*\ (T,P,\bar{n}_i)$ for ionic species. At the present time there is a very limited set of data for this parameter and all of them were measured at temperature less than 85 °C (Lvov et al., 1986; Lvov et al., 1993). A great deal of effort should be directed toward developing both experimental and theoretical methods for obtaining ionic entropy of transport data at temperatures up to 374 °C.

It is also necessary to analyze electrode design and procedure of operation to obtain a precise knowledge of the internal solution composition.

Expected Results

The proposed work should result in the development of a reference electrode of sufficient accuracy (1-2 mV) to permit reliable potentiometric studies to be carried out in aqueous solutions at temperatures to 374 °C.

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