Effect of Inhibitors on the Kinetics of Electrochemical Hydrogen Absorption in Metals

H. W. Pickering, F. M. Al-Faqeer and K. G. Weil

Department of Materials Science and Engineering

The Pennsylvania State University

University Park, PA 16802

This paper will review some recent developments that address the issue of how the addition of certain species to the electrolyte inhibits the kinetics of hydrogen adsorption on, and absorption into, metals. It extends the so-called IPZ mechanistic analysis that has previously been developed to evaluate the kinetics of the hydrogen evolution and absorption reactions on otherwise clean metal surfaces, i.e., metal surfaces that are otherwise free of adsorbates other than hydrogen. Finally, it considers the addition of other species to the electrolyte that specifically adsorb on the metal surface and compete with hydrogen for available surface sites. This recently derived (newly named IPZA) analysis will be described and illustrated for different inhibiting species that compete with hydrogen for the available surface sites. The coverage, θ_I, of these inhibitor species is also obtained from the IPZA analysis along with the above mentioned surface parameters. This θ_I value can then be compared to values of θ_I independently obtained by two other methods, the electrochemical quartz crystal microbalance (EQCM) and the electrochemically measured corrosion rate in the absence and presence of the inhibitor.

The IPZ analysis can determine the individual rate constants of the hydrogen evolution reaction, k_1 and k_2, (from the steady state hydrogen permeation data or from the polarization curve); the kinetic-diffusion rate constant, k, and its components, the absorption rate constant, k_{abs} and the desorption rate constant, k_{des}; the hydrogen surface coverage, θ_H; and the hydrogen concentration at the charging side of the membrane, C^o. The original IPZ analysis derived for Langmuir adsorption conditions has been used extensively in the literature. A newer generalized version of the original IPZ analysis has been derived for Temkin-Frumkin adsorption conditions. It has been recently utilized for characterizing the effect of hydrogen sulfide additions to an acidic electrolyte on modifying these rate constants and related surface parameters during the hydrogen evolution and absorption reactions on iron. The IPZA analysis determines these same parameters for the adsorbing hydrogen species in the presence of the competitively adsorbing inhibiting species, as well as the surface coverage, θ_I, of the inhibiting species.

The IPZA analysis has been applied to steady state hydrogen permeation data obtained for iron in acidified aqueous solution containing either hexamethylenetetramine (HMTA) or iodide ion, I^-, inhibitor species for the hydrogen adsorption and absorption reactions. Agreement of the coverage, θ_I, of the inhibitor species provided by the IPZA analysis with the θ_I values obtained from the EQCM and the corrosion rate experiments was good for both inhibiting species. These results will be presented at the meeting.