



Challenges in the theory of electron transfer at passive interfaces

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Abstract

Electron transfer (ET) has been described as the simplest of chemical reactions, because it generally does not result in the change in identity of a chemical species, but merely results in a change in the oxidation state of a single atomic center. In principle, ET is the ideal vehicle within which to develop the theory of rate processes, because of the inherent simplicity of the reaction dynamics. However, the development of an effective theory that can predict reaction rates from first principles has proven to be elusive and scientists are no closer to that goal than they were three decades ago. However, starting with the groundbreaking work of Gurney in 1931, which was hailed as one of the first triumphs of quantum mechanics, QET (quantum electron transfer) theory has provided an unassailable explanation of Tafel's law; the exponential dependence of the rate of a charge transfer reaction on the applied potential. This paper provides a brief review of QET theory with the particular goal of accounting for Tafel's law on passive surfaces. The inverse Tafel's law, where the current decreases exponentially with increasing voltage for an anodic (oxidation) reaction, is also discussed. In this case, the decrease in the current is due to the thickening of an oxide layer on the surface and the resulting decrease in the quantum mechanical tunneling probability of charge carriers across the film. Both phenomena (the normal and inverse Tafel's law) occur in electrochemical and corrosion systems and, indeed, often occur in the same system, such as the reduction of a cathodic depolarizer on a passive surface. Finally, the use of the inverse law as a tool for probing the dynamics of formation of thin oxide films on metal surfaces is discussed with emphasis on the

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oxidation of hydrogen on oxidized platinum in alkaline solution at ambient and elevated temperatures.

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1. Introduction

A hundred years have now passed since Tafel formulated his famous equation

$$\eta = a + b \ln(i) \quad (1)$$

where η is the overpotential ($\eta = E - E^\circ$), E is the applied potential, E° is the equilibrium potential, i is the current density, and a and b are constants [1]. This most basic equation of electrochemical kinetics was originally developed empirically for the hydrogen evolution reaction (see Ref. [2]), but since that time it has been demonstrated, with suitable modifications for incorporating mass transfer effects, to hold for most, if not all, charge transfer reactions. Subsequent work demonstrated that the originally empirical constants, a and b , could be written in terms of fundamental quantities as $a = b \ln(i_0)$ and $b = RT/z\alpha F$, where T is the Kelvin temperature, R is the universal gas constant, F is Faraday's constant, z is the charge number, i_0 is the exchange current density (current density for the partial anodic or the partial cathodic reaction at the equilibrium potential), and α is the transfer coefficient.

The importance of Eq. (1) is manifold, but the most significant feature is that it demonstrates the exponential relationship between current and voltage for charge transfer reactions occurring at interfaces under activation control. This empirical relationship is the foundation of electrochemical kinetics, and all theories and models that are advanced to account for the kinetics of charge transfer reactions at interfaces must account for Tafel's Law [Eq. (1)]. These theories and models extend from Gurney's pioneering model of 1931 [3,4] to explain hydrogen evolution, which was regarded as a one of two early triumphs for quantum mechanics (the other being the explanation of α particle emission in radioactive decay), to the award of the Nobel Prize in 1992 to Marcus [5–7] for a model that incorporated solvent reorganization. Numerous quantum mechanical models, each becoming successively refined in terms of some aspect of the original Gurney treatment of 1931, have appeared over the years and it may now be claimed (by some) that charge transfer in an elementary reaction is now well understood, although prediction of the rate constant for any given reaction is seldom better than being qualitative or semi-quantitative, at best. In parallel with the development of the quantum mechanical models, various classical models have been devised, mostly upon the basis of the activated complex or transition state theory (TST) that was originally devised by Eyring [8]. TST has had a profound impact on almost all branches of the physical sciences and engineering, and it remains one of those deserving advances that were never awarded the ultimate prize. Many of these models have combined the two approaches, by using quantum

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