modern aspects of electrochemistry

no. 37

Edited by RALPH E. WHITE

MODERN ASPECTS OF ELECTROCHEMISTRY

No. 37

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Modern Aspects of Electrochemistry

Modern Aspects of Electrochemistry, No. 36:

- The study of electrochemical nuclear magnetic resonance (EC-NMR); *in situ* both sides of the electrochemical interface via the simultaneous use of ^{13}C and ^{193}Pt NMR.
- Recent impressive advances in the use of rigorous ab initio quantum chemical calculations in electrochemistry.
- Fundamentals of ab initio calculations, including density functional theory (DFT) methods, help to understand several key aspects of fuel cell electrocatalysis at the molecular level.
- The development of the most important macroscopic and statistical thermodynamic models that describe adsorption phenomena on electrodes.
- Electrochemical promotion and recent advances of novel monolithic designs for practical utilization.
- New methods for CT analysis and an explanation for the existing discrepancy in Li diffusivity values obtained by the diffusion control CT analysis and other methods.

Modern Aspects of Electrochemistry, No. 35:

- Impedance spectroscopy with specific applications to electrode processes involving hydrogen.
- Fundamentals and contemporary applications of electroless metal deposition.
- The development of computational electrochemistry and its application to electrochemical kinetics.
- Transition of properties of molten salts to those of aqueous solutions.
- Limitations of the Born Theory in applications to solvent polarization by ions and its extensions to treatment of kinetics of ionic reactions.

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Preface

This volume of Modern Aspects contains seven chapters. The major topics covered in the first six chapters of this volume include fundamentals of solid state electrochemistry; kinetics of electrochemical hydrogen entry into metals and alloys; oxidation of organics; fuel cells; electrode kinetics of trace-anion catalysis; nano structural analysis. The last chapter is a corrected version of chapter four from Volume 35.

Faisal M. Al-faqeer and Howard W. Pickering begin the first chapter by going back to 1864 and Cailletet who found that some hydrogen evolved and was absorbed by iron when it was immersed in dilute sulfuric acid. The absorption of hydrogen into metals and alloys can lead to catastrophic failures of structures. They discuss the kinetics of electrochemical hydrogen entry into metals and alloys.

In chapter three, Clyde L. Briant reviews the electrochemistry, corrosion and hydrogen embrittlement of unalloyed titanium. He begins by reviewing the basic electrochemistry and general corrosion of titanium. He also discusses pitting and galvanostatic corrosion followed by a review of hydrogen embrittlement emphasizing the formation of hydrides and the effect of these on titanium's mechanical properties.

Christos Comninellis and György Fóti discuss the oxidative electrochemical processes of organics in chapter three. They begin by defining direct and indirect electrochemical oxidation of organics. They introduce a model that allows them to distinguish between active (strong) and non-active (weak) anodes. Different classes of organic compounds are used for kinetic models of organic oxidation at active and non-active type anodes.

In chapter five, Kas Hemmes presents a comprehensive discussion of fuel cells and Carnot engines; Nernst law; analytical fuel cell modeling; reversible losses and Nernst loss; and irreversible losses, multistage oxidation and equipartition of driving forces. He compares two analytical models with experimental results on a 110 cm^2 Molten Carbonate Fuel Cell. He also discusses fuel cell configurations and geometries, and numerical fuel cell modeling of various cells such as the Alkaline Fuel Cell, Polymer Electrolyte Membrane Fuel Cell, Direct Methanol Fuel Cell, Phosphoric Acid Fuel Cell, Molten Carbonate Fuel Cell, and Solid Oxide Fuel cell. He ends with a discussion of new developments and applications of fuel cells: fuel cells in trigeneration systems; coal/biomass fuel cell systems; indirect carbon fuel cells; and direct carbon fuel cells.

Zoltán Nagy discusses in chapter five the catalytic effect of trace anions in outer-sphere heterogeneous charge-transfer reactions. He begins with the observations of H. Gerischer and continues with the observations of D. C. Johnson and E. W. Rosnick. The measurements of J. Weber, Z. Samec, and V. Marecek are explored as well. A discussion of the observations of F. R. Smith and J. T. Wadden and the work of Z. Nagy and L. A. Curtis, and H. C. Hung and Z. Nagy are included. He states that it is reasonable to conclude that trace-anion catalysis of outer-sphere charge-transfer reactions may be a very general phenomenon.

Chapter six by M. Abraham and M. C. Abraham discusses the results of experimental and theoretical investigations on bridging electrolyte-water systems as to thermodynamic and transport properties of aqueous and organic systems. This chapter is a corrected version of chapter four in Volume 35. In the course of editing Volume 35, the authors provided a final set of edited and corrected diskettes. However, in conversion to CD format for the final pagination and indexing stage, using supposedly the same software, many errors and transpositions of diagrams occurred in the final production stage of the chapter. The Editors and Publisher find it necessary and appropriate to reprint this corrected chapter in its entirety in this volume. We apologize to the authors and our readers for any inconvenience this may have caused.

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Kinetics of Electrochemical Hydrogen Entry into Metals and Alloys

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I. INTRODUCTION

In 1864, Cailletet found that when an iron sample was immersed in dilute sulfuric acid, some hydrogen evolved and some was adsorbed by the iron.[1-3] In 1922, Bodenstein found that application of a cathodic current would result in an increase in the amount of hydrogen entering iron.[4] His results showed that the amount of hydrogen permeating an iron membrane was directly proportional to the square root of the applied current density.[2-4] These two observations demonstrated that some of the hydrogen atoms produced electrochemically during corrosion of iron may enter the metal lattice and permeate through the metal and that the quantity of hydrogen entering the metal can be increased by applying a cathodic current. The entry of the electrolytic hydrogen into metal is related to the hydrogen evolution reaction.

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Atomic hydrogen has a uniquely high diffusivity being able to rapidly diffuse through some metals at room temperature. The diffusivity of hydrogen within iron, with its rather loosely packed bcc crystal lattice, is extremely high. The diffusion coefficient of hydrogen in fully annealed iron is of the order of 10^{-5} cm^2 s^{-1} at room temperature.[5,6] This is about 12 orders of magnitude greater than that of other interstitials such as carbon and nitrogen. The high mobility of hydrogen atoms into metals is commonly attributed to the small size of its atom.[7]

The entry of these hydrogen atoms into the metal lattice is an undesirable reaction because of the damage that the absorbed hydrogen causes to the physical and mechanical properties of the metal.[3,7-10] Internal bursts and blisters may be realized during corrosion or cathodic polarization if large amounts of hydrogen collect in a localized area.[3,8,9] The absorbed hydrogen causes hydrogen embrittlement and, as a result, possible catastrophic failure of structures in service.[3,8,11]

There are many sources of absorbed hydrogen in metals. Hydrogen can enter metals and alloys during cleaning, pickling, welding or electroplating processes, to name a few. Or, it may be picked up from the service environment as a result of cathodic protection or corrosion.[3,5] In all of these processes, the hydrogen evolution reaction (HER) is a possible cathodic reaction with atomic hydrogen as a byproduct.[3,6,12-18] It is usually an unavoidable electrode reaction proceeding simultaneously with these processes.

Mechanistic analyses have been developed which evaluate the kinetics of hydrogen entry into metals via the hydrogen evolution (HER) and absorption (HAR) reactions. These analyses can determine the individual rate constants of the hydrogen evolution reaction, k_1 and k_2, (from the steady state permeation data or the polarization curve) and the kinetic-diffusion rate constant, k, the hydrogen surface coverage, θ_H, and the hydrogen concentration in the charging side of the membrane, C^o, (from permeation data). The surface coverage of a second adsorbate, θ_A, can also be evaluated. Example applications of these analyses are given for characterizing the effects of hydrogen sulfide and hexamethylenetetramine (HMTA) on the HER and HAR. They are known as The IPZ and IPZA (Iyer, Pickering, Zamanzadeh, Al-Faqeer) analyses. The surface coverage's of HMTA were determined using the newer IPZA analysis, which takes into account competitive adsorption under Langmuir isotherm. Good agreement was obtained with its coverage's determined by two other independent