BOOK REVIEWS

The use of single-crystal electrodes, a host of new surface probes and the ability to analyze a working electrochemical interface in situ and then ex situ using ultra-high-vacuum (UHV) techniques have led to rapid experimental advances. The first three chapters of the book provide an introduction to structural characterization and behavior of single-crystal metal-electrode surfaces. The tools of surface crystallography as applied in UHV are expertly reviewed by Michel Van Hove. Phillip Ross and Dieter Kolb go on to describe in situ methods of characterizing working 'wet' electrodes by such techniques as surface extended X-ray absorption fine structure (SEXAFS), grazing-incidence X-ray scattering (GIXS), scanning tunneling microscopy (STM), atomic-force microscopy (AFM) and surface secondharmonic generation (SHG). Coupled wet electrochemistry and ex situ UHVanalysis studies are described, in which low-energy electron diffraction (LEED) and other electron spectroscopies are employed for structural analysis in UHV. These tools, coupled with cyclic voltammetry, are used to understand and discuss the structure of underpotentially deposited metal overlayers and potential-induced reconstruction of electrode surfaces.

The precise structure of directly adsorbed ions and diffusely ordered solvated ions that make up the electrochemical double layer at the electrochemical interface is difficult to characterize using any of the techniques above. In order to begin to understand the issues involved, Manuel Soriaga reviews molecular adsorption at single-crystal electrodes. Vibrational spectroscopy, via high-resolution electron energy-loss spectroscopy (HREELS) and infrared absorption spectroscopy (IRAS), is used to provide structural information on adsorbate bonding geometries through surface selection rules and analogies to inorganic cluster compounds. (It should be noted that recent dynamical LEED and SEXAFS studies have repudiated several nitric oxide site assignments based on vibrational spectroscopy, and this has diminished the enthusiasm for extrapolating the structures of cluster compounds to surfaces.) A metal electrode tempered by co-adsorbed ions and water defines an inner electrochemical layer, and Gerhard Pirug and Hans Bonzel discuss the simulation of such lavers in UHV by co-adsorption of alkali metals and water. Wolfgang Schmickler and Karl Heinzinger provide analytical and molecular-dynamics-based theoretical chapters on the electrochemical interface. The final experimental chapters of the book, by Zofia Borkowska and Ulrich Stimming and by Fred Wagner, examine the relationship between UHV simulations of electrochemical lavers at cryogenic temperatures and 'wet' electrochemistry. Water typically desorbs from metal electrodes at temperatures below 200 K. Nevertheless, the consensus of the authors is that diffusion and conductivity in favorable acid/water systems can be sufficient for purposes of electrochemical simulations at temperatures as low as 150 K. The chapter by Wagner is truly delightful as he thoughtfully catalogs the difficulties of connecting cryogenic UHV surface science with wet electrochemistry from experimental and theoretical points of view. Impressive results from UHV simulations of the electrochemical interface include the ability to count water molecules of ion hydration by thermal desorption and the spectroscopic identification of the hydronium ion (H₃O⁺) by HREELS when HF or HCl is co-adsorbed with H₂O on Pt(111).

The text provides a fine introduction to the field of interfacial electrochemistry. Its emphasis on current research and the many references to the primary literature suggest it will be much appreciated by the electrochemical community. Crystallographers will be particularly interested in the important role that diffraction techniques (LEED, GIXS and SEXAFS) have played in structural determinations of the inner electrochemical layer. At the same time, they may pause to reflect on how difficult it is to characterize the structure of the outer Helmholtz, or diffuse Gouy–Chapman, layer of solvated ions. Despite the difficulties of microscopically characterizing the electrochemical double layer, the text clearly indicates that rapid progress is being made in the emerging field of interfacial electrochemistry. Excellent accounts of the recent advances in and future prospects of the field are provided.

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Books Received

J. Appl. Cryst. (1994). 27, 132

The following books have been received by the Editor. Brief and generally uncritical notices are given of works of marginal crystallographic interest; occasionally, a book of fundamental interest is included under this heading because of difficulty in finding a suitable reviewer without great delay.

Infrared transmission spectra of carbonate minerals. By G. C. Jones and B. Jackson. Pp. xv + 222. London: Chapman & Hall, 1993. Price £75.00. ISBN 0-412-54650-7. The stated purpose of this compilation is 'to make available recently acquired spectra of as many well-characterized carbonate minerals as possible in order to further the use of infrared spectroscopy in mineralogy.' Fourier-transform IR spectra and relevant physical and chemical data are presented on facing pages for over 100 minerals arranged in alphabetical order. In a few cases, expanded spectra are provided on an additional page. Cross references are provided, where available, for specimens that have been examined by X-ray powder diffraction.