J Solid State Eletrochem (2003) 7: 731–732
DOI 10.1007/s10008-003-0432-6

BOOK REVIEW

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James A. Wingrave (ed.), Oxide surfaces (Surfactant sciences series, vol. 103).

Dekker, New York, 2001, Hardcover, 536 pp (ISBN 0-824-70000-7), US $185.00

Inorganic oxide surfaces are everywhere, not only on ceramics and technical glasses. Oxide layers help to passivate many metals, otherwise they may be on the first step towards corrosion. The editor even claims that "most of the surfaces in the universe are covered with oxides of some sort". A book on such a general topic cannot be exhaustive. Wingrave's monograph does not try to give a general overlook but is, in spite of its title, an accumulation of articles with different levels of specialization and quality.

For me, the most important part is that on materials science. Chapters 2 and 3 by Netz and Andelman and by Cohen Stewart and De Keizer, respectively, review the physics of polymers on surfaces and the adsorption kinetics. The most interesting examples, polymer brushes and polymer grafted hydrophobic oxide surfaces, are exposed in chapter 8 by Cohen et al. All three articles contain a lot of interesting polymer physics, both theory and experiments. In this context I only missed an explicit discussion of the issue of fractal dimensions, which is really suggested by fig. 7 on page 123. Chapter 9 by Hernandez et al. on ceramic membranes is a highlight: a history of applications, synthesis methods, and the characterization by pore size distribution and SEM measurements are all of great interest for engineers and scientists working in related fields. This chapter will indeed "assist the reader in solving problems encountered in ... interfacial science".

Much of the inorganic chemistry of the insulating oxides and especially of clays is summarized in chapters 5 and 6 by Casey et al. and by Brady et al., respectively. The formal thermodynamics and kinetics of the adsorption in aqueous solutions is the subject of chapter 1, written by the editor himself. This is a lengthy discussion (113 pages), with a vast number of formulas. I doubt that any reader can make use of just these specialized expressions as on pages 10 and 11, e.g. The titration curves for a "hypothetical metal oxide" (fig. 4) are trivial, but the basic question has not been addressed at all: the state of hydroxylation of an oxide surface depends on its morphology, and this is still an object of vivid research and controversy, even for simple systems. Chapter 4 is an extension of chapter 1 by the same author, including activity coefficients from the Debye–Hückel-model. Aprotic liquid–mineral oxide systems are studied in the context of corrosion inhibition (chapter 7 by Førland and Høiland). Other nonaqueous solvents are alcohols, which show association by hydrogen bonding and are, in this respect, more similar to water. Adsorption isotherms with a stepped ("sigmoidal") shape are presented, but what is the origin of this characteristic feature?

Chapter 10 by Vayssilow on vibrational interactions between substrate and adsorbent is the only attempt to account for the very detailed picture that molecular physics has drawn of adsorption processes during the last decades. A well-funded discussion on vibrations of adsorbed species and the transfer of energy to other modes and stochastic motions is given. Unfortunately, the drawings are reproduced with low resolution and the text contains a number of sometimes misleading errors. Figure 7 deals with ammonia dimers, not dimmers, and without too much searching I found further misprints in equations 44, 82, 86, 128, 132, ... The article treats an interesting subject, but it was not written with much relationship to the respective experiments, such as He scattering for the dispersion of surface phonons and others. The rotation (in fact rotational tunnelling) of ammonia on MgO has been studied in much more detail in neutron scattering experiments by Prager et al. than in the cited work by Girardet (cf. page 430).

I found the last chapter 11 the *least* useful. It contains a fundamental discussion on the thermodynamics of adsorption by Tóth and starts essentially from his equation 10, which is derived in a way similar to the textbook proof of the Clausius–Clapeyron formula:

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$$\left(\frac{\partial \pi}{\partial p}\right)_T = (v^{\mathrm{g}} - v^{\mathrm{s}})\frac{n^{\mathrm{s}}}{A} \tag{1}$$

The author shows that for common isotherms, such as the Langmuir formula, the derivative of the surface tension π with respect to external pressure p diverges when the coverage Θ attains 1, but claims that the right side, with the difference of the molar volumes of gas v^{g} and adsobate v^{s} and the excess amount of adsorbate n^{s}, must be finite, since the denominator only contains the constant surface area A. This leads him to the conclusion that generally accepted adsorption isotherms (as actually used in other parts of the book) are "thermodynamical nonsense".

I have several objections against this article. Firstly, the subject has no specific relation to oxides, and will certainly not help engineers and students, as is claimed by the editor for his book. Secondly, I think that most of this is based on fundamentally wrong assumptions. It is very clear from equation 4 in the same text that A signifies the area of the empty rather than of the total surface and goes to zero for $\Theta \to 1$. It is further clear that divergence of this derivative does not imply divergence of π itself and, therefore, cannot be discarded by principal reasons. The singularity of the derivative is probably related to the very low entropy of a monolayer filled up to the last site. Further confusion is made between complete coverage of the first surface layer and a total coverage amounting to that of one monolayer. In contrast to filling one distinct layer up to the very last site, a total coverage equivalent to one monolayer, Θ_{m}, is easily obtained and exceeded by multilayer adsorption. The author refers to a series of typical BET systems (fig. 2) showing that Θ_{m} is reached at pressures around one half of the saturation pressure, and then "cures" the Langmuir isotherm by multiplying the coverage with a factor >1, with the result that at a finite pressure the monolayer is filled, rather than at infinite pressure as to be expected (equation 65). To my understanding, all this is "thermodynamical nonsense".

The book deserves attention as a reference for specialists such as surface chemists, but has to be read with some scepticism. I could not recommend it to students or to engineers looking for some general information.