EDITORIAL

Editor's note

Galina Tsirlina [1]

The article "Perspective on experimental evaluation of adsorption energies at solid/liquid interfaces" by A. R. Zeradjanin, I. Spanos, J. Masa, M. Rohwerder, and R. Schlögl induced rather intensive discussion of the corresponding author with Reviewers and Editor. We believe that publication of this work can cause more wide discussion in electrochemical community in respect to understanding of adsorption phenomena, which complexity is far beyond any simplified correlations and descriptors.

Just in case, we would like to remind the readers what was treated as the hydrogen adsorption energy E_{M-H} used by Trasatti in his widely known correlations [1] (Ref.6 in the article under discussion). There were three sources of E_{M-H} values. First, E_{M-H} were used estimated by Krishtalik from the differences of activation energies of hydrogen discharge step, with using E_{M-H} for Hg as the benchmark. There are many strains and limitations for these estimates (recent discussion is available [2]), and surely *the resulting values for various metals are related to different surface coverages*. Second, the heats of formation of metal hydrides were considered a source of E_{M-H}, and some values of this type demonstrated essential difference from Krishtalik's values. *It is hardly possible to assign these values to any coverage*, but probably they are more close to hypothetic high H coverages in the absence of water. Third, for transition metals, the direct "dry" (gas phase) data for adsorption heats *mostly at high H coverages* were considered. In case of Cu, Au, and Ag (*low H coverages*), the spectroscopic dissociation heat values were also attracted. These sets of diverse data allowed to obtain volcano plots, but never allowed to interpret these plots straightforwardly and quantitatively.

Interpretation was impossible because of dramatic difference of volcano ascending and descending branches in respect to (i) hydrogen coverage (low and high respectively) and (ii) the nature of the limiting step (Volmer step for the former branch, but never for the latter).

Surely modern activities related to correlations of this type are important (either with E_{M-H} or with work function, as these two quantities being also correlated by some means). First of all, new experimental data are required to separate the roles of certain factors. It is very important to form the link between the physics of hydrogen evolution elementary act and E_{M-H} as the key parameter of reaction terms. In particular, *it is of primary importance to combine the work function experiments started by the authors with direct measurements of hydrogen coverage*. At this stage we can only assume from the rough estimate based on Nernst equation that for 5% of hydrogen in humid nitrogen at atmospheric pressure the coverage on platinum group metals corresponds to H upd coverage at ca. 40 mV RHE; i.e., the coverage is high enough if the system is equilibrated. Simultaneously, very low H coverage is expected for Au and Cu. What is the reason of the difference in exchange current densities, the coverage as is or E_{M-H} (and, correspondingly, work function)? The coverage is affected by E_{M-H} but also finds itself independently in equations for the rates of certain elementary steps.

Let us also remind the reader that Breiter and Kennel [3] documented hydrogen adsorption heats for various H coverages on Pt in various electrolytes. This quantity (and correspondingly E_{M-H}) undergoes dramatic Temkin-type decrease with coverage: the difference for low and high coverage achieves 0.5 eV in acids and appears to be even higher in alkaline solutions. This huge effect should be surely taken into account when the observed effects are of the same or lower values.

Finally, we would like to stress that at the current step of electrocatalysis development, it is probably more important to analyze not correlations themselves but just deviations from these correlations, to shed light on the origin of complex phenomena.

✉ Galina Tsirlina
tsir@elch.chem.msu.ru

1 Department of Electrochemistry, Faculty of Chemistry, Moscow State University, Moscow, Russia

References

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