Langmuir **1995,** *11,* 2845−2846

Comments

Comments on "Complementarity in Radiochemical and Infrared Spectroscopic Characterization of Electrode Adsorption"

Editor's Note: The paper by Wieckowski (*Langmuir* **1994**, *10*, 920), which is the subject of the following comment, should preferably have been published as a Comment on the original paper by Parry et al. (*Langmuir* **1993**, *9*, 1878).

We wish to comment on the paper "Complementarity in Radiochemical and Infrared Spectroscopic Characterization of Electrode Adsorption".[1] In his article, Wieckowski criticizes two sentences from the introduction to a recent paper of ours,[2] which had to do with an infrared spectroelectrochemical study of anionic adsorption during underpotential deposition (UPD). The author singles out comments made about radiotracer techniques but ignores those made by us about other methods. Additionally, Wieckowski makes no statements whatsoever about our data in ref 2, nor does he question our interpretations of those data. Furthermore, the author presents no new data, but instead republishes data (and the discussion of those data) from a separate publication.[3]

The statements that Wieckowski questions are as follows: "Radiotracer experiments,[4,5] which do indeed provide data on electrolyte behavior in a thin-layer cell, cannot differentiate between surface and solution species. Furthermore, radiotracer techniques do not allow for the determination of the orientation of adsorbed anions, and does not provide information on the behavior of surface water." We contend that in his criticism of our paper, Wieckowski took these two sentences partially out of context, in order to make a case that our statements misrepresented the capabilities of radiotracer techniques.

In his "polemical" paper,[1] Wieckowski makes the case that "none of the statements of [ref 2] quoted above is strictly correct and ... the first assertion is simply incorrect." Examination of our paper (ref 2, p 1879) will show the reader that our statements regarding radiotracer techniques were made within the context of studies of copper UPD on gold electrodes. A thorough introductory section to any research paper should include background on alternative and complementary methods that have been applied to investigations of similar systems. We believe that we did just this in our paper, where we provided information on a host of other methods that have been used (for UPD studies of Cu on Au) besides radiotracer techniques, including both in-situ and ex-situ methods. Our intention was to point out the utility and limitations of various techniques that may be used to study electrochemical interfaces, within the context of UPD studies.

The experimental conditions for the radiotracer results presented by Wieckowski[1,3] are well removed from those used for surface infrared investigations in Parry et al.;[2] however, Wieckowski sidesteps this issue. Our studies were conducted in electrolyte solutions which were aqueous 0.5 M SO_4^{2-}; yet Wieckowski attempts to support his objections to our comments with data from solutions that are aqueous 5×10^{-4} M SO_4^{2-}, with significant excess concentration (in relation to SO_4^{2-}) of (nonadsorbing[6]) perchlorate anion, ClO_4^-. There is absolutely no doubt that radiotracer techniques could *not* distinguish between solution and surface sulfate species (be they SO_4^{2-} or HSO_4^-) under the *solution and electrode surface conditions* that we used. This distinction can only be accomplished by radiotracer techniques in solutions of very low concentration of sulfate species ($<10^{-2}$ M[7]), and only then by subtraction of solution count rates from total count rates (thereby requiring at least two experiments). Surface infrared techniques are not subject to such a limitation; this is the issue that we attempted to point out in the introduction of our paper. Elsewhere in our paper, we showed clearly that we could distinguish between surface and solution sulfate species and also between sulfate and bisulfate. These are capabilities which the radiotracer technique does not have for the systems that we studied.

Additionally, it was possible for us to observe the potential-dependent reorientation of adsorbed water by using surface infrared spectroelectrochemistry.[2] Radiotracer techniques would not be useful for providing surface or orientational information on adsorbed water on smooth electrodes in aqueous solutions. In no way can one make the case that in the solutions that we used, compared to those used by Wieckowski,[1] the electrode/solution interfaces in the two systems were "morphologically equivalent", as he asserts.

Wieckowski alludes to our purported supposition that infrared and radiotracer techniques, as applied to investigations of the electrode−solution interface, are not complementary. In fact, no such claim was made nor intended. Indeed, in a recent electrochemical quartz-crystal microbalance study of copper UPD on Au{111},[8] one of us noted corroborating data from similar systems in which both infrared and radiotracer methods (not to mention other techniques) were utilized. Furthermore, complementarity of surface infrared and radiochemical techniques has been presented by one of us in recent reviews of infrared spectroelectrochemistry.[9−11]

In deference to Wieckowski's criticism of our first statement in question above, we admit that this first

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[1] Wieckowski, A. *Langmuir* **1994**, *10*, 920.

[2] Parry, D. B.; Samant, M. G.; Seki, H.; Philpott, M. R.; Ashley, K. *Langmuir* **1993**, *9*, 1878.

[3] Shi, Z.; Lipkowski, J.; Gamboa, M.; Zelenay, P.; Wieckowski, A. *J. Electroanal. Chem.* **1994**, *366*, 317.

[4] Horanyi, G.; Rizmayer, E.; Joo, P. *J. Electroanal. Chem.* **1985**, *152*, 211.

[5] Zelenay, P.; Wieckowski, A. In *Electrochemical Interfaces*; Abruña, H. D., Ed.; VCH Publishers: New York, 1991.

[6] Samant, M. G.; Kunimatsu, K.; Seki, H. *Anal. Chem.* **1994**, *66*, 1781.

[7] Lipkowski, J.; Stolberg, L; Morin, S.; Irish, D. E.; Zelenay, P.; Gamboa, M.; Wieckowski, A. *J. Electroanal. Chem.* **1993**, *355*, 147.

[8] Borges, G. L.; Kanazawa, K. K.; Gordon, J. G.; Ashley, K.; Richer, J. *J. Electroanal. Chem.* **1994**, *364*, 281.

[9] Ashley, K.; Pons, S. *Chem. Rev.* **1988**, *88*, 673.

[10] Ashley, K. *Spectroscopy* **1990**, *5* (1), 22.

[11] Ashley; K. *Talanta* **1991**, *38*, 1209.

0743-7463/95/2411-2845$09.00/0

sentence was, if taken by itself, unfortunately somewhat ambiguous. We therefore offer a revision to this sentence as follows: "Radiotracer experiments ... cannot differentiate between surface and solution species *under the experimental conditions used in this work.*"

It is regrettable that Wieckowski's criticism of our paper's[2] introductory comments (which were but a very minor component of our work) was published as an "article", rather than as a "comment". Wieckowski's "polemic"[1] presented no new data and did not discuss the data presented in our paper. A proper "polemical" argument would discuss *data*, and/or the interpretation of data that are controversial. We urge that in the future, under similar circumstances, a more appropriate forum is used to clear up issues of this kind.

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Received October 17, 1994

LA940808V

Reply to Comments on "A Complementarity in Radiochemical and Infrared Spectroscopic Characterization of Electrode Adsorption"

At the end of their comment, Parry *et al.* write: "we admit that the first sentence (*Radiotracer experiments, which do indeed provide data on electrolyte behavior in a thin-layer cell, cannot differentiate between the surface and solution species ...*[1] *)* was, if taken by itself, unfortunately somehow ambiguous". However, they are unhappy that an article rather than a comment publication format was chosen in this author response to ref 1.[2] The use of an article was indeed appropriate considering the severity of the ambiguity. The statement, as written,[1] leads the reader to believe that surface concentrations cannot be determined using radiotracer techniques. This is in direct contrast to work being performed in our and other research laboratories. This author felt it extremely important to clarify this point. Oddly, Perry *et al.* also insist that new data were needed in ref 2 (to comment on their original paper[1]). Since "polemical" means "pertaining to a controversy, argument",[3] and the controversy related to the past events (publication date 1993[1]), the past and then current (ionic, 1994) data were used to illuminate the seed of the controversy.

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Received February 2, 1995

LA950080Y

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[1] Parry, D. B.; Samant, M. G.; Seki, H.; Philpott, M. R.; Ashley, K. *Langmuir* **1993**, *9*, 1878.

[2] Wieckowski, A. *Langmuir* **1994**, *10*, 920.

[3] *The American Heritage Dictionary*, 2nd ed.; Houghton Mifflin Co.: Boston, MA, 1985.