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Author(s)	HORIUTI, Juro; KEII, Tominaga; MITUYA, Atusi
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VELOCITY OF HYDROGEN EVOLUTION AT LOW OVERVOLTAGE: ANSWER TO COMMENTS OF BOCKRIS

By

Juro HORIUTI, Tominaga KEII and Atusi MITUYA

We might proceed on discussing the points raised by BOCKRIS[1] commenting on the paper[2] of the two of the present authers.

His point I is that KEII's calculation be inadequate because that (a) Eq. (6) in the latter paper be wrong and (b) the dissolution of platinum effected favourably by $Pt \rightarrow Pt^{2+} + 2e_0^-$ rather than by $Pt \rightarrow Pt^{4+} + 4e_0^-$ assumed KEII.

As pointed out by him, the latter equation should be read,

$$C^{Pt^{++++}} = \frac{(C^{H^+})^4}{(P^{H_2})^2} e^{-4FE_H/RT} \qquad (1)$$

exponent 4 to C^{H^+} being missing by misprint in the paper, the actual calculation being however carried out correctly as shown by the numerical result given there.

As to (b) we might mention that the conclusion of the contamination by dissolution of being impossible remain unchanged whichever reaction be taken responsible for the dissolution, only difference being that the period required for one platinum atom to deposit on the mercury surface is reduced from 10^{73} years to 10^{19} years, by taking $Pt \rightarrow Pt^{2+} + 2e_0^-$ in place of $Pt \rightarrow Pt^{4+} + 4e_0^-$, completly in agreement with his remark that the period is thus reduced by 10^{54} factor, which puts the same thing in other way.

As regards his latter two points II and III, the present authors wish to emphasize the importance of measuring so small a rate of hydrogen evolution at equilibrium of every electrode reaction but that of the latter, since otherwise the current due to the former would appreciably mask the latter. The cathodic current of a solution containing plenty of mercury ion would thus consist of the reaction,

1) BOCKRIS, J. Res. Inst. Catalysis, vol. 2, (1953), 105.
2) HORIUTI and MITUYA, ibid. vol. 2, (1951), 79.

$$Hg_2^{++} + 2\varepsilon = 2Hg \qquad (2)$$

as well as of that of the hydrogen evolution, principally, perhaps, of the former. But the absence of mercury ion in the solution does not assure on the other hand, as would seem to do at first sight, the true rate of the hydrogen evolution to be measured, inasmuch as the current measured is the resultant or the algebraic sum of that of the hydrogen evolution and that of (2), which latter would then proceed reversely reducing the measured current from that due to the hydrogen evolution.

The concentration of mercury ion at equilibrium of (2) being now particular to the electrode potential, the latter equilibrium can be brought about by keeping the mercury electrode at a definite potential in a strictly closed vessel until the mercury ion concentration finally adjusts itself to that of equilibrium at the potential when the current settles at a steady value appropriate to that of hydrogen evolution. This is however practicable with possibly small volume and simple geometry of the solution, since otherwise the mercury ion would steadily diffuse away towards the remoter part of the solution giving apparently steady current constantly compensated by that of the reversal of (2), as inferred from the finding of our experiment conducted with the above precaution that it took even a few hours for a steady current to set in. That the rate of (2) did reduced the measured current irreversibly in our case, but reversibility vanished at prescribed potential, may be deduced from the result described in the paper that "The current measured at a definite potential of the mercury electrode was found asymptotically decreased or increased to a definite value as expected according as the cathode potential was raised or lowered*) from the former definite value to the present one, the asymptotic current being quite reproducible irrespective of the history".

So far as the present authors know, the quantity of solution used by the other authers[3)**)] was big enough compared with the area of the mercury cathode and its geometry complicated enough, so that it seems hardly possible for the mercury ion concentration to settle at that of equilibrium. This would be the principal cause that the other

3) Bockris and Parsons, Trans. Farad. Soc., 45, (1949), 916.
Post and Hiskey, J. Am. Chem. Soc, 73, (1951), 161.

*) The words "lowered" and "raised" were inverted by misprint in our previous paper [Ref. 2], although they were correct as they were if referred to the overpotential.

**) We could not read Joffa's work quoted by Bockris [Ref. 1].

authors have obtained much smaller current than that of the present authors, as raised by BOCKRIS as his point III.

As regards to his point II, it would be sufficient to refer the commenter to the above quoted fact that the steady current finally attained was reproducibly observed throughout repetition of the above persue of the steady current with one and the same sealed cell. If the migration of platinum particle by disintegration caused the increase of the electrolytic current at the cathode, and if the latter effect were in turn caused by electrolysis, at so low a polarization as less than 5.10^{-4} volt[2], why should the final steady current not increase along with the continuation and repetition of the electrolysis? Or is there any ground for that the disintegration should occur once for all at the outset and never later, thus leaving the final steady current reproducible?

Further cause of the diminution of current observed with unsealed vessel may be attributed to the effect of the trace of oxygen in the electrolyte.

In the case of our sealed vessel, this effect, if any, would vanish in the course of time, automatically in the presence of big catalyser, the platinum anode, similarly as the nervous precaution, even introduced by experience, of placing paste at the top of mercury, of the calomel electrode, protects, with this unleaded redoxy system at the top, the leaded one at the bottom from the attack of oxygen to fluctuate its potential. We will not go further into this point at the moment, since the above argument would be sufficient to defend the validity of the present authors' result.

The Research Institute for Catalysis
Hokkaido University
Sapporo, Japan