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01 Jan 1971

Anodic Dissolution Of Beryllium In Anhydrous Media

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Recommended Citation

Discussion of "Anodic Dissolution of Beryllium in Anhydrous Media" [H. Aida, I. Epelboin, and M. Garreau (pp. 243–248, Vol. 118, No. 2)]

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DISCUSSION

—— SECTION ——

Electrochemical Studies in Liquid and Solid AgBr

D. O. Raleigh and H. R. Crowe
(pp. 79-86, Vol. 118, No. 1)

R. D. Armstrong and T. Dickinson[1]: It is difficult to understand why Raleigh and Crowe attribute the measured capacitance of the interface Pt/AgBr to an inner layer effect whilst continuing to attribute the capacitance of the C/AgBr interface to a diffuse layer effect. The inner layer capacitance, which arises from the finite size of ions, is always in series with the diffuse layer, so that it is the smallest capacitance of the combination which is dominant. Thus, if a diffuse layer capacity is important in one case (C/AgBr), it is also likely to be important in another (Pt/AgBr). Our own opinion is that in both cases the capacitance arises from an inner layer effect, the differences in magnitude reflecting different true contact areas; and we think that in fitting the measured C-E curve to the theoretical one for C/AgBr, Raleigh[2] is unjustified in placing the theoretical C-E curve at a particular point on the E axis since this point was determined by a calculation of the absolute (*sic*) potential difference between Ag and AgBr.

D. O. Raleigh: We did not attribute the measured Pt/AgBr interface capacitance to an ideal inner layer, but to a layer of adsorbed Ag^+ and/or Br^- ions (depending on potential) on the Pt surface. In this instance, the simple series model for the diffuse and compact layer capacitances is invalid and large over-all capacitances may result[3]. Armstrong and Dickinson are of course entitled to their own interpretation of such data, and the simplicity of a purely inner layer model is admittedly attractive. It seems necessary, however, to deal with diffuse layer capacitance in some manner, and the Grimley-Mott model[4,5] seems reasonable. I have discussed this model for ionic solids at some length in a recent publication[6].

To be sure, the Grimley-Mott estimate of the Ag/AgBr absolute electrode potential may be considerably in error, but the C/AgBr capacitance data[7] match the theoretical curve both in general magnitude and in relative invariance to the potential. Dominance by an ideal inner layer capacitance would require the diffuse layer capacitance to be comparatively large. The theory does not predict this large a diffuse layer capacitance anywhere in the voltage range, regardless of the assignment of the absolute electrode potential. Our way out of the dilemma has been to suggest specific ion adsorption in the Pt/AgBr case.

At this point, it seems useful to state that we are indeed open to alternative explanations and also to point out the dangers in carrying over interface concepts developed for aqueous systems (a practice in which we share some guilt). The solid electrode-solid electrolyte interface is physically unique in a number of respects. Interface models based on a detailed consideration of the microscopic situation would seem to be needed in developing appropriate theoretical treatments.

Anodic Dissolution of Beryllium in Anhydrous Media

H. Aida, I. Epelboin, and M. Garreau
(pp. 243-248, Vol. 118, No. 2)

W. J. James and M. E. Straumanis[8]: The recent article regarding the anodic dissolution of Be in anhydrous media by Aida *et al.*, is most interesting in that it appears to provide further proof that the two concepts of "anomalous" dissolution, namely the presence of transitory species of uncommon valence or the "chunk effect" (film and/or metal spalling) are not incompatible.

The authors approach in attributing greater stability to Be^+ in a water solvent-poor interface as opposed to the greater stability of Be^{+2} in a water solvent-rich, appears to us to be a reasonable one. Our disagreements with proponents of unusual transitory ionic states as being responsible for the anomalous dissolution behavior of metals have been based on the fact that these studies were carried out in dilute aqueous media. Thermodynamic considerations of the stability of ions such as Be^+, Al^+, Zn^+, Mg^+, *etc.* in aqueous solutions virtually rules out the possibility of their existence at any measurable distance from the anodic surface. This is not to say, of course, that the anodic expulsion of, *e.g.* Be, does not occur in two consecutive electron discharges to form Be^{2+}.

Consequently, it is not surprising that the attempts by several investigators to detect directly the existence of such unstable species at considerable distances from the electrodes were doomed to failure.

Furthermore, the undisputable detection of such comparatively stable ions (for references see the article under discussion here) as Cu^+ and In^+ can hardly be considered as verification that anomalous dissolution of considerably more active metals occurs as a consequence of formation of uncommon transitory species.

In their discussion of the nature of the Be surfaces, the authors state that the appearance of a gray coloration on the surface or actual identification of metallic particles in the anode region cannot be taken as indisputable evidence of the chunk effect because the formation of metallic particles may always be attributed to the reaction $2\ Be^+ \rightarrow Be^{++} + Be \downarrow$

Whereas the concept of such a disproportionate reaction is supported by knowledge of other more noble metals which undergo this reaction, *e.g.* Cu, there is absolutely no evidence of direct nature that Be undergoes this reaction either in aqueous or anhydrous media.

On the contrary, experimental evidence suggests that this reaction is very unlikely, taking into account the failure to detect Be^+ in aqueous solutions, the inability to plate Be out of such solutions, the presence of deformation twins on the comparatively large Be-chunks and on the etched Be surfaces, indicating that the former initially belonged to the solid Be piece. In fact, the process of detachment of Be platelets from the Be substrate, dissolving in acids, could be observed optically[9].

[1] Electrochemistry Research Laboratories, Department of Physical Chemistry, University of Newcastle-upon-Tyne, Newcastle-upon-Tyne, England.
[2] D. O. Raleigh, *J. Phys. Chem.*, 70, 689 (1966).
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[4] T. B. Grimley and N. F. Mott, *Discussions Faraday Soc.*, 1, 3 (1947).
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[8] Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, Missouri 65401.
[9] M. E. Straumanis and D. L. Mathis, *J. Less-Common Metals*, 4, 213 (1962).

Similar behavior has been observed for Al, Mg, Zn, Cd, and Sn in acidic or aqueous salt solutions[10-17]. If the same reasoning were applied to Zn to explain the presence of the gray to black coloration on its surface and the x-ray evidence of metallic particles in the anolyte, how can one explain why, when the Zn surface is amalgamated, no gray coloration is observed together with no metallic particles, and that a valence state of two is obtained in the same electrolytes[18]? Clearly, whereas in the first case Zn particles were detached from the bulk during the dissolution, which resulted in a calculated ionic state less than two, no such process could occur when the metal was amalgamated, since the Zn particles could not penetrate the Hg-surface layer and a valence of two, therefore, resulted.

Furthermore, we have also examined recently by SEM techniques Zn and Mg electrodes exhibiting surface films after anodic dissolution in aqueous media and can state that in all cases the microscopy confirms the source of the metal-like particles as arising from the electrode surface.

The foregoing discussion is not meant to detract from this excellent paper by Aida et al. The authors have presented strong evidence for the existence of Be^+ in anhydrous media. Further studies of this nature should go far in accounting on a more quantitative and general basis for the apparently anomalous behavior of many metals in both aqueous and anhydrous media.

H. Aida, I. Epelboin, and M. Garreau: We are pleased to see that W. J. James and M. E. Straumanis agree that anomalous anodic dissolution can be interpreted in terms of the two different basic concepts which have long been opposed in the literature. The protracted discussion on this topic, in which the editors of this Journal allowed us to take part (Discussion Section of June 1957 and June 1959), has been fruitful since it led to a better though still partial understanding of this difficult problem.

We think it necessary, however, to give further information about certain points of our paper that seemed disputable to W. J. James and M. E. Straumanis.

1.—First, we do not think that the transitory species of uncommon valency can only exist in anhydrous solutions. In our experiments, the absence of water in the electrolyte (O, 1 g/liter) highly favors the formation, near the anode, of a layer which is permeable to monovalent ions and almost impermeable to electrons. However, in certain cases, this layer can be partially formed in solutions richer in water. Thus, aluminum dissolves with an apparent valency of about two in an alcoholic solution of $LiClO_4$ containing 100g of water per liter, and this at anodic potentials sufficiently high to cause electrolytic polishing, which is incompatible with the "chunk effect."

2.—Concerning the chunk effect more particularly, the main point seems no longer to be whether the different methods, either those cited by Straumanis and James or ours, may reveal unambiguously its existence. We agree with Straumanis and James and admit that this effect can occur under various conditions; and we think that efforts should henceforth focus on its interpretation rather than on its identification. This is what we are doing at the present time, using the following new approaches: (a) study of the influence of changes in the crystal structure of the dissolved sample, caused either by various thermal treatments or by replacement of polycrystals by very pure single crystals; (b) kinetic study by modern electrochemical methods.

(a) The first results on crystal structure effects show that the disintegration of the metal occurs at the level of the subgrains of the lattice. This might be due to a phenomenon which would start under the influence of the very small differences in the reticular energy which exist between the sites constituting the boundaries of dislocation of the crystal substructure and the unperturbed parts of this crystal.

(b) By improving the analysis of the polarization curves (which have been roughly described in our paper) using a current interruption method completed by electrochemical impedance measurements, we recently showed that the anodic potential necessary to create the layer in which Be^+ is stable was actually much lower than the one predicted by curve c' in Fig. 2. The current-potential curve, corrected for ohmic drop, shows a marked change in the slope at an anodic potential of 1V as measured relative to an Ag/Ag^+ (0.2M) reference electrode. This change corresponds to the border separating the potential range within which Ne equals unity, and the surface is bright, from the range within which Ne differs from unity, and the dissolution is heterogeneous. Consequently, the electric energy actually available at the anode within the field where the chunk effect is observed is not very high. Dissolution can occur rapidly only at the weakest parts of the metallic lattice constituted by the boundaries of dislocation. The surface of the anode is thus divided in two zones: the first one has a small area (emergence of the dislocation boundaries) where the current density is high; the second has a larger area but scarcely contributes to dissolution. The relative importance of the contributions of these zones depends on the potential. Faradaic impedance diagrams obtained at these low potentials provide support for this interpretation since they show, at very low frequencies, more than one time constant.

3.—The fact that beryllium cannot be plated out from the solutions we used is not in disagreement with the formation of stable Be^+ ions moving sufficiently far from the electrode to modify the faradaic yield of the dissolution. In fact, this formation needs a minimal anodic potential which is incompatible with the cathodic reaction $Be^+ + e \rightarrow Be \downarrow$ in the cases considered here.

4.—As for the results obtained with amalgams, we think that the canceling of the anomaly may be related to an easier adsorption of anions on solid surfaces than on liquid surfaces. This might be the reason why the quasi-crystalline anhydrous layer cannot be formed. This interpretation is strongly supported by our results on the anodic dissolution of gallium in $LiClO_4$ solutions in ethanol: with solid Ga ($t = 25°C$) Ne = 1, whereas with liquid Ga ($t = 35°C$) Ne = 3[19].

Crystal Structures of the Elements of the Periodic Table and the Mechanisms of Electrolytic Hydrogen Evolution Reaction

A. K. Vijh (pp. 263-264, Vol. 118, No. 2)

S. Trasatti[20]: Some points of Vijh's reasoning seem to be questionable. First of all, Vijh divides the metals into two main classes according to whether or not the hydrogen evolution reaction (h.e.r.) proceeds with significant steady-state chemisorption of hydrogen. However, copper, silver, and gold are included by Vijh into the class of metals adsorbing hydrogen (Vijh's class II), and in fact, this does not seem to be the case.

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[18] W. J. James and G. Stoner, *J. Am. Chem. Soc.*, 85, 1354 (1963).

[19] See M. Garreau, *Métaux*, 544, 425 (1970).
[20] Laboratory of Electrochemistry, University of Milan, Milan, Italy.