Electroanalytical Chemistry and Interfacial Electrochemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

J. Electroanal. Chem. 1972. V. 39, N 1. P. 225-228

SHORT COMMUNICATION

Effect of the structure of the zinc surface on the adsorption of tetrabutylammonium iodide

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(Received 28th February 1972)

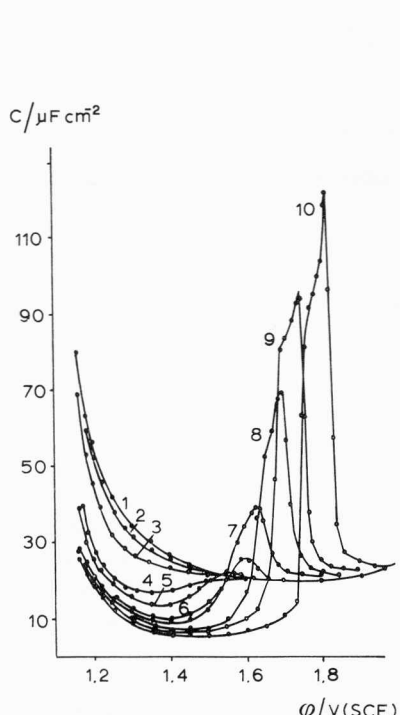
It was pointed out earlier[1] that the structure of a zinc surface affects the adsorption of hexyl alcohol, particularly the height and width of the cathodic adsorption–desorption peaks. It was of interest to study the effect of the surface structure on the adsorption of a substance characterized by a high attraction constant in the adsorbed layer. Tetrabutylammonium iodide (TBAI) was chosen for this purpose[2].

The adsorption behavior of polycrystalline and single crystal (basal face (0001)) zinc, containing 99.999% Zn was investigated. The face (0001) was formed by cleaving a zinc single crystal at liquid nitrogen temperature. The electrodes were electrochemically polished and prepared as already described[3]. The reagents were twice recrystallized. Doubly-distilled water purified with activated carbon was used for solutions. The capacity measurements were carried out at a frequency of 65 Hz; the electrode potential was measured against SCE.

Figures 1 and 2 show the differential capacity curves measured on polycrystalline and single crystal zinc in the presence of TBAI. In the region of adsorption of tetrabutylammonium (TBA) cations the double layer capacity decreases with increasing TBAI concentration, the capacity minimum shifting into the region of more negative potentials. At more cathodic potentials, well-defined adsorption–desorption peaks appear on the C, φ-curves. Thus, in the presence of 10^{-2} M TBAI, the height of the peak on zinc single crystal is 275 μF cm^{-2}. No desorption peaks in the presence of TBA cations were observed by Chuan-sin and Iofa[4] for single crystal zinc, but as was discussed in ref. 3, this discrepancy is mainly due to the fact that the C, φ-curves were measured at a high a.c. frequency (10^4 Hz). Our measurements showed that at this frequency the TBA desorption peaks practically disappear.

The heights of the desorption peaks for polycrystalline and single crystal zinc are compared in Fig. 3.

It follows from a comparison of the capacity measurements data (Figs. 1, 2 and 3) that the height and shape of the peaks depend on the microstructure of the zinc surface. The differences appear at a TBAI concentration of 3×10^{-4} M, when the surface coverage with adsorbate is sufficiently high. The peaks obtained on the face (0001) are higher and almost one-third of the width of those on a polycrystalline electrode, which points to an increase of surface homogeneity when passing from



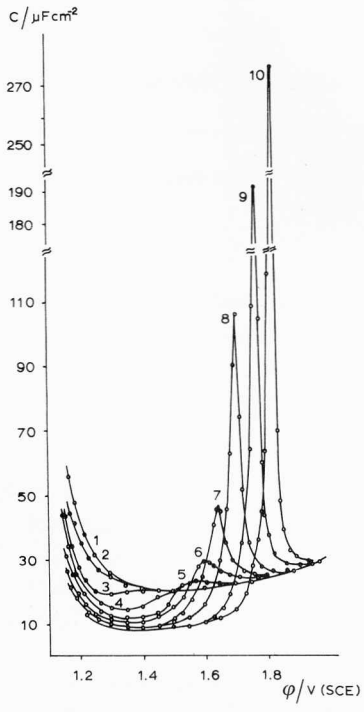


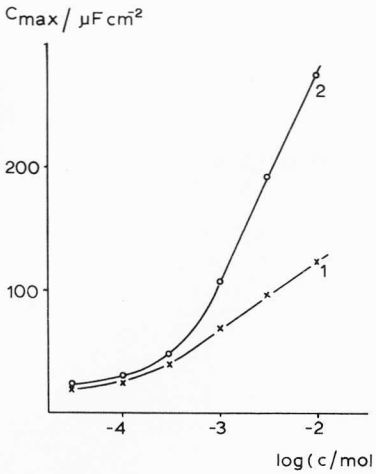
Fig. 1. Differential capacity curves measured on polycrystalline zinc in 0.1 *M* KI containing TBAI. TBAI concns.: (1) 0, (2) 10^{-6}, (3) 3×10^{-6}, (4) 10^{-5}, (5) 3×10^{-5}, (6) 10^{-4}, (7) 3×10^{-4}, (8) 10^{-3}, (9) 3×10^{-3}, (10) 10^{-2} *M*; frequency 65 Hz.

Fig. 2. Differential capacity curves measured on the face (0001) of zinc single crystal in 0.1 *M* KI containing TBAI. TBAI concns. and frequency as in Fig. 1.

polycrystalline to single crystal zinc. The homogeneity of the face (0001) seems to approach that of a mercury surface.

The shape of the desorption peaks testifies to the existence of considerable attractive forces between the adsorbed particles, which is accounted for by the coadsorption of TBA cations and iodine ions. The measurements of the C, φ-curves in the presence of TBA in different supporting electrolyte solutions showed that the anionic composition of the solution significantly affects the height of the peaks. The height increases with change of the supporting electrolyte anion in the sequence: $SO_4^{2-} < Br^- < I^-$, the narrowing of the peak occurring in the same sequence. The TBA cations being adsorbed on zinc surface, draw iodine ions into the electric double layer, as in the case of TBA adsorption on mercury[5].

The desorption peaks obtained on polycrystalline zinc are distorted: at potentials near to the potential of the peak maximum they show a step, the height and shape of which change somewhat when passing from one polycrystalline sample to another. A more detailed study showed that the appearance of the step is associated with the microstructure of the zinc surface. On large-grained polycrystalline zinc we obtained split adsorption–desorption peaks (Fig. 4, curve 1). The first maximum lies at the potential -1.69 to -1.70 V, corresponding to the beginning of the step



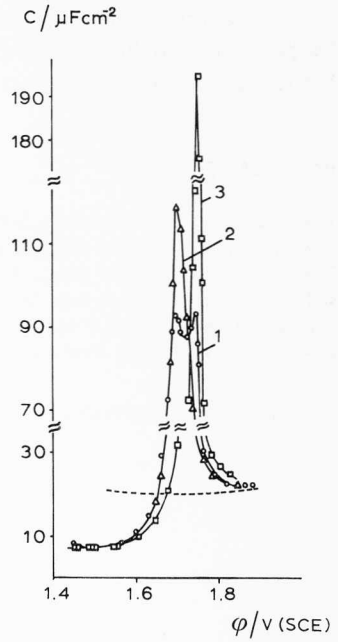


Fig. 3. Dependence of desorption peak height on TBAI concn.: (1) polycrystalline zinc, (2) face (0001).

Fig. 4. Differential capacity curves measured on zinc in 0.1 *M* KI + 3×10^{-3} *M* TBAI: (1) polycrystalline zinc, (2) set of prismatic faces of single crystal, (3) face (0001). (----) Curve for polycrystalline zinc in the supporting electrolyte soln.

(Fig. 1, curve 9); the potential of the second maximum at -1.75 V almost coincides with the potential of the maximum on the C, φ-curve for the basal face at the same TBAI concentration ($\varphi = -1.76$ V, Fig. 2, curve 9). The splitting of the desorption peak is apparently due to the presence on the polycrystalline electrode surface of faces with different indices. This is supported by the results of the capacity measurements on single crystal electrodes, the preparation of which will be described in another communication (Fig. 4). The surface of one of the electrodes was formed by a set of prismatic faces, and constituted the lateral surface of a cylinder, the base of which (basal face) was perpendicular to the cylinder axis and isolated from the solution by polystyrene. The face (0001) was used as the second electrode, as in the case of Fig. 2.

From a comparison of the results of measurements presented in Fig. 4 it can be concluded that the maximum at the potentials -1.69 to -1.70 V corresponds to the desorption of TBAI from the surface of prismatic faces, and the maximum at -1.75 V to desorption from the face (0001). Probably, the difference between the values of the desorption potential is mainly due to the difference between the potentials of zero charge of individual faces of the single crystal, although the position of the peak can be affected also by differences in the adsorption energies. From the ratio of the peak heights in the capacity measurements it is possible to assess the texture of polycrystalline zinc. Thus, on the surface of zinc for which the curves in Fig. 1 were obtained, the fraction of crystallites oriented with the face (0001) to the surface is larger than for the sample used for curve 1 in Fig. 4.

A comparison of the results of capacity measurements with different substances leads to the conclusion that the effect of surface structure on adsorption is greater for substances having high attraction constants.

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