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Citation for published version (APA):
Smit, W., & Stein, H. N. (1978). Note on the adsorption of sodium ions in the compact part of the electrical double layer of oxides. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *91*(3), 393-394.

Document status and date:
Published: 01/01/1978

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Preliminary note

NOTE ON THE ADSORPTION OF SODIUM IONS IN THE COMPACT PART OF THE ELECTRICAL DOUBLE LAYER OF OXIDES

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(Received 5th May 1978)

In a recent paper Uchida et al. [1] investigated the shifts of the flat band potential (V_f) of tin oxide electrodes as a function of pH in the presence of divalent cations. The measured values of ΔV_f were considered to be an indication of the penetration of divalent cations into the Helmholtz region. The flat band potentials of SnO_2 electrodes as a function of pH without addition of divalent cations were found to be linearly dependent on pH in neutral and acid solutions. The deviations in basic solutions were interpreted in terms of adsorption of cation impurities such as Mg^{2+} and Ca^{2+} present in alkaline solution. This interpretation resulted from the consideration that Na^+ ions are surface-inactive and are supposed to be located at the outer Helmholtz plane without any specific interaction with the oxide surface.

Recently [2], we developed a radiochemical method for the determination of the penetration depth of counter ions in the solid phase. This method consists essentially of the equilibration of rods of the material to be investigated in a double tracered solution, f.i. $^{24}Na^{82}Br$, seven 1-s washings with acetone-water mixture (96:4 w/w) followed by a layerwise dissolution of the surface layer of the solid. An additional result of such experiments on vitreous silica was, that the adsorption of sodium ions in the compact part of the electrical double layer became evident. The results of measurements, which are in progress on α-Al_2O_3 single crystal rods with c-axis parallel to the cylindrical axis, indicate that with this oxide sodium ions are incorporated into the Helmholtz region as well. The charge densities, calculated with an assumed surface roughness of one, of the sodium and bromide ions, adsorbed from 0.01 M NaBr solutions, are plotted as a function of pH in Fig. 1. Apart from the small charge in the diffuse part of the double layer, the sum curve of these curves with inversed sign is the surface charge density curve. Details of these experiments and the elaboration of the results will be published elsewhere in the future.

In our opinion, the relatively large deviations of V_f from linear dependence on pH in basic solutions, reported by Uchida et al. [1] for SnO_2, furnish also evidence of the penetration of univalent cations into the Helmholtz region of this oxide.

It must be noted that the site-binding model of the oxide aqueous electrolyte interface, introduced by Yates et al. [3] in order to account for the dis-
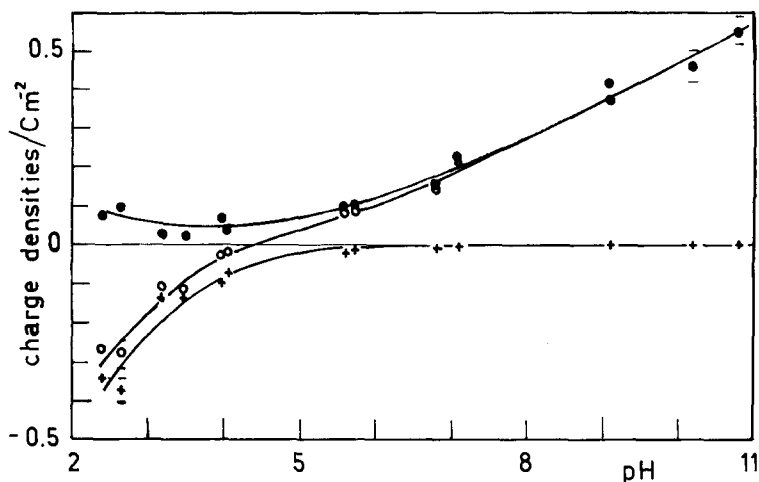
Fig.1. Charge densities vs. pH curves of ions adsorbed in the compact part of the double layer of α-Al$_2$O$_3$ single crystals in about 0.01 M NaBr solution. ($\bullet$)σ_{Na^+}, (+)σ_{Br^-}. The sum curve ($\circ$) is nearly equal to the surface charge density (σ_0) curve with inversed sign.

tinctive properties of the oxide/aqueous electrolyte interface, viz. high charge and moderate zeta potential, involves an interfacial ion pair formation between cations and anions of the supporting (1—1) electrolyte with oppositely charged primary surface groups. The inner Helmholtz plane is considered to be the locus of centres of the ions which form ion pairs with surface groups.

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