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OPTICAL STUDIES OF ELECTROLYTE FILMS ON METAL SURFACES

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The thickness of liquid films on metal electrodes, formed by partial withdrawal of polished flat and cylindrical metal surfaces from electrolytic solutions has been measured by light interference. After a thinning period in the order of 10 hours stationary film thicknesses in the order of 0.5 microns have been observed with the exact values depending on the parameters of the system such as electrochemical polarization and electrolyte concentration.
OPTICAL STUDIES OF ELECTROLYTE FILMS ON METAL SURFACES

by

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Liquid films extending beyond the apparent liquid-solid-gas interface have long been suspected to exist on gas-consuming electrodes and attention to their importance for the mass transfer in gas diffusion electrodes has recently been drawn by F. G. Will. An analysis for porous electrodes by J. A. Rockett has supported the concept of an electrolyte film inside pores. An important parameter for understanding the processes occurring in such an electrolyte film is its thickness. If the electrochemical charge transfer takes place in the film its thickness will affect mass transfer and ohmic potential drop and thus influence the spatial distribution of the reaction.

The direct observation of liquid films on metal surfaces is difficult because of their sensitivity to most types of probes. Optical techniques have the advantage of allowing a continued observation with a minimum disturbance to the object. Preliminary experiments had indicated that the expected dimensions were in the order of magnitude measurable by light interference, however the large difference in light intensity reflected from the two film surfaces results in practically unobservable interference minima and therefore the usual techniques cannot be applied. The use of polarized light incident under certain angles, however, has resulted in well defined interference fringes and colors, suitable for quantitative evaluation.

Using the above interference technique, the thickness of liquid films formed by partial withdrawal of polished flat and cylindrical surfaces from aqueous solutions has been measured for several systems as a function of time. A typical result obtained on a flat, rectangular nickel electrode (1.7 cm wide, 3 cm high) is shown in figure 1 for two different heights x above the liquid level. At time zero the liquid in the cell (3.4 M KOH) is rapidly lowered and cathodic reduction of oxygen is initiated under a constant current (100 mA). Down to a thickness of about one micron, where surface effects appear to become noticeable, the film thinning follows the relationship (inverse square root of time) expected from a consideration of viscous and gravitational forces only. A stationary film thickness is first reached in the upper parts of the electrode (after 2.5 hrs. at x = 1.4 cm) and considerably longer times are necessary in the lower parts (6 hrs. at x = 0.4 cm). After these periods electrolyte films have been found
in other experiments to remain unchanged over several weeks.

The thermodynamic stability of electrolyte films on vertical electrodes is due to a lower surface energy of the wetted as compared to the dry metal surface. One should therefore expect a spontaneous film formation on a dry electrode upon partial immersion. The inability to observe this process as yet may be due to adsorption phenomena or surface contamination to which film formation is extremely sensitive.

REFERENCES

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