A Shadow Schlieren Method for the Study of Diffusion Boundary Layers at Electrodes

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The Schlieren method described below corresponds to the method developed by Schmidt¹ for the study of temperature boundary layers. It so far seems to have been seldom used for the investigation of concentration boundary layers². Like all Schlieren methods, it is based on the fact that light rays passing through a medium with a continuously changing refractive index are deviated into the optically denser parts of the medium. Since in this case the image is formed by the projection of a shadow without the use of lenses the designation "shadow Schlieren method" seems appropriate³.

A microscope lamp (Fig. 1) with a small spiral (2×2 mm) acts as a point source of light. It is placed at the focus of a condenser lens with a small focal length. This lens gives a beam of approximately parallel light. A high degree of parallelity is achieved by placing two slits at a large distance from each other in the light path. The slits 1 and 2 are 2–3 mm wide and the distance between them is 10 m which means that the deviation from parallelity can be neglected. For qualitative purposes, as in lecture experiments, the distance between the slits can be reduced to about 1 m. The electrolysis cell, consisting of planoparallel plates of optical glass, is placed behind slit 2 in the light path. The light beam passes along and parallel to a copper plate, 1 mm thick, occupying the whole cross section of the cell. A shadow image is obtained on a screen or

Fig. 1. Optical arrangement for the study of electrode films, viewed from above.

Fig. 2. a) Current shut off b) Cathode with 2 A/dm^2 on right side c) Anode with 2 A/dm^2 on right side d) Transition from laminar to turbulent flow at 1.5 A/dm^2 e) Fully developed turbulence at 4 A/dm^2 . With a), b) and c) slit 2 was 2 mm wide and $a = 25$ mm, $b = 7$ mm. With d) and e) slit 2 was 3 mm wide and $a = 45$ mm, $b = 10$ mm. In exps. d) and e), the total cathode height was 180 mm, but only the height between 80 and 140 mm from the lower end of the cathode was photographed.

photographic plate. When no current is flowing, a photograph like the one in Fig. 2 a is obtained.

Upon electrolysis, the concentration gradients produced will manifest themselves on the image. In all the cases shown in the photographs here, the electrolyte consisted of 1 M CuSO_4 and the temperature was 20°C . If a cathodic current is applied on one side of the copper plate, the photograph in Fig. 2 b is obtained. In the cathode diffusion layer (cathode film), the concentration and refractive index are lower than those in the bulk solution. The light beam is therefore deviated away from the electrode. The deviation is proportional to the refractive index gradient. Since the gradient is greatest close to the cathode surface, the light

rays that enter the solution near the cathode surface will undergo the greatest deviation. The width of the bright band is, therefore, a measure of the concentration gradient on the cathode surface. The deviation may be expected to be proportional to the current density and to the width of the electrode, *i.e.* the length of the light path within the cell. However, this seems to be valid only up to a certain c.d. and electrode width, above which the deviation is constant. This is probably due to the fact that the cathode film is so thin (about 0.5 mm) that the light ray soon enters the bulk solution in which its path is rectilinear. Besides the bright band, a broadening of the cathode shadow is observed, obviously because the light is deviated out of the cathode film. The thickness of this film can therefore be estimated. In the upper part of Fig. 2 b, it seems to be about 0.4 mm.

For photographic purposes, the distance *b* between the cell and the plate should not be greater than 10 mm, otherwise the shadow image of the cathode will not be sharp. For accuracy in measurement however, this distance should preferably be increased to 100 mm which gives a corresponding increase in the displacement on the screen.

The shadow Schlieren method is less valuable for the investigation of the anode film. The light passing through the boundary layer will be deviated towards and deflected by the electrode. This will result in a broadening of the electrode shadow. There is, however, also an opposing effect, which results in a narrowing of the shadow, due to the light passing close to the rear edge of the electrode. Both these effects seem to appear in Fig. 2 c.

The free convective flow ⁴ caused by the difference in gravity between the electrode film and the bulk solution is also revealed by the method described, particularly at the cathode. In the case corresponding to

Fig. 2 b, horizontal dark lines can be seen in the bright band adjacent to the cathode shadow. These lines move upwards with an increasing speed which seems to correspond to the vertically accelerated laminar flow in the cathode film. Since the velocity of this flow increases with the current density and with the electrode height, the flow will turn turbulent if these variables are increased. The transition from laminar to turbulent flow at a certain distance from the lower edge of the cathode is shown in Fig. 2 d. The diffuse bright band at the upper part of the cathode in Fig. 2 d appears to the naked eye much like the flickering of a flame, obviously due to the formation of eddies. Finally, Fig. 2 e shows fully developed turbulence due to a higher c.d.

While useful information is obtained by this simple method without lenses, it would be of interest to analyse the whole concentration profile in the boundary layer. According to Lamm ⁵, this could be done by the addition of lenses to the apparatus so as to correspond to Lamm's slit method ⁶. The investigation will be continued.

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