

Change in Potential of Silver-Silver Chloride Electrodes with Time

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An aging effect with freshly prepared silver-silver chloride electrodes was first noted by MacInnes and Parker,¹ who found it to be always in the same direction. This effect was investigated by Smith and Taylor,² who attributed its origin to concentration-polarization and made tests, the results of which harmonized with this explanation. When silver electrodes are coated electrolytically with silver chloride, the solution within the pores of the silver chloride becomes more dilute than the surrounding solution and these electrodes, freshly prepared, therefore, act as cathodes toward electrodes previously aged in the solution, since the latter have had the electrolyte within their pores replenished. Because the aging behavior is always in the same direction and, for relatively thick coatings of silver chloride, amounts at least to several tenths of a millivolt, it appears to be an effect different from the fluctuating bias of a few hundredths of a millivolt frequently observed after the electrodes have apparently come to equilibrium. If sufficient time is allowed, the freshly prepared electrodes attain the same average potential as the aged electrodes. The time required for this equilibrium to be attained depends on several factors, among which are the amount of silver chloride deposited per unit area, *i. e.*, the thickness of the layer through which the diffusion must occur, and the current density at which the layer is formed. The smaller the current density of silver chloride formation, the nearer is the concentration within the pores of the layer kept to equilibrium with the surrounding solution and consequently the smaller is the aging effect.

In some recent work, Hornibrook, Janz and Gordon³ made experiments, the results of which they consider to contradict the conclusions of Smith and Taylor. Their results, however, instead of being contradictory to these conclusions are in agreement with what is to be expected for thin films of silver chloride formed at low current densities. It should be emphasized that no dispute as to the facts is involved and no criticism

of the validity of the technique and results of the excellent work of Hornibrook, Janz and Gordon is intended.

From the dimensions of the electrodes and the time and current used for coating with silver chloride, it appears that the thickness of the coatings and the magnitude of the current density used by Smith and Taylor were, respectively, about 13.4 and 5.6 times as large as those used by Hornibrook, Janz and Gordon. The latter point out that concentration differences tend to disappear with $\exp(-\pi^2 kt/x^2)$, where k is the diffusion constant, t the time, and x the distance from the plane where the concentration is constant. The time required for the exponential to fall to a given value increases as the square of the distance, x , which can be taken as the thickness of the layer of silver chloride. Hornibrook, Janz and Gordon found no indication of aging after twenty-five minutes in one experiment and after forty minutes in another. If the time of aging with their relatively thin layer was of the order of ten minutes, it would escape detection, while with a layer 13 times as thick, about twenty-eight hours would elapse before the aging was over, and the effect would be readily found.

Present conditions of work make it unjustifiable for us to spend the time required to show experimentally how the aging period of freshly prepared silver-silver chloride electrodes varies from a negligible time for a very small thickness of silver chloride deposited at a low current density to an appreciable time for a thicker layer deposited at a higher current density. Our previous work, however, has shown the latter, and the results of Hornibrook, Janz and Gordon not only show the former, but are what would reasonably be expected on the basis of our explanation of the aging effect.

Because of the various factors, such as film thickness, current density, temperature, concentration and agitation of the solution, which affect the time of aging, different investigators using different conditions of preparation of their silver-silver chloride electrodes will find marked differences in the magnitude and duration of the aging effect. In any case, however, it is important to recognize the possibility of the occurrence of the effect and to make sure it has been eliminated from the results of the final measurements.

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(1) D. A. MacInnes and K. Parker, *THIS JOURNAL*, **37**, 1445 (1915).

(2) E. R. Smith and J. K. Taylor, *J. Research Natl. Bur. Standards*, **20**, 837 (1939).

(3) W. J. Hornibrook, G. J. Janz and A. R. Gordon, *THIS JOURNAL*, **64**, 514 (1942).