[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF REED COLLEGE]

A STUDY OF THE SILVER CHLORIDE ELECTRODE

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Although the silver chloride electrode in various forms has been used for a good many years as a reference electrode, authors have reached no agreement as to the best method of preparing this electrode. Various investigators using different methods of preparation and manipulation have obtained different results and to a certain degree the potential of the silver chloride electrode still remains in doubt, the separate electrodes varying from 0.1 mv. to as much as 1.0 mv. It was the writer's object to study the factors which cause these relatively large differences in potential in an effort to produce an electrode that would be reproducible and constant within 0.01 mv.

The silver chloride electrode has been prepared most often by electrolytically depositing silver upon platinum gauze from a cyanide solution. After being washed for a day in water the electrode is covered with a layer of silver chloride by electrolysis as the anode in dilute hydrochloric acid solution.[1] Electrodes prepared according to the directions of MacInnes and Parker have been used by several investigators,[2] and have been discarded by others[3] as being not reproducible or constant in potential. The writer selected this form of electrode for study to determine whether a constant and reproducible silver chloride electrode could be produced by this method of preparation.

Factors that Influence the Potential of the Electrode.—The factors involved in the preparation and use of the silver chloride electrode that influence the potential are: (1) cyanide ion absorbed in the silver-plated electrode, (2) light, (3) time and (4) concentration of chloride solution. The writer has investigated these factors in the desire to determine acceptable methods of preparation and of use of the silver chloride electrode.

The directions of MacInnes and Parker[1b] produce electrodes of "reddish-brown color the shade of which was the same whether the electrolysis was carried out in the light or in complete darkness." Noyes and Ellis[4] prepared silver chloride electrodes that were, they state, "not appreciably affected" by the action of daylight. Several years ago the writer noted

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[1] (a) Jahn, *Z. physik. Chem.*, **33**, 545 (1900); (b) MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915).

[2] (a) Harned and Brumbaugh, *ibid.*, **44**, 2729 (1922); (b) Harned and Fleysher, *ibid.*, **47**, 82 (1925); (c) Scatchard, *ibid.*, **47**, 641 (1925); (d) Harned and Swindells, *ibid.*, **48**, 126 (1926); (e) Nonhebel *Phil. Mag.*, [7] **2**, 1085 (1926).

[3] (a) Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917); (b) Güntelberg, *Z. Electrochem.*, **17**, 179 (1911); (c) Randall and Young, THIS JOURNAL, **50**, 989 (1928).

[4] Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

that the odor of cyanide remained with the silvered electrodes after a period of five or six days of washing,[5] and that the shade of the color of electrodes that had been washed for two weeks *did* vary according as the deposition of the silver chloride was made in darkness or in daylight. Güntelberg[6] protected his electrodes from contact with light but does not mention the effect, light had upon them.

The writer prepared his silver chloride electrodes in complete darkness and protected them from exposure to light while they were being used. Results from the experimental work outlined below show that an electrolytically deposited silver–silver chloride electrode, reproducible and constant to within 0.01 mv., can be prepared if precautions are taken to protect the electrode during its preparation and use from being affected by those factors which change its potential. Both the absorption of cyanide in the silvered electrode and the exposure of the silver chloride electrode to daylight have been found to alter the potential of the electrode appreciably in the positive direction. The effect of cyanide absorption may be eliminated by washing the silvered electrode over a period of two weeks. The absorption, which determines the time of washing necessary, may be decreased by depositing the silver in an H-cell from a solution of $KAg(CN)_2$ that has been purified by careful recrystallization. The effect of daylight is eliminated by working in a dark room or by the light from an incandescent lamp, or by covering the cell with opaque cloth.

The writer has had occasion to use about fifty of these silver chloride electrodes prepared according to the directions given later in this paper. They have been found to be quite as reproducible and constant as the platinized platinum–hydrogen electrode.

Experimental

To test the effect of the time of washing of the silvered electrodes, several series of electrodes were prepared according to the directions of MacInnes and Parker[1b] in which the time of washing was varied from one to twenty days. The color and potential of the resulting electrode gradually changed until about the fourteenth day of washing, after which the silver chloride electrode produced was pure white and constant in potential. Electrodes chloridized after twenty-four hours of washing, were red-brown in color and, although checking very well within each series, were usually about 0.2 mv. positive to the white silver chloride electrodes. An attempt was made to lessen materially the time required for washing by boiling the electrodes for several hours in water and in dilute hydrochloric acid. These methods did not lessen the time appreciably.

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[5] Carmody, "Dissertation," Catholic University of America, **1926.**

[6] Güntelberg, *Z. physik. Chem.*, **123,** 199 (1926).

The darkening of the electrodes which had not been sufficiently washed is due evidently to the reduction of the silver chloride by the traces of cyanide that are absorbed during electrolysis. In order to decrease the possibility of this absorption of the cyanide ion, the electro-deposition of the silver was carried on in an H-cell in which the two compartments were connected by a long tube, an arrangement designed to prevent hydrocyanic acid, formed at the anode, from diffusing into the cathode chamber. Also, the time of electrolysis was shortened from twenty-four to eight hours with a corresponding increase in current from three to eight milliamperes per electrode. To further insure a low concentration of the cyanide ion, the potassium silver cyanide used in the electrolysis was precipitated from a solution free from excess potassium cyanide and recrystallized twice from distilled water. The silvered electrode carried no odor of cyanide after being washed. After being washed for two days and then coated with silver chloride it was light pink in color and reproducible and constant within 0.02 mv. When the period of washing was extended to five days the resulting electrode was white and reproducible to well within 0.01 mv.

Several series of white electrodes were prepared and subjected to the action of daylight and the light from an incandescent lamp. All became brown in color, the shade increasing with the time of exposure, and becoming positive to the control electrodes. The results are shown in Table I.

TABLE I

RESULTS OF EXPERIMENTS

Kind of light	Diffused daylight	Direct sunlight	Incandescent lamp
Time of exposure	1 minute	1 minute	12 hours
Average change, mv.	0.05	0.2	0.01

As would be expected, daylight has a much greater effect upon the potential and color than has the light from the incandescent lamp.

To determine the effect of the concentration of the electrolytic solution, two groups of silver chloride electrodes were prepared, one group in 0.1 *M* hydrochloric acid and the other group in 0.01 *M* acid. When placed in 0.1 *M* hydrochloric acid they all acquired the same potential within an hour. This demonstrates the practicability of using silver chloride electrodes in solutions of different concentration from that in which the electrodes are made. The precaution of chloridizing the silvered electrodes in a solution of the same concentration as that in which the electrode is to be used seems to be unnecessary.

The effect of time on the electrodes noted by Scatchard[2c] and Nonhebel and Hartley[7] was not noted. Several electrodes that had stood in distilled water for a month as well as several that had been in constant use

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[7] Nonhebel and Hartley, *Phil. Mag.*, (6) **50**, 729 (1925).

in lead chloride solutions showed no difference in potential when being compared with electrodes freshly prepared. The change in potential noted by former investigators is evidently due to the action of light on the electrodes and not to any simple aging effect.

Directions for Preparing Electrodes

1. Clean platinum gauze electrodes by boiling in concentrated nitric acid for a few minutes.
2. Electrolyze as cathodes in an H-cell from a solution of potassium silver cyanide that has been prepared free from excess potassium cyanide and purified by recrystallization. The electrolysis is carried on for eight hours, a current of eight milliamperes per electrode being used.
3. Wash in running water for five days.
4. Electrolyze as anodes in dilute hydrochloric acid for one hour. A current density of 3 milliamperes per electrode is employed.
5. Keep in distilled water and protect from contact with direct or diffused sunlight.

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Summary

A study of the factors that affect the potential of the silver chloride electrode has been made.

Directions are given for its preparation and care while being used.

Results show that the electrolytically deposited silver–silver chloride electrode when carefully prepared and used is quite as reproducible and constant as the hydrogen electrode.

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