

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

A Type of Silver Chloride Electrode Suitable for Use in Dilute SolutionsBY ALFRED S. BROWN¹

Silver chloride electrodes have proved to be an important aid in many studies of solutions of electrolytes. In this Laboratory we have recently had occasion to use them in several investigations. Although many forms of these electrodes have been described, they may be grouped into three main classes, those prepared: (a) with precipitated silver chloride,² (b) by the electrolytic chloridizing of reduced silver oxide paste³ and (c) by the electrolytic deposition of both silver and silver chloride.⁴ As preliminary tests have indicated that electrolytically formed electrodes (type c) are best suited to the problems at hand, this investigation is concerned with some of the factors involved in the preparation of that type of electrode. The study has been limited to electrodes of small bulk and surface, as these may be expected to have the least disturbing effect on dilute solutions.

The Construction and Cleaning of the Electrode Base.—Platinum wire, 0.040 to 0.045 cm. in diameter is sealed directly through the end of a Jena "Thermometer Glass" tube, leaving about 1 cm. of wire outside of the tube. The end of the wire is fused in order to remove the sharp edges formed when the wire is cut. It is essential that the wire have a smooth surface. Carmody's⁴ method of cleaning the electrodes in boiling concentrated nitric acid has been found to be satisfactory.

The Silver-Plating Solution.—An excess of silver cyanide is added to a hot, filtered solution containing 20% of potassium cyanide.⁵ After stirring for about half an hour, the undissolved silver cyanide is filtered off and the solution cooled. The precipitated potassium silver cyanide is recrystallized from water and may be dried by centrifuging. Jena sintered glass filters have been used in the filtrations.

The silver plating solution is prepared by dissolving about 10 g. of the potassium silver cyanide in a liter of distilled water. Free cyanide is reduced to a minimum by adding enough dilute silver nitrate solution to produce a faint cloud of silver cyanide. After this has settled, the clear solution is decanted. It is desirable to precipitate a little silver cyanide from the solution each time the solution is used.

The Electrolysis.—The electrodes are supported by rubber stoppers inserted into holes drilled through a plate glass disk. This disk, which is 13 cm. in diameter and 0.6 cm. thick, also provides an easily cleaned, non-corro-

dible cover for the beaker used as electrolyzing bath. A platinum anode is used in the silver plating since silver anodes were found to polarize readily (due, possibly, to the absence of free cyanide). At a platinum anode, hydrocyanic acid is evolved and silver cyanide precipitated from the solution. Contamination of the main body of the solution by the products of the anode reaction is effectively eliminated by isolating the anode with a porous diaphragm. This consists of a Pyrex tube (about 1 cm. in diameter and 8 cm. long) into which an alundum disk (9 mm. in diameter and 2 mm. thick) has been sealed. The tube is flared at the top so that it may be hung from the edge of the central hole in the glass disk.

Each group of six electrodes is silver plated by electrolysis for two to six hours at a total current of 2 to 0.5 milliamperes. The electrodes are then carefully rinsed and kept (usually overnight) in distilled water until they are chloridized.

The group of electrodes is chloridized by electrolysis for half an hour in 0.1 normal hydrochloric acid at a total current of about 2 milliamperes. The platinum cathode is introduced through the central hole in the glass disk. Electrodes prepared in this manner have a purplish-brown color. As these electrodes are not affected, either in color or in electrical behavior, by sunlight, they may be prepared and used without the inconvenience of working in rooms with restricted illumination.

Tests of the Electrodes

Electrodes prepared according to the directions given in this paper have been tested in sodium chloride solutions, silver nitrate solutions, alkaline solutions containing a chloride ion constituent⁶ and hydrochloric acid solutions.⁷ Since the results of the tests in the first division are representative, they alone will be presented in detail.

Table I contains a summary of about a thousand observations of the differences in the potentials assumed by several pairs of electrodes in neutral sodium chloride solutions, each pair being tested at two or more salt concentrations in the range 0.2 to 0.0002 normal. In this table, the first two columns indicate the electrodes measured, the third and fourth columns show the average and maximum potential differences between the electrodes, and the last column contains the number of days over which the tests extended. These results give 0.02 millivolt as the average reproducibility of the electrodes, and show that while

(6) MacInnes and Belcher, *THIS JOURNAL*, **55**, 2630 (1933).

(7) Unpublished data very kindly furnished by Mr. Donald Belcher.

(1) National Research Council Fellow.

(2) Linhart, *THIS JOURNAL*, **41**, 1175 (1919).(3) Electrode Type 2, Harned, *ibid.*, **51**, 416 (1929).(4) Carmody, *ibid.*, **51**, 2901 (1929); **54**, 188 (1932).(5) Bassett and Corbet, *J. Chem. Soc.*, **125**, 1660 (1924).

differences as high as 0.05 millivolt are sometimes observed, it is possible to select electrodes that agree to 0.01 millivolt.

Electrodes of different groups and different ages have been inter-compared in numerous solutions. These tests are important because they show that the reproducibility of the electrodes from group to group is the same as that within a single group, and is independent of the age of the electrodes. The data in Table I, then, are sufficiently representative of the behavior of this type of silver chloride electrode under all the conditions to which they have been subjected.

TABLE I
REPRODUCIBILITY OF SILVER CHLORIDE ELECTRODES IN
SODIUM CHLORIDE SOLUTIONS

Electrodes Group	Pair	Potential diff. between electrodes, mv.		Duration of tests in days
		Average	Maximum	
A	1-2	0.01	0.01	54
	3-4	.01	.01	
B	1-2	.02	.02	9
	3-4	.01	.01	
C	1-2	.01	.01	1
	3-4	.04	.07 ^a	
D	1-2	.03	.03	1
	3-4	.03	.03	
E	1-2	.02	.02	16
	3-4	.02	.02	
F	1-2	.01	.01	
	3-4	.01	.01	
G	1-2	.02	.02	31
	3-4	.03	.05	
Misc.	1-2	.01	.02	4
	3-4	.01	.02	
	5-6	.01	.02	
	7-8	.01	.01	

^a Only one observation greater than 0.05.

Discussion

Carmody, in an interesting paper,⁴ has described a method of preparing reproducible, white silver chloride electrodes. He emphasizes the necessity of (a) removing free cyanide from the silver-plating solution, (b) washing the silver-plated electrodes for at least five days, (c) protecting the silver chloride electrodes from daylight, and expresses the opinion that the electrodes must be white in order to be reproducible and stable. It unfortunately is impossible to duplicate his technique exactly since he does not specify the current densities that he used. However, if

the effective area of his platinum gauze is assumed to be the area of a piece of foil having the same over-all dimensions, Carmody's current densities fall within the ranges suggested in this paper.

The present investigation has confirmed his observation that the silver-plating solution must be free from excess cyanide and a simple method of obtaining this result is described. On the other hand, the author, in spite of repeated attempts, has been unable to prepare white electrodes similar to those described by Carmody. The duration of the washing to which the silver-plated electrodes were subjected has been varied from a few hours to three weeks without affecting either the color or the electrical behavior of the electrodes. It seems probable, therefore, that some factor other than this washing is responsible for the production of white electrodes. Prolonged washing may even be disadvantageous as it increases the chance of contamination of the silver by the dust and fumes in the laboratory atmosphere.

The color of the electrodes described in this paper has been found to be governed by the current density used in chloridizing. Uniformly dark-colored electrodes always resulted from chloridizing at a total current between 2 and about 0.5 milliamperes (current density of 2.5 to 0.6 milliamperes per square centimeter), whereas electrodes prepared at lower current densities were spotted with grayish patches which did not darken on exposure to sunlight. The spotted electrodes exhibited a somewhat erratic electrical behavior in the silver nitrate solutions in which they were tested. A white but insufficiently adherent form of silver chloride is probably produced at very low current densities.⁸

The author wishes to express his appreciation of the advice and assistance so generously given him by Dr. Duncan A. MacInnes.

Summary

A simple and rapid electrolytic method of preparing silver chloride electrodes is described. The stability and reproducibility of these electrodes are within a few hundredths of a millivolt, even in extremely dilute solutions.

NEW YORK, N. Y.

RECEIVED DECEMBER 11, 1933

(8) MacInnes and Parker, *THIS JOURNAL*, **37**, 1445 (1915). Compare also Reedy, *Am. J. Sci.*, [4] **40**, 281 (1915).