Preparation of Ag/AgCl Electrodes

The preparation of Ag/AgCl electrodes by electrolysis has been described. Serviceable electrodes can be made, but cleaning and replating of polarized electrodes have not been successful. Procedures are reported here for preparation of fresh electrodes with low rest potentials and cleaning and replating of used electrodes to increase their serviceability.

Disks (1 cm in diameter and 1 mm thick) were machined from a sheet of silver (T. B. Hagstoz and Son, Philadelphia, Pa. 19106) and were perforated with 0.5 mm holes for use in a streaming potential cell. The disks were polished to a finish obtained with 15 μm alumina and cleaned with hot, concentrated HNO₃. The Ag/AgCl electrodes were prepared by anodic electrolysis (Model 143-1 Electroformer, Hanau Engineering, Buffalo, N.Y. 14225) in 1.0 N HCl solution and a current density of about 6.5 mA/cm² for five minutes. A wire of pure silver (T. B. Hagstoz and Son) was used as a cathode. The electrodes were dark purple in color and were not affected by daylight or fluorescent room lights when stored in 10⁻³ N KCl solution. The rest potential of a pair of electrodes was obtained by streaming various concentrations (10⁻³ to 10⁻⁵ N) of KCl solutions through the cell at a pressure of about 10 cm Hg. The rest potential was low and reproducible for a given pair of electrodes, but was dependent on the concentration of KCl as shown in Figure 1. The coefficient of determination (r²) obtained from analysis of variance of the least-squares regression was 0.985. A new Ag/AgCl electrode is shown in Figure 2A.

Upon polarization or contamination, the AgCl layer must be removed from the silver disk before replating. Parreira and Ottewilla have recommended dipping the electrode into hot, concentrated HNO₃ to remove the AgCl. Instead of AgCl being removed evenly from the surface of the electrode, selective areas were attacked more severely than others resulting in incomplete removal of the AgCl and in destruction of the electrode (Fig. 2B).

The aforementioned procedure was modified by use of reverse electrolysis (25 mA for up to 30 min) to strip the AgCl layer evenly from the silver disk, after which the electrode was dipped into hot, concentrated HNO₃ for 5 sec for a final cleaning. The electrode obtained from this modified procedure had a smooth surface and was free of residual AgCl. Replating was accomplished in the manner described already for original plating. An electrode upon polarization and after cleaning and replating by this procedure is shown in Figures 2C and 2D, respectively. The latter electrode was designed to have increased distance among the 24 holes. The modified procedure increased the number of times that a used electrode could be cleaned and replated by several-fold and resulted in Ag/AgCl electrodes with low reproducible values of rest potential comparable to those shown in Figure 1.

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Fig. 1. Rest potential of Ag/AgCl electrodes as a function of concentration of KCl solution.

Fig. 2. Ag/AgCl electrodes: (A) new electrode; (B) electrode in (A) after dipping in hot, concentrated HNO₃; (C) polarized electrode; (D) electrode in (C) after cleaning by the modified procedure and replating.
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References


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