Cost-Effective Teacher

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Easy-to-Make Ag/AgCl Reference Electrode

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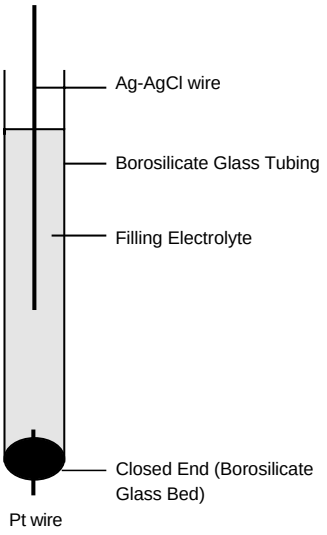
We are all aware of the importance of the use of the right reference electrode in voltammetric and potentiometric measurements. A practical reference electrode should be readily and reproducibly prepared and maintained, relatively inexpensive, stable over time, and usable under a wide variety of conditions. Of the two most common secondary reference electrodes, calomel and silver–silver chloride, the latter meets these requirements quite well. In addition, it is more rugged and easily miniaturized than is the calomel electrode. Many designs of such devices can be found in the literature (*1*).

The Sawyer-type electrode (*2*) (cracked-glass joint) employed for some time in our laboratories, proved to be hard to prepare and often our goal was achieved only after several trials. Our need for a reliable, easy-to-construct, small-size Ag–AgCl reference electrode to be used in electropolymerization by cyclic voltammetry led us to design a new type of electrode that can be assembled in any laboratory using readily available materials, such as Ag/AgCl wire from a broken glass electrode for pH measurements, a small piece of Pt wire, and a short piece of borosilicate glass tubing of the desired diameter.



Our prototype, depicted in the figure, has been successfully utilized in our laboratories in both aqueous and nonaqueous solvents. It can be assembled in a few minutes and no special skill (apart from very elementary glass-blowing) or tools are necessary. All that is needed is to weld a short piece of Pt wire (e.g., 0.5 mm in diameter and 5 mm long) to the closed end of a piece of borosilicate glass tubing (e.g., 4 mm in diameter and 5–10 cm long). The imperfect seal of Pt with borosilicate glass accounts for the very low leak rate of the filling electrolyte, which permits the necessary electrolytic contact with the working solution. The dimensions quoted above are those used in our experiments, but electrodes of any other size can be constructed to match the dimensions of the electrolytic cell. If a coated Ag wire is not available, this can be readily prepared following any of several methods described in the literature (*2–4*). This procedure usually takes no more than 30 min.

The filling solution depends on the medium utilized. We used a 3.5 M KCl solution in aqueous medium, while aqueous tetramethylammonium chloride adjusted to 0.000 V vs SCE was employed in nonaqueous medium. In our work, the reference electrode was located inside a Luggin capillary containing the working solution.

A reference electrode of this kind can be continuously used for at least 2 months without refilling or changing the inner filling solution. Eventually, the AgCl coating may need to be rebuilt following some of the method mentioned above. The actual value of the resistance has not been measured, but a typical value of the cell resistance (given by the Voltammetric Analyzer System, BAS model CV-50W) is about 30 Ω or less in aqueous medium (0.1 M supporting electrolyte concentration).

Literature Cited

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