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Short communication

A simple and effective porous plug for a practical standard reference electrode in nonaqueous media

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The calomel electrode, a practical standard reference electrode for aqueous solution, has no counterpart in nonaqueous electrochemical work. Several different reference electrodes are described and employed for each nonaqueous solvent, such as acetonitrile, *N*,*N*-dimethylformamide or dimethylsulfoxide [1]. The use of different solvents for the reference electrode and the electrochemical cell solutions has been avoided, not only because of the uncertainty of contact potentials, but because of the practical need to avoid mixing of the solutions.

Sintered glass cannot impede the mixing of solutions, specially during long experiments. Special porous glass plugs, such as those made with Vicor®, are extremely effective as diffusion barriers and provide good electrical contact. However, they are fragile and tend to crack easily when placed between different solvents or solutions of different ionic strength. Certain proposed porous plugs, such as that of Moe [2], resulted, in my experience, difficult to use with both a satisfactory closure and an adequate electrical resistance.

We have designed and constructed very simple and effective reference electrode holders with the following procedure: One of the ends of a Pyrex-glass cylinder, of appropriate length and 2–3 mm diameter, is sealed by fusion in a torch flame. The closed cylinder is filled, to a 0.5–1.0 cm height, with an homogeneous mixture of finely ground Pyrex glass and porous ceramic material (suitable proportions are given below), such as white bathroom tiles. The end of the tube that contains the mixture is heated in a laboratory burner flame until it glows red. This sinters the inner mixture without fusing the outer Pyrex cylinder. The end of the tube is marked and cut with a glass-cutter, thus exposing the sintered mixture which will constitute the porous plug end of the reference electrode.

The Pyrex-glass cylinder is filled with the solution and the components of the RE. We commonly use, with excellent results, the $AgNO_3$(ACN)/Ag reference electrode, which is the most commonly used in nonaqueous solvents. This device was tested with classical couples such as ferrocene/ferrocenium by cyclic voltammetry (C.V.). The results obtained showed a good correlation with literature data [3].

An important advantage of the device is the ability to easily change the porosity and electrical resistance of the plug through the variation of the ratio of glass to porous material. The essays showed that a 20–40 wt% of porous material gave satisfactory results.

$AgNO_3$(ACN)/Ag reference electrodes thus built, have been in use in our laboratory for *several years*, in different systems such as quinones, 1,2,5-thiadiazoles and its derivatives, alcohols, thiols and amides [4–9] dissolved in electrolytic solutions of almost all common protic and aprotic nonaqueous solvents (occasionally in the presence of strong acids – trifluoracetic or perchloric – or bases – sodium ethoxide), without solution leakage or contamination problems. Routinely, C.V. and long electrolysis were employed. Their mechanical resistance is high and is comparable to that of a solid glass-rod or porcelain of similar diameter.

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