MINIATURIZED REFERENCE ELECTRODES FOR AQUEOUS, AQUEOUS-ORGANIC, AND ORGANIC MEDIA

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INTRODUCTION

Following already published results on miniaturized reference electrodes (MREs) [1] a new reference system was devised and tested, with the inclusion of a Ag/Ag_2S internal reference element (IRE) in a photopolymerized acrylic hydrogel with tetramethylammonium chloride (QAS) as the supporting electrolyte. These MREs can serve as reproducible reference half-cells in various electroanalytical measurements performed in aqueous, mixed aqueous-organic, and organic media. They have proven extremely useful in voltammetric measurements, where a component dissolved in an organic solvent is added to an aqueous supporting electrolyte. [2] New applications were explored, including electrochemistry in low volumes of analyte, *e.g.* 1 µL, and in protein solutions, *e.g.*, bovine serum albumin (BSA). [3]

EXPERIMENTAL

Silver wires (0.25 mm diameter, 99.9% pure, Strem Chemicals) were cleaned electrochemically at -0.5 V vs. Ag/AgCl, 3 mol L^{-1} KCl (60 s), then coated with Ag_2S by immersion in $(NH_4)_2S$ solution (5 wt.% in water, Fisher Scientific) for 12-24 h, at room temperature. Black-gray, adherent, and uniform Ag_2S coatings were obtained.

Gel-type electrolytes of modified polymer composition were prepared according to our previously reported procedure. [1,3] The polymer matrix has been further optimized for improved electrolyte retention. The highest molar ratio QAS/acrylic acid (AA) attained was 0.85, yielding an AA/acrylonitrile (AN) molar ratio of 1/1.3. [3] The accuracy of these numbers is crucial for the behavior of the MREs; a 5% weighing error of the mixture components results in a polymer that will cause the MRE to fail.

Electrochemical measurements were performed with a Model 660a Electrochemical Workstation (CH Instruments, Austin, TX) equipped with a Faraday cage, using either a two- or a three-electrode setup.

RESULTS

The stability of the electrode potentials was evaluated by recording open-circuit potential *vs.* time (OCP), in aqueous 3 mol L^{-1} Cl^- solution, relative to a commercial Ag/AgCl 3 mol L^{-1} double junction reference electrode (DJRE). Potential stability of ±1 mV/30 h was achieved, while the chloride and pH response of the MRE were conveniently low: -0.9 mV/p[Cl^-], and 0.1 mV/pH, respectively. MREs do not contaminate the analytical sample, even when the sample volume is of 1-30 µL.

Low-volume cyclic voltammetry (CV) experiments were performed in a two-electrode setup, where MRE functioned as both RE and counter electrode (CTR). When using very small samples of analyte, it is sometimes difficult, or even impossible, to employ three electrodes in the same droplet. Therefore it is important to have a reference electrode that can allow current flow, and function simultaneously as both RE and CTR. Fig. 1 displays a CV recorded in the two-electrode mode, in 1 µL aqueous solution (0.5 mmol L^{-1} $K_4Fe(CN)_6$). This type of application requires electrodes with low impedance; for MREs the impedance values were determined to be on the order of 10^2 to 10^3 Ω.

For possible in vivo applications, we examined the stability of our MREs in the presence of proteins. Our choice was albumin, which represents almost half of human blood protein. Fig. 2 presents an OCP measurement in a 3.5 wt.% BSA, 0.9 wt.% NaCl solution. The potential is stable within ±1mV. Two separated half-cells were used, connected through a salt bridge; one half-cell contained DJRE at room temperature, and the other cell (with MRE) was kept on ice to prevent protein degradation.

In addition to aqueous solutions, our MREs behaved extremely satisfactorily in organic media (*e.g.*, CH_3OH, C_2H_5OH, CH_3CN, CH_2Cl_2, propylene carbonate).

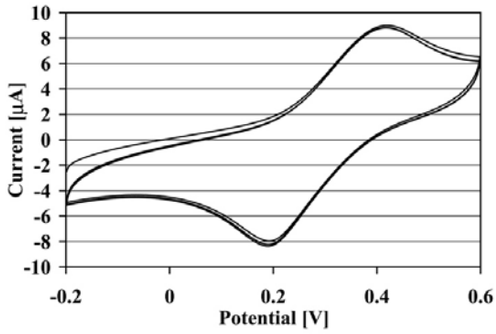

Fig. 1 Low-volume CV with no CTR in 1 µL aqueous solution (0.5 mmol L^{-1} $K_4Fe(CN)_6$).

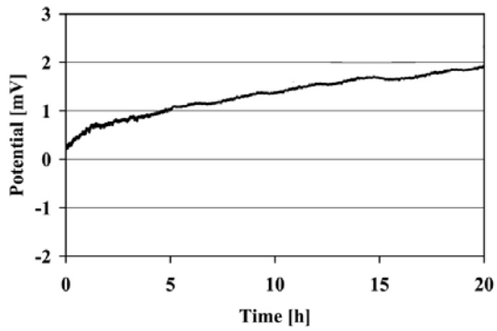

Fig. 2 OCP in 3.5 wt.% BSA, 0.9 wt.% NaCl solution, two half-cell setup (reference half cell at 298 K, half-cell with protein and MRE on ice).

REFERENCES

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