SOLID STATE MINIATURIZED REFERENCE ELECTRODES BASED ON STAINLESS STEEL

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INTRODUCTION

Stable reference electrodes (REs) can be obtained by keeping a metal-metal oxide (M/M_xO_y)-type internal reference element (IRE), *e.g*, stainless steel, in an environment of constant pH. [1] Such macro-scale REs were constructed initially using a stainless steel wire immersed in an aqueous solution of 2 mol L^{-1} HCl. [1] We miniaturized the above REs by imbedding stainless steel IREs (SSIREs) in a polymer matrix of fixed and constant pH value, [2,3] to yield miniaturized REs (SSWMREs). These deliver a stable and constant potential value ($E^{0'}$) over the range of pH 1-13. Their $E^{0'}$ value is constant ($\pm$ 1.5 mV) over time periods of up to 30 h; hence they are suitable for potentiometric and voltammetric determinations, performed in both aqueous and organic solutions. SSWMREs are practically free of undesired leakage; therefore they do not contaminate the analytical sample, even when used in very small volumes. The very low cost and relatively easy preparation of SSWMREs makes them good candidates for disposable REs.

EXPERIMENTAL

SSIREs (diameter 0.254 mm; type 304, Alfa Aesar, Ward Hill, MA) had the following wt.% composition: Fe (70), Cr (19), and Ni (11). [2] Such wires were activated by combined chemical and thermal methods: (i) etched with HCl (36.5 wt%) and rinsed with de-ionized water, then (ii) heated, in the presence of air, at 190 ^{0}C for 2 weeks or at 450 ^{0}C for 24 h. This procedure increases the thickness of the naturally occurring oxide layer on the surface of the stainless steel wire. Next, the activated SSIREs were incorporated in an acrylic-type hydrogel matrix (1-2 μL), obtained by photo-polymerization [2,4] to yield SSWMREs.

These half-cells were subjected to various tests for assessing the chemical and dimensional stability of their polymer matrix.

Electrochemical measurements were performed with a Model 660a Electrochemical Workstation (CH Instruments, Austin, TX) equipped with a Faraday cage, in both two and three-electrode configurations

RESULTS

Stability of electrode potential was established by open circuit potential *vs.* time (OCP) measurements (Fig. 1). After 5 h (OCP) the $E^{0'}$ of the electrode stabilizes within $\pm$1.5 mV.

The response mechanism of SSWMREs can be explained as follows. A native oxide layer, M_xO_y, covers stainless steel. This coating reacts reversibly with H^+ ions (Eq.1); hence it acts as a metal-metal oxide type pH-sensor, responding to protons with a Nernstian slope (Eq.2):

$$M/M_xO_y\ (s) + 2y\ H^+ + 2y\ e^- \rightarrow M\ (s) + y\ H_2O \quad (1)$$

$$\Delta E = E - E^0 = RT/2F\ \ln(a_{H^+})^2 \approx -0.059\ pH \quad (2)$$

When maintained in an environment of constant pH value, the SSIRE detects the same H^+ activity and delivers a constant potential value, to which other electrodes can be referenced. [1-3]

The exchange current density (i_o) of SSWMREs was determined in both aqueous and organic media, providing throughout values on the order of 10^{-2} A cm^{-2}, greater than the literature values [2]. (The larger i_0 is, the better the electrode can act as a non-polarizable system.) SSWMREs maintain a constant potential value (-0.378 V *vs.* Ag/AgCl, 3 mol L^{-1} KCl) over the pH range 1-13. The pH sensitivity of this reference system is < 0.1 mV / pH unit (at 298 K). SSWMREs may serve as internal or external reference electrodes. SSWMREs are suitable for both potentiometric and voltammetric analyses. The electrodes were employed in aqueous solutions and in five organic media (*i.e.*, CH_3OH, C_2H_5OH, CH_3CN, CH_2Cl_2, propylene carbonate). The reference system behaved reproducibly in each medium. Multiple scans from a cyclic voltammetry (CV) experiment are perfectly overlaid, *i.e.*, reproducible (see Fig. 2, CV in 1 mmol L^{-1} ferrocene methanol (Fc-CH_2OH), CH_2Cl_2). All components and materials that compose SSWMREs are potentially biocompatible and, therefore, these reference electrodes show promise for biomedical applications.

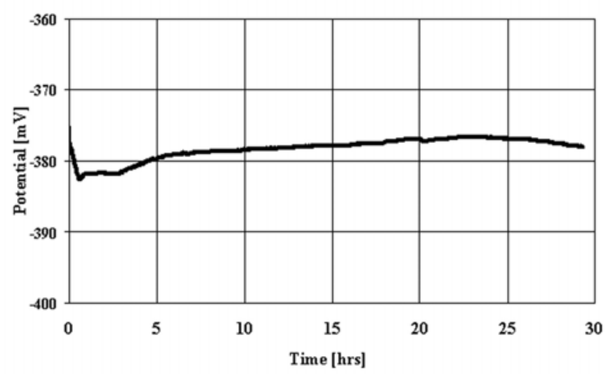

Fig. 1: OCP of SSWMRE *vs.* Ag/AgCl, 3 mol L^{-1} KCl RE

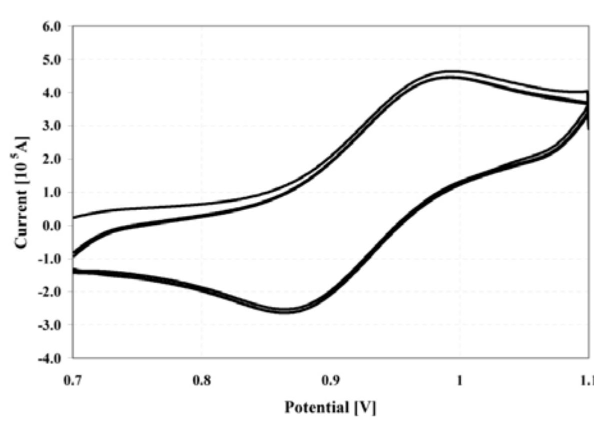

Fig. 2: CV (6 scans) in 1 mmol L^{-1} Fc-CH_2OH, CH_2Cl_2

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