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Plasticizer-free solid-contact pH-selective microelectrode for visualization of local corrosion

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ABSTRACT

The pH-sensitive solid-contact microelectrode (SCME) was developed for micro-potentiometric measurements for corrosion applications. A needle-shaped metallic body of the microelectrode was insulated with the exception of the 5 micron long apex where a layer of conductive polymer, poly(3-octhylthiophene-2,5-diyl) and then a pH sensitive membrane was deposited. The pH-selective membrane was based on plasticizer-free poly(methylmetacrilate–decylmetacrilate). The pH sensitivity was imparted on the membrane by a pH ionophore 4-nonadecylpyridine. The developed microelectrode is more robust than traditionally used glass capillary microelectrodes as it does not include any liquid in its construction nor is it as fragile. Thus, the main disadvantages of glass capillary microelectrodes, most importantly fragility and leakage of the liquid membrane, were eliminated. The properties of the improved microelectrodes, important for corrosion applications, were characterized. These include the slope, long- and short-term stability and reproducibility of potential, detection limits, selectivity coefficients, response time and life-time of the microelectrodes. The developed microelectrodes showed stable potential and short response time assuring reliable results during scanning measurements. Corrosion of hot dip galvanized steel sample was monitored by measuring local pH and current density quasi-simultaneously. The designed SCME showed its efficiency for practical applications for localized, scanning measurements in the field of corrosion.

1. Introduction

Solid contact electrode is an ion-selective sensor that does not include liquid in its construction. Miniaturization of these ion-selective sensors is easier to realize compared to downscaling of traditional ion-selective electrodes with plasticized or glass membranes. Miniaturized sensors are highly demanded in corrosion research to study the localized electrochemical processes caused by differences in microstructure and microcomposition of a substrate [1]. Any corrosion process results in change of local (and often bulk) pH due to anodic and cathodic reactions. pH microelectrodes provide valuable information about processes occurring at metal-solution interface of any corroding system and as such are the most frequently used among other ion-selective microelectrodes (ISMEs) [2]. The chronology of development of ion-selective electrodes from invention to miniaturization is described in several excellent reviews [3–5].

Glass capillary microelectrodes (GCMEs), widely used as miniaturized sensors, suffer from several major drawbacks with the most prominent being leakage of a liquid membrane and fragility resulting in a limited lifetime that usually does not exceed one day. The solid-contact microelectrodes (SCMEs) were suggested as an alternative that is free of these disadvantages. The SCMEs are less fragile than glass capillary microelectrodes. The inner filling solution is eliminated and hence its leakage. Detection limit, response time, short- and long-term stability are improved in comparison with glass capillary ion-selective microelectrodes [6].

Various types of solid-contact and solid-state pH-selective microelectrodes were reported by many groups [6–21]. Among solid-state microelectrodes Ir/IrO$_x$ microelectrodes are the most widely used due to their advantageous characteristics. They possess wide working pH range from 2 to 13 [7] and enable pH monitoring under high temperature and pressure, and in aggressive environments. Another important advantage is their capability for miniaturisation down to nanoscale [14]. However, the characteristics of Ir/IrO$_x$ electrodes are very sensitive to the microstructure and composition of the oxide film which is defined by fabrication conditions [15,16] and may demonstrate large hysteresis reaching 100 mV [17]. Often, fabrication methods are not practical due to their high cost [15]. Cheaper production techniques may yield Ir/IrO$_x$ electrodes that show significant potential drift

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unacceptable for scanning measurements and super-Nernstian slope in a range of 59–90 mV/dec [15].

Besides iridium-based microelectrodes, tungsten/tungsten oxide (W/W_xO_y) [22] and antimony/antimony oxide (Sb/Sb_2O_3) [23] needle shaped solid-state microelectrodes were reported to be used in corrosion research [8,12,13]. The main disadvantages of these microelectrodes are the sub-Nernstian slope (below 46 mV/dec at 25 °C) indicating non-Nernstian mechanism of response and rather narrow range of linear response (e.g. from pH 5.2 to 10.6 [8,13]) that is only satisfactory for a limited number of corrosion applications.

Metal/metal oxide based microelectrodes are usually sensitive to pH only. General feature that can be called disadvantage of all these microelectrodes is that once optimized, production methodology does not allow for fabrication of microelectrodes sensitive to other ions. The way to extend the range of ions assessable for detection is application of an ion-selective membrane on tip of needle shaped metallic substrate. Within this approach the way of fabrication of SCME can be optimized just once and production of the microelectrode sensitive to another ion only consists in optimization of membrane composition. We successfully used this approach to develop pH and Mg^{2+} selective SCMEs in our previous publication [6].

The development of solid-contact sensors with ion-selective membrane started with the invention of a coated wire electrode [24]. First generation of solid-contact ISEs had several drawbacks, in particular the potential drift, resulted from the indefinite transition from ionic (membrane) to electronic (metallic substrate) conductivity. An intermediate layer of electrically conductive polymer functioning as ion-to-electron transducer between an internal reference element and an ion-sensitive membrane significantly improved the performance solid-contact electrodes [25–27]. As for the ion-sensitive part of the microelectrode, the poly(vynilchloride) (PVC) has been the most widely used polymer matrix for years. However, recent publications show that electrodes with membranes based on copolymer methylmethacrylate–decylmethacrylate (P(MMA-DMA)), demonstrate better selectivity, detection limit and lifetime[28–31]. This is because the diffusion coefficients of ions in that co-polymer are much lower than in conventional PVC membranes (around 10^{-11} cm^2/s in P(MMA-DMA) vs. 10^{-8} cm^2/s in plasticized PVC). P(MMA-DMA) is a self-plasticized polymer and was specifically designed for ion-selective electrode applications by Hall's group [29,30]. P(MMA-DMA) is also better water repellent than PVC and helps to slow down the formation of a detrimental aqueous layer between solid contact and ion-selective membrane. Meanwhile, gradual formation of water pockets between the membrane and the metallic substrate is responsible for the deterioration of the characteristics of microelectrodes [32,33]. Elimination of aqueous layer stabilizes the potential of SCMEs and decreases the detection limit and response time [28,34], essential parameters for microelectrodes used for spatially resolved measurements [35].

There were several successful approaches towards miniaturization of solid-contact electrodes comprising rigid metallic substrate, conducting polymer and ion-selective membrane potentially suited for scanning measurements. However, each construction has certain features that could be improved: fragility of the glass microelectrode body [12,19–21], insufficiently long for localized scanning measurements response time and poor stability of potential [21] or relatively large tip (300 μm–3 mm) [18,19]. P(MMA-DMA) was first applied for fabrication of miniaturized solid contact electrodes with ultralow detection limit by Backer's group [18]. A layer of P(MMA-DMA)-based membrane and a layer of POT were applied over a gold wire. The resulting size of the measuring tip was ca. 300 μm which is not sufficiently small for high resolution localized measurements.

The aim of the presented research is to develop a solid-contact ion-selective microelectrode with a plasticizer-free membrane based on P(MMA-DMA) copolymer. Once optimized, the same polymeric matrix can be used to manufacture SCMEs selective to other ions. Not aiming for a universal tool, we focused on optimizing the properties of the new microelectrode for corrosion related studies: Nernstian slope, stability of the potential, short response time, lifetime and selectivity to Na^+ (as that is the most common interfering ion in corrosion research [36]) and applicability for localized scanning measurements [37]. The construction of the microelectrode presented in [6] was taken as a starting point, but the PVC based membrane used in [6] was substituted by P(MMA-DMA) plasticizer-free copolymer. The designed SCME is proven to be adequate for practical applications in the field of corrosion research and demonstrated better performance than its PVC-based counterpart.

2. Experimental

2.1. Reagents

The following reagents were used to fabricate the pH sensitive membranes: sodium tetrakis[3,5-bis(triflouromethyl)phenyl] borate (NaTFPB, Ref. 72017), tridodecylamine (Hydrogen Ionophore I, Ref. 95292) and 4-nonadecylpyridine (Hydrogen Ionophore II, Ref. 95295) of Selectophore grade and p-Xylene (pure for analysis) obtained from Fluka, regioregular poly(3-octylthiophene-2,5-diyl) (POT) of electronic grade obtained from Aldrich (Ref. 682799). P(MMA-DMA) was synthesized according to [38]. Amount of DMA in the final polymer is 81 wt.%. The number average molecular weight Mn is 13,600 g/mol. The weight average molecular weight M*w* is 23,200 g/mol. The set of pH buffer solutions with pH 2 (Ref. 82564); 3 (Ref. 82565); 4 (Ref. 82566); 5 (Ref. 33544); 6 (Ref. 33545); 7 (Ref. 33646); 8 (Ref. 33547); 9 (Ref. 82574); 10 (Ref. 82575); 11 (Ref. 82576); 12 (Ref. 33651) was purchased from Fluka and used for calibrating the developed SCMEs. The solutions with the constant concentration of NaCl (0.05 M) were obtained by mixing 6.93 ml of a corresponding pH buffer solution with 70 μl of 5 M NaCl solution. The aqueous solutions were prepared using MilliPore water (ρ > 18 MΩ cm).

2.2. Preparation of the pH-sensitive microelectrode

Electron micrographs and optical photograph of the SCME used in this work are presented in Fig. 1. The construction of the microelectrode is similar to that described in our previous work [6]. The ion-selective SCME comprises a needle-shaped rigid conductive substrate with a shaft diameter of 250 μm. It is made of 70/30 wt.%, platinum/iridium alloy to assure the stiffness of the

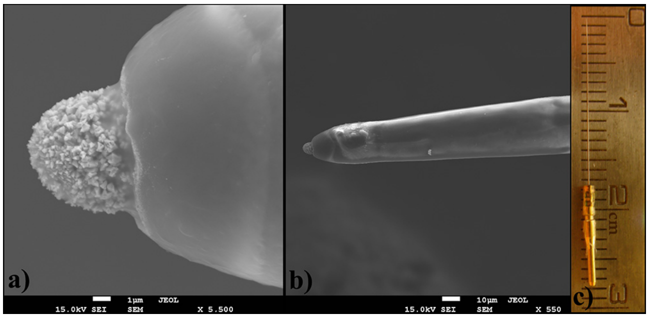

Fig. 1. (a) Electron micrograph of the exposed apex with the Au layer deposited over the Pt–Ir needle-like substrate, (b) electron micrograph of the body of a microelectrode and (c) optical photograph of SCME with the contact.