



Fabrication of a novel casein phosphopeptides/multi-walled carbon nanotubes/micro hybrid resin as mixed matrix membrane-junction reference electrode



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ARTICLE INFO

Article history:

Received 14 August 2014

Received in revised form 29 January 2015

Accepted 8 February 2015

Available online 14 March 2015

Keywords:

Mixed matrix membrane

Reference electrode

Casein/nanotube/micro hybrid resin composite

Chloride isotherm

Casein phosphopeptides

ABSTRACT

A novel reference electrode was fabricated via modification of a Pt electrode with a solid-state mixed matrix membrane generated by mixing casein phosphopeptides as Ca^{2+} and Cl^- ionophores, multi-walled carbon nanotubes (MWCNTs) as an electrical support (inorganic phase) and micro hybrid resin as binder (organic phase) with the weight ratios of 25:25:50 (wt.%), respectively. The selectivity of casein toward Ca^{2+} during formation of casein phosphopeptides– Ca^{2+} nanocomplex (average diameter: ~ 250 nm) was evidenced using UV–Vis spectrometry. Linear adsorption behavior was also estimated for the fabricated nanocomposite. Potentiometric technique revealed the strong adsorptivity of the nanocomposite to the chloride ion. The fabricated reference electrode showed adequate stability in various ionic strengths generated in the presence of ions such as Na^+ , K^+ , Mg^{2+} , Cl^- , I^- , I_3^- , SO_4^{2-} , PO_4^{3-} , ClO_4^- , etc. The non-polarization behavior of the fabricated reference electrode was confirmed during passing at least 10.0 mA electrical current thorough the electrode. The fabricated half-cell of the reference electrode with notation of “Pt | KCl(sat.) | Ca^{2+} (1.0 μm) nanocomposite membrane|” had a fixed reduction potential equal to -0.070 ± 0.002 V vs. standard hydrogen electrode. The electrical stability of the electrode was originated from irreversible adsorption behavior of the nanocomposite to the Cl^- as well as from the stability of casein phosphopeptides– Ca^{2+} nanocomplex during the conditioning steps. The reliability of the fabricated reference electrode was studied during testing in a three-electrode system including two Pt disks as working and counter electrodes during evaluating the nerstian behavior of cyclic voltammetry of 1.0 mM $\text{Fe}(\text{CN})_6^{4-/3-}$ solution with anodic and cathodic peak potential difference (ΔV) of 59.0 ± 0.1 mV. The lifetime of the fabricated reference electrode was estimated to at least 12 months.

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1. Introduction

In electrochemistry, a reference electrode is an electrode which is stable with a fixed composition and constant electrode reduction potential [1]. Reference electrodes are generally adopted in the electrochemical systems for various purposes such as estimation of the electroactive behavior as well as the redox strength of redox half reactions, in measuring the electrode potential in potentiometry, during applying a fixed electrical potential in voltammetry and in the controlled potential electrolysis [2–4]. Stable composition, fixed electrode potential, ideally non-polarizability, simplicity,

low cost, and ease of use are considered as the main characteristics of an ideal reference electrode [5].

Over the past decades, various types of reference electrodes such as standard hydrogen (SH), calomel, Ag/AgCl, and quasi-reference electrodes have been introduced [6–8]. Among these references electrodes, SH with 0.000 V standard reduction potential is considered as an acceptable reference electrode [7]. This electrode operates well in the non-aqueous electrolyte solution, but serious limitations such as need of H^+ standard solution with 1.00 M activity, introduction of hydrogen gas with a fixed pressure (1.000 atm), and finally control of the temperature to 25 °C have limited the direct applications of SH electrode in the commercial electrochemical cells [9]. Other reference electrodes such as calomel ($\text{Hg}/\text{Hg}_2\text{Cl}_2$) and Ag/AgCl, in spite of their great advantages like simplicity, availability and their low cost [10,11], sometimes suffer

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from shortcomings including temperature dependency of the electrode potential, instability and polarization during carrying high electrical currents, foul of the reference electrode (porous disk) with various adsorbents, and leakage of the internal electrolyte [7,12]. Quasi-reference electrodes are also limited to the special use due to low stability as well as polarization of the electrode using an internal standard such as ferrocene (II/III), cobaltocene, etc. [13]. All these challenges point to the strong demand of electrochemists for developing more reliable reference electrodes.

Various modifications have been applied to the reference electrode technology for its use in various conditions such as high temperature, large electrical currents, variable junction potential, etc. [14]. For instance, the stability of Ag/AgCl reference electrodes has been approved via modification of ionic liquids (ILs) as a salt bridge [15]. The performance of activated carbon has also been promoted via bounding activated carbon with polytetrafluoroethylene to provide a quasi-reference electrode for the use in pure IL electrolytes [16]. Zheng et al. reported that Pd-coated Pt wire provides stable potential during its use in the alkaline polymer electrolyte membrane fuel cells [17]. Moreover, Zuliani et al. proposed a junction-based reference electrode preparing on screen printed substrates using poly-3,4-ethylenedioxythiophene [18]. Despite all efforts, the efficient use of these probes has still been limited to only special applications [19]. Furthermore, scientists have recently focused on the fabrication of miniaturized reference electrodes based on the lab-on-chip technology [20]. Factors such as low cost and fast response time are considered as major advantages of this kind of electrodes. However these electrodes are not so reliable because of polarizability during passing large electrical currents [21]. Therefore the performance of the reference electrodes, the efficient use of these probes has still been limited to only special applications.

Different kinds of membranes such as glass, crystal, liquid media, etc. have been adopted as the junction of the potentiometric electrodes [20–22]. Moreover, various solid supports such as PVC, activated carbon or silica have been utilized as membranes during homogeneous mixing with a selective ionophore and solid salt as an ionic cite followed by plasticizing using a suitable plasticizer [23,24]. These membranes in spite of their simplicity as well as their renewability may extremely undergo problems such as low flexibility and small permeability to selected ion species [25,26]. In addition, toxicity, fragility and low capability for miniaturization have limited the *in vivo* clinical applications of these potentiometric electrodes [25]. It has been reported that mixed matrix membranes (MMMs) due to their intrinsic properties including high selectivity for adsorption and permeation of inorganic species, flexibility and also because of the presence of void volume and capillary channels in their organic/inorganic matrix [26] seem to be a suitable candidate for formation of membrane-based potentiometric electrode.

Casein is also a protein which makes up ~80% of the proteins in cow milk [27]. According to the surface activity property of this molecule, it exists in the form of a supermolecular structure known as micelle [28]. Micelle has amphiphilic characteristic which causes attractions and repulsions of this molecule with some inorganic species such as cations and phosphate metal ions [29]. It has been reported that casein phosphopeptides stabilize ions such as Ca^{2+} or Cl^- through the formation of nanocomplexes [30,31]. Presence of these ions in the nanocomplexes is biologically available for ventral absorption and remineralization of subsurface abrasion in tooth enamel [32,33]. Compared to other cations, significant ion binding energy (~4.0 eV) has been evaluated for Ca^{2+} [34,35]. Based on these results, formation of Ca^{2+} -based nanocomplex with high complex formation constant [36] can be considered as suitable ionophore during construction of membrane-junction reference electrodes.

Here a novel and reliable membrane-junction reference electrode is introduced based on modification of an inert electrode such as Pt disk with a new MMM fabricated via mixing multi-walled carbon nanotubes (MWCNTs) as inorganic phase, micro hybrid resin as organic phase and casein phosphopeptides as Ca^{2+} and Cl^- ionophores.

2. Experimental

2.1. Synthesis of MWCNTs

In this study, MWCNTs were selected as inorganic phase. MWCNTs due to their intrinsic properties such as high active surface area, large aspect ratio (surface–volume ratio), and presence of plenty of edge planes (roughness) in their matrix have been considered as good candidate for fabrication of electrodes [37,38]. In addition, compared to other types of carbon allotropes such as single-walled carbon nanotubes, carbon nanofibers and activated carbons, MWCNTs possess lots of porosity in their matrix [39,40]. This nanostructure was adopted as an inorganic phase during construction of the MMM. According to our previous report [41], higher permeation and more flexibility are estimated for MMMs constructed using activated MWCNTs as inorganic phase.

2.2. Materials

Micro hybrid resin composite was purchased from Vericom Company (Korea). To generate the nanocomposite, 0.236 g of calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Merck, Darmstadt, Germany) was dissolved in 100 mL of triply-distilled water to prepare 10.0 mM Ca^{2+} stock solution. Different concentrations of Ca^{2+} ranging between 1.0×10^{-8} and 1.0×10^{-2} M were daily prepared via dilution of the Ca^{2+} stock solution. Other reagents such as NaCl, $\text{CH}_3\text{COONH}_4$, KNO_3 , NaNO_3 , NH_4Cl , $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, ascorbic acid ($\text{C}_6\text{H}_7\text{NaO}_6$), ethylenediaminetetraacetic acid (EDTA), $\text{CO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, K_2SO_4 , $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$, I^- , I_3^- , and Na_3PO_4 were purchased from Merck, Darmstadt, Germany, and prepared by dissolving the appropriate compound in deionized water.

2.3. Casein phosphopeptides extraction

In this study, casein phosphopeptides were extracted from milk using procedure reported in Refs. [42,43]. For this purpose, briefly, ~8.0 g-powder of nonfat milk (Nestle, P.J.S. Co., Qazvin, Iran) was dispersed in 85.0 mL of triply-distilled water and heated at 40 °C. Afterwards, 40 drops of acetic acid (27%, w/w) were added with the rate of ~5 drops per minute. This process led to generate white precipitate as casein. Afterward, ~0.4 g of calcium carbonate (Merck, Darmstadt, Germany) was added to the milk solution to neutralize the pH. Finally, casein phosphopeptides were extracted from the solution by centrifuging the precipitation and decanting the solution above it.

2.4. Electrode preparation

To fabricate the nanocomposite-based membrane, casein phosphopeptides, MWCNTs and the hybrid resin composite material were mixed with the ratios of 25:25:50 (wt.%) followed by packing inside one end of a Teflon tubing (diameter 2.0 mm). An inert electrode such as a Pt wire was selected as internal electrode. ~3.2 mL solution including 1.0 μM Ca^{2+} and 3.0 M Cl^- was selected as internal standard solution.

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