

Potentiometric Response Characteristics of Oxide-Coated Gallium Electrodes in Aqueous Solutions



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ABSTRACT

This paper reports on the potentiometric response characteristics of gallium electrodes coated with native or anodic oxide layers in aqueous solutions. Solid metallic gallium electrodes were prepared by cooling liquid gallium monoliths supported either on planar silicon substrates or incorporated within glass capillaries. These metallic gallium electrodes showed potentiometric pH responses with a slope of *ca.* -38 mV/pH in the pH range between 3 and 9. The potentials measured could originate from redox processes involving surface oxide that was formed as a result of reactions between the metallic gallium and water (and/or OH⁻), as observed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Similar potentiometric measurements were examined for planar and capillary-incorporated gallium electrodes that were anodized in ice-cooled aqueous H₂SO₄ at 10 V. Although the resulting nanoporous anodic oxide-coated electrodes did not initially show potentiometric pH responses, they exhibited pH responses with a smaller response slope (*ca.* -30 mV/pH; pH 3–9) after potentiometric measurements in a solution of pH ≤ 3. This observation could be explained by the acid-induced dissolution of an oxide-based barrier layer that passivated the underlying gallium electrode. This explanation was compatible with the observation of an additional gallium oxide layer over the nanoporous anodic oxide after the potentiometric pH measurements. Interestingly, in contrast to the metallic gallium electrodes, the anodic oxide-coated electrodes exhibited potentiometric Nernstian responses to SO₄²⁻ at ≥ 10⁻⁴ M, reflecting the presence of sulfate doped into the oxide during the anodization. These results provide fundamental knowledge required to design miniaturized electroanalytical probes based on gallium electrodes.

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1. Introduction

Because of its low melting point (*ca.* 30 °C), metallic gallium has been utilized to fabricate μm-scale electrodes within confined spaces such as glass capillaries [1] and polydimethylsiloxane (PDMS)-based microchannels [2–4]. These electrodes have been prepared by introducing liquid gallium into the space of interest, followed by the solidification of the metal at the lower temperature. The presence of its native surface oxide layer [5] facilitates introducing liquid gallium into the relatively hydrophilic microstructures [1]. In addition, slight volume expansion during solidification [6] permits the fabrication of leakage-free solid electrodes within the confined spaces. Previously, solid gallium electrodes within microfluidic channels were used for localized

plasma generation [2], electrohydrodynamic mixing [3], and conductivity detection [4]. Capillary-incorporated solid gallium microelectrodes were employed as amperometric probes for scanning electrochemical microscopy in aqueous solutions [1].

In contrast to its utilization as amperometric indicator electrodes, the use of metallic gallium for potentiometric measurements has been very limited. Metallic gallium was explored as an indicator electrode for potentiometric neutralization titration in non-aqueous solutions [7]. However, to the best of our knowledge, potentiometric responses at metallic gallium electrodes in aqueous solutions have not been reported, most likely due to their high reactivity with water that involves the formation of an oxide-based passivation layer and their corrosion in acidic and basic solutions [8]. This high reactivity plays essential roles in the gallium-involved depassivation of aluminum for use as an anodic material in batteries [9] and in the preferential formation of gallium-based oxides on the surfaces of gallium-based alloys [10]. On the other hand, a number of metal electrodes have been used as potentiometric pH sensors in

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spite of their limited applicable pH ranges defined by the stability of the metal and/or its oxide [11]. Their potentiometric pH responses reflect proton-involved redox processes based on a metal–metal oxide couple or metal oxides having different oxidation states [11]. These electrodes have been used to fabricate μm -scale or smaller potentiometric pH sensors [12], including probes in scanning probe microscopy [13,14].

Recently, we have reported the formation of self-organized nanoporous gallium oxide via anodization of solid metallic gallium in ice-cooled H_2SO_4 [15]. The resulting oxide layer, which was anticipated to be based on a wide band-gap semiconductor ($\sim 4.8\text{ eV}$) [16], was comprised of uniform cylindrical nanopores aligned perpendicular to the underlying gallium electrode. The diameter of the resulting cylindrical nanopores was controllable in the range of 18–40 nm by adjusting the H_2SO_4 concentration and anodization voltage. Importantly, very similar nanoporous oxide structures could be obtained on both substrate-supported planar electrodes and capillary-incorporated electrodes. Thus, the anodization of solid gallium provides a simple means not only to prepare nanostructured functional materials [17], but also to fabricate miniaturized electrodes coated with functional nanoporous thin layers [18]. The nanoporous layers can serve as platforms to control biocompatibility [19] and chemical selectivity [20] in potentiometric sensing as well as permit for designing miniaturized amperometric sensors that measure analyte-induced changes in nanopore permeability [18,21,22].

In this study, we investigated the potentiometric response characteristics of gallium electrodes coated with native or anodized oxide layers in aqueous solutions. Planar electrodes and electrodes incorporated at the end of glass capillaries were employed to study potentiometric response behavior to pH and anions. The surface morphologies and chemical compositions of planar electrodes were measured using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) to gain insight into potentiometric response mechanisms.

2. Experimental

2.1. Chemicals and Materials

Gallium metal (99.99%) was purchased from GalliumSource and used as received. Si (100) wafers (p-type) and borosilicate Pasteur pipets were purchased from University Wafer and Fisher Scientific, respectively. Sulfuric acid (Fisher Chemical), lithium chloride (Acros Organics), lithium hydroxide (Fisher Chemical), sodium chloride (Fisher Chemical), potassium chloride (Fisher Chemical), potassium bromide (Aldrich), potassium nitrate (Fisher Chemical), potassium sulfate (Fisher Chemical), sodium perchlorate (Aldrich) and hydrochloric acid (Fisher Chemical) were of reagent grade or better, and used as received. All solutions were prepared with water having a resistivity of $18\text{ M}\Omega\text{ cm}$ or higher (Barnstead Nanopure Systems).

2.2. Electrode Preparation

Planar gallium electrodes on Si-substrates and capillary-incorporated gallium electrodes were prepared under Ar atmosphere according to the procedures described previously [15,23]. An electrical connection was made using a piece of conductive copper tape (Electron Microscopy Science) for a planar electrode and a copper wire for a capillary-incorporated electrode. Metallic gallium samples were anodized in ice-cooled 4 or 6 M aqueous H_2SO_4 at 10 V (vs. carbon counter electrode) with a CH Instruments model 618B electrochemical analyzer or a NuVant EZstat-HV potentiostat/galvanostat. As shown previously [15], the anodization in 4

and 6 M H_2SO_4 led to the formation of anodic oxide nanopores with average diameters of 28 and 19 nm, respectively. The anodized samples were washed thoroughly with water, and kept immersed in water or 0.01 M LiCl overnight before the potentiometric measurements were performed.

2.3. Potentiometric Measurements

Potentiometric measurements were performed at room temperature (ca. 20°C), which was sufficiently lower than the melting point of metallic gallium, using cells shown in Fig. 1. For a planar electrode, the geometric area exposed to a solution was defined by an O-ring (6 mm in inner diameter) used in the cell (Fig. 1a) [24], which was smaller than that used during the anodization (8 mm in inner diameter). The exposed geometric area for a capillary-incorporated electrode was defined by the opening of the capillary (ca. 1 mm in diameter) (Fig. 1b) [15]. The potential of a gallium sample and the pH of a solution were simultaneously recorded every 30 seconds using a Jenco 672 digital mV meter and a Denver Instrument UB-10 pH/mV meter equipped with a Fisher Accumet combination pH glass electrode, respectively. The input impedance of the pH/mV meter was significantly larger (greater than 10^{10} – $10^{12}\ \Omega$) than the resistance of the oxide-coated electrodes (10^5 – $10^7\ \Omega$) measured in 0.01 M LiCl using electrochemical

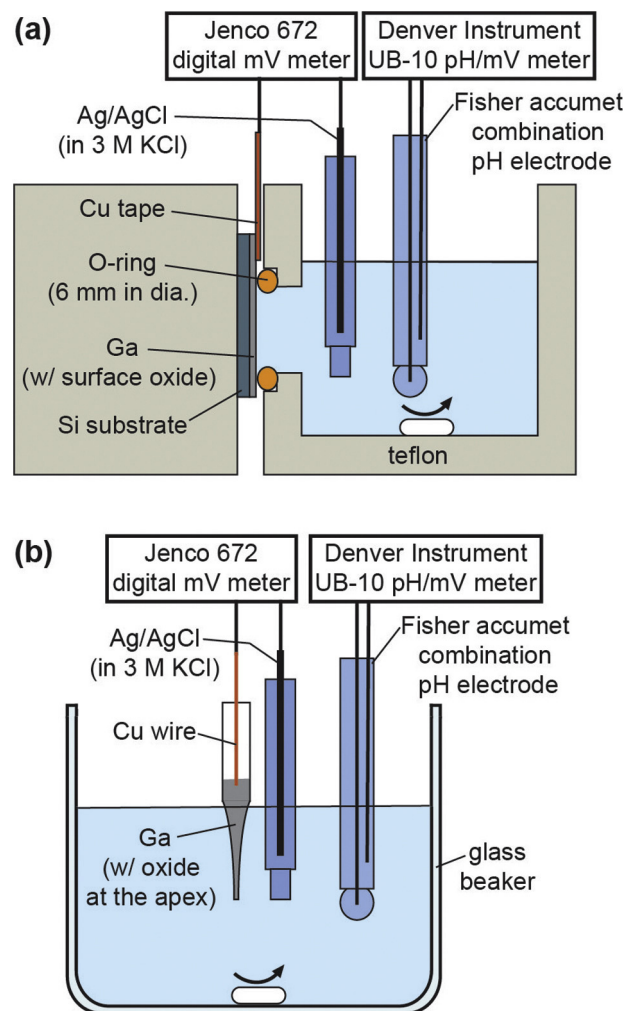


Fig. 1. Schematic illustrations of the experimental apparatus used (a) for a planar electrode on a silicon substrate and (b) for a capillary-incorporated electrode.

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