[Prepared for publication in *Electrochim. Acta*]

Ms. Ref. No.: SS14-185

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 (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.

Keywords:

Gallium electrode, nanoporous anodic gallium oxide, oxide layer formation, potentiometric responses, aqueous solutions

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 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 (~ 4.8 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 M Ω 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 H₂SO₄ 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 H₂SO₄ 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 UV-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 impedance spectroscopy (data not shown). All of the solutions contained 0.01 M LiCl as a supporting electrolyte, and were stirred during the potentiometric measurements [24]. The pH of a sample solution was adjusted by adding LiOH and HCl solutions containing 0.01 M LiCl to the sample solution. The anion concentration of a sample solution was increased by stepwise addition of stock solutions (0.010 and 1.0 M for KBr, KNO₃ and NaClO₄; 0.010 and

0.40 M for K₂SO₄) to 0.01 M LiCl (5.0 mL). It should be noted that negligible response to Na⁺ and K⁺ was found at the gallium electrodes, as verified by potentiometric measurements at different NaCl and KCl concentrations (data not shown). The potential and pH values for potential vs. pH curves were obtained when the differential quotient ($\Delta EMF/\Delta t$) in a potential-time curve was smaller than 1 mV/min.

Fig. 1

2.4. SEM-EDX Measurements.

A LEO 1550 field-emission scanning electron microscope equipped with an EDX detector was used to measure the surface morphology and chemical composition of planar electrodes according to the procedures reported previously [15]. All of the SEM images reported were obtained at an acceleration voltage of 15 kV with an in-lens detector. The EDX spectra were measured during the acquisition of SEM images with 5000-times magnification. The elemental compositions of anodized gallium surfaces were slightly different from those obtained previously [15] probably because of different conditions used for the EDX measurement (e.g., acceleration voltage).

3. Results and Discussion

3.1. Time Courses of Potentiometric pH Responses Measured at Planar Gallium Electrodes with and without Anodic Oxide Layers.

Fig. 2a shows time courses of EMF measured at planar gallium electrodes with and without nanoporous anodic oxide layers just after the overnight immersion in 0.01 M LiCl. The solution pH was adjusted by stepwise addition of an HCl solution containing 0.01 M LiCl, and measured

using a glass pH electrode. The EMF of the metallic electrode became more positive with decreasing pH from 4.6 to 4.1 and from 4.1 to 3.1. Considering the presence of a surface oxide layer, the potentiometric pH response is attributable to proton-involved redox processes based on metallic gallium and its oxide such as [8]:

In contrast, the gallium electrodes anodized in 4 M and 6 M H_2SO_4 , which were covered with anodic oxide layers comprising nanopores of 28 and 19 nm in average diameter [15], exhibited a negligible change in EMF from pH 5 to 4, followed by EMF becoming more positive from pH 4 to 3. The positive EMF response at these anodized electrodes was slower than that at metallic ones. In addition, the anodized electrodes exhibited a very small EMF change in the range of pH 4-9 prior to immersion in a solution of $\text{pH} \leq 3$ (data not shown). The absence of the potentiometric pH response probably reflects the complete passivation of the underlying metallic gallium by a barrier oxide layer formed at the bottom of the nanopores during the anodization, as shown for nanoporous anodic alumina [25]. At $\text{pH} \leq 3$, the barrier layer was gradually dissolved to expose the underlying metallic gallium, as reported for an oxide passivation layer on metallic gallium (*e.g.*, $\text{Ga}_2\text{O}_3(\text{s}) + 6\text{H}^+ \rightleftharpoons 2\text{Ga}^{3+} + 3\text{H}_2\text{O}$) [8] and also for the barrier layer of nanoporous anodic alumina [25]. The exposure of the metallic gallium ultimately allowed the observation of the potentiometric pH response that is primarily defined by the aforementioned proton-involved redox processes based on the gallium–gallium oxide equilibrium. As shown in **Fig. 2a**, both types of anodized electrodes exhibited similar trends in the potentiometric pH responses even though the chemical compositions of the anodic oxide layers were slightly different (*vide infra*). Thus, potentiometric data measured at gallium electrodes anodized in 6 M H_2SO_4 will not be discussed below.

Fig. 2

Fig. 2b shows the time courses of EMF recorded for planar metallic and anodized gallium electrodes after being used for potentiometric measurements at $\text{pH} \leq 3$. Both electrodes exhibited a more positive EMF at lower pH, as expected from the potentiometric response mechanism based on proton-involved redox processes. The response time of the anodized electrode was fairly short as compared with that shown in **Fig. 2a**, reflecting the exposure of metallic gallium during the measurements at $\text{pH} \leq 3$. Although the metallic electrode exhibited a larger potentiometric response, the slopes of the potentiometric pH responses at pH 3-9 were significantly smaller than the Nernstian slope of -58.2 mV/pH (at 20°C). In contrast, both electrodes exhibited much larger potentiometric responses at $\text{pH} > 9$ as compared with the Nernstian slope, probably due to chemical processes behind the corrosion of the surface oxide layer [8]. The EMF of these electrodes gradually became more negative upon immersion in a solution of $\text{pH} < 3$ (data not shown), probably due to the gradual dissolution of the oxide layer [8].

3.2. Potentiometric pH Responses Measured at Metallic and Anodized Gallium Electrodes.

Fig. 3 depicts EMF vs. pH curves measured at (a) metallic and (b) anodized gallium electrodes. As described above, the metallic and anodized electrodes exhibited potentiometric pH responses smaller and significantly larger than the Nernstian response at pH 3-9 and $\text{pH} > 9$, respectively. Similar potentiometric pH responses were observed regardless of the solutions employed for preconditioning (*i.e.*, water (filled circles) and 0.01 M LiCl (filled triangles)), suggesting that the influences of reactions of Cl^- with metallic gallium [8] on potentiometric response behavior were negligible under the concentration examined. The potentiometric pH

responses were very similar for planar (filled triangles) and capillary-incorporated (open triangles) electrodes: The response slopes (average and standard deviation from multiple samples) at pH 3~9 were -38 ± 9 (mV/pH; $n = 7$) and -37 ± 11 (mV/pH; $n = 6$) for planar and capillary-incorporated metallic electrodes, respectively. The slopes at the same pH range were -28 ± 4 (mV/pH; $n = 4$) and -28 ± 12 (mV/pH; $n = 7$) for planar and capillary-incorporated, anodized electrodes, respectively. These results indicate that miniaturized potentiometric pH sensors can be fabricated based on gallium, though the precision of the potentiometric measurements may be limited as shown by the relatively large standard deviations of the slopes. The relatively small response slopes may reflect the sluggish proton-involved redox reactions, as metallic gallium may be less stable than its oxide in aqueous solution.

Fig. 3

3.3. SEM-EDX Characterization of Metallic Gallium.

The high reactivity of metallic gallium in aqueous solutions can be recognized from changes in its surface appearance upon potentiometric measurements at pH 3-10. **Fig. 4a** and **4d** shows optical images of a planar metallic gallium electrode before and after potentiometric pH measurements, respectively. The area exposed to an aqueous solution, which was defined by an O-ring, changed from reflective to cloudy, suggesting the compositional and/or morphological changes of the gallium surface. The SEM image of the latter sample (**Fig. 4e**) showed sub- μm -scale grains that were not observed prior to the potentiometric measurements (**Fig. 4b**). In addition, the EDX spectrum of the latter surface (**Fig. 4f**) indicated the presence of oxygen, which was not found on the metallic gallium (**Fig. 4c**). These results verify the formation of an oxide layer via the reactions of metallic gallium with water and/or OH^- [8]. The almost

stoichiometric composition of the dried oxide (Ga_2O_3) (**Table 1**) suggests the formation of a relatively thick oxide layer, considering μm -scale depth in X-ray generation. Importantly, the successful observations of the potentiometric pH responses suggest that the surface oxide layer exposed to an aqueous solution was hydrated and gel-like with high water- and ion-permeability [26], but not thick and compact passivation layers [12]. The sub- μm -scale grain structures shown in the SEM images probably resulted from the shrinkage of the gel-like layer due to removal of water in the ultrahigh vacuum environment used for SEM measurements.

Fig. 4

Table 1

3.4. SEM-EDX Characterization of Anodized Gallium.

In contrast to metallic gallium, the surface of anodized gallium did not show any changes in the unreflective and dark appearance upon potentiometric measurements at pH 3-10 (**Fig. 5a** and **5e**). However, SEM-EDX results revealed changes in microscopic surface morphology and chemical composition. Prior to the potentiometric measurements, a well-organized nanoporous structure was observed on the anodized surface (**Fig. 5c**) as reported previously [15]. The EDX spectrum (**Fig. 5d**) verified the presence of gallium oxide on the surface [15]. The sulfur signal in the EDX spectrum originated from sulfate incorporated into the anodic oxide during anodization, as observed in anodic alumina [27]. The sulfate incorporation was supported by the higher sulfur content in samples anodized at the higher H_2SO_4 concentration and also by the observation of residual sulfur after potentiometric pH measurements (**Table 1**).

Upon potentiometric measurements, sub- μm -scale grains (**Fig. 5f** and **5g**) as shown in **Fig. 4e**, rather than the well-organized nanoporous structure (**Fig. 5c**), were observed. The surface

was covered with gallium oxide, as indicated by the EDX data (**Fig. 5h** and **Table 1**). Importantly, the nanoporous structure could be seen through a gap between grains (**Fig. 5g**), indicating that the nanoporous anodic oxide was covered with a hydrated oxide layer formed via reactions of exposed metallic gallium (*vide supra*) with water (and/or OH⁻). The growth of the oxide layer is consistent with the smaller sulfur content measured after the potentiometric measurements (**Table 1**), considering that the additional layer was grown in sulfate-free solutions. The formation of the additional oxide layer is attributable to the high reactivity of metallic gallium exposed to an aqueous solution, which involves the formation of gallium oxide/hydroxide in a solution containing gallium ion caused by the dissolution of metallic gallium. The oxide layer deposition limits the electroanalytical applicability of the nanoporous structure.

Fig. 5

3.5. Potentiometric Responses to Anions.

Interestingly, these oxide-coated gallium electrodes exhibited potentiometric responses to anions in 0.01 M LiCl (pH ~ 5.3). As shown in **Fig. 6a**, metallic gallium electrodes exhibited a potentiometric response to Br⁻, *i.e.*, an EMF change to the more negative direction with an increase in Br⁻ concentration with a slope of -19 ± 3 mV/decade at $\geq 10^{-4}$ M. The response time was relatively short (*ca.* 2-3 min). In contrast, anodized gallium electrodes exhibited potentiometric responses to SO₄²⁻ with a slope of -29 ± 6 mV/decade at $\geq 10^{-4}$ M, in addition to Br⁻ with a sub-Nernstian slope of -19 ± 10 mV/decade at $\geq 10^{-4}$ M (**Fig. 6b**). The responses were slower upon changing an anion concentration from 10^{-4} to 10^{-3} M (*ca.* 5 min), and were faster at the higher concentration (*ca.* 2-3 min). The response to Br⁻ probably reflects the strong

adsorption of Br^- to gallium and its oxide [8]. The Nernstian response to SO_4^{2-} at the anodized electrodes probably originates from the partition of sulfate into the oxide layer, as the anodized oxide contains sulfate as a dopant during the anodization (**Table 1**). Importantly, the anodized electrodes offered very similar potentiometric responses (-29 ± 6 mV/decade) after immersion in 0.01 M LiCl for one week. The observation of the potentiometric Nernstian response to SO_4^{2-} suggests that the doping of anion(s) during the anodic oxide formation provide a unique means for controlling the potentiometric selectivity of oxide-coated metal electrodes.

Fig. 6

4. Conclusions

This study clarified the potentiometric response characteristics of metallic and anodized gallium electrodes in aqueous solutions through a series of potentiometric and SEM-EDX measurements. The high reactivity of gallium and its oxide in aqueous solution strongly affects the potentiometric response behavior of these electrodes regardless of electrode shapes. These electrodes exhibited potentiometric pH responses at pH 3-9 with response slopes smaller than the theoretical Nernstian slope. The smaller response slope and the limited measureable pH range could be explained by the intrinsic reactivity of metallic gallium and its oxide with water, H^+ and OH^- . The high reactivity of these materials led to the formation of a hydrated, gel-like oxide layer on the electrode surface. The oxide deposition will prevent the utilization of the nanoporous anodic oxide layers to control the molecular accessibility to the underlying electrode, and thus the exposed gallium surface needs to be modified with chemically stable, functional materials for their future electroanalytical applications in microfluidics and scanning probe microscopy [4, 13, 14, 28, 29]. More interestingly, the anodized gallium electrodes showed

potentiometric Nernstian responses to SO_4^{2-} that were attributable to the partition of the analyte anion into the sulfate-doped anodic oxide layer. This finding suggests that the anion doping induced by the anodic oxide formation provides a simple and unique means for developing potentiometric sensors.

Acknowledgements

This work was partly funded by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy (DE-FG02-12ER16095). The authors also acknowledge Terry C. Johnson Center for Basic Cancer Research and Targeted Excellence Funds of Kansas State University for partial financial support of this work.

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Table

Table 1

Elemental Composition (at%) Obtained from EDX Data ^{a)}

sample	before potentiometric measurements			after potentiometric measurements		
	Ga	O	S	Ga	O	S
no anodization	100	– ^{b)}	– ^{b)}	40.2 ± 0.7	59.8 ± 0.7	– ^{b)}
anodized in 4 M H ₂ SO ₄	35.3 ± 1.0	61.4 ± 0.9	3.3 ± 0.1	37.4 ± 0.6	61.8 ± 0.6	0.7 ± 0.1
anodized in 6 M H ₂ SO ₄	30.5 ± 0.6	65.2 ± 0.8	4.3 ± 0.2	37.1 ± 4.1	62.1 ± 4.3	0.8 ± 0.3

^{a)} Average ± 90% confidence interval from data measured at five different areas on one or two samples.

^{b)} Not detected.

Figure Captions

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.

Fig. 2. Potential vs. time curves measured at a planar metallic gallium electrode (red circles), a planar electrode anodized in 4 M H₂SO₄ at 10 V (black triangles) and a planar electrode anodized in 6 M H₂SO₄ at 10 V (blue squares). Measured (a) just after overnight immersion in 0.01 M LiCl and (b) after use for potentiometric measurements at pH ≤ 3. EMF was recorded every 30 seconds in aqueous solutions containing 0.01 M LiCl at *ca.* 20 °C. Solution pH represented by the numbers shown in the figures was adjusted by adding solutions of LiOH (for increasing pH) or HCl (for decreasing pH) containing 0.01 M LiCl.

Fig. 3. Potential (EMF) vs. pH curves measured for (a) metallic gallium electrodes and (b) gallium electrodes anodized in 4 M H₂SO₄ at 10 V. Planar electrodes preconditioned in water (filled circles), those in 0.01 M LiCl (filled triangles) and capillary-incorporated electrodes preconditioned in 0.01 M LiCl (open triangles) were examined. The data for the anodized gallium electrodes were recorded after the electrodes were used for EMF measurements at pH ≤ 3. The solution pH was measured with the glass pH electrode, and was adjusted by adding solutions of LiOH (for increasing pH) or HCl (for decreasing pH) containing 0.01 M LiCl.

Fig. 4. (a, d) optical images, (b, e) SEM images and (c, f) EDX data of planar gallium electrodes before and after the potentiometric pH measurements, respectively. **Fig. 4a** and **4d** was measured for an identical sample, and the area contacted with samples solutions is shown as a circle shown in the latter image, which was defined by an O-ring (6 mm in diameter).

Fig. 5. (a, e) Optical images, (b, f) SEM images measured at low magnification, (c, g) SEM images measured at higher magnifications, and (d, h) EDX data of planar gallium electrodes anodized in 4 M H₂SO₄ at 10 V before and after the potentiometric pH measurements, respectively. **Fig. 5a** and **5e** was measured for an identical sample, and the dark area in these

images reveals the anodized region that was defined by an O-ring (8 mm in diameter). A part of the dark area, which was defined by a 6-mm diameter O-ring, was exposed to sample solutions during potentiometric measurements.

Fig. 6. Potentiometric responses of planar (a) metallic and (b) anodized gallium electrodes to anions (Br^- , NO_3^- , SO_4^{2-} and ClO_4^-). Measured at three different electrodes in aqueous solutions containing 0.01 M LiCl (pH $\sim$ 5.3) at room temperature (*ca.* 20 °C). The error bars represent the standard deviations of ΔEMF values measured at the three electrodes.

Figs. 1-6

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.

Fig. 2. Potential vs. time curves measured at a metallic gallium electrode (red circles), a planar electrode anodized in 4 M H₂SO₄ at 10 V (black triangles) and a planar electrode anodized in 6 M H₂SO₄ at 10 V (blue squares). Measured (a) just after overnight immersion in 0.01 M LiCl and (b) after use for potentiometric measurements at pH ≤ 3. EMF was recorded every 30 seconds in aqueous solutions containing 0.01 M LiCl at *ca.* 20 °C. Solution pH represented by the numbers shown in the figures was adjusted by adding solutions of LiOH (for increasing pH) or HCl (for decreasing pH) containing 0.01 M LiCl.

Fig. 3. Potential (EMF) vs. pH curves measured for (a) metallic gallium electrodes and (b) gallium electrodes anodized in 4 M H₂SO₄ at 10 V. Planar electrodes preconditioned in water (filled circles), those in 0.01 M LiCl (filled triangles) and capillary-incorporated electrodes preconditioned in 0.01 M LiCl (open triangles) were examined. The data for the anodized gallium electrodes were recorded after the electrodes were used for EMF measurements at $\text{pH} \leq 3$. The solution pH was measured with the glass pH electrode, and was adjusted by adding solutions of LiOH (for increasing pH) or HCl (for decreasing pH) containing 0.01 M LiCl.

Fig. 4. (a, d) optical images, (b, e) SEM images and (c, f) EDX data of planar gallium electrodes before and after the potentiometric pH measurements, respectively. **Fig. 4a** and **4d** was measured for an identical sample, and the area contacted with samples solutions is shown as a circle shown in the latter image, which was defined by an O-ring (6 mm in diameter).

Fig. 5. (a, e) Optical images, (b, f) SEM images measured at low magnification, (c, g) SEM images measured at higher magnifications, and (d, h) EDX data of planar gallium electrodes anodized in 4 M H_2SO_4 at 10 V before and after the potentiometric pH measurements, respectively. **Fig. 5a** and **5e** was measured for an identical sample, and the dark area in these images reveals the anodized region that was defined by an O-ring (8 mm in diameter). A part of the dark area, which was defined by a 6-mm diameter O-ring, was exposed to sample solutions during potentiometric measurements.

Fig. 6. Potentiometric responses of planar (a) metallic and (b) anodized gallium electrodes to anions (Br^- , NO_3^- , SO_4^{2-} and ClO_4^-). Measured at three different electrodes in aqueous solutions containing 0.01 M LiCl (pH $\sim$ 5.3) at room temperature (*ca.* 20 $^{\circ}C$). The error bars represent the standard deviations of ΔEMF values measured at the three electrodes.

Graphical Abstract