Gas phase nucleation core electrodes for the electrolytical method of measuring the dynamic surface tension in aqueous solutions

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Abstract

The design and operation of a new type of single nucleation site electrode, the gas phase nucleation core (GPNC) electrode, is described in this paper. The GPNC is basically an artificial Harvey nucleus which is made on a microelectrode. It is experimentally shown that it is possible to generate monosized gas bubbles with a periodical evolution by this method. The gas bubble evolution process is monitored electrically by means of overpotential and impedance measurements as well as optically observed. It is concluded that a possible use of the devices could be as a surfactant concentration sensor.

Keywords: Sensor actuator system; Dynamic surface tension, Electrolysis

1. Introduction

Gas evolution reactions at metal electrodes during electrolysis processes have been thoroughly described in the literature [1]. The attention of most authors has mainly been focused on the mass transfer processes and the reaction kinetics at gas evolving electrodes and on the various components of the electrode overpotential during the gas evolution reaction. Macroad electrodes as well as microelectrodes were used for these studies. The applications in mind have been quite different, from mass transfer enhancement by local stirring [2,3] to industrial electrolysis processes [4] and dynamic surface tension measurements [5].

On any existing flat electrode the place where the bubbles nucleate is unknown, independently of the active nucleation mechanism. It is generally accepted that nucleation of gas bubbles takes place in natural microcavities randomly distributed on the surface of the electrode. One way to fix the nucleation place is the miniaturisation of the electrode down to the same order of size as the bubble size. The chance that only one active site is present on the electrode surface increases in this way. Even on such microelectrodes, the reproducibility still remains a problem because bubbles might form at random places in an uncontrolled manner. For instance, two bubbles can nucleate at the same time and remain so small that they do not coalesce [6] and thus release separately while other small bubbles may coalesce and form a larger bubble. To fix the nucleation place it is useful to investigate and understand the nature of the nucleation processes and to create an electrode with a single reproducible nucleation site.

A literature scan has shown that virtually no publications deal with artificial nucleation sites for gas evolving electrodes. The published papers concerning artificial nucleation sites for gas phase nucleation were either made for nucleated pool boiling [7] or for nucleation by dissolution [8]. Except for paper [9], no reference could be found in literature in which artificial nucleation sites for reproducible single bubble generation are used during electrolysis.

A short review is given in Ref. [9] of the various nucleation mechanisms, i.e., homogeneous nucleation, heterogeneous nucleation, and nucleation from Harvey nuclei. Here only the bubble nucleation from Harvey nuclei is discussed. A Harvey nucleus is basically a trace of gas that may be present in a pocket (small cavity) on the surface of an electrode or the wall of the containing vessel which is in equilibrium with the liquid environment [10]. If the concentration of dissolved gas exceeds a maximum value depending on the dimensions of such a gas contain-
ing pocket, the corresponding Harvey nucleus becomes active and a bubble will grow from that pocket. When a bubble grows from one Harvey nucleus, its presence prevents other nucleation events in the neighbourhood of this bubble \[11\]. If an artificial nucleus can be created on an electrode, nucleation of bubbles only from one nucleation centre can be obtained. Artificial Harvey nuclei were proposed in Ref. \[8\], for the case of bubble growth by dissolution.

The monitoring of the bubble evolution can be done optically as well as electrically \[12\]. The electrical monitoring of the bubbles is based on the fact that the electrode surface in contact with the liquid solution is fluctuating during the bubble evolution process. These fluctuations induce fluctuations of the electrode overpotential and of the electrode impedance. A discussion of these phenomena can be found in Refs. \[9,13\].

In this paper, the evolution of gas bubbles from artificial Harvey nuclei during electrolysis of water was chosen for further investigation. One such artificial Harvey nucleus was made on an electrode in the form of a gas phase nucleation core (GPNC) electrode. A schematic representation of the GPNC electrode is given in Fig. 1.

2. Experimental

2.1. Technology of the GPNC electrodes

For practical reasons, concerning mainly the reproducibility of the fabrication process, the gas phase nucleation core electrodes (Fig. 1) were made in silicon technology. Silicon wafers with a (100) crystal orientation were used. The cavities were isotropically etched in silicon through a SiO\(_2\) mask (insulator layer in Fig. 1). The etching of silicon was performed by reactive ion etching (RIE) in a SF\(_6\) atmosphere (12 sccm, 20°C, 40 W HF, 50 mT) for 30 min. The isotropic etching is quite well controlled in silicon substrates. The mouth opening of the cavity can be changed by changing the mask used in the photolithography process. Devices with mouth diameters of 2, 3, 5, or 10 μm were fabricated. The cavity depth and volume can be adjusted by changing the etching time.

A sandwich of Ti/Au/Ti with a thickness of 25/25/25 nm, respectively, was evaporated and patterned on the wafers. Three metal strips were patterned on one chip, resulting in three GPNC electrodes (WE) with a common silicon bulk electrode (BE). The active area of the electrodes was defined by a passivation layer consisting of a sandwich of SiO\(_2\), Si\(_3\)N\(_4\), and photocurable polyimide (HTR3-200, OCG Microelectronic Materials, Inc.) as shown in Fig. 1. It should be noted that the polyimide cannot be directly deposited on the electrode metal because of its capability to undergo redox reactions in electrolyte solutions \[4\]. The SiO\(_2\), Si\(_3\)N\(_4\) interlayers were included to avoid this problem. At the end of this patterning process, the titanium top-layer was removed in the active area (hydrofluoric acid diluted in demineralised water, 1:20), allowing the gold surface a free contact with the aqueous solution. It is mentioned in the literature \[4,12\] that gas bubbles grown by electrolysis on microelectrodes have diameters in the order of 10-200 μm. To detect the bubbles evolving at the microelectrode by means of overpotential or impedance fluctuations, the size of the electrode active area also has to be comparable with the bubble size. The active area of the microelectrodes used during the experiments was determined by the SiO\(_2\), Si\(_3\)N\(_4\), polyimide window to a circle with a diameter of 35 μm. The wafers were then cut into pieces and the chips were glued on 8 x 100 mm\(^2\) printed circuit board carriers. The three metal strips were wire bonded and the silicon bulk was contacted with silver glue. The devices were then encapsulated by hand with Hysol resin (Dexter Electronic Materials Division, USA).

For the investigation of the behaviour of silicon as cathode material, some devices were made, where a squared area (100 x 100 μm\(^2\)) was allowed to contact the solution through a Si\(_3\)N\(_4\) window. The devices were mounted on PCB carriers in a similar way as the GPNC electrodes. The electric contact between the silicon and the printed circuit board was done with silver glue.

2.2. Operation of the GPNC electrodes

The gas phase nucleation core electrodes were used as cathodes. Correspondingly, the counter electrode was used as anode. Hydrogen bubbles were produced at the GPNC electrodes, according to the hydrogen evolution reaction (in alkaline medium):

\[
e^- + H_2O \rightarrow 1/2 H_2 + OH^-\]

A schematic representation of the input configuration needed for the operation of the GPNC electrodes is given in Fig. 2. The gold top electrode was used as working
electrode (WE). Current control was chosen because the amount of gas generated is linearly related to the current injected into the electrode. A voltage controlled current source ($I_{we}$) was connected between the working electrode and a counter electrode (CE), a platinum plate with a much bigger area than the working electrode (approx. 1 cm$^2$). The purpose of the bulk silicon electrode (BE) was only to generate the actual gas phase nucleation core. This was achieved by connecting a second voltage controlled current source ($I_{be}$) between the bulk electrode and the same counter electrode (CE).

The balance between the two currents, $I_{we}$ and $I_{be}$, is important for the operation of the GPNC electrode. The sum of the two currents is proportional to the total amount of gas produced by electrolysis. There are in principle two options for the use of the current source $I_{be}$, either interrupt it after the generation of the nucleus, or keep a low current through the bulk electrode to compensate for the gas taken by the bubbles from the cavity during their detachment and to improve in this way the stability of the gas phase nucleus.

2.3. Measurement set-up

A schematic of the complete measurement set-up used for the electrical monitoring of the gas bubbles is shown in Fig. 3. The functioning of this set-up was already described in Ref. [9]. The overpotential and impedance fluctuations are measured between the working electrode (WE) and a calomel reference electrode (RE). The signal processing unit was designed with two channels, to allow a simultaneous measurement of the overpotential and impedance fluctuations due to bubble evolution. The overpotential channel automatically removed the mean value of the potential measured between the RE and the WE, making it possible to monitor only the absolute value of the fluctuations around this mean value. For the impedance measurements, a signal (ACin) with a frequency of 100 kHz and a small amplitude (typically 50 mVpp) was added to the control voltage of the current source (DCin) by means of a summing amplifier, $\Sigma$. The amplitude of this small signal voltage was chosen in such a way that also the fluctuations of the resulting current of the current source could be considered to fulfill the small signal condition. No phase difference could be measured between the two channels of the amplifier. The outputs of the two channels ($V_{out1}$ and $V_{out2}$) were monitored and recorded on a dual channel digital oscilloscope ( Nicolet model 310). The bubble frequency was estimated from these recordings. For the characterisation of the suitability of silicon as cathode material, a potentiostat (EG&G PAR, model 263A) was used.

The experiments were done in a 10 mM solution of sodium acetate (NaAc, Merck, analytical grade), at different concentrations of non-ionic surfactant (Novel EO 4.5, courtesy of Unilever). Where needed, the pH was adjusted by adding small amounts of sodium hydroxide (NaOH, Merck, analytical grade).

The bubble evolution process was also optically observed with a Volpi TV Modular Microprobe system and a miniature CCD colour camera (Teli, type CS5131) connected to a video recorder. An external light source (Highlight 2000) was used in addition to the internal light source of the TV Microprobe (Intralux 6000-1). The magnification of the optical system was about x400.

3. Results and discussion

3.1. Silicon as electrode material

The behaviour of the silicon as cathode material in aqueous solutions was investigated by chronopotentiometry. Chronopotentiometry was chosen because the experimental conditions are in this case similar to those used during the normal operation of the microelectrodes for gas evolution under current control. For this technique, a current is injected through the working electrode (in this case silicon or gold) and the resulting potential is measured.

A typical chronopotentiometric response of a gold electrode (active area 35 x 35 $\mu$m$^2$) and of a silicon electrode (active area 100 x 100 $\mu$m$^2$) to a cathodic current step corresponding to a current density of 50 A m$^{-2}$ is
shown in Fig. 4. It can be seen that it is possible to inject a cathodic current through both materials. At the same current density, the resulting potential of the silicon electrode is much more negative than that of the gold electrode. This can be explained by the presence of a thin silicon oxide layer on the silicon surface. This layer is called the native oxide layer and is always present on silicon, especially in aqueous solutions. The charge transfer occurs via a breakthrough mechanism through this oxide layer or by the electrolytical dissolution of the silicon oxide. This is why silicon is not generally used as an electrode material. However, for the generation of the gas phase nucleation core, the value of the overpotential is not important and thus it can be concluded that silicon can be used for this purpose. The use of silicon as electrode material for the generation of the gas phase nucleus highly simplifies the design and the fabrication of the GPNC electrodes. A rough estimation gives a value of 5 MΩ for the resistance between the silicon electrode and the reference electrode at the current density of 50 A m⁻².

After the design of the devices was completed, an attempt was done to measure the influence of the mouth opening of the GPNC electrode on the resistance between the bulk electrode and the reference electrode. The measurements were carried out with the potentiostat, where the bulk electrode (BE) was connected as a normal working electrode in a three electrode configuration. Additionally, the concentration of background electrolyte was changed (NaAc with a concentration of 10 mM, 100 mM, and 1 M). No influence of the electrolyte conductivity or mouth opening could be measured. This result can be explained by the fact that the resistance of the oxide layer is much higher than the electrolyte resistance, which seems reasonable for the breakthrough conduction mechanism. Through optical observation under the microscope, it turned out that all four sizes of mouth openings under investigation were suitable for the generation of the gas nucleus with the bulk electrode (BE).

3.2. Single bubble nucleation

The need for the creation of the gas phase nucleus is pointed out by the results shown in Fig. 5 where the overpotential fluctuations due to the gas bubble evolution were recorded. For this experiment, the bulk silicon electrode was not connected \( i_{\text{inc}} = 0 \mu A \) and a current \( i_{\text{we}} = 0.58 \mu A \) was injected through the working electrode. The experiment was performed in a solution of 10 mM NaAc with 0.1 g l⁻¹ non-ionic surfactant (Novel EO 4.5). By optical observation of the gas evolution process it could be seen that several bubbles evolved at the same time, even from this small electrode surface (35 × 35 μm²). It can be concluded that the reproducibility of the gas bubble evolution process is not good enough in case the gas phase nucleus is not previously generated in situ.

The reproducibility of the bubble evolution was improved when the gas phase nucleus was generated from the bulk silicon electrode. The nucleation of single bubbles with a constant frequency from the GPNC electrodes
Fig. 7. Constant frequency during the bubble evolution from GPNC electrodes illustrated by means of the recording of the overpotential fluctuations. Measurement in 10 mM NaAc with 0.25 g l\(^{-1}\) Novel E04.5 surfactant. The estimated frequency is 8.25 Hz. The experiment was performed at \(l_{\text{we}} = 1 \mu\text{A}\) and \(l_{\text{be}} = 0.8 \mu\text{A}\). The origin of the overpotential fluctuations is arbitrary.

is illustrated in Fig. 6 where a photograph of the resulting bubble train is given. The equal distances between the bubbles on the photograph point out the periodicity of the nucleation process. The corresponding recording of the overpotential fluctuations is given in Fig. 7. Again, the periodicity of the signal is obvious. The experiment was performed at \(l_{\text{we}} = 1 \mu\text{A}\) and \(l_{\text{be}} = 0.8 \mu\text{A}\). It can be deduced from this periodicity that, as mentioned in the Introduction, the gas generated with the gold top electrode (WE) diffuses to the already existing gas phase in the nucleation core leading to a growing bubble rather than nucleating an independent bubble.

It can be seen in Fig. 7 that the amplitude of the overpotential fluctuations due to the bubble evolution is about 20 mV. This small amplitude represents only about 1% of the DC value of the overpotential of the gold electrode (Fig. 4). This difference points out the need for the DC shifting block in the overpotential channel of the signal processing unit.

There are in principle two possibilities for the use of \(l_{\text{be}}\) for the generation of the gas phase nucleus. One possibility is to continuously pass a current through the bulk electrode and the other is to apply only a pulse on the bulk electrode, before starting the actual measurements. The difference between the two situations is the total amount of gas that is produced at the GPNC electrode, namely the sum of the gas amounts produced by the working and the bulk electrodes. If \(l_{\text{be}}\) is turned off during the actual experiment and after generating the gas phase nucleus the situation is referred to as \(l_{\text{be}} = 0 \mu\text{A}\) in the following experiments. In this case, the total amount of gas produced at the GPNC electrode is directly proportional to the current through the gold working electrode \(l_{\text{we}}\).

To illustrate the possibility of simultaneous monitoring of the overpotential and impedance fluctuations, a gas bubble evolution process with an estimated frequency of approximately 0.5 Hz was recorded at an electrolysis current \(l_{\text{we}} = 0.37 \mu\text{A}\) and \(l_{\text{be}} = 0 \mu\text{A}\). The results are given in Fig. 8. It can be seen that, when a bubble grows on the electrode, both the absolute value of the overpotential and the impedance increase. The maximum is reached right before the bubble detachment. This is due to the continuously increasing surface screening of the electrode during the bubble growth. The abrupt fall occurs when the bubble detaches from the electrode. It can be concluded from Fig. 8 that either the overpotential or the impedance fluctuations can be used for the monitoring of the bubble evolution process. The difference between the shapes of the overpotential fluctuations in Figs. 7 and 8 is due to the different frequency of the two signals that is caused by a different current injected through the electrodes.

It has to be noticed that it is impossible to monitor only the bubble nucleation on the GPNC electrodes. By measuring the overpotential or the impedance fluctuations, the detachment of the bubbles is actually monitored. It has to be assumed that the conditions at the detachment moment do not vary from one bubble to the other in case all the external parameters are kept unchanged, which seems reasonable. A constant bubble detachment frequency corresponds to a constant bubble nucleation frequency. However, the external parameters can change in practice. Among these parameters the solution pH, the surfactant concentration, and the electrolysis current are the most important. Their influence on the bubble detachment frequency has been experimentally investigated in the present study and the discussion of the results follows.

3.3. Influence of the experimental parameters on the bubble frequency

The measurement result of the effect of changing the
pH of the solution on the bubble frequency is presented in Fig. 9. It can be seen that the bubble detachment frequency increases slightly when the pH of the solution increases. This effect can be explained by the influence of the pH change on the charges of the materials immersed in the solution, which is a known fact [15]. For the GPNC electrode, the materials that could change their surface electrical charge are gold, polyimide and the bubble surface (gas-liquid interface). In the considered pH range, these materials are negatively charged which means that the electrostatic interaction forces are of repulsive nature. Higher repulsive forces are expected for higher pH values. If the charges change on the surface of these materials, also the balance of the forces acting on the bubble at the detachment moment changes. Consequently, the bubble detachment diameter changes as well. At a higher pH a smaller bubble diameter and thus a higher bubble frequency should be obtained and is also measured experimentally.

The influence of the electrolysis current injected through the working electrode of a gas phase nucleation core electrode \( (I_{we}) \) on the bubble frequency is shown in Fig. 10. As it was expected, a higher bubble frequency corresponds to a higher amount of gas produced by electrolysis (the current \( I_{we} \)).

In Fig. 11 the effect of the surfactant concentration on the bubble frequency is presented for an electrolysis current \( I_{we} = 0.6 \mu A \) and \( I_{be} = 0 \mu A \). At this constant current, an increase of the bubble frequency is observed for a higher surfactant concentration and thus for a lower dynamic surface tension. This increase in the bubble frequency was expected because by increasing the surfactant concentration, the surface tension of the solution decreases, and the attachment force that keeps the bubble on the electrode becomes smaller. The solution used had a high pH. This pH was chosen to avoid the pH effect mentioned earlier. It can be concluded from Fig. 11 that the GPNC electrodes can be used as sensors for measuring the surface tension in aqueous solutions.

4. Conclusions

It is shown in this paper that it is possible to control the nucleation process of gas bubbles and to create a reproducible single nucleation site with an artificial Harvey nucleus. By isotropically etching the bulk silicon under the working electrode through a small hole, an artificial Harvey nucleus is made. It is demonstrated that the silicon can be used as cathode material. The micro cavity under the electrode surface is then filled with gas by electrolysis between the silicon bulk electrode and a remote counter electrode. Electrolysis is also carried out between the working electrode and the same counter electrode. The gas produced at the working electrode no longer gives rise to nucleation of bubbles all over the electrode surface. Rather than creating a new bubble, the gas produced by the working electrode is diffusing to the gas phase nucleation core generated in the cavity underneath the working electrode.

The functioning of the gas phase nucleation core (GPNC) electrodes is studied in this paper. The effect of various parameters like the solution pH and the surfactant concentration on the bubble detachment frequency are
also investigated in this paper. Based on the results presented, it is concluded that a possible application of the GPNC electrodes is as a surface tension sensor, if appropriate care is taken for keeping constant the parameters that could influence the behaviour.

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References


Biographies

Alex Volanschi was born in Bucharest, Romania, on May 6, 1967. He received the M.Sc. degree in electrical engineering from the Department of Electrical Engineering of the Polytechnical Institute of Bucharest, Romania, in June 1991. Since October 1991 he has been with the Biosensor Technology Group of the MESA Research Institute at the University of Twente, The Netherlands, doing research on chemical sensors. He is currently working towards his Ph.D. degree on the development of a surface tension sensor.

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Piet Bergveld was born in Oosterwolde, The Netherlands, on January 26, 1940. He received the M.Sc. degree in electrical engineering from the University of Eindhoven, The Netherlands, in 1965 and the Ph.D. degree from the University of Twente, The Netherlands, in 1973. The subject of his dissertation was the development of ISFETs and related devices, the actual invention of the ISFET, since then also investigated by many international research groups of universities as well as industry. Since 1965 he has been a member of the Biomedical Engineering division of the faculty of Electrical Engineering (University of Twente) and was in 1984 he was appointed as full Professor in Biosensor Technology. He is one of the project leaders in the MESA Research Institute. His research subjects still concern the further development of ISFET technology as well as physical sensors for biomedical and environmental applications, resulting in more than 200 papers to date.