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SHORT COMMUNICATION

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Voltammetric analysis using a self-renewable non-mercury electrode

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Abstract Galinstan is a new kind of electrode material and the galinstan electrode is a promising alternative to the commonly used mercury electrodes. The eutectic mixture of gallium, indium and tin is liquid at room temperature (m. p. −19°C) and its voltammetric behaviour is similar to that of mercury. The potential windows of use were determined for different pH values and are similar to those obtained with conventional mercury electrodes. Furthermore, the high hydrogen overpotential, which is characteristic for mercury, can be observed when galinstan is used as electrode material. Galinstan can be employed as a liquid electrode in the voltammetric analysis of different metal ions, such as lead and cadmium, in different supporting electrolytes. Our results indicate that the non-toxic liquid alloy galinstan could therefore become immensely important in electrochemical research as a potential surrogate material for mercury.

Keywords Galinstan · Voltammetry · Potential window

Abbreviations HMDE: hanging mercury drop electrode · DME: dropping mercury electrode · SMDE: static mercury drop electrode · MFE: mercury film electrode · HGDE: hanging galinstan drop electrode

Introduction

A number of different electrodes have been used for the determination of a wide range of reducible and oxidizable organic and inorganic compounds. Mercury, being the dominant and also the only liquid electrode material available so far, has been applied extensively in this field. Since mercury is a liquid under standard conditions and is applicable in an unusually large variety of forms, such as the hanging mercury drop electrode (HMDE) [1, 2], the dropping mercury electrode (DME) [3, 4], the static mercury drop electrode (SMDE) [5, 6] and the mercury film electrode (MFE) [7, 8], it still remains the most attractive electrode material. One of the major advantages of these mercury electrodes is their high hydrogen overpotential which expands the negative potential window without affecting the electrochemical behaviour (low background current and noise).

Because solid electrodes have a comparatively low hydrogen overpotential it has always been difficult to achieve a wide potential range with them. In addition, solid electrodes are subject to memory effects and, in most cases, a mechanical (e.g. polishing) or (electro-) chemical pretreatment of the surface is required. These factors limit the possible applications of solid electrodes like glassy carbon [9], carbon paste [10], pyrolytic carbon film [11, 12] and noble metal electrodes [13].

Because mercury is highly toxic and because its sustainable disposal is very difficult and expensive, the use of the material is strictly limited or even prohibited in certain countries. Therefore it seemed desirable to find an alternative material which is less toxic than mercury but displays similar characteristics. Consequently, an elaborate search for new electrode materials to be used in the polarographic and voltammetric analysis has been going on during the past fifty years. In order to acquire a dropping electrode with a highly reproducible and renewable electrode surface, the liquid state of aggregation is particularly important. Despite such efforts no publications whatsoever have explored the potential use of galinstan as an electrode material in electroanalytical chemistry. Galinstan has merely appeared in recent reports concerning electrochemically induced oscillation phenomena [14]. Thanks to its thermosensitive expansion, galinstan has also be used as a microinjection system [15, 16] and found its principal mode of

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Table 1 Selected physical and chemical properties of galinstan and mercury under normal conditions

	Galinstan	Mercury
Melting point (°C)	−19	−39
Boiling point (°C)	>1,300	357
Vapour pressure (Pa)	$<10^{-6}$ (at 500°C)	16.3×10^{-6} (at 20°C)
Mass density (kg m^{-3})	6,440	13,546
Viscosity (Pas)	0.0024	0.0015
Thermal conductivity (W mK^{-1})	16.5	8.65
Electric resistance (Ωm)	0.435	0.96×10^{-6}
Solubility in water	Very low solubility, data not available	20 µg L^{-1}

application as an alternative metallic liquid to mercury in clinical thermometers [17].

We would like to propose that galinstan can be potentially employed as an attractive alternative to the commonly used electrochemical working electrodes, since it combines the advantages of a high hydrogen overpotential, good electrochemical behaviour, a simple surface renewal at drop-formation and the non-toxicity of this alloy.

Herein we present the first study of the use of galinstan as an electrode material in voltammetric analysis.

Experimental

Apparatus

All measurements were performed using a VA Trace Analyzer 746 with a pertinent VA Stand 747 (Metrohm, Herisau, Suisse), supported by a VA Database 2.00 (Metrohm) software.

Electrodes

When using the multimode electrode from Metrohm, the capillary clogged after approximately 2 h. A possible cause is the large adhesive force to the glass. Thus we used melting point tubes: these were filled with the alloy using a syringe and a copper wire inside dipped to allow electrical contact with the VA Stand. This construction served as working electrode in which the surface area of the galinstan electrode was about 1 mm^2.

An Ag/AgCl electrode (3 M KCl) and a platinum coil were used as reference and as auxiliary electrodes, respectively, according to the three-electrode technique. We therefore worked at the hanging galinstan drop electrode (HGDE).

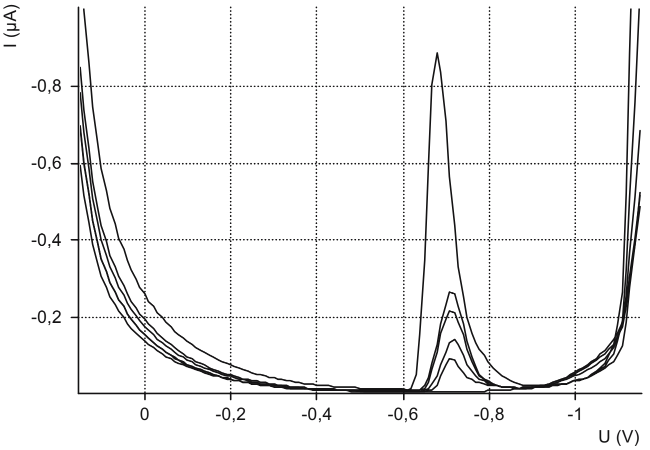

Fig. 1 Differential pulse voltammogram of Pb^{2+}, obtained with the hanging galinstan drop electrode (HGDE) at pH=6.0 and at different concentrations of Pb^{2+}

Chemicals

All chemicals were of analytical grade purity and were obtained from Merck (Darmstadt, Germany). Aqueous solutions were prepared with doubly distilled water. Galinstan was obtained from Geratherm Medical (Geschwenda, Germany, commercial price ≈1 € g^{-1}).

Recording the voltammograms

Prior to electrochemical measurements, the solutions were deoxygenated by purging them for 10 min with pure nitrogen (99.999 vol%, Air Liquide Berlin, Germany) after having been purified by pyrogallol, dissolved in 3 M KOH. For subsequent measurements, the solution was just purged for 100 s. The measurement method we chose was differential pulse polarography (DPP) with a pulse amplitude of −50 mV and a scan rate of 10 mV s^{-1}. We used acetate buffer solutions with a pH=4.4 and pH=6.0 as supporting electrolytes. Before each investigation, 20 mL of the blank

Table 2 Analyte concentration and peak potential of Pb^{2+} at the HGDE and at pH 6.0

Pb^{2+} concentration (mmol L^{-1})	Peak potential of Pb^{2+} (mV)
0.25	−710
0.49	−715
0.74	−709
0.98	−712
1.8	−677

supporting electrolyte was pipetted into the voltammetric cell.

Preparation of acetic buffer solution pH=4.4

A 136-g sample of sodium acetate and 77 g of ammonium acetate were dissolved in 1 L of doubly distilled water. This solution was mixed with 250 mL of acetic acid (98%).

Preparation of acetic buffer solution pH=6.0

A 100-g sample of ammonium acetate was dissolved in 300 mL of doubly distilled water. After the addition of 4.1 mL of acetic acid (98%) the pH was corrected by adding either ammonia solution (25%) or acetic acid (98%), if required.

Results and discussion

The standard potential of each single component of galinstan, which, depending on the pH value, usually lies in the voltammetrically important potential window between −100 mV and −1,000 mV, does not actually arouse the expectation of a generally high potential area of the material. In spite of this, we commenced our investigations assuming that the interactions between the single components, which effect oxidation overpotentials in each compound, would have a positive influence on the potential range of the entire alloy. Besides, the electrode surface could be made passive by growing an oxide layer, which also resulted in an expansion of the potential window towards the anodic direction. As is commonly known, galinstan forms an oxide layer after a certain time when exposed to air but this can be removed by simply stripping it off. Considering the short lifetime of a drop and the deoxygenation of the sample solutions, we would argue that the measurements could not be influenced by an oxide layer because it would not have a chance to occur under these conditions. Further studies regarding this postulation are in progress.

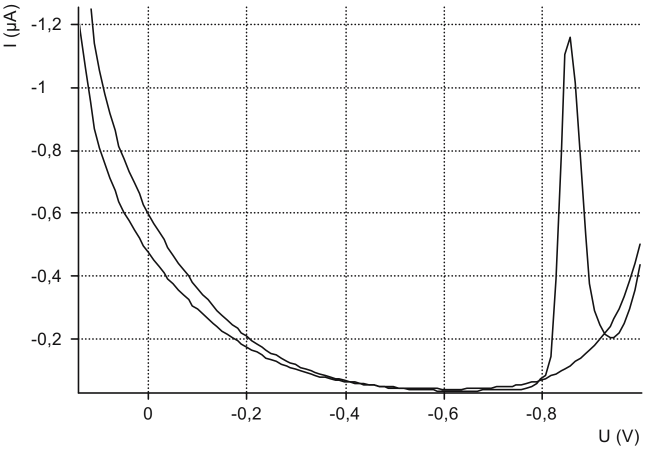

Fig. 2 Differential pulse voltammogram of Cd^{2+} (2.8 mmol L^{-1}, peak potential −854 mV), obtained with HGDE at pH 4.4

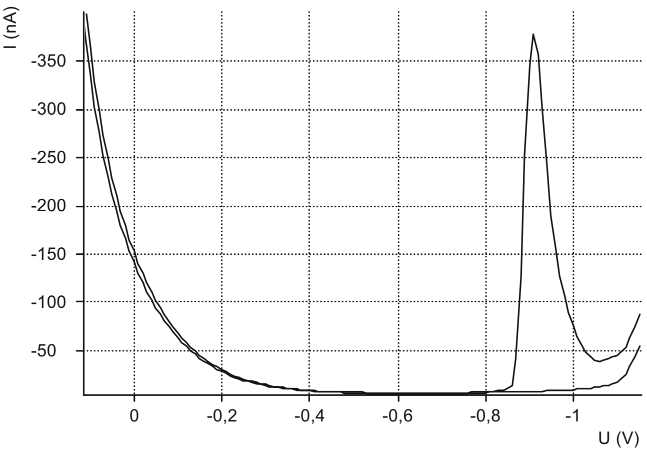

Fig. 3 Differential pulse voltammogram of Cd^{2+} (0.93 mmol L^{-1}, peak potential −905 mV), obtained with HGDE at pH 6.0

Mercury has a high vapour pressure (1.63×10^{-6} Pa) at room temperature. The particular danger of mercury vapour results from the absence of warning properties such as odour, colour, taste or irritation to the eyes or respiratory organs. Accordingly, the threshold limit value (TLV) of 0.025 mg m^{-3}, as it has been determined by the American Conference of Governmental Industrial Hygienists (ACGHI), is reached quite easily when elemental mercury is distilled or stored openly [18]. If mercury occurs in higher concentrations it is immediately absorbed by inhalation and then passes into the lungs where it is oxidized in the red blood cells. From there it is transferred to all parts of the body as a neurotoxin. Galinstan, on the other hand, has a comparatively low vapour pressure ($<10^{-6}$ Pa at 500°C) and therefore could not be absorbed by inhalation. Even if resorption of galinstan was assumed, it would not be followed by intoxication.

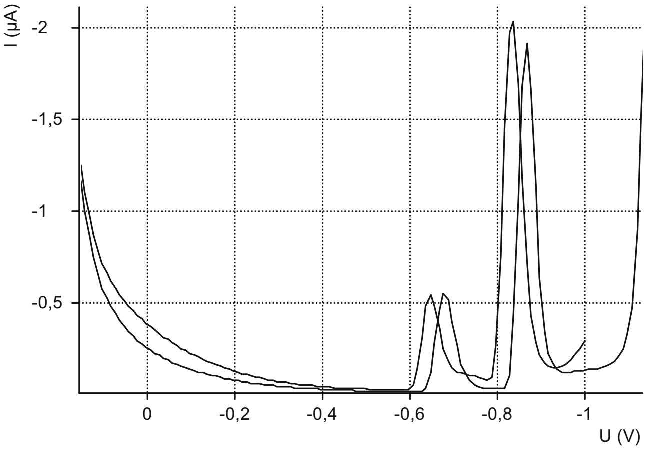

Fig. 4 Simultaneous determination of Pb^{2+} (0.95 mmol L^{-1}) and Cd^{2+} (0.47 mmol L^{-1}) at different pH values, pH 4.4 (Pb^{2+} peak potential −646 mV, Cd^{2+} peak potential −833 mV) and pH 6.0 (Pb^{2+} peak potential −696 mV, Cd^{2+} peak potential −873 mV)

Table 3 Several metal ions and their peak potential using differential pulse anodic stripping voltammetry with an accumulation time of 900 s, obtained with the HGDE

Metal ion and its concentration (mol L^{-1})	pH	Accumulation potential (mV)	Peak potential (mV)
Cu^{2+} (7.2 10^{-6})	4.6	−400	24
Cd^{2+} (7.7 10^{-8})	4.6	−900	−515
Pb^{2+} (9.1 10^{-7})	6.0	−800	−611

The physical and chemical properties of galinstan are listed in Table 1 and compared to those of mercury under standard conditions, unless otherwise indicated.

Depending on the material, the adhesion forces of galinstan can be greater than the cohesive forces, which complicate the use of glass capillaries for example. To avoid this problem it is necessary to use plastic or coated glass capillaries instead. When galinstan is used in thermometers, the measuring tubes are usually coated with a gallium oxide layer [17]. However, in our experiments we were able to use simple glass capillaries with a diameter of about 1 mm, because we worked at the hanging galinstan drop electrode; in that case the great adhesive force towards the glass capillary is not a problem. Furthermore, the formation of a new drop could be achieved quite easily by a mechanical knock off at the VA Stand.

Another advantageous feature of galinstan is that it forms an alloy at its surface with other metals, such as copper, tin, lead, zinc, gold and silver, especially if all surfaces are free from oxides. That means that galinstan, like mercury, is able to produce an amalgam if the investigated metal ions are electrochemically reduced to the metallic state.

We decided to use lead (as Pb^{2+}) and cadmium (as Cd^{2+}) as exemplary metal ions because of their well-known reduction behaviour at moderate potentials and above all because they are two of the environmentally critical metal cations.

The voltammograms were recorded from +0.15 V to −1.15 V with a pulse amplitude of −50 mV. We chose a pulse time of 40 ms (with time step=1.00 s) and a measuring time of 20 ms. The resulting sweep rate was 10 mV s^{-1}. Prior to the measurement the electrode was kept in solution for 10 s to allow equilibration. The reproducibility was tested by repeating a scan three times. The repeatability of the scans is satisfactory, especially with higher concentrations.

Figure 1 shows the differential pulse (DP) voltammograms for five different concentrations (Table 2) of $Pb(NO_3)_2$ in acetic buffer solution pH=6.0. The potential window in this supporting electrolyte reaches from 0 V up to −1.1 V. Thus, the oxidation potentials of the components of galinstan are anodically shifted with regard to the standard potentials, and the hydrogen overpotential of galinstan is high, and thus comparable to that of mercury. Hence galinstan, like mercury, extends the negative potential window.

The peak potential of Pb^{2+} measured at galinstan electrodes is shifted cathodically by approximately 200 mV compared to the mercury electrode. It can furthermore be observed that the current mutually increases with the concentration of the analyte. In the case of galinstan as well as mercury the peak potential of Cd^{2+} depends on the pH value. With an increasing pH, the electrode potential of Cd^{2+} becomes more negative. The peak potential of Cd^{2+} at pH=4.4 lies at −854 mV (Fig. 2), whereas at pH=6.0 the potential is −905 mV (Fig. 3). As in the case of Pb^{2+}, the Cd^{2+} peak shows a cathodic shift of about −200 mV compared to mercury electrodes.

The simultaneous determination of Pb^{2+} and Cd^{2+} also becomes possible by using galinstan as electrode material in the differential pulse voltammetry (Fig. 4).

Conclusion and outlook

This study presents the galinstan electrode as a novel liquid electrode. There are the two major advantages of this new electrode material:

- it is a metallic non-toxic electrode with an electrochemical behaviour similar to that of mercury (low background, high hydrogen overpotential) and
- it is a simply renewable electrode surface which allows a high reproducibility.

With diverse experiments we were able to confirm the wide potential window of galinstan. Towards the anodic side the limit is comparable to that of mercury, and is the case for the cathodic potential limit, which indicates a high hydrogen overpotential. Accordingly, the potential window of galinstan is comparable to that of mercury. By using other supporting electrolytes like KNO_3, Britton–Robinson buffer solutions, phosphate buffer solutions etc., it is possible to expand the potential window in both directions; and so other metal ions, such as zinc and copper, can be reduced on galinstan electrodes. We observed the general

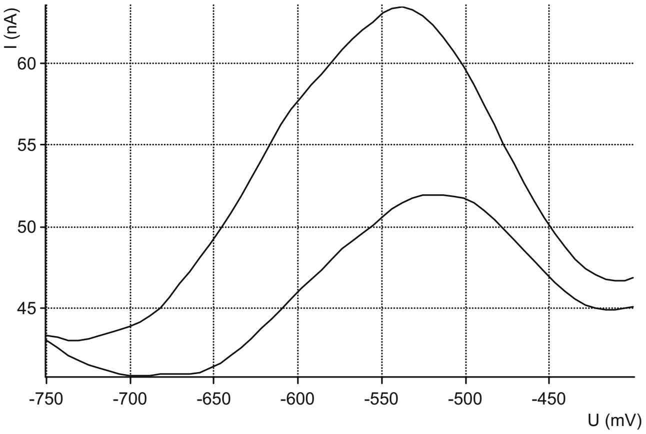

Fig. 5 Differential pulse anodic stripping voltammetry of Cd^{2+} (1.5 10−7 mol L^{-1}, peak potential −532 mV and 7.7 10−8 mol L^{-1}, peak potential −515 mV) with an accumulation time of 900 s

tendency that the potential window can be expanded towards the cathodic direction by using supporting electrolytes with high pH values. To define the potential window it is necessary to specify the current defining the limits and the measuring technique. A large horizontal baseline is reached if the limit current is set to 200 nA. For the acetic buffer solution pH=6.0 used the potential range was about 0 to −1.1 V, whereas the potential window at pH=4.4 reaches from −0.1 V up to −1 V using the DPV.

The limit of detection (LOD) depends on the method used. Operating with this new electrode and recording differential pulse voltammograms the LOD lies between 10^{-4} and 10^{-6} mol L^{-1} and can be optimized by varying the experimental parameters and by using other measuring methods like stripping voltammetry. First investigations show that we obtain good signals with concentrations in the order of 10^{-8} mol L^{-1} using differential pulse anodic stripping voltammetry. Table 3 gives some metal ions determined with ASV. Figure 5 shows one example using the differential pulse anodic stripping voltammetry in the investigation of Cd^{2+}.

Even organic compounds with one or several electroactive groups, as in nitrofurantoin (C=N and nitro groups) or phenazopyridine (C=N and azo groups), can be reduced at the galinstan electrode using differential pulse voltammetry. Further studies are in progress and results will be published in due course.

It is generally possible to use this galinstan electrode like the HMDE, DME and SMDE because of its property to form renewable drops. Whether it is possible to determine smaller concentrations with the help of film electrodes like in the case of mercury film electrodes cannot be clarified easily. The in situ realization of the galinstan film electrode is not an easy task, since the three components have to be reduced in the correct mass ratio to build up the eutectic mixture.

We hope that this electrode can partly or even completely replace mercury in voltammetric analysis, which would ideally render it unnecessary to work with mercury at all in the idealistic case.

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