

A METHOD FOR REACTIVATING THE SURFACE OF WORKING ELECTRODES DURING ELECTROCHEMICAL MEASUREMENTS

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A method was worked out for recovering the surface of stationary working electrodes during polarographic and other electrochemical measurements. The method consists in continuously reducing mercuric ions, added purposely to the supporting electrolyte, on the electrode surface. The reduced ions thus form a fresh, constantly renewed layer of mercury on the surface of the electrode where at the same time the reduction of the substance to be determined occurs. The overall limiting current is then the sum of the current corresponding to the reduction of the species tested and that corresponding to the reduction of the mercuric ions. The necessary concentration of the mercuric ions depends on the type and concentration of impurities present and varies in the range of $1 \cdot 10^{-5}$ to $2 \cdot 10^{-4} M$.

The applicability of the method was demonstrated on a continuously operating analyser with a mercury pool electrode, employed for measuring oxygen concentration in gases.

Long-term polarographic and other electrochemical measurements, carried out on electrodes with a stationary nonrecovered surface, are often accompanied by undue changes in the activity of the working electrode. Consequently, the current measured varies with time even in cases where the concentration of the species tested is constant. If these changes are small and gradual, they may be eliminated by periodic calibrating but in some cases they are so big that long-term measurements are no longer possible. The origin of this phenomenon varies from one case to the next; it may be due to changes in the surface area of the electrode, to the adsorption of electroactive substances, to the formation of oxide films or other species, to secondary electrode reactions, *etc.* In most cases, the current measured decreases but in some cases an increase of the current with time has also been observed. This is mostly due to the changes of the surface of the electrode, induced by the deposition of impurities of a low hydrogen overvoltage, on which a secondary reduction of hydrogen ions takes place.

It is, therefore, necessary that the working electrode be periodically or continuously recovered. A series of methods has been devised for this purpose, *e.g.* agitating the surface of the pool electrode and bubbling a gas above its surface¹, continuously circulating the mercury from the pool electrode through a washing device², restoring the surface by periodic switching to another potential³, and cleaning the surface mechanically in various ways. The present paper describes a new method for recovering the electrodes with the aid of a constant formation of a fresh surface of mercury deposited electrolytically from the solution⁴.

EXPERIMENTAL

Experiments were made with a polarographic analyser employed for determining oxygen in gases, operating with a stationary mercury level washed by a current of the gas to be tested¹. The analyser is schematically designed in Fig. 1. The working mercury pool electrode was formed by the level of mercury contained in a glass tube and had a surface area of 0.87 cm^2 . The mercurous sulphate reference electrode had an area of 7.6 cm^2 and was held in a separate compartment. The electrical contact was of platinum wire of 0.5 mm diameter welded into glass under the mercury level. The $0.1\text{ N-H}_2\text{SO}_4$ supporting electrolyte was fed to the working electrode compartment at the rate of 0.15 ml/min , preceded to the reference electrode compartment, and was let out. The rate of flow was set to such a value as to just surmount the rate of diffusion and thus prevent contaminating the working electrode compartment with mercuric ions from the reference electrode compartment. Both electrode compartments were separated by fritted glass and the part of the tube, forming the electrolytical connection between the two electrodes, was filled with glass wool.

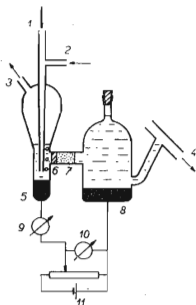


FIG. 1

Oxygen Analyser with Stationary Mercury Electrode

1 Inlet of air from the manostat; 2 inlet of H_2SO_4 ; 3 outlet of gas; 4 outlet of used $0.1\text{ N-H}_2\text{SO}_4$; 5 working mercury electrode; 6 fritted glass; 7 glass wool; 8 mercurous sulphate reference electrode; 9 microamperemeter; 10 voltmeter; 11 battery.

All chemicals used were of A. R. grade. The mercury was first washed with diluted nitric acid and then re-distilled *in vacuo*. The gas to be tested was fed directly above the surface of the working electrode, agitating thus intensively the electrolyte. The flow rate was kept constant at 140 ml/min with a liquid manostat and a flow restricting element (capillary). The temperature varied in the range of $20\text{--}22^\circ\text{C}$.

The potential imposed on the electrode was supplied from a 4 V storage battery *via* a potentiometer of 100 ohm internal resistance. The current was registered with a point recorder Regula, type Z 61 N3 of 400 ohms internal resistance. Its maximum sensitivity, $50\text{ }\mu\text{A}$ for the full scale, was adjusted by a shunt. The working electrode was made the cathode. Its potential was kept at -1.2 V against a mercurous sulphate reference electrode in $0.1\text{ N-H}_2\text{SO}_4$ which corresponded to the potential of the oxygen plateau on the $i\text{-}E$ curve. The information about the state of the surface of the working electrode was obtained in 24 h intervals by recording an $i\text{-}E$ curve. During this measurement, the potential was varied in steps of 200 mV , the current was registered on reaching a steady-state value after $5\text{--}10\text{ min}$.

The Principle of the Reactivation Method

The method takes advantage of the possibility of a constant renewal of the electrode by depositing on its surface metallic mercury from the supporting electrolyte. The layer of the newly formed mercury thus covers the surface of the pool electrode inclusive the impurities contained thereon.

The method is applicable to cases where the electrode potential during the measurement is more negative than the reduction potential of mercuric ions, *i.e.* practically to all reduction reactions. The resulting limiting current obtained by this method is the sum of the limiting current of the reduction of mercuric ions and the limiting current of the reduction of the species tested. The former does not interfere with the measurement as it has a constant value, and may, therefore, be easily deducted. In practice it means that the zero concentration of the substance tested has not the value of the respective residual current but a value raised by the reduction of the mercuric ions.

The optimum concentration of mercuric ions to be added to the electrolyte is found by experiment as it varies with the type and concentration of the impurities present. A concentration as low as 10^{-5} M favourably influences the course of the i - E curve and its time stability, although its reduction current is low and is virtually concealed in the residual current. For determining oxygen in the air an addition of $1 \cdot 10^{-4}$ of Hg^{2+} to the $0.1\text{N-H}_2\text{SO}_4$ has proved satisfactory.

RESULTS OF MEASUREMENTS

The behaviour of the mercury pool electrode during continuous determination of the concentration of oxygen in the air will be seen in Fig. 2. The electrode has not been recovered. Curve 0 was registered two hours after switching on and shows a well developed plateau of the limiting current of oxygen in the range of almost 400 mV. On further curves, the plateau gets gradually shorter and deformed, as may be seen on curve 6, registered after six days of operation. The deformations, of course, affect the accuracy of the measurement. The time during which no apparent deformation of the curve occurs is not reproducible and varies from one case to the next. This effect cannot be eliminated by agitating the mercury.

The influence which the renewal of the surface by depositing mercury had on the course of the curves, is seen in Fig. 3. The $0.1\text{N-H}_2\text{SO}_4$ contained $5 \cdot 10^{-5}$ M- HgSO_4 , the other experimental conditions being the same as in Fig. 2. It will be seen from

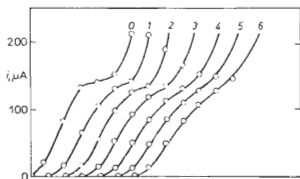


FIG. 2

i - E Curves of O_2 Reduction on a Non-Reactivated Stationary Mercury Electrode in $0.1\text{N-H}_2\text{SO}_4$

From -0.4V against a mercurous sulphate electrode; the potential difference between the experimental points is always 200 mV. 0 2 h after switching on the analyser, 1—6 in 24 h intervals. The number of the curve denotes also the number of days the analyser was in operation.

the curves that a steady state between the contamination and restoration of the surface was established and that there was no change in the shape of i - E curves with time.

The deposition of mercury restores even those mercury electrodes which have already been partly deactivated. An electrode was operated for six days without recovery until the i - E curve obtained exhibited noticeable deformation (Fig. 4). At this point, HgSO_4 was added to the supporting electrolyte to the concentration $1 \cdot 10^{-4}\text{M}$. Curves $6'$ and $6''$, registered after two and five hours, respectively, exhibit a restored plateau of the limiting current which was subject to no more changes with time. The inception of curves $6'$ -14 is shifted by $10 \mu\text{A}$ in the direction of the current axis in agreement with the value of the limiting current of Hg^{2+} reduction.

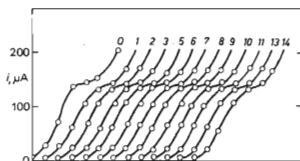


FIG. 3

i - E Curves of O_2 Reduction on a Stationary Mercury Electrode Recovered by the Cathodic Deposition of Mercury

$0.1\text{N-H}_2\text{SO}_4$ containing $5 \cdot 10^{-5}\text{M-HgSO}_4$. From -0.4V against a mercurous sulphate electrode in 200 mV steps (to negative potential values). 0 2 h after switching on the analyser; between curves 3 - 5 and 11 - 13 there is a time difference of 48 h , between other curves 24 h . The number of each curve also gives the number of days the analyser was in operation.

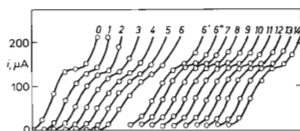


FIG. 4

Deposition of Mercury on a Partly Deactivated Surface

From -0.4 V against a mercurous sulphate electrode, points in 200 mV steps (to negative potential values). 0 2 h after switching on the analyser, 1 - 6 in 24 h intervals. After registering curve 6 , the Hg^{2+} concentration was adjusted by adding HgSO_4 to $1 \cdot 10^{-4}\text{M}$; $6'$ 2 h , $6''$ 5 h after adding the mercury; 7 - 14 in 24 h intervals.

On the surface of the mercury electrode, $6,2 \cdot 10^{-7}$ g/min of mercury was deposited which corresponds to the rate of growth of $5,58 \cdot 10^{-8}$ cm/min. Assuming a uniform deposition of the mercury, this would correspond to an increment of 100 atomic layers per hour. A layer of 1 mm thickness would thus take 1320 days to grow, and there is, therefore, no danger of an undue change in the distance between the electrode surface and the inlet tube of air, influencing thus agitation of the electrolyte or the transport of the depolariser.

The mercuric ions necessary for recovering the surface are added directly into the supporting electrolyte flowing slowly through the analyser. For experimental setups with stationary electrolyte, the concentration of the mercuric ions may be kept constant by the solubility product of a sparingly soluble mercurous or mercuric salt as well, or they may be supplied by diffusion from the reference electrode compartment. A good way of producing the Hg^{2+} is the anodic dissolution of an auxiliary mercury electrode by imposed current. It seems that this method might also be administered in coulometry in those cases where undue hydrogen evolution occurs on the impurities deposited on the electrode.

Depositing a thin film of mercury proved useful in oxygen analysers containing a silver working electrode as well; in these cases the gradual deactivation of electrodes was eliminated⁵.

It is evident that the above method may also be used for further polarographic, coulometric, and other measurements where a constantly renewed electrode surface is required. The reactivation described above found use in continuous polarographic analysers thanks to its simplicity and long-term effect which is only with difficulties or not at all attained by other methods.

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