

AN INVESTIGATION OF THE OXYGEN CATHODE WITH A SILVER CATALYST POLARIZED IN THE REGION OF NEGATIVE POTENTIALS

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Summary

Different types of oxygen diffusion cathodes have been tested to determine whether cathodic polarization of the electrodes at negative potentials has an influence on their further catalytic activity for oxygen ionization, and whether under these conditions potassium from the KOH solution penetrates into the silver catalyst.

The results show that even if these electrodes were kept in the hydrogen evolution potential range for a long time, there were no changes in the catalytic activity of the silver in oxygen gas electrodes. No evidence of potassium penetration into the silver catalyst was found.

Introduction

Silver is often used as a catalyst for the electrochemical reduction of oxygen in alkaline solutions. A silver catalyst provides relatively positive potentials owing to the intensive decomposition of hydrogen peroxide ions. High current densities at relatively low polarisations are obtained when this metal in the form of fine particles is built into the electrode. When the oxygen supply to the working interface of a cathodically loaded electrode is stopped, the electrode potential shifts in the negative direction till it reaches the region where, simultaneously, hydrogen ions and alkaline metal ions are reduced during the process called "cathodic incorporation of metals", according to the ideas presented by Kabanov [1 - 3].

This paper attempts a solution to the problems of whether the cathodic polarization of the silver catalyst at negative potentials can influence its further catalytic activity for oxygen ionization (this possibility has been suggested by Giles and Harrison [4] but has not been confirmed) and the extent to which the alkaline metal penetrates into the porous electrode during this polarization. In addition, using a porous electrode with a large surface could provide some details that are very difficult to observe on a small surface area of smooth silver metal, such as was used in previous measurements.

Experimental

Electrodes

Several types of electrodes were used:

(a) Porous electrodes made by sintering (450 °C) a pressed 7:3 mixture of silver powder and a filler (grain size under 40 μm) with total porosity of 73%. The pore diameter was under 20 μm ; specific catalyst loading 120 mg cm^{-2} .

(b) Overpressure gas diffusion electrodes with an unsintered catalyst layer made from a mixture of Raney silver (grain size under 25 μm) and carbonyl nickel in a 1:2 ratio, bonded with 2% PTFE. An asbestos cover layer of 78% porosity prevented gas penetration into the electrolyte. Specific catalyst loading 80 mg cm^{-2} ; gas overpressure 0.07 MPa.

(c) Hydrophobic porous electrodes operating without gas overpressure, having a catalytic layer of silver prepared by reduction of a water suspension of a solid silver salt.

(d) Smooth silver electrodes prepared from silver wire, working surface 15 mm^2 .

Measurements

The electrodes were immersed in 7N KOH solution for 24 h and then measured by the chronopotentiometric method against a Hg/HgO reference electrode in a half cell assembly (7N KOH, 22 °C). Potential changes were recorded by means of a high speed compensation potentiometer (Servogor Goertz, Austria).

To stop the oxygen supply to the electrodes, which changes them from oxygen to silver electrodes, the following procedures were adopted:

- for the hydrophilic electrodes the gas supply was stopped, which resulted in immediate flooding of the porous system;
- for the hydrophobic electrodes, by covering the gas side or by immersing the electrode in a solution through which nitrogen was bubbled.

Results and discussion

The chronopotentiometric curve of a cathodically polarized porous electrode with silver catalyst without oxygen supply is shown schematically in Fig. 1. When the surface area of the catalyst layer is covered with oxide, a reduction wave appears in the potential range 0.00 - 0.15 V (curve 1). By using low current densities a second wave can be observed in the potential range -0.2 to -0.4 V, corresponding to the reduction of oxygen dissolved in the electrolyte or adsorbed on the catalyst surface (curve 3). An electrode previously reduced at a potential of -0.8 V or above and then measured in the solution without oxygen supply does not show these waves (curve 2). The further shift to more negative values of hydrogen evolution and the final negative potential depends on the current density. With the current densities

used in practical cells it is possible that the silver cathode shifts to a potential value of -1.3 V.

A potential arrest appears in the range -1.0 to -0.7 V (curve 4) during the reverse anodic polarization after the initial sharp potential drop. Next, two potential waves occur in the positive region (silver oxides formation) followed by oxygen evolution. These qualitative characteristics are basically the same for all the electrodes used.

From the point of view of the problem under examination, an essential point is that the anodic curve has only one arrest in the negative potential region (Fig. 2), which becomes the most important part of the chronopotentiometric curve of the anodic branch of the silver electrode polarization. The search for conditions under which the anodic wave appears on type (a) electrodes has shown its dependence on temperature, cathodic current and potential, and simultaneously on anodic current which is in qualitative agreement with refs. 1 - 3. The anodic wave becomes more apparent with increase in temperature, cathodic potential and period of cathodic polarization, and also with decrease in anodic current. The conditions are expected to vary with different types of electrode. It is important to note that in our work on porous electrodes polarized with high cathodic current densities to a potential value of -1.5 V, only one potential wave was found on subsequent anodic polarization, although ref. 5 reports a second one.

According to the literature the observed changes undoubtedly result either from the oxidation of hydrogen formed during previous cathodic water reduction [6 - 8] and adsorbed on the silver surface or from the simul-

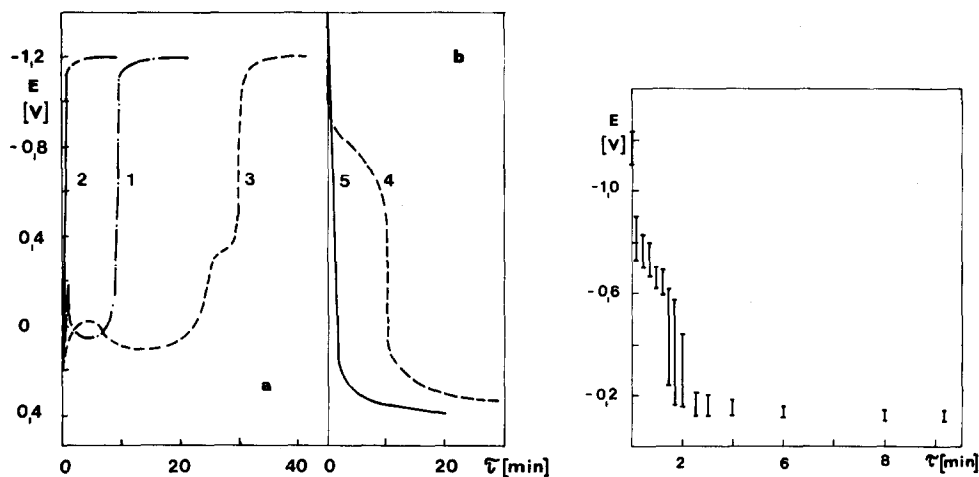


Fig. 1 (left). Chronopotentiometric curves of porous Ag electrode type (a). The cathodic polarization: 1, oxidized surface, $i_c = 50 \text{ mA cm}^{-2}$; 2, reduced surface, solution without oxygen, $i_c = 50 \text{ mA cm}^{-2}$; 3, oxidized surface, oxygen in solution, $i_c = 5 \text{ mA cm}^{-2}$. The anodic polarization: 4, $i_a = 50 \text{ mA cm}^{-2}$; 5, $i_a = 100 \text{ mA cm}^{-2}$.

Fig. 2 (right). Chronopotentiometric curves of five anodically polarized Ag electrodes type (a) after cathodic polarization (2 h) in the flooded state; $i_a = 50 \text{ mA cm}^{-2}$.

taneous oxidation of hydrogen and precipitated alkali metal [8 - 10]. Our further work was aimed at determining which of these processes actually occurs.

According to the literature, precipitation of alkali metal and its incorporation into the cathodic metal (Ag, Zn, Pb, Al, Cd) occurs in a similar manner to the formation of mercury amalgams in aqueous solutions, *i.e.*, at more positive potentials than the equilibrium potential [1 - 9]. A part of the precipitated alkali metal diffuses into the cathode metal [5, 11] where intermetallic compounds are formed and another part is immediately oxidized by water [1, 5, 12]. Each of the phases formed shows its appropriate wave on the anodic curve. This must be recorded at low current densities for their distinct differentiation [1 - 3].

We expected that more precise resolution of the single phases would take place in chronopotentiometric tests of an unloaded electrode, the potential changes of which are controlled by direct self decomposition by water of the formed phases. It was shown that such measurements could be carried out with type (c) hydrophobic electrodes, which because of their small size and large surface area could be polarized to the very negative potential of -3.0 V. Only one anodic wave was found in the potential region mentioned above (Fig. 3). The wire electrodes (type (d)) were similarly tested to investigate some disproportions in anodic waves at negative potentials greater than -1.0 V, reported by Kiseleva *et al.* [5]. The record of the dependence of the changes occurring in cathodic potential is shown in Fig. 4, which confirms the wave in the potential range -1.3 to -1.4 V, and a minor break at a potential of -1.8 V. Neither of these potential breaks occurs with a porous electrode. This fact may be ascribed to a difference in the structure of the cathodic material, as was observed, for example, with Cd [9, 13].

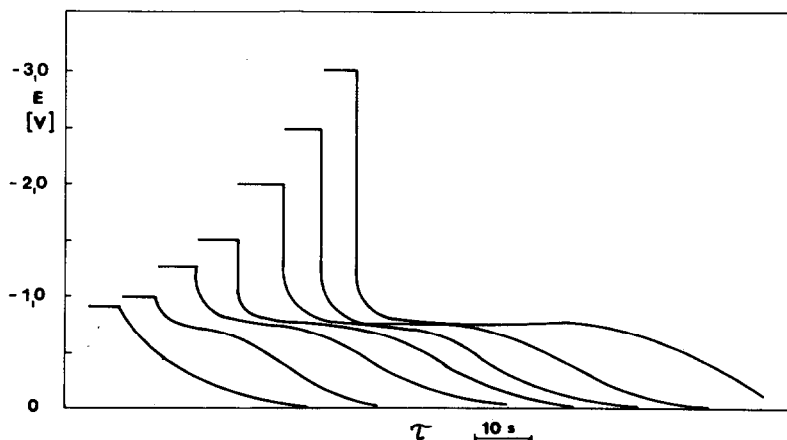


Fig. 3. Chronopotentiometric curves of immersed type (c) silver electrode, unloaded, after cathodic polarization (1 h) at different negative potentials. Electrolyte bubbled with hydrogen.

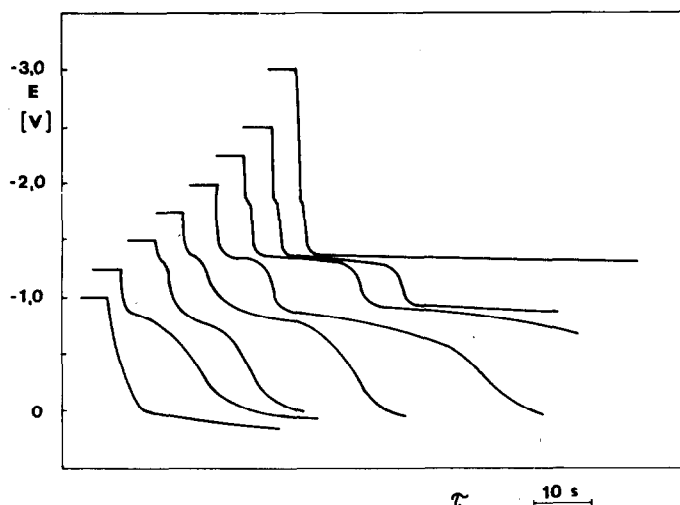


Fig. 4. Chronopotentiometric curves of immersed type (d) silver electrode, unloaded, after cathodic polarization (1 h) at different negative potentials. Electrolyte bubbled with hydrogen.

It is evident that the waves at potentials more positive than -1.0 V are identical for all types of electrode. The explicit analytical proof of whether the examined wave is due to the oxidation of alkali metal is difficult to determine due to the impossibility of removing the electrolyte from the electrode. In our work therefore we concentrated on trying to determine the extent to which the examined waves in the potential region more positive than -1.0 V appertain to hydrogen.

The existence of adsorbed hydrogen formed by electrochemical reduction is, in the given potential region, considered to be possible [9, 14, 15], even though previous opinions were to the contrary [16]. The real catalytic activity of silver to ionize hydrogen has been stated to be negligible [6].

To confirm this statement we investigated a type (c) electrode (functional area 10 cm^2) directly in contact with hydrogen in KOH solution. The electrochemical characteristics are shown in Fig. 5. Curve 1 shows the course of the open circuit potential as a function of temperature; curve 2 shows that even at a temperature of 80°C the electrode can be loaded only by a low current of a few mA cm^{-2} at a low overpressure of gas bubbling through it. These results confirm that the catalytic activity of silver to ionize hydrogen is negligible.

A further fact is found when the same electrode immersed in KOH solution is polarized by a cathodic current from 50 to 100 mA cm^{-2} for different lengths of time. After switching off the cathodic current the electrode adjusts to the potential of the hydrogen electrode. This potential is maintained for a length of time dependent on the length of the cathodic period, as shown in Fig. 6. These potentials cannot correspond with the ionization

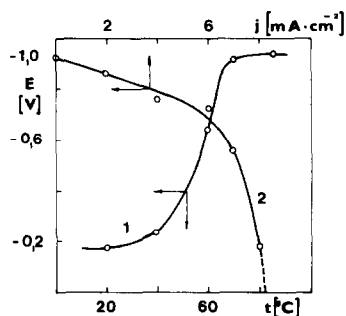


Fig. 5 (left). Electrochemical behaviour of type (c) Ag electrode in contact with hydrogen. 1, temperature dependence of open circuit potential; 2, polarization curve at 80 °C.

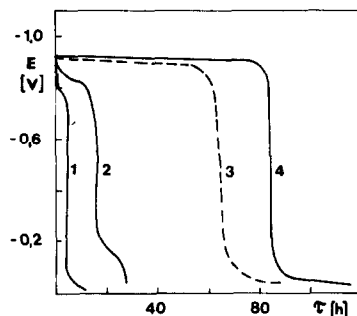


Fig. 6 (right). Chronopotentiometric curves of immersed type (d) Ag electrodes, unloaded, after cathodic polarization, $i_c = 50 \text{ mA cm}^{-2}$, for different times: 1, 10 h; 2, 15 h; 3, 24 h; 4, 42 h.

of an alkali metal, having regard to its activity with water and the length of the arrest.

According to some authors [6 - 8] it can be shown that the potential waves on the anodic branch of the chronopotentiometric curve (Fig. 2) belong predominantly to adsorbed hydrogen. Finally it has been stated that the major part of the cathodic current is used in hydrogen evolution and only a small part in the precipitation of alkali metal [9, 10]. This metal is not firmly incorporated into the electrode metal and mostly reacts immediately with water during the cathodic process. In addition a negligible residue is able to react chemically or electrochemically (together with hydrogen) after the current ceases.

We also investigated the amount of adsorbed hydrogen. The actual quantity is small, which is shown by the relation between the lengths of the arrests of cathodic and anodic polarization (Fig. 7).

When the electrochemical process described takes place under defined conditions on silver catalysts a question which arises in connection with working cathodes is whether their catalytic surface may not be altered at the same time and consequently their catalytic activity be lost. It is well known that catalyst history can influence the behaviour of an electrode [4]. This possibility was investigated by using electrodes of types (b) and (c) in long term tests. The former operated under oxygen overpressure at a temperature of 70 °C, and the latter operated with air (CO_2 had not been significantly removed) at normal air pressure and temperature. Two rows of electrodes in parallel were loaded at a current density of 50 mA cm^{-2} . The first row operated with, the second without, gas supply. Gas was supplied to the second row of electrodes at selected intervals. The shift in potential from negative values to the values of a working oxygen electrode was very sharp; however, in spite of this the gas supply was maintained for 1 h before the final potential was recorded. The potentials of electrodes loaded permanently

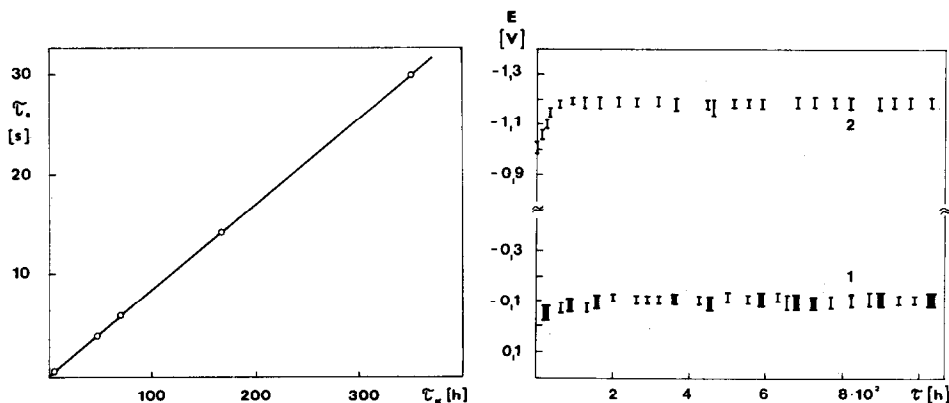


Fig. 7 (left). Dependence of the anodic arrest (t_a) on the duration of the cathodic polarization (t_k) for a type (c) electrode. Cathodic current $i_c = 50 \text{ mA cm}^{-2}$; anodic current $i_a = 1 \text{ mA cm}^{-2}$, 60°C , electrode area 10 cm^2 .

Fig. 8 (right). Time dependence of potentials of type (c) oxygen electrodes. 1, row of three electrodes polarized with oxygen supply; 2, row of three electrodes polarized without oxygen supply. Cathodic current $i_c = 100 \text{ mA cm}^{-2}$, 20°C . Heavy lines indicate the measurements of the 2nd row working with oxygen supply.

without gas supply during these 1 h test periods reached the same potential as the electrode operating with gas supply, as shown by the results in Fig. 8.

Conclusions

Cathodic polarization of oxygen electrodes in the range of potentials from -1.0 to -1.3 V does not affect the catalytic activity of the silver for oxygen reduction. Even if these electrodes were kept in the potential range of hydrogen evolution for a long time, there were no changes in the activity of the silver catalyst in oxygen gas electrodes.

Direct determination of potassium, which may be precipitated in the electrodes during cathodic polarization at more negative potentials, is difficult, but it can be stated that predominantly hydrogen evolution takes place so the amount of alkali metal simultaneously precipitated will be very small.

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