

COMPARATIVE METHODS FOR THE ESTIMATION OF THE ACTIVITY AND THE TRANSPORT HINDRANCES OF AIR GAS-DIFFUSION ELECTRODES

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Summary

Comparative methods are developed for the estimation of the activity and the transport hindrances of air gas-diffusion electrodes. The value of the intercept with the abscissa of the polarization curve on a semilogarithmic scale in the low current density range is accepted as a measure of the activity of air electrodes. The difference $\Delta E = E_{O_2} - E_{air}$ between the electrode potential when operating with pure oxygen, E_{O_2} , and with air, E_{air} , at the same current density is used for the estimation of the transport hindrances in air electrodes.

These methods are successfully employed for the investigation of air electrodes in alkaline solution. Different porous hydrophobic materials are investigated and the transport hindrances in their porous structure are compared. The activity and the transport properties of various active carbon catalysts are studied. The activity and the transport hindrances of catalysts of active carbon promoted with different amounts of silver are investigated, and the optimum content of silver in the catalyst is found. The methods proposed for estimation of the activity and the transport hindrances of gas-diffusion electrodes are successfully used for the investigation of some types of complex catalysts, *e.g.*, catalysts of active carbon and pyrolyzed chelate compounds.

Introduction

Wet-proofed "fixed zone" air gas-diffusion electrodes are commonly used in metal-air systems and fuel cells. The stability of the gas/electrolyte interface in similar electrodes is achieved by wet-proofing some of the pores with an hydrophobic agent, so that the electrodes can operate in free air without any gas overpressure.

A great variety of wet-proofed air gas-diffusion electrodes exists at the present time which differ both in overall structure and in materials used

[1 - 8]. It is very difficult rigorously to compare experimental data for different types of wet-proofed gas-diffusion electrodes. Usually the basic information for the electrochemical performance of an air electrode is obtained from its current-voltage characteristics [9, 10]. In most cases the current density generated by the electrode at a specific potential is used for comparison of the performance of air electrodes of different overall structure or with catalysts [11]. The shape of the current-voltage curve of an air electrode, however, is influenced simultaneously by the activity of the catalyst and by all transport processes which take place in the porous structure of the electrode. In addition the transport hindrances in the air electrode are a function not only of its overall structure, but also of the porous structure and the surface properties of the catalyst. Therefore it is very difficult to compare the performance of different air electrodes by using their current-voltage characteristics alone. In this respect the use of some simple experimental methods for the estimation of the activity and the transport properties of the air electrodes would prove to be very helpful.

Comparative methods for the estimation of the activity and the transport hindrances of the air gas-diffusion electrodes will be described in this paper.

Experimental

Double-layer, "fixed zone", carbon-air electrodes [6] were investigated. The electrodes consist of a porous, highly hydrophobic, electrically conductive gas-supply layer made of a special hydrophobic material [12] and a catalytic layer consisting of a mixture of the same hydrophobic material and a porous catalyst.

Electrodes of area 10 cm^2 were prepared. The current collector (nickel-plated iron grid) was pressed on the gas side of the electrode.

Steady-state current-voltage characteristics of the electrodes when operating with air and with pure oxygen were measured in a 7N KOH solution at room temperature using a half-cell arrangement. The potential was measured against an Hg/HgO reference electrode in the same solution.

Results and discussion

Figure 1 presents a polarization curve on a semilogarithmic scale of an air electrode of the structure described and with an active carbon catalyst. It is seen that at high current densities the polarization curve is substantially influenced by the transport hindrances in the electrode. With decrease in current density the transport hindrances are reduced, and at current densities lower than 10 mA/cm^2 their influence is slight. In this current density range a linear relation between the potential and the logarithm of the current density is observed.

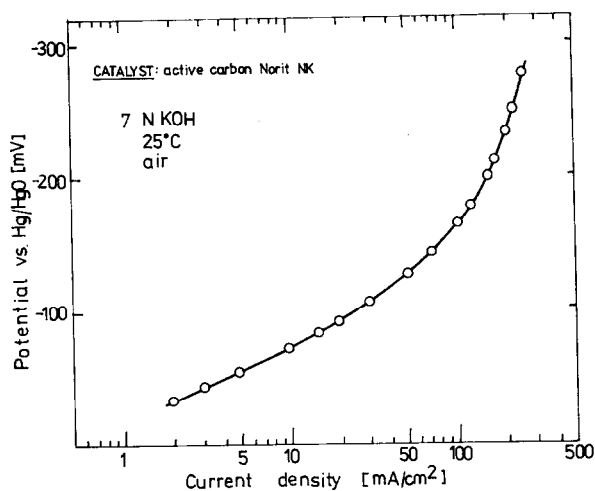


Fig. 1. Polarization curve of air electrode with active Norit NK carbon catalyst.

It can be accepted that within the low current density range the whole surface of the catalyst which is in contact with the electrolyte is participating equally in the electrochemical reaction. In this case the current generated from the electrode can be described by the expression:

$$i = S\vec{k}(k_0P_0) \exp\left(\frac{\alpha z F}{RT} E\right) \quad (1)$$

Here S is the wetted surface of the catalyst, \vec{k} is the rate constant of the electrochemical reaction, k_0 the solubility, and P_0 the partial pressure, of the oxygen. E is the potential of the air electrode measured against a reference electrode.

This expression can be presented in the form:

$$E = \frac{RT}{\alpha z F} \ln S\vec{k}(k_0P_0) - \frac{RT}{\alpha z F} \ln i \quad (2)$$

which is a linear relation between the potential and the logarithm of the current density with an intercept a with the abscissa:

$$a = \ln S\vec{k}(k_0P_0) \quad (3)$$

The value of the intercept a can be used as a measure of the activity of the real air gas-diffusion electrodes.

Figure 2 presents, on a semilogarithmic scale, the polarization curves within the low current density range of air electrodes differing in the type of active carbon catalysts used. It is seen that the value of the intercept a for these electrodes is different. The slopes of the presented curves are identical (ca. 50 mV/decade). The electrodes are operating under identical conditions, so that the product, k_0P_0 , is constant in all cases. Under these conditions the

observed difference in the values of the intercepts, a , of the curves may be attributed to the differences either in the rate constants \bar{k} , or in the wetted surface S of the catalyst, or both. It can be concluded that a higher value of the intercept a corresponds to a more pronounced activity of the air electrode.

By the use of this simple comparative method, different air electrodes can be compared in respect of their catalytic activity.

This is illustrated in Fig. 3 where similar curves are presented for air electrodes with catalysts of active carbon and active carbon with some quantity of silver [13]. It is seen that the intercepts, a , for these electrodes are different, which means that their activities differ. Electrodes with silver in the catalyst are more active than electrodes of pure, active carbon. Moreover, an increase in the amount of silver [14] in the catalyst results, as expected, in an increased activity of the electrode.

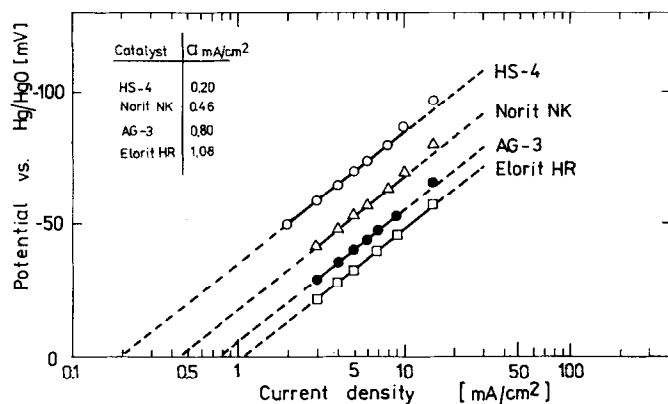


Fig. 2. Tafel portions of the polarization curves of air electrodes with active carbon HS-4; Norit NK; AG-3; Elorit HR catalysts (a [mA/cm²] — intercept with the abscissa).

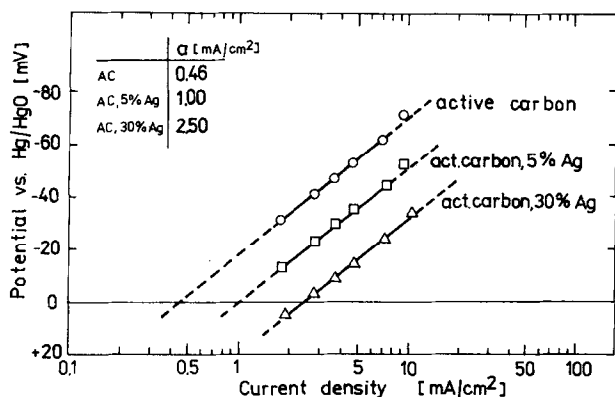


Fig. 3. Tafel portions of polarization curves of air electrodes with active carbon; active carbon + 5% Ag; active carbon + 30% Ag catalysts (a [mA/cm²] — intercepts with the abscissa).

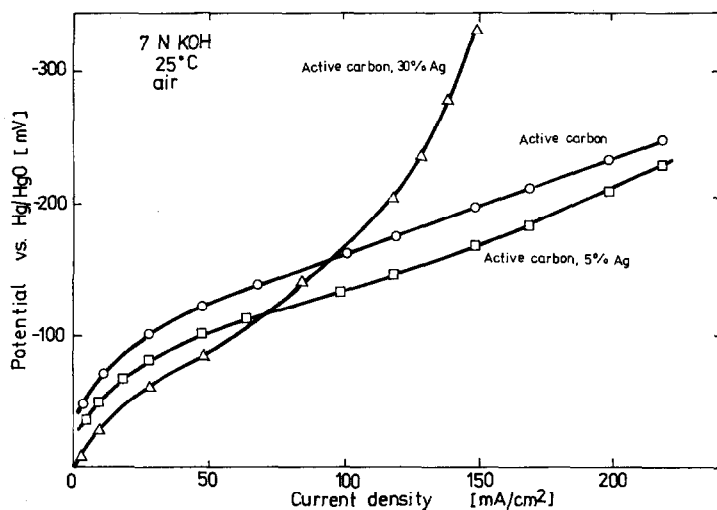


Fig. 4. Polarization curves of air electrodes with the same catalysts as in Fig. 3.

Nevertheless, a comparison of the current-voltage characteristics of the same electrodes (Fig. 4) shows that the performance of the most active electrode in the high current density range is drastically reduced. Apparently the increase in the silver content of the catalyst influences not only its activity but also its porous structure. At very high silver contents the porous structure of the catalyst becomes unfavourable for transport [14].

In general, the problem of transport hindrances in wet-proofed gas-diffusion electrodes is of prime importance for their practical application.

An experimental method has been proposed [15] for the estimation of the transport hindrances in air gas-diffusion electrodes.

In order to assess the influence of the transport hindrances on the electrode performance it is convenient to introduce an efficiency factor, f , for the electrode [16] defined by the ratio:

$$f = \frac{I(E)}{I^{\text{id}}(E)} \quad (4)$$

of the current density of the real electrode $I(E)$ and the current density of the corresponding ideal electrode $I^{\text{id}}(E)$ at an identical potential E . The ideal electrode corresponding to a particular real electrode has the same overall structure and catalytic activity, but the transport processes in it are not hindered. This means that the rates of all transport processes in the ideal electrode are infinitely high. The activation hindrances are the same both in the real and in the corresponding ideal electrode.

The value of the efficiency factor, f , of the electrode is equal to, or smaller than, unity. Its value depends on the current, I , on the porous structure of the electrode, on the type of the electrolyte, etc. Its value depends also on the partial pressure of oxygen, P_0 . The value of the efficiency factor

f will be different for the same electrode when operating at different partial pressures of the reactant.

The efficiency factor of a particular electrode operating with air and with pure oxygen can be compared easily at the same current density:

$$I = I(E_{\text{air}}) = I(E_{\text{O}_2}) \quad (5)$$

Apparently under these conditions the potential of the electrode when operating with air (E_{air}) and with pure oxygen (E_{O_2}) will be different:

$$E_{\text{air}}(I) \neq E_{\text{O}_2}(I) \quad (6)$$

From expression (5) and from the definition of the efficiency factor of the electrode, eqn. (4), the following equation can be obtained:

$$I_{\text{air}}^{\text{id}}(E_{\text{air}})f_{\text{air}} = I_{\text{O}_2}^{\text{id}}(E_{\text{O}_2})f_{\text{O}_2} \quad (7)$$

For cases where the current density of the ideal electrode can be described by eqn. (1), the following expression for the difference between the potentials of the electrode when operating with air and with pure oxygen at the same current density can be obtained:

$$\Delta E = E_{\text{O}_2}(I) - E_{\text{air}}(I) = \frac{RT}{\alpha z F} \ln \frac{P_{\text{O}_2}}{P_{\text{air}}} + \frac{RT}{\alpha z F} \ln \frac{f_{\text{O}_2}(I)}{f_{\text{air}}(I)} \quad (8)$$

At sufficiently low current densities the transport hindrances are slight, so that the efficiency factors of the electrode, both when operating with air and with pure oxygen, tend to unity. In this case the value of ΔE_0 will be given by:

$$\Delta E_0 = \frac{RT}{\alpha z F} \ln \frac{P_{\text{O}_2}}{P_{\text{air}}} \quad (9)$$

which should be independent of the current density.

With increase in the current density, both the efficiency factors of the electrode operating with air and with pure oxygen will decrease. The efficiency factor of the electrode operating with air will decrease more rapidly with increase in the current density than the efficiency factor of the same electrode operating with pure oxygen. It follows from eqn. (8) that with increase in the current density the value of ΔE will increase.

Figure 5 presents the current-voltage characteristics of an electrode with active carbon catalyst operating in 7N KOH with air and with pure oxygen. By subtracting the potential from the two curves at the same current density the values of ΔE are easily obtained. The values of ΔE obtained, as a function of the current density, are presented in Fig. 6. It can be seen that the values of ΔE increase with current. At low current densities the values of ΔE are practically independent of current density. This is seen in Fig. 7 where the same curve is presented for current densities up to 10 mA/cm².

It should be noted that the ΔE values are free from the IR drop in the electrolyte between the air electrode and the reference electrode.

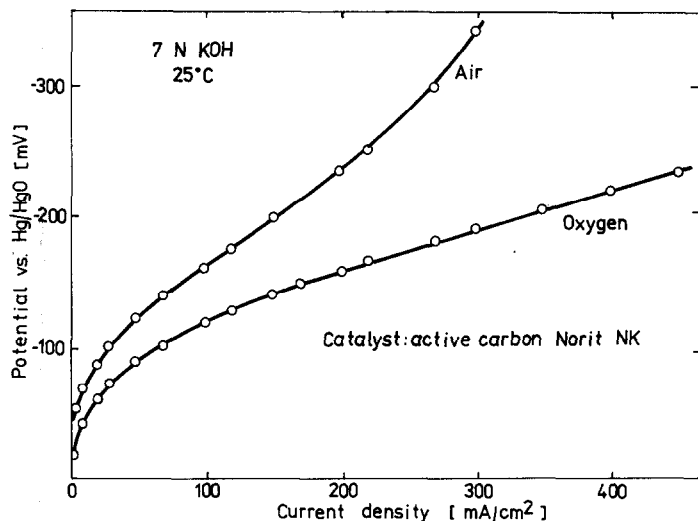


Fig. 5. Polarization curves of an electrode when operating with air and with pure oxygen.

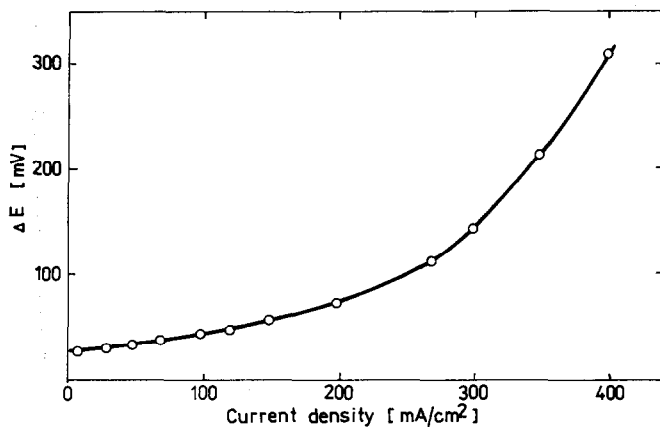


Fig. 6. ΔE - I curve obtained from Fig. 5 ($\Delta E = E_{O_2}(I) - E_{air}(I)$).

Experimental ΔE - I curves can be used for comparison of gas-diffusion electrodes in relation to the transport hindrances. In order to illustrate this possibility, Fig. 8 shows ΔE - I curves for air electrodes with identical catalytic layers and with gas-supply layers differing only in their thickness [17]. Apparently, the increase in the thickness of the gas-supply layer will result in an increase in the hindrances in the transport of the molecular oxygen through this layer. As would be expected, the ΔE - I curves of the electrodes with thicker gas-supply layers increase more rapidly with increase in current density.

The estimation of the transport hindrances in air electrodes using ΔE - I curves can be performed in two ways: by comparison of the shape of the

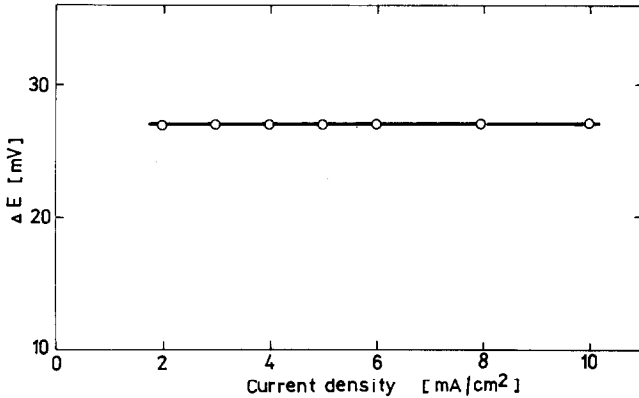


Fig. 7. ΔE - I curve obtained from Fig. 5 at current densities up to 10 mA/cm^2 .

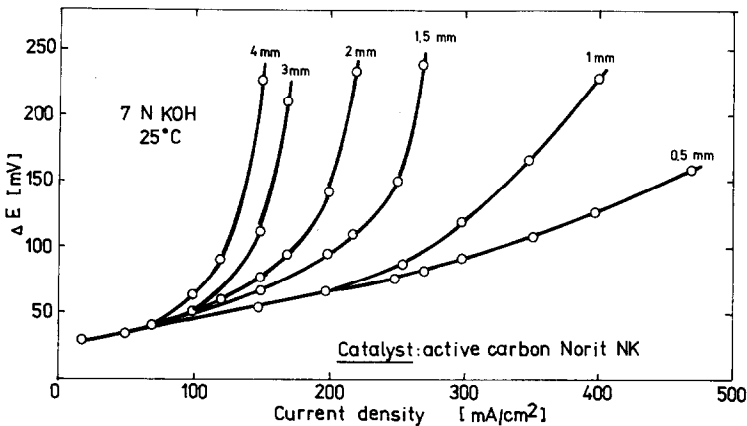


Fig. 8. ΔE - I curves of electrodes with identical catalytic layers and gas-supply layers of thickness 0.5; 1.0; 1.5; 2.0; 3.0; 4.0 mm.

corresponding ΔE - I curves, or by comparison of the values of ΔE at a constant current density. This constant current density should be sufficiently high, in the range where the transport hindrances are pronounced.

The comparative method can be used for the investigation of different porous materials for gas-diffusion electrodes. For example, Fig. 9 presents ΔE - I curves for electrodes with identical catalytic layers. The gas-supply layers of these electrodes have a thickness of about 1 mm and are prepared from different porous materials: from a porous Teflon sheet and from a special hydrophobic material [6]. Apparently, the difference in the shape of the ΔE - I curves of these electrodes is due entirely to differences in the type of gas-supply layers. It is seen that hindrances to the transport of oxygen through the gas-supply layer made from porous Teflon sheet are much more pronounced.

The method described also offers the possibility of obtaining information about the transport hindrances in porous catalysts.

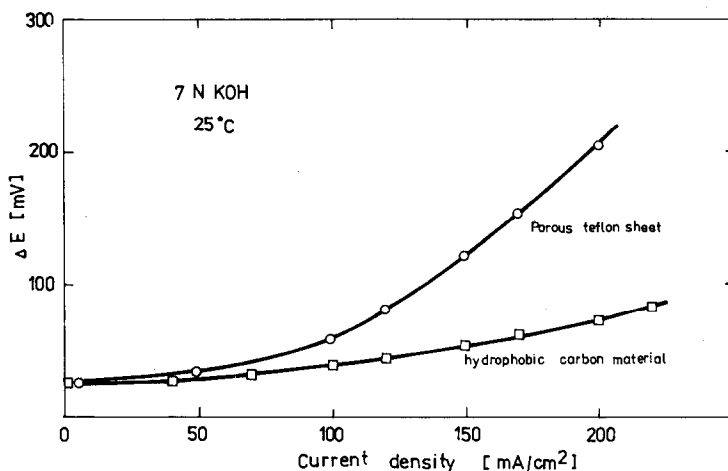


Fig. 9. ΔE - I curves of electrodes with identical catalytic layers and gas-supply layers prepared from a porous hydrophobic carbon material and from a porous Teflon sheet.

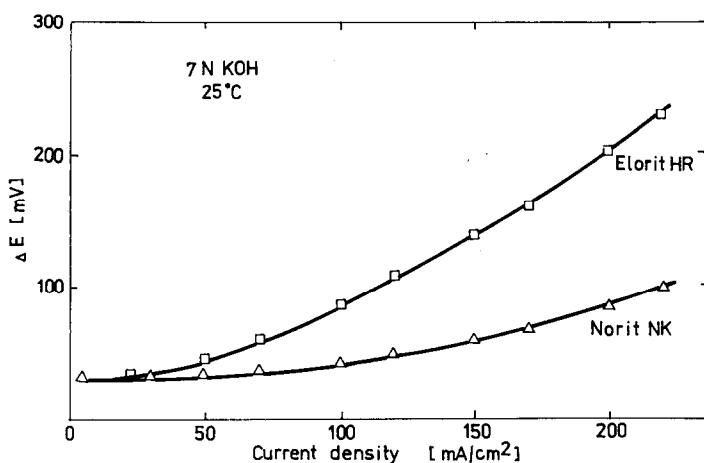


Fig. 10. ΔE - I curves of electrodes with identical gas-supply layers and with active carbon Elorit HR and active carbon Norit NK catalysts.

The construction and the method of preparation of the described electrodes allow different porous catalysts to be introduced into them without any changes in their hydrophobic matrix [18]. If the ΔE - I curves of such electrodes differ, this can only be attributed to differences in the porous nature of the catalyst. In this way various porous catalysts can be compared with regard to the transport hindrances in their porous structure. Such a comparison is very useful for the selection of porous catalysts for air electrodes.

Figure 10 shows, as an example, the ΔE - I curves for air electrodes with two types of active carbon catalysts — Elorit HR and Norit NK [19]. It can

be seen that the transport hindrances in the electrode with Elorit HR are much more pronounced than those in the electrode with Norit NK. From Fig. 2 it is seen that the activity of the electrode with the Elorit HR carbon is higher than that of the electrode with Norit NK. It can be concluded that for operation at low current densities (up to 10 mA/cm^2) the more active Elorit HR carbon is to be preferred, but for operation at high current densities (above 20 mA/cm^2), where the influence of the transport hindrances is considerable, the Norit NK carbon is more suitable.

The proposed method can also be used in the assessment of some promoted catalysts. Active carbon promoted with silver is often used as a catalyst in air gas-diffusion electrodes [13, 20 - 22]. It has been shown (Fig. 3) that the increase in the amount of silver in such catalysts results in an increase in their activity, but as is seen in Fig. 11, the introduction of a large amount of silver in the active carbon results in a drastic increase in the transport hindrances of air electrodes.

The method described for estimating the transport hindrances in air electrodes allows the optimal silver content in such catalysts to be determined. Figure 12 presents the ΔE values of air electrodes at a constant current density of 200 mA/cm^2 as a function of the amount of silver in the catalyst. It is seen that the introduction of more than 10% of silver to the active carbon results in a significant increase in the transport hindrances of the air electrodes. It can be concluded that the amount of silver introduced into the porous structure of the active carbon should not exceed 10%. Catalysts from active carbon promoted with a larger amount of silver are suitable only for air electrodes operating at low current densities.

The comparative methods described for the estimation of the activity and the transport hindrances in the air electrodes were used in an investigation of some new types of catalysts.

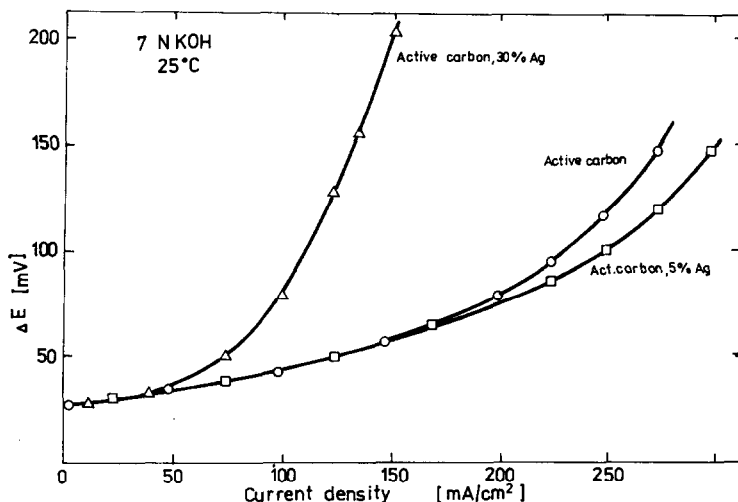


Fig. 11. ΔE - I curves of electrodes as in Figs. 3 and 4.

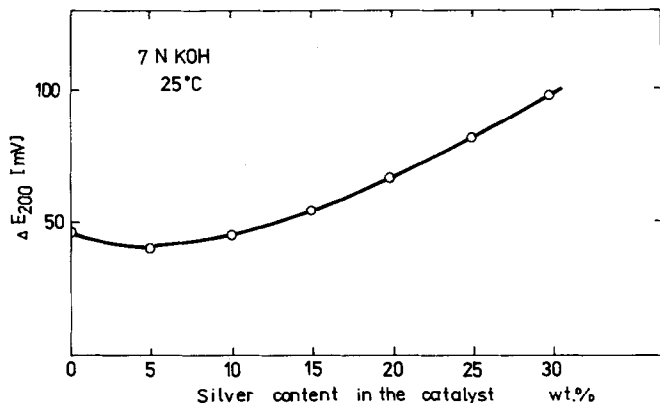


Fig. 12. ΔE_{200} as a function of silver content in the catalyst (ΔE_{200} = the value of ΔE at a current density of 200 mA/cm²).

This is illustrated for catalysts, prepared by heat treatment at elevated temperatures, of active carbon impregnated with the organic chelate cobalt tetramethoxyphenylporphyrin (CoTMPP). This type of catalyst ensures very high electrochemical performance of the air gas-diffusion electrodes and an improved stability in their long-time performance [23 - 29].

It was found by X-ray diffraction [30] that by heat treatment at sufficiently high temperatures, the chelate compound CoTMPP decomposes, the pyrolytic products being metallic β -cobalt and some graphite-like residues of the porphyrin ring. During heat treatment of the CoTMPP impregnated active carbon these pyrolytic products are formed in the porous structure of the active carbon. By using the comparative methods described the influence of each of the two types of pyrolytic product of the CoTMPP chelate compound on the activity and on the transport properties of the catalyst can be studied.

Catalysts were prepared by impregnating separate batches of P-33 active carbon with a solution of cobalt acetate, with a solution of metal-free tetramethoxyphenylporphyrin (H₂TMPP), and with a solution of the CoTMPP compound [31]. After removing the solvent, the impregnated carbons were heated for 5 h in an argon gas flow at 830 °C. The amounts of the Co acetate and of the H₂TMPP were selected so as to ensure that the content of cobalt and of H₂TMPP corresponded to the quantities of the same components in the catalyst prepared with the CoTMPP compound.

Figure 13 presents, on a semilogarithmic scale, the current-voltage characteristics of air electrodes with the above mentioned catalysts, over the low current density range. The electrodes differ only in the type of catalyst used. The same Figure also presents the curve for an electrode with heat treated active carbon catalyst under the same conditions. It is seen that the activity of the electrode with catalyst based on CoTMPP is substantially higher than that of the electrode with pure, active carbon. The electrode with metal-free H₂TMPP has the same high activity as the electrode with

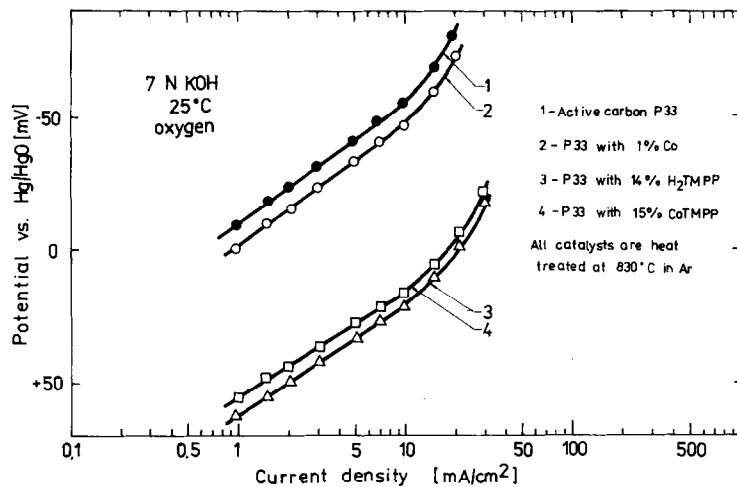


Fig. 13. Polarization curves of oxygen electrodes with different heat-treated catalysts: 1, active carbon P-33; 2, P-33 + 1% Co; 3, P-33 + 14% H₂TMPP; 4, P-33 + 15% CoTMPP.

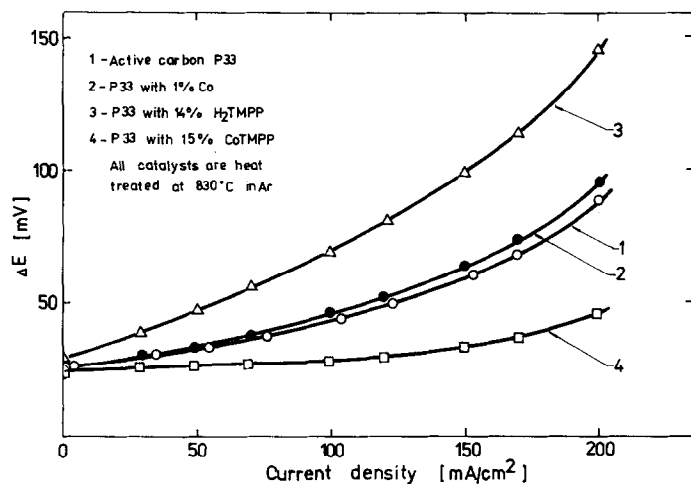


Fig. 14. ΔE - I curves of the electrodes as in Fig. 13.

CoTMPP. Apparently, the presence of the decomposition products of the porphyrin ring determines the enhanced activity of these catalysts. The introduction of cobalt alone does not influence the activity of the carbon.

Figure 14 presents the ΔE - I curves of the same electrodes. It is seen that the transport hindrances in the electrode with CoTMPP are significantly lower than those in the three other electrodes, and the electrode with metal-free H₂TMPP shows the highest transport hindrances. This is also seen in Fig. 15, where the current-voltage characteristics of air electrodes with both metal-free H₂TMPP and CoTMPP are presented.

It was suggested that the decreased transport hindrances in the catalyst with CoTMPP were connected with the presence of cobalt. In order to confirm this hypothesis, the heat-treated catalyst prepared with metal-free H_2TMPP was subsequently impregnated with Co acetate and once more heat treated at $830^\circ C$ under argon. The electrode with this catalyst shows (Fig. 15) a polarization curve identical with that of the electrode with a catalyst based on the compound CoTMPP. It can be concluded that the presence of cobalt influences the porous structure of the catalyst.

Similarly, catalysts with identical amounts of metal-free H_2TMPP and various cobalt contents were prepared, and the $\Delta E-I$ curves of air electrodes with these catalysts were investigated. Figure 16 shows the ΔE values of these electrodes at a current density of 200 mA/cm^2 as a function of cobalt content. It is seen that the presence of small amounts of cobalt (up to 5%) results in a significant decrease in the transport hindrances of the electrodes, followed by their slow, gradual increase at higher cobalt contents. The activity of these electrodes is quite independent of the amount of cobalt in the catalyst. This experiment shows that the presence of cobalt in the catalysts investigated exerts a beneficial effect upon their porous structure.

The described comparative methods for the estimation of the activity and the transport hindrances were also successfully used in the investigation of the long-term performance of air gas-diffusion electrodes [32 - 34]. These methods can be applied for optimization of air gas-diffusion electrode catalysts [35].

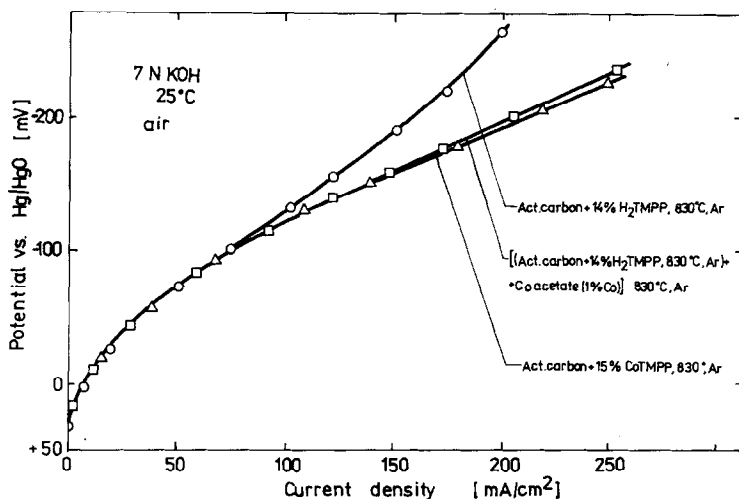


Fig. 15. Polarization curves of air electrodes with catalysts: active carbon + 14% H_2TMPP , heated at $830^\circ C$ in argon; active carbon + 15% CoTMPP, heated at $830^\circ C$ in argon; (active carbon + 14% H_2TMPP , heated at $830^\circ C$ in argon), impregnated with Co acetate (1% Co) and reheated at $830^\circ C$ in argon.

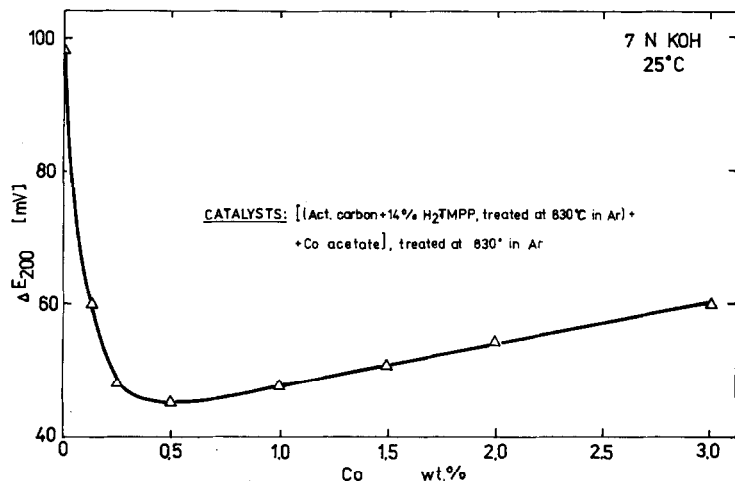


Fig. 16. ΔE_{200} values as a function of cobalt content in heat treated catalysts from active carbon + 14% H₂TMPP + Co.

Conclusions

Comparative methods are proposed for the estimation of the activity and transport hindrances in air gas-diffusion electrodes.

It is shown experimentally that these methods can be successfully used in an investigation of air electrodes in alkaline solutions.

The proposed comparative methods allow the total structure of the air electrodes and the structure of their gas-supply layer to be optimized in relation to the transport hindrances in the electrodes. The study of the activity and the transport hindrances in various porous catalysts allows the optimal catalyst to be chosen for air electrodes suitable for a particular application.

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