

ANODIC OXIDATION OF ETHYLENE GLYCOL WITH NOBLE METAL ALLOY CATALYSTS*

H. KOHLMÜLLER

Siemens Research Laboratories, Erlangen (F.R.G.)

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Summary

Potentiodynamic investigations have shown that the intermetallic compound Pt_3Pb exhibited an activity approximately ten times higher than pure platinum in the anodic oxidation of ethylene glycol to oxalic acid.

The results obtained with smooth electrodes have been confirmed with noble metal coated nickel screen-electrodes which are suitable for application in fuel cells.

Introduction

Ethylene glycol is of particular importance as an energy carrier for fuel cells because of its high energy densities, ease of transport, favourable storage, low vapour pressure, non-toxic nature and ready availability.

The catalytic activity for the conversion of methanol on the active surfaces of noble metals on which lead has been deposited has been reported previously [1, 2]. Further work has been carried out to determine the catalytic activity of platinum-lead alloys for the oxidation of ethylene glycol.

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Experimental

Runey-platinum

For the conversion of alcohols in fuel cells, noble metal catalysts have proved to be particularly useful. On the basis of this experience the behav-

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four of such catalysts and the intermetallic compounds of platinum and lead was investigated for the anodic oxidation of glycol.

Platinum-lead

Among the various intermetallic compounds known in this system, the compound with the highest platinum content, Pt₃Pb, containing about 25% of lead is of particular interest.

This substance is formed by melting the elements and also by electrolysis from aqueous acidic solutions.

The corrosion behaviour of different platinum-lead alloys was investigated by potential-sweep measurements. The result is shown in Fig. 1.

A peak attributed to the oxidation of the intermetallic compound Pt₃Pb is observed at a potential of -300 mV. Only at a lead concentration above the stoichiometric composition of Pt₃Pb is the appearance of a further peak observed at a potential of -600 mV. This peak shows the oxidation of lead.

Potentiodynamic measurements in the investigation of platinum catalysts

The surface of the catalysts can vary considerably. In order to make comparative measurements, the catalysts should have uniform surfaces. Investigations with polished surfaces are especially suitable. For this purpose, the sample which is mostly available as regulus is contacted, embedded in epoxy resin and ground or polished.

The potential sweep method has proved to be particularly useful for screening and for obtaining a first insight into the behaviour of the catalyst. In the potential sweep diagram (Fig. 2) the conversion of ethylene glycol appears at B and during the potential reverse sweep at F.

High conversion rates of glycol were attained only in the transition range between hydrogen and oxygen coverage of the electrode.

Similar results to those shown in Fig. 2 were obtained with platinum-lead alloys, only the peak heights were different. The hydrogen peaks were barely visible and were extremely small by comparison with the glycol peaks.

Results and Discussion

Determination of the activity and the order of reaction

At constant scan rate and a reaction order of 1 a linear relation between the peak height and the concentration may be expected.

$$i_p = \text{const} \cdot c^b$$

$$\log i_p = a + b \cdot \log c$$

$$b = \frac{d(\log i_p)}{d(\log c)}$$

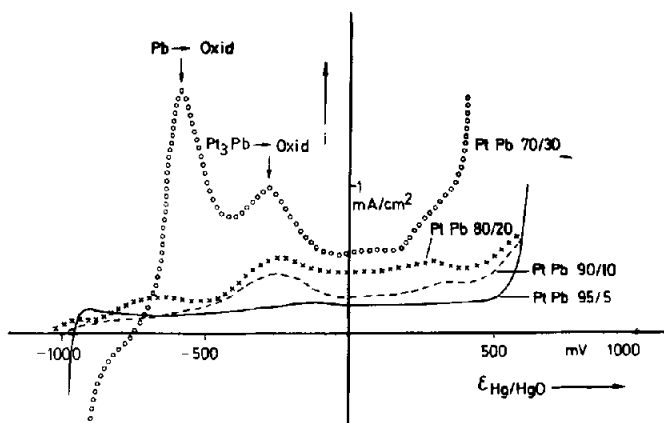


Fig. 1. Current-voltage curves showing the corrosion of platinum-lead alloys; electrolyte: 6 M KOH, 50 °C; scan rate: 0.01 V/s.

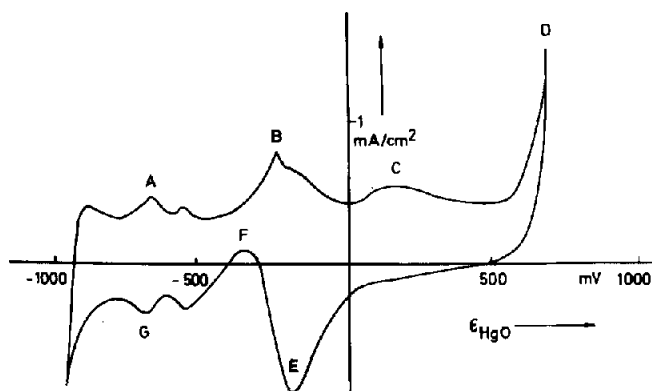


Fig. 2. Current-voltage curve showing the anodic oxidation of ethylene glycol on platinum; electrolyte: 6 M KOH, 50 °C; scan rate: 0.1 V/s.

- | | |
|----------------------------------|----------------------------------|
| A Oxidation of adsorbed hydrogen | D Oxygen evolution |
| B Oxidation of glycol | E Reduction of oxygen layer |
| C Surface coverage with oxygen | F Oxidation of glycol |
| | G Surface coverage with hydrogen |

The quantity a is a measure of the activity of the catalyst.

Also with reaction orders which deviate from 1, straight lines are obtained by log-log plotting of peak current and concentration. The reaction order b can be evaluated from the slope of these straight lines.

Activity of Raney-platinum alloys

The presentation of peak height with respect to concentration allows the different activities of various electrodes to be recognized (Fig. 3).

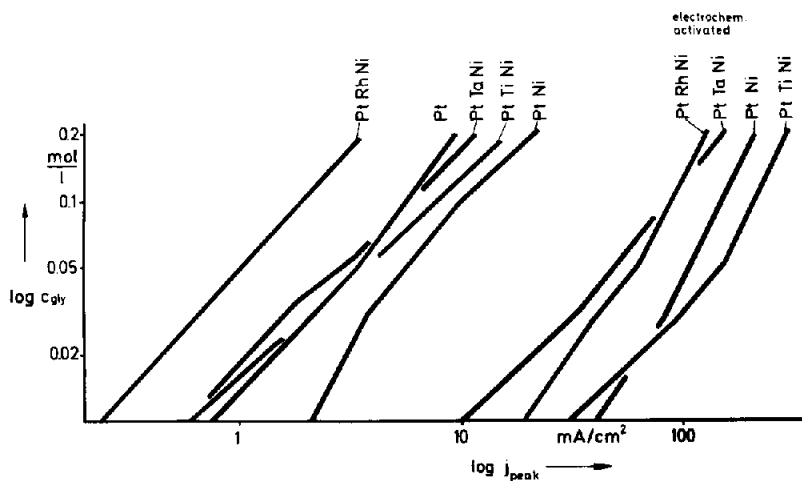


Fig. 3. Peak height in dependence on concentration in the Raney-Pt series; electrolyte: 6 M KOH, 50 °C, scan rate: 0.01 V/s.

Smooth electrodes of the alloys do not differ substantially from pure platinum. Electrochemical extraction of the non-noble alloy component (Ni) in sulphuric acid by anodic charging leads to a more than tenfold increase in the activity. This increase is attributed to enlargement of the surface area caused by the extraction of nickel.

Activity of platinum-lead alloys

Pt-Pb alloys belong to the second group of noble metal catalysts which we have investigated. Even in this case, preliminary attention was paid to the dependence of the glycol peak height on the concentration (Fig. 4). In this Fig. and Fig. 3 a correction has been made for the current carried by the supporting electrolyte.

The measure of the catalyst activity α shows that with low additions of lead a very strong change in activity occurs. A further increment up to 30% brings about only modest changes. A change in the slope of the lines can be observed. A relation between activity and reaction order is to be expected. At catalysts having a low activity, the conversion of ethylene glycol proceeds with an apparent reaction order lower than one (Fig. 5). This phenomenon can be explained by the assumption that with catalysts of low activity the coverage is roughly one and is only little influenced by the glycol concentration. The current densities with active catalysts become so high that the coverage deviates from one. The coverage obeys Henry-Dalton's adsorption law. Therefore, a reaction order of one is to be expected.

Determination of the apparent energy of activation

The activation energy for glycol conversion was determined at some representative platinum-lead alloys (Fig. 6).

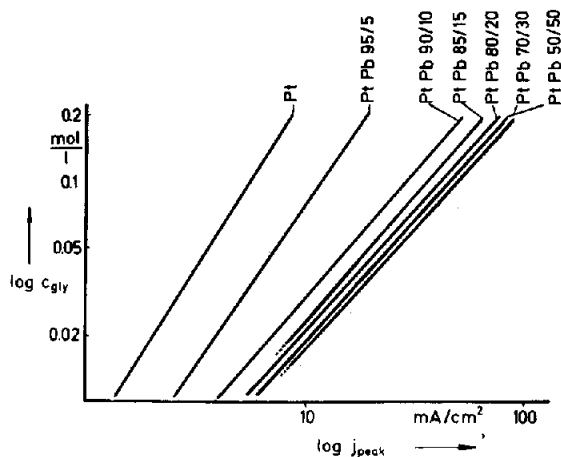


Fig. 4. Peak height in dependence on concentration in the Pt-Pb series; electrolyte: 6 M KOH, 50 °C; scan rate: 0.01 V/s.

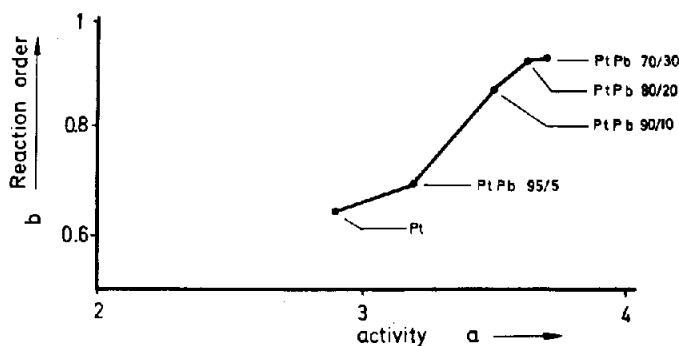


Fig. 5. Reaction order in dependence on activity; electrolyte: 6 M KOH, 0.1 M glycol, 50 °C.

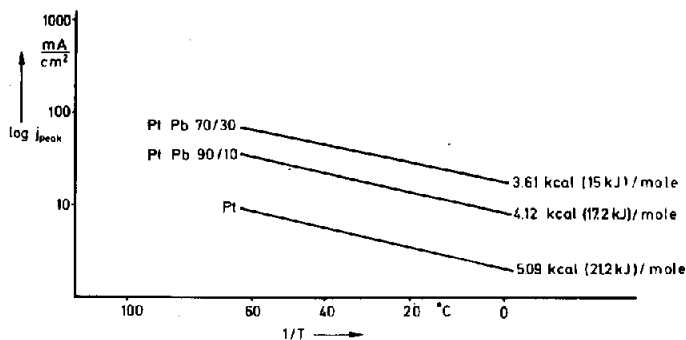


Fig. 6. Peak height in dependence on temperature; electrolyte: 6 M KOH, 0.1 M glycol; scan rate: 0.01 V/s.

A relation can also be established by comparing the activity and the activation energy (Fig. 7). The more active catalysts have a greater value for α . They exhibit a lower activation energy for glycol conversion than the less active ones.

Determination of the current function

A picture of the reaction mechanism can also be gained from the relation between peak height and scan rate. In the case of pure diffusion limiting the peak height is dependent on the expansion of the diffusion layer. Using Fick's second law and the expansion time of the diffusion layer which is dependent on the scan rate, the following equation can be formulated [3]:

$$\psi = \frac{i_p}{n \cdot F \cdot D^{1/2} \cdot (v \cdot n \cdot F / RT)^{1/2} \cdot c}$$

The value of the current function and its dependence on the scan rate allow the different reaction mechanism to be distinguished.

With pure platinum and the essentially more active platinum-lead alloy catalysts the dependence of the current function on the scan rate indicates an advanced chemical reaction (Figs. 8 and 9).

The reaction products of the ethylene glycol oxidation were precipitated by cooling the electrolyte. X-ray analysis shows only oxalic acid monohydrate in this precipitate. Considering the chemical nature of ethylene glycol there are two hydroxyl groups which can be alternately or successively oxidized to carboxylic acid via the aldehyde stage. Accordingly, two different reaction paths might result.

The catalytic activity of the various catalysts can be summarized at this point as follows: with Raney-platinum and ternary Raney-platinum alloys the increase in activity can only be attributed to an enlargement of specific surface area; with platinum-lead more than a tenfold increment in activity is attainable in comparison with pure platinum. This improvement of activity is to be attributed to the intermetallic compound Pt_3Pb .

Platinum-lead catalysts in fuel cell electrodes

The positive results that we obtained with smooth electrodes are confirmed in fuel cells. The construction of a fuel cell employing noble metal coated screens as an anode and a supported electrode as cathode is illustrated in Fig. 10 [4].

Ni-screens are especially suitable as catalyst supports for fuel cell electrodes. Platinum-lead compounds can be readily deposited in these supports. Such screens which are used as fuel cell electrodes, confirm the results obtained with smooth electrodes. Current densities in the range of 50 mA/cm² are achieved at a reasonable overpotential (Fig. 11).

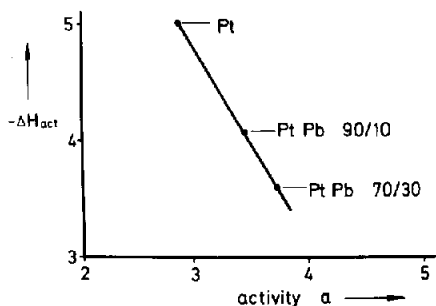


Fig. 7. Activation energy in dependence on activity; electrolyte: 6 M KOH, 0.1 M glycol, 50 °C.

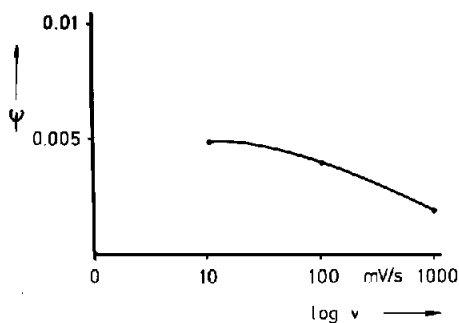


Fig. 8. Current function in dependence on scan rate on Pt; electrolyte: 6 M KOH, 0.1 M glycol, 50 °C.

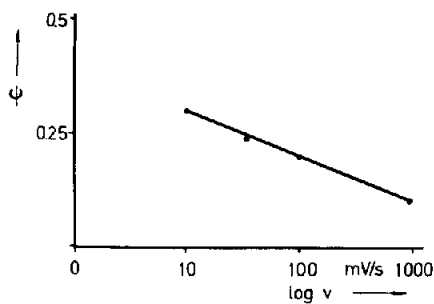


Fig. 9. Current function in dependence on scan rate on Pt-Pb 90/10; electrolyte: 6 M KOH, 0.1 M glycol, 50 °C.

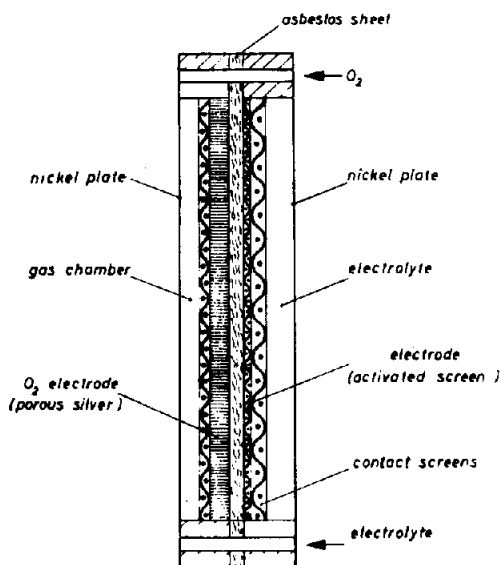


Fig. 10. Cross-section of a fuel cell working with dissolved fuel.

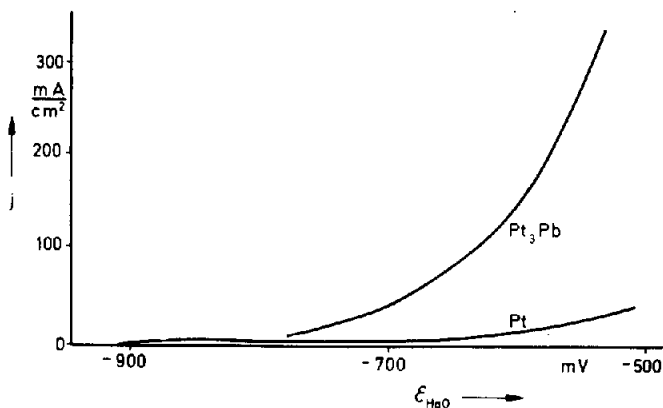


Fig. 11. Current-voltage curves showing the different activities of pure platinum and platinum-lead compound as fuel cell electrodes; electrolyte: 6 M KOH, 2 M glycol, 60 °C. Electrodes: Pt (black) on Ni screen; 5 mg/cm², Pt₃Pb (black) on Ni screen; 5 mg/cm².

Acknowledgement

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