SYMPOSIUM ON FUEL CELLS
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY
AMERICAN CHEMICAL SOCIETY
CHICAGO MEETING, September 3-8, 1961

DSK - ELECTRODES FOR THE CATHODIC REDUCTION OF OXYGEN

By

Heiner M. Dittmann, Edward W. Justi and August W. Winsel
Institute of Technical Physics
Braunschweig Institute of Technology, Braunschweig, Germany

1. INTRODUCTION

At the Spring Meeting of the Electrochemical Society in Indianapolis this year, Justi and Winsel (1) reported on their DSK-system (2) and its application to fuel cell technology. Previously, (in the monograph "High-drain hydrogen-diffusion-electrodes operating at ambient temperature and low pressure") Justi, Pilkuhn, Scheibe, and Winsel (3) had described in detail the method employed in preparing the DSK-hydrogen electrode, using nickel as the basic material, as well as its electro-chemical properties. To complete the picture of these fuel cells, this paper will deal with the DSK-oxygen-electrode. We trust that we may be allowed to present only a brief description of how DSK-electrodes are made, confining ourselves to the specific properties of the oxygen-electrodes.

2. THE METHOD BY WHICH THE DSK-OXYGEN-ELECTRODE IS PREPARED

It is characteristic of the DSK-electrode that it contains a Raney catalyst in an electronic conducting supporting matrix. (4) To make a DSK-electrode, the powered Raney alloy is mixed with the supporting matrix powder, the resulting mixture formed into an electrode under pressure and then sintered. The non-noble components of the Raney alloy (Al, Zn, Si) are then leached out while the Raney metal is retained in the pores of the electrode as a highly effective catalyst. Instead of first pressing the electrode and then sintering it, the hot-pressing technique permits preparation in one process. (5) The DSK-oxygen-electrode contains Raney silver as the catalyst. For many years it has been known that silver possesses good properties as an oxygen-carrier and as a decomposition catalyst for H_2O_2. (6, 7)

These same properties are reinforced in the Raney silver owing to its larger specific surface area. (8) The Raney silver is formed in the pores of a supporting matrix which 1) possesses good sintering properties, 2) has good electrical conductivity, and 3) is not attacked by the activating solvent and the fuel cell electrolyte at the oxygen potential. These conditions reduce considerably the number of substances which can be considered. We should like to mention that the noble metals, including silver, are too expensive to be used in great amounts. However, nickel and nickel alloys, which passivate in alkaline solution, and finally carbon can be employed. At first we used a silver supporting matrix and later a nickel one. The many difficulties which arose in the development of oxygen-electrodes described here have been eliminated largely by K.-H. Friese (9) in our laboratories. They originated for the most part in the Raney alloy.

2.1 The Raney Silver-Alloy

The first condition which must be fulfilled by a Raney alloy for use in DSK electrodes is its ready malleability. The Raney alloy should therefore be as brittle as possible. In the most often used Raney nickel alloys of the Ni/Al system this condition is ideally fulfilled; however, this is not the case for the Raney silver alloys in the Ag/Al systems. The latter alloys as normally produced are so thoroughly ductile that when placed under a press flattening into wide sheets rather than fracturing occurs. When placed in a ball mill thin plates result which are not at all suitable for sintering.

Friese, Justi and Winsel (4) managed to increase considerably the brittleness and also improve the electrochemical properties of the oxygen electrode by adding a small quantity of manganese (less than 0.3 weight percent). Later it turned out that this method was inferior when compared with a thermal treatment of controlled melting.

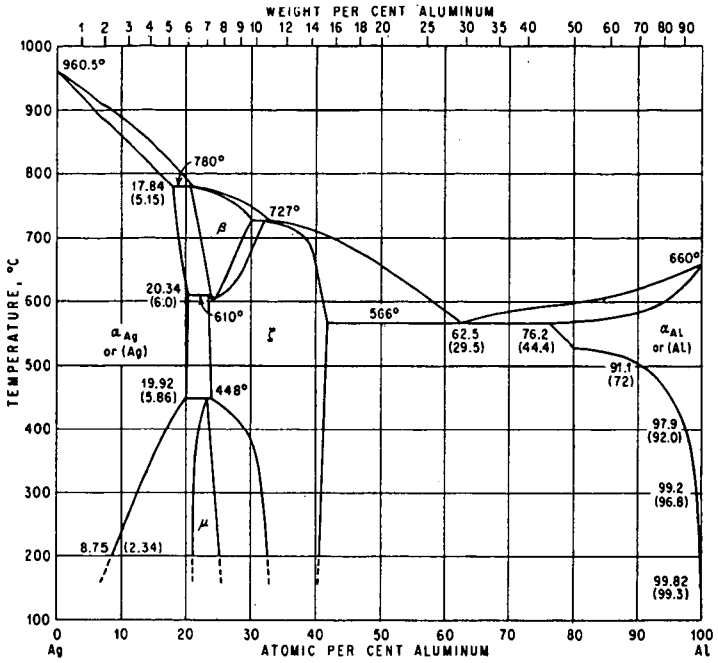

Fig. 1 - Phase Diagram of the Binary System Ag/Al.

Fig. 2 - DSK Oxygen electrode with plexiglas attachment, used for the present experiments. The pipe serves both as gas inlet and as conductive lead.

Under a calcium chloride protective melt 65% by weight of silver is melted with 35% by weight of aluminum in a carbon crucible. As can be seen in the Ag/Al phase diagram (Fig. 1) a solid melt appears as a crystalline mass from the ζ and α_{Az} phases slightly above the eutectic temperature of 566°C. (10). Both phases are attacked by potassium hydroxide, yielding chiefly the sought-after Raney silver from the ζ phase.

If one can produce a melt of this composition and quenches it from 800° to less than 100°C., a brittle regulus is obtained which shows strong texture formation at the fractured surfaces. According to Friese one can obtin a good malleable Raney alloy for DSK electrodes by means of this treatment.

The second condition which a Raney alloy must fulfill is the capacity to be formed into a stable electrode element when mixed with the supporting matrix powder. Our experience has taught us that this condition is not easily met. A supporting matrix made of nickel requires a sintering temperature of at least 600°C. However, at this temperature according to the phase diagram the liquid α_{Az} phase in the alloy 65% Ag, 35% Al is already present. This liquid phase reacts spontaneously with the nickel supporting matrix in KOH solution to yield the non-attackable intermetallic compound AlNi. The result is a very homogeneous product from which no Al can be dissolved, therefore permitting no Raney silver to be obtained. The product is therefore not suitable for oxygen electrodes. The only possible way to prepare DSK electrodes with Raney Ag as a catalyst on a supporting nickel matrix is the hot pressing method. (5) By the use of the latter it is possible to make use of the increased reactivity of metals in the plastic flow state. (11) Applying temperatures between 300 and 500°C. and pressures to one ton/cm^2 the individual powder grains are welded together. As a consequence of this treatment the composition of the grains in the interior regions does not change. Potassium hydroxide solution is then able to activate the electrode element which remains mechanically stable.

By means of this hot pressing technique we were able, with Dr. Friese's aid, to produce single layer electrodes which yielded current densitites over 500 ma/cm^2 below 100°C. - though at the cost of rather high gas losses. (8, 9)

2.2 Double Layer Electrodes

To avoid a situation whereby gas bubbles escape through large pores into the electrolyte without reacting we have prepared, as did Bacon (12) electrodes consisting of two layers. (13) The fine-pore protective layer is made from carbonyl nickel alone, or with the addition of a fine-grained Raney alloy which yields Raney silver upon activation. The large-pore operating layer is produced likewise from carbonyl nickel and Raney alloy powder. The porosity is influenced both by the particle size of the alloy and through the addition of KCl powder as filler. After hot pressing the filler is easily dissolved. (14)

In many cases electrodes were prepared in our laboratory with an additional gas conducting layer to increase the mechanical rigidity. This third layer contains no silver but consists of porous nickel.

All of the following electrochemical properties of our DSK oxygen electrodes are the results of experiments on multilayered electrodes which permitted no gas bubbles to escape unreacted into the electrolyte.

3. THE ELECTROCHEMICAL PROPERTIES OF AG-DSK-ELECTRODES USED FOR THE CATHODIC REDUCTION OF OXYGEN

3.1 The Experimental Procedure

Disk shaped electrodes about 2 mm thick and 40 mm in diameter were pressed into plexiglass, the borders made gastight, leaving a 10 cm^2 surface area to yield current, see Fig. 2. Nickel foil was employed chiefly as the counter electrode on which oxygen was envolved. The polarization was measured with the aid of a saturated calomel electrode employed as reference electrode. In addition the siphon of the electrode was fitted with a Luggin capillary for use as a potential measuring device and placed directly on the surface of the oxygen electrode. In this manner the resistance polarization is for the most part excluded, except for that which unavoidably originates within the pores. (3, 15) A D. C. voltage amplifier with a high threshold resistance (Knick-Berlin) was used to measure the potential while a milliampere meter of the 0.2 class recorded the current.

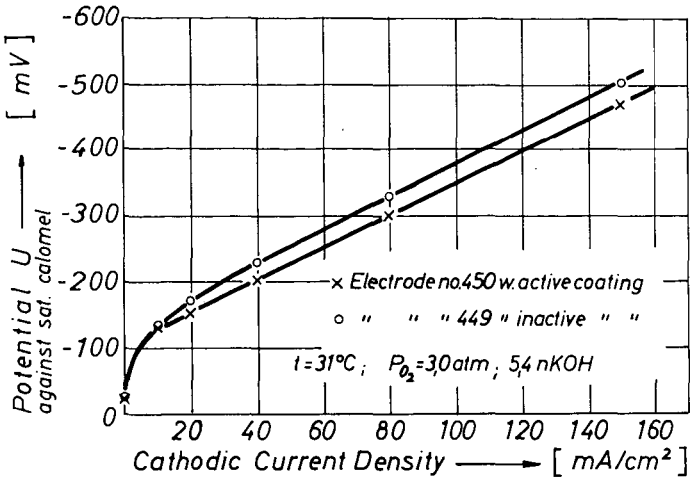

Fig. 3. Comparison between the performances of two electrodes, the upper having an active, the lower an inactive protecting layer. Electrolyte: 5.4 n KOH; temperature: 31°C; p=30 atm.

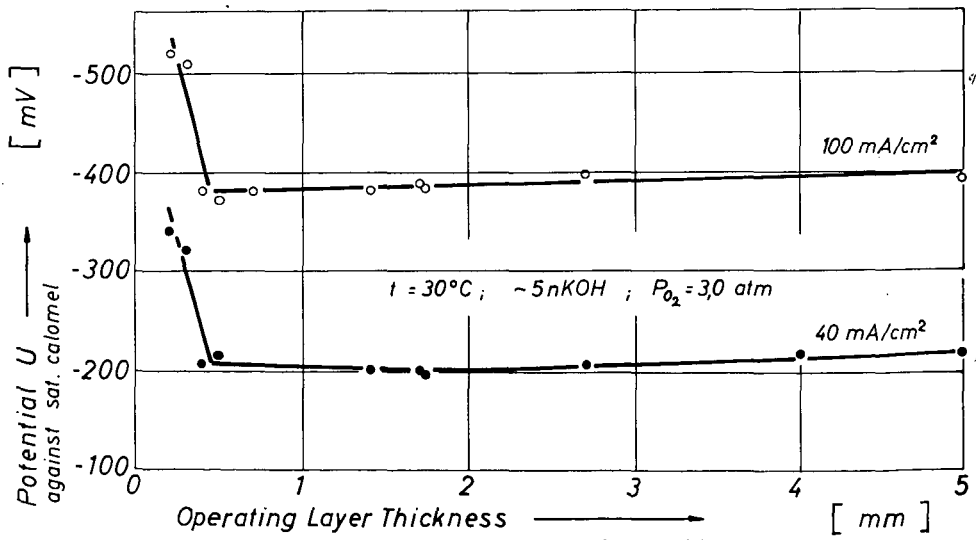

Fig. 4. Voltage of DSK oxygen double layer electrodes vs. thickness of operating layer. Parameter: operating current densities. Electrolyte: 5 n KOH; temperature: 30°C; p=3.0 atm.

3.2 The Influence of the Protective and Operating Layers

The significance of the individual layers during the cathodic reduction of oxygen was investigated in two series of measurements. In this manner we hoped to determine where the silver, as the active as well as most expensive electrode component, could be most suitably placed.

3.21 The Protective Layer

The significance of the protective layer during the polarization of an electrode is completely clear when it is limited to the voltage drop which occurs in the electrolyte located within the pores. However, it is not clear whether the protective layer itself also participates directly in the cathodic oxygen reaction. The latter might be expected if, or example, the diffusion of oxygen molecules into the electrolyte-filled protective layer was of a comparable order of magnitude to the current yielding ability of the electrodes. It might also have been the case if, within the scope of the Berl reaction, (16) hydrogen peroxide were formed which then diffused into the protective layer where it could be electrochemically reacted.

These questions are most simply resolved by employing similar electrodes, once with and once without Raney silver in the protective layer. In Fig. 3 the comparison is shown. The current density - polarization curves of electrodes with and without Raney silver in the protective layer differ only by a few hundredths of a volt. This difference can probably be ascribed to the somewhat increased broadening resistance in the inactive protective layer which is due to a lesser porosity. In no case, however, is there a characteristic co-functioning of the protective silver layer on the oxygen reduction.

3.22 The Operating Layer

In answer to the question how thick should one make the operating layer of the DSK-silver-electrode, we have plotted, in Fig. 4, the polarization as a function of operating layer thickness of otherwise similar electrodes for two different current densities. Here one sees that approximately 0.5 millimeter thick layers yield the largest effects with the smallest amount of material. Increasing layer thickness does not improve the electrode performance; however, thicknesses below 0.5 mm show a strong performance deterioration. One may then conclude that the reaction zone of the electrochemical oxygen reduction penetrates approximately 0.5 mm. into the working layer.

In Figure 5 the silver content of the working layer has been changed, the latter being limited due to demands of mechanical rigidity. As would be expected the electrode with the largest silver content reveals the least polarization at equal current densities in the pressure range of 1 to 4 atmospheres.

Considering these facts we have been able to reduce the amount of silver for optimal electrodes to 0.05 g/cm^2 electrode surface by using a gas conduction layer with increased mechanical rigidity. This amount is insignificant with respect to the price of the electrode.

3.3 The Influence of Operating Conditions

3.31 The Oxygen Pressure

The influence of oxygen pressure on the electrochemical properties of the oxygen electrode can be seen in Fig. 5. At a certain pressure at which the operating layer is pressed free, the electrode commences to function. At constant current density the polarization diminishes with increasing pressure. However, in the region of approximately 2 to 4 atmospheres it becomes almost pressure independent. A further increase in pressure causes the protective layer to be pressed free permitting the gas to escape unreacted into the electrolyte as fine bubbles.

3.32 The Electrolyte Concentration

On account of its nickel supporting matrix our DSK electrode functions only in alkaline solution. It has been tested at various concentrations of potassium hydroxide whose conductivity maximum lies at about six normal. In Figure 6 the cathodic current density for varying degrees of polarization is plotted as a function of the concentration of potassium hydroxide. Between three and four normal all curves show a maximum which is shifted to lower concentrations with increasing polarization. The resistance minimum of the electrode can be explained as follows:

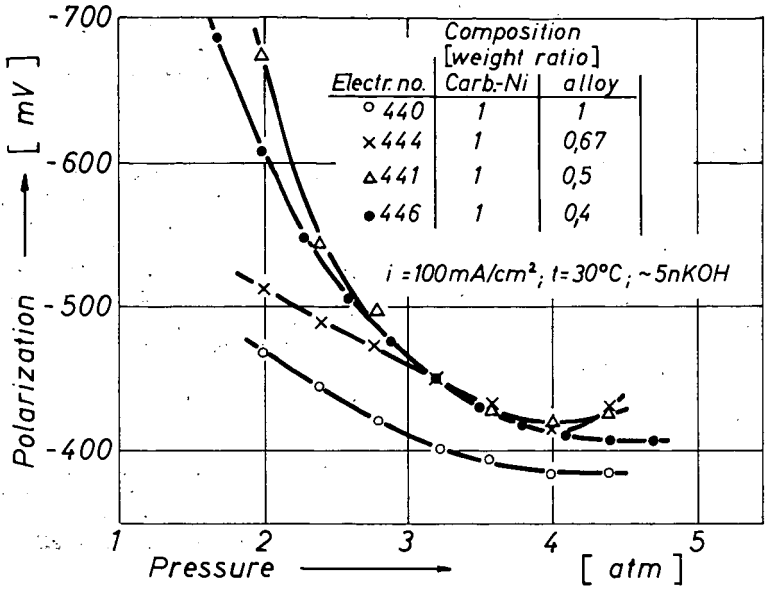

Fig. 5. Voltage of different DSK oxygen double layer electrodes against sat. calomel vs. operating oxygen pressure. Constant current density i = 100 ma/cm^2, electrolyte 5 n KOH; t=30°C.

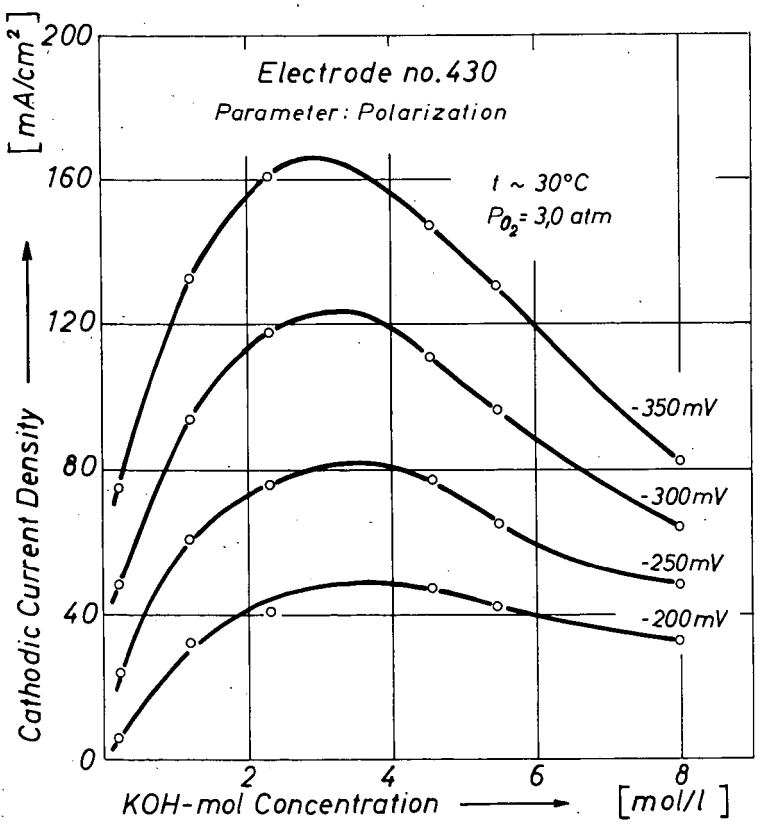

Fig. 6. Current density i vs. KOH concentration at t=30°C and p=3.0 atm. Parameter: polarization.

During cathodic current flow the KOH concentration increases within the pores as compared to that in the bulk electrolyte. The electrolyte resistance minimum is then reached when the alkali in the pores attains the optimal concentration. The greater the polarization is this will be the case the lower the concentration is.

3.4 The Stability of the Catalyst

In order to determine if Raney silver ages with time an oxygen electrode has been exposed to alternating loads since December 1959. Since March 23, 1960, it has been placed in an hydrogen-oxygen cell which operates during the day at 50 ma/cm^2 and overnight at 30 ma/cm^2. During this period (15 months) the electrode did not change. (17)

3.5 The Gas Efficiency

The current yield is, of course, important in judging the economic efficiency of an electrode. For example, if one admits one mole of oxygen to an oxygen electrode, then one can obtain maximally 4 x 96,500 Ampere-secs. as the electrical change. Deviations from this may be caused by gas bubbles which have escaped into the electrolyte electrochemically unreacted, by back diffusion of oxygen molecules into the electrolyte, and also by the fact that the electron yield of the electrochemical elementary process is not complete. If the reduction of the oxygen molecule is carried to H_2O four electrons per oxygen molecule are liberated. But if the reduction is carried only as far as H_2O_2 then only two electrons are released. (16) Between these ideal cases many intermediate values are conceivable. These occur as a result of the electron yield obtained by the catalytic or electrochemical decomposition of the H_2O_2 formed in the Berl reaction. (18)

The current yield of our DSK electrodes was determined by measuring at the electrodes the current flow of the flowing gas streams. The left diagram in Figure 7 shows the gas flow to the stationary loaded hydrogen electrode, the right diagram to the stationary loaded hydrogen electrode, the right diagram to the oxygen electrode. The drawn-in thick lines are calibration curves of the flowmeter which correspond to a complete gas utilization. The experimental points determined at three different temperatures confirm the almost 100 per cent electrochemical reaction of the admitted gases. (17)

In the right diagram the standard calibration plot for the Berl process is seen on the dashed curve. Apparently within the scope of our measuring accuracy the true electron yield of the single process is four. From this we should like to conclude that perhaps the H_2O_2 formed in accordance with the Berl mechanism occurs as a short-lived intermediate product.

4. CONCLUSION

This report has been presented as a review of the technology as well as the capacity of our DSK electrodes. It would not be complete if nothing were said about the future development. We believe that through further improvements, especially of the technology of the protective layers, the polarization characteristics of our electrodes may be improved. Allied with this our efforts are primarily concerned with the further technical development of hydrogen-oxygen cells and other fuel cells for carbon monoxide (3) and with liquid fuel-electrolyte (19) mixtures.

ACKNOWLEDGMENTS

The authors express their grateful appreciation to their sponsoring firms, the Ruhrchemie AG at Oberhausen and the Steinkohlen Elektrizitat AG at Essen for support of this work and publishing permit. The authors are also indebted to Dr. K.-H. Friese for many stimulating discussions and to Dr. Bernard R. Stein, ARO, Frankfurt, Germany, for the skillful translation.

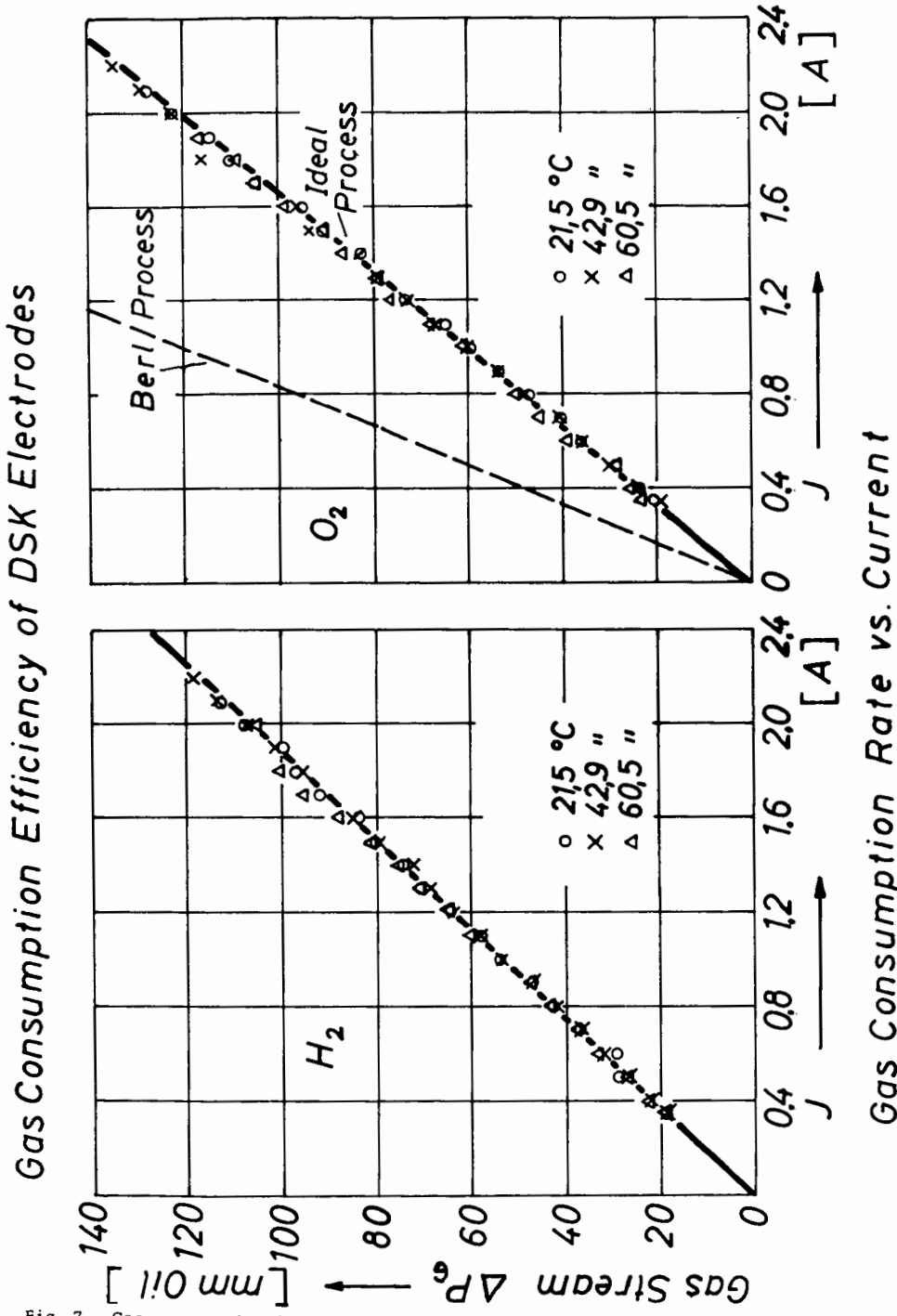

Fig. 7. Gas consumption (Faraday efficiency) of DSK double layer electrodes with hydrogen (left) and oxygen (right) vs. current. The thick lines are calibrating lines for the flow-meters, indicating complete electrochemical reaction of the gases according to $H_2 + \frac{1}{2}O_2 = H_2O$. The dotted line (right) applies to the Berl reaction $H_2 + O_2 = H_2O_2$.

LITERATURE CITED

(1) Justi, E., and Winsel, A., 119th Meeting of the Electrochemical Society, Indianapolis (1961); J. electrochem. Soc., to be published; Naturwiss. 47, 298 (1960).

(2) Winsel, A., Dissertation, Braunschweig, T. H., (1957), Justi, E., Scheibe, W., and Winsel, A., DBP 1 019 361 (1954); USA pat. 2 928 891; Brit. pat. 806 644; French pat. 1 132 762; Scheibe, W., Dissertation, Braunschweig, T. H. (1959).

(3) Justi, E., Pilkuhn, M., Scheibe, W., and Winsel, A., "High Drain Hydrogen-Diffusion-Electrodes Operating at Ambient Temperature and Low Pressure", Abh. d. Math. -Nat. Kl. d. Akad. d. Wiss. u. d. Lit. Mainz, No. 8, Komm. Verlag Steiner, Wiesbaden, 1959.

(4) Friese, K. -H., Justi, E., and Winsel, A., Austrian pat. 207 429 (1957).

(5) Friese, K. -H., Justi, E., and Winsel, A., Austrian pat. 205 089 (1958).

(6) Kordesch, K., and Marko, A., Osterr. Chem. Ztg. 52, 125 (1951).

(7) Witherspoon, R. R., Urbach, H., Yeager, E., and Hovorka, F., Tchn. Report No. 4, Navy Research (1954).

(8) Friese, K. -H., Diplomarbeit, Braunschweig, T. H. (1956).

(9) Friese, K. -H., Dissertation, Braunschweig, T. H. (1959).

(10) Hansen, M., "Constitution of Binary Alloys", McGraw-Hill Book Co., New York, 1958.

(11) Sully, A. H., "Metallic Creep and Creep Resistant Alloys", London, 1949.

(12) Bacon, F. T., Brit. pats. 667 298 (1952) and 725 661 (1955); USA pat. 2 716 670 (1955).

(13) Dittmann, H., Diplomarbeit, Braunschweig, T. H. (1961).

(14) Heuer, W., Diplomarbeit, Braunschweig, T. H. (1959).

(15) Winsel, A., Z. Elektrochem. To be published.

(16) Berl, W. G., Trans. Electrochem. Soc. 83, 253 (1943).

(17) Winsel, A., Z. Elektrochem. To be published.

(18) Vielstich, W., Z. physik. Chem. (N. F.) 15, 409 (1958).

(19) Justi, E., and Winsel, A., USA pat. 2 925 454; Brit. pat. 821 688; French pat. 1 148 012; DAS 1 071 175 (1955).