Cathodic Reduction of Nitrobenzene on the Packed-bed Copper Electrode

Shiro Yoshizawa, Zenichiro Takehara, Zempachi Ogumi, and Toshio Tsuji

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

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An application of a packed-bed copper electrode to the formation of aniline by the cathodic reduction of nitrobenzene was investigated. As the particles for the packed-bed, spherical particles of an anion exchange resin chemically plated with copper were successfully used. Though the current efficiency for the aniline formation on the packed-bed electrode in a batch cell decreased with continuing electrolysis, the efficiency was improved by the electrolysis under a flowing electrolyte and became very high, *i.e.*, near 100%. This is due to the removal of the accumulated products on the electrode surface by the flowing electrolyte. The effective depth of the bed electrode on which the nitrobenzene reacted cathodically was also determined from the measurement of the potential profile in a packed-bed electrode: the result was about 3 mm. This low value of the effective depth is ascribed to the low conductivity of the electrolyte and to the high electronic conductivity of the packed-bed. This may be improved by using bed particles of lower electronic conductivity and a higher cell capacity may be expected.

The electrochemical production of organic compounds at a high rate is generally difficult due to the low exchange current density of the electrode reaction and the disturbance of the electrode reaction by the accumulation of the reaction products on the electrode surface, in the case of the formation of low solubility products. Thus, an application of a packed-bed electrode, which is a three-dimensional electrode may be considered. By its operation under a flowing electrolyte the accumulation of the reaction products on the electrode surface may be avoided. Such a packed-bed electrode was applied to the cathodic reduction of nitrobenzene in acidic solution, which is an electrode process which has a well-known reaction mechanism,[1] and the probability of scaling up the cell capacity was examined.

Experimental

Electrolytic Cell. The anode compartment of the electrolytic cell (Fig. 1) was separated from the cathode one by a diaphragm of an ion exchange membrane. A platinum plate was utilized as the counter electrode (anode), and the working electrode (cathode) was made from a packed-bed. The diameter of the working surface was 25 mm and the distance between the diaphragm and the current feeder was 40 mm. A copper net was used as the current feeder. A 2% (volume) aqueous sulfuric acid solution was used as an anolyte. A catholyte was prepared from an EWS solution, which consisted of 35 parts of ethanol, 10 parts of water, and two parts of sulfuric acid and nitrobenzene. The catholyte flowed through the bed from top to bottom and the anolyte was circulated. The electrolysis was operated at room temperature. The particles for the packed-bed electrode were prepared from an anion exchange resin, Amberlite IR-410 as follows:[2] Pretreatment: 1. Stir in ethanol. 2. Keep in a 15% aqueous solution of potassium carbonate for 15 min below 70 °C under stirring. 3. Wash with distilled water. 4. Keep in a solution composed of 1 part of 1% aqueous silver nitrate solution and 1 part of ethanol at room temperature for 5 min under stirring (surface activation). 5. Vacuum dry below 40 °C. Each particle thus pretreated was chemically plated. A plating bath was prepared by dissolving 180 g of glycerine and 180 g of copper carbonate in 1 liter of 20% NaOH solution. The solution was kept for a day before use. A 28% formaldehyde solution was used as a reducting reagent. One gram of particles was put in 10 ml of plating bath and a reducing reagent was added 1 ml at a time until the color of the copper ions disappeared. Particles plated with copper were dried under a reduced pressure after being washed with distilled water, and were kept in a desiccator.

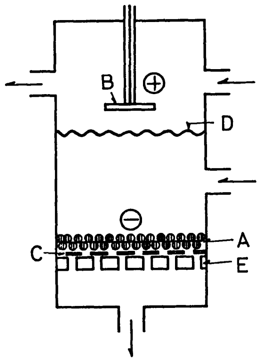

Fig. 1. Electrolytic cell.
A: Working bed electrode. B: Counter electrode.
C: Current feeder. D: Anion exchange membrane.
E: Plastics net.

Analysis. Each fraction of the effluent electrolyte was analyzed as follows: It was first neutralized by a NH_3 solution and then it was extracted by ether. The extract was analyzed by utilizing a liquid chromatography technique.

Potential Measurement. A probe was devised to measure the particle potential in a bed electrode. A copper wire of 0.5 mm diameter was covered with polyethylene. One end of it was bare only at an edge and the other was bare for the contact to the measuring circuit. This probe was supported by a glass pipe. A fine Luggin capillary was attached, with a porous porcelain tip on its edge to prevent bed particles from coming into the capillary. If that occurred, the solution potential measured by the capillary would be disturbed by the dissolution of copper.

Results and Discussion

Current-Potential Relationship. The potential on the copper-plate electrode where the nitrobenzene reacted in a mixed solution (EWS) was examined by cyclic voltammetry (Fig. 2). The reduction of nitrobenzene begins at about −0.2 V (*vs.* SCE) and hydrogen evolution begins at about −0.5 V. Accordingly, only the reduction of nitrobenzene occurs between −0.2 and −0.5 V.

Electrolysis in a Batch-Cell. The current efficiency for aniline formation was examined at a copper-plate

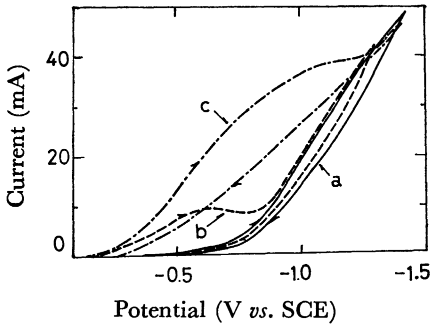

Fig. 2. Current-potential curves on the copper-plate electrode in EWS solution by a cyclic voltammetry with sweep rate of 0.1 V/s.
a: Without nitrobenzene, b: with 1% nitrobenzene, c: with 5% nitrobenzene.

electrode in an H-shaped batch-cell which was equipped with an ion exchange membrane as a diaphragm. At the early stage of electrolysis under a constant current, of 10 mA/cm^2, for example, the current efficiency of aniline formation was very high, about 70—80%. However, the electrode surface was covered by a colloidal product with continuing electrolysis and the current efficiency decreased with electrolysis time. After a few hours electrolysis the current efficiency decreased to 30—40% and hydrogen evolution occurred as a side reaction. Besides the copper plate, a copper-particle bed was used as the electrode in a batch-cell. As the latter electrode, 1 g of particles was inserted in a glass vessel (10 mm diameter, 10 mm height). A copper wire which was set at the bottom of the vessel was utilized as a current feeder. The rate of aniline formation on this electrode was examined under a constant current electrolysis (Fig. 3). A solid product accumulated on the bed electrode; it was identified as anilinium sulfate by its IR spectrum. No other compound was observed. A straight line in this figure represents the calculated rate of aniline formation by supposing that the current efficiency of aniline formation is 100%. The experimentally obtained rate was lower than the calculated one. This may be due to the hydrogen evolution as a side reaction. The rate of aniline formation hardly decreased after about 48 h electrolysis.

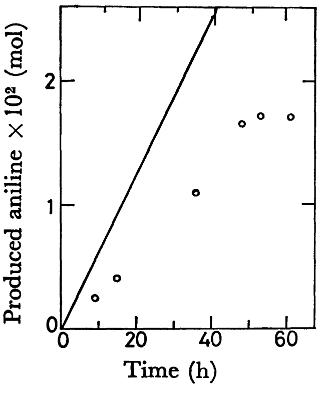

Fig. 3. Current efficiency for aniline formation at constant current (100 mA) electrolysis by using packed-bed copper electrode in a batch cell.
—: Calculated rate as 100% current efficiency,
○: observed value.

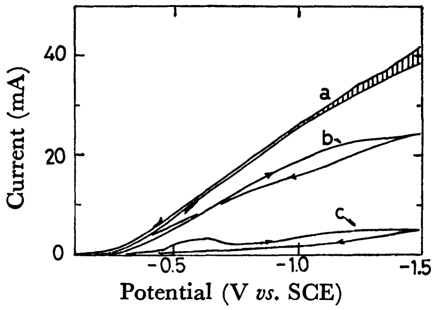

Fig. 4. Current-potential curves on the copper-plate electrode in EWS solution containing 5% nitrobenzene by a cyclic voltammetry with sweep rate 0.1 V/s.
a: By using copper electrode not covered by a colloidal product,
b: by the use of the solution added with 0.3% aniline after the measurement of "a",
c: by using copper electrode after 3 h electrolysis at 10 mA covered by a colloidal product.

The potential-current curve by cyclic voltammetry on the copper-plate electrode covered by the colloidal product was measured (Fig. 4). The current in the potential region in which the reduction of nitrobenzene occurred decreased exceedingly after being covered by the colloidal product. By adding aniline, which is the reaction product, the decrease of current was also observed, but it was very slight. This may show that a colloidal product retards the cathodic reduction of nitrobenzene very much and accelerates the hydrogen evolution, due to the shift of the potential to a more negative value during the constant current electrolysis. Thus, the current efficiency for aniline formation may be decreased with continuing constant current electrolysis in a batch-cell.

Electrolysis at a Packed-Bed Electrode. By using a packed-bed electrode (Fig. 1), an EWS solution containing 5% nitrobenzene was electrolyzed at a constant current (100 mA) under flow. The effluent electrolyte was collected by 10 ml at a time. Each fraction was analyzed for the aniline content, and the rate of aniline

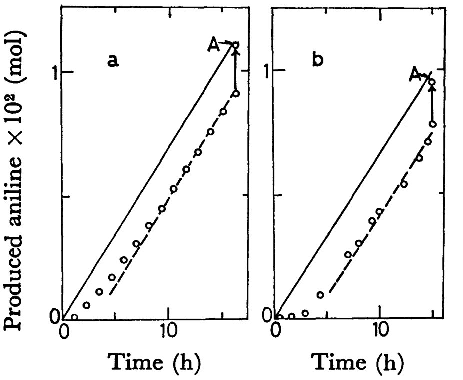

Fig. 5. Current efficiency for aniline formation at constant current (about 100 mA) electrolysis by using packed-bed copper electrode under flowing electrolyte.
a: bed depth, 30 mm, b: bed depth, 10 mm.
—: Calculated rate as 100% current efficiency,
○: observed value.

formation was calculated (Fig. 5). a and b in this figure represent results obtained by the cells of 30 and 10 mm heights, respectively. Straight lines represent results which were calculated by assuming that the current efficiency of aniline formation was 100%. At the early stage of electrolysis, the rate is apparently slow. This is due to the induction period before the flowing out of the solution under the bed electrode. The experimental results fell almost on the dotted lines which represent the current efficiency of 100%. It becomes clear from this fact that the current efficiency is very high. The electrolyte contained in the cell flowed out after electrolysis and was analyzed for the aniline content. Then the amount of aniline became point A in Fig. 5. These results also show that the current efficiency is very high, approximately 100%.

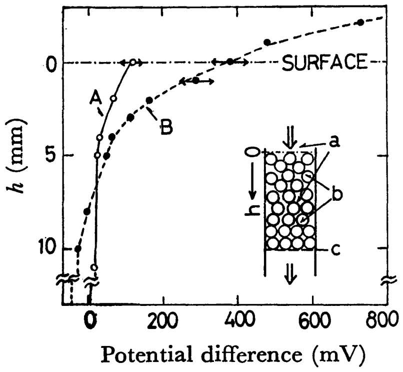

Fig. 6. Potential profile in a packed-bed copper electrode at 75 mA/cm^2 electrolysis under flowing electrolyte.
A: Potential difference between particles and feeder at various positions (b—c),
B: potential difference between solution and feeder at various positions (a—c).

Potential Profile in a Packed-Bed Electrode. The potential profile in a packed-bed electrode was examined under the conditions of constant current electrolysis (Fig. 6). The change of solution potential was measured along the bed depth by using a fine Luggin capillary. The change of particle potential was measured also along the bed depth by the probe described in the experimental section. Both potentials were referred to a current feeder which was at the furthest position from a counter electrode. In this experiment the total current was 100 mA and the apparent current density per cross sectional area of packed-bed electrode became 75 mA/cm^2. Potential changes became very small at the current densities lower than 10 mA/cm^2 and, on the other hand, the convection occurred in the bed at the current densities higher than 400 mA/cm^2. This convection is ascribed to the large Joule heat. Accordingly, the same profile as in Fig. 6 was observed between 10 mA/cm^2 and 400 mA/cm^2. The effective depth of the bed electrode on which nitrobenzene reacts is considered from Fig. 6 to be less than 3 mm, because the particle potential must be more negative by 200 mV than the solution potential for the reduction of nitrobenzene, as shown in Fig. 2. The low value of the effective depth is ascribed to the low conductivity of the electrolyte and to the high electronic conductivity of the packed-bed. At deeper positions in the packed-bed electrode, the potential of the particle electrode became more positive than the solution potential at the same position. This may cause the dissolution of copper. In order to increase the effective depth of the packed-bed electrode, bed particles of lower electronic conductivity must be used.

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References

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