Modification of the Packed-bed Electrode and Its Potential Distribution

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The packed-bed electrode has been investigated in order to scale up the cell capacity by introducing three-dimensional electrode. The reactions of aniline formation by cathodic reduction of nitrobenzene and Fe(II) ion formation by cathodic reduction of Fe(III) ion were studied. When bed particles with high electric conductivity were used, the effective depth of the packed-bed where the electrode reaction took place was very small. However, when particles with moderate resistance were used, the effective depth increased. This is because the potential distribution in the bed material is the same as that in the electrolyte in the bed, the potential difference between particles and electrolyte thus being maintained constant at any position in the bed. From the standpoint of scaling up the cell capacity, this type of electrode can be effectively applied.

Application of a packed-bed or porous electrode[1,2] has been investigated by many workers, in order to scale up the cell capacity by introducing three-dimensional electrode. The packed-bed electrode was also recently studied as regards application to the treatment of waste water.[3,4] The increase in cell current was not large since the effective depth of packed-bed or porous electrode where the electrode reaction took place was very small. This is ascribed to the high electronic conductivity of bed material or porous material and to the apparent low conductivity of electrolyte in the bed which is caused by small void between particles in the bed. Under these conditions, the potential of solution in the bed and that of bed particles are distributed as represented by curves φ_s(P) and φ_m(P). Thus the potential difference between particles and electrolyte changes in the bed (curve $\Delta\varphi$(P), Fig. 1).[5] This shows that the potential difference between particles and electrolyte enough for an electrode reaction to proceed exists only at the part of bed nearest to the counter electrode.

Fleischman *et al.*, [5] Hiddleston and Douglas[6] and Janssen[7] introduced a fluidized-bed electrode. The apparent resistance of bed material in the bed which changes with the expansion of bed causes a potential distribution in the bed (curve φ_m(f), Fig. 1).[5] The potential distribution of solution in the bed also changes at the same time as the change of expansion (curve φ_s(f)). The potential distribution formed thus in both sides of the solution in the bed and bed particle causes an adequate potential difference between particles and electrolyte for an electrode reaction at any position in the bed as shown by curve $\Delta\varphi$(f). Accordingly the effective depth of bed electrode where the electrode reaction took place could be expected to become large.

If particles with moderate resistance are used as bed material of a packed-bed electrode, the same potential distribution in a packed-bed electrode as in a fluidized-bed electrode can be expected. We have examined the potential profile in a packed-bed constructed with particles having a moderate resistance and also the increase of effective depth of this type of electrode.

Experimental

Carbon particles (14—20 mesh) partly graphitized were used as bed material. The resistance of the particles was about 3.4 Ωcm. Two other kinds of particle were also used, a glass bead (1—2 mm diam) chemically plated with copper, and a carbon particle (about 0.5 mm diam), also chemically plated with copper because of high resistance. Copper deposition of the particles was carried out by the same technique as that given in a previous paper.[2]

The electrolysis cell (Fig. 2) was made of polyvinyl chrolide. The bed size was 3 cm in width and 1.5 cm in thickness. The bed depth was changeable. The bed was supported on a glass filter through which electrolyte was distributed. The bed was also covered with a glass filter. A graphite plate

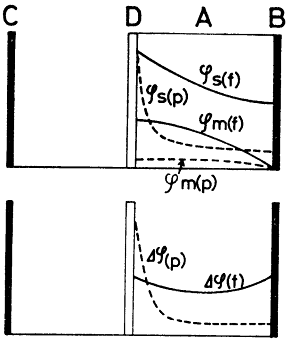

Fig. 1. Potential profiles in packed-bed and fluidized-bed electrodes.
A: Bed electrode. B: Feeder electrode. C: Counter electrode. D: Diaphragm. φ_s: Solution potential. φ_m: Particle potential. $\Delta\varphi$: Potential difference between φ_s and φ_m. Suffix f and p means fluidized-bed and packed-bed, respectively.)

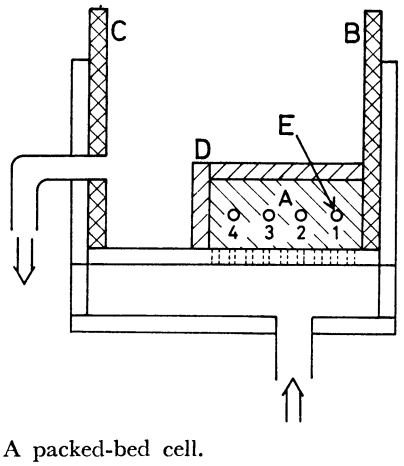

Fig. 2. A packed-bed cell.
A: Packed-bed. B: Feeder electrode. C: Counter electrode. D: Diaphragm. E: Luggin capillaries and probes.

was used as a counter electrode. A graphite or copper plate was used as a feeder electrode which was set at the opposite end of the bed from the counter electrode. Both electrodes were positioned parallel to each other. The electrolyte fed into the cell flowed across the bed.

Three kinds of electrolyte were used: 1 M HCl saturated with nitrobenzene, 0.02 M $FeCl_3$+1 M HCl and 0.5 M $FeCl_3$+1 M HCl.

Four graphite rods or four copper wires were inserted into the bed from one side for use as probes, with which the potential of the bed particle at each position was measured. Four glass capillaries were inserted into the bed from the other side for use as Luggin capillaries, with which the solution potential in the bed was measured. Potential distributions in the direction of depth in the bed* were measured. Two saturated calomel electrodes (SCE) were used for measuring the potential distribution in the solution. Electrolysis was carried out at room temperature.

Results and Discussion

Dissolution of copper occurred when glass beads or carbon particles plated with copper were used as bed material. This may be ascribed to the high conductivity of the bed material. In this case, most of the cell current came from the part of the bed electrode nearest to the counter electrode. The potential of the particle at a part farther from the counter electrode can become so positive to the solution potential at the same position as to make the dissolution of copper possible. These two kinds of particle are not suitable as bed material. In most of the experiments a third material, 14—20 mesh carbon particles, was used.

Reduction of Nitrobenzene. A nitrobenzene solution was reduced to aniline by a bed electrode constructed with carbon particles. A feeder electrode and probes were made of copper. Potential distribution was measured by constant current electrolysis at 500 mA/cm^2 (Fig. 3). A distribution of particle potential took place in the bed as expected. $\Delta\varphi$, the difference between particle potential and solution potential at the same position in the bed, becomes large near a feeder electrode, hydrogen evolution being observed in this region. The reduction of nitrobenzene takes place at fairly negative potential. On the other hand, hydrogen overvoltage of carbon is not so high. The potential region where the reduction of nitrobenzene occurs predominantly is narrow. The reduction of nitrobenzene to aniline is accompanied by many side reactions. $\Delta\varphi$ can not be set at a given potential throughout the bed (Fig. 3); we can not accurately control $\Delta\varphi$ throughout the bed. This causes the reduction of current efficiency of aniline formation, as confirmed experimentally. The current efficiency became less than 50%.

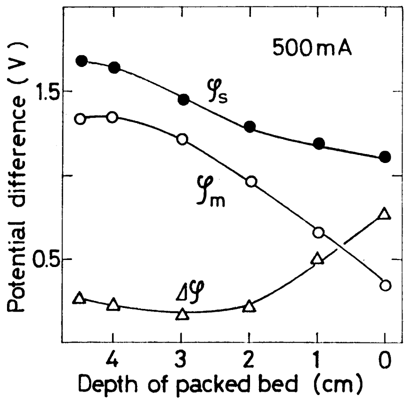

Fig. 3. Potential profiles at the reduction of nitrobenzene in 1 M HCl saturated with nitrobenzene. Total current: 500 mA.

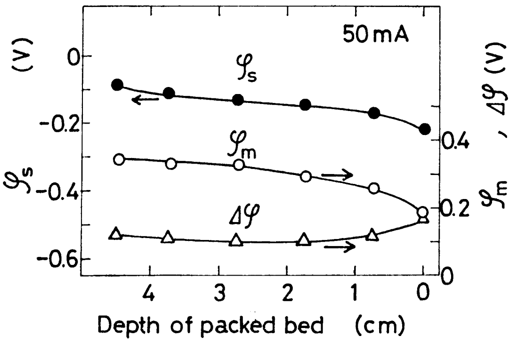

Fig. 4. Potential profiles at the reduction of Fe(III) ion in 0.5 M $FeCl_3$+1 M HCl. Total current: 50 mA.

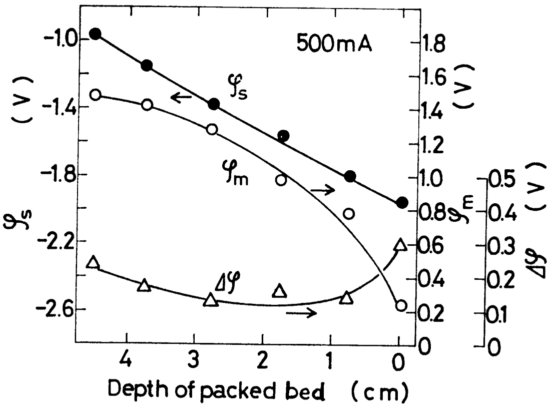

Fig. 5. Potential profiles at the reduction of Fe(III) ion in 0.5 M $FeCl_3$+1 M HCl. Total current: 500 mA.

Reduction of Iron(III) Ion. The reduction of iron(III) ion was examined as an example of the reaction with a low overvoltage. The feeder electrode and probes consist of graphite. The potential distribution was measured at a high concentration of iron(III) ion, 0.5M in 1M HCl, under conditions of constant current electrolysis (Figs. 4 and 5). The solution potential, φ_s was referred to that at a position just next to the diaphragm on the side of the counter electrode. The particle potential, φ_m, was referred to the potential of feeder electrode. The value of φ_m at zero position was due to the contact

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* A small moving Luggin capillary and a small probe made from graphite rod or copper wire were also used, for measuring the potential distribution of solution in bed and that of bed particles in the directions of width and thickness in the bed. In these directions, uniform potential distributions were observed.

resistance between particles and the feeder electrode.** $\Delta\varphi$ corresponds to the potential difference at each position in the bed from an equilibrium potential 650 mV (*vs.* SCE).

The fact that the change of $\Delta\varphi$ along the depth was not so large at the small cell current (Fig. 4) indicates that the packed-bed is active throughout. On the other hand, Fig. 5 shows that at a large cell current, $\Delta\varphi$ becomes larger near both ends than at the center. This means that a larger part of the cell current comes from the parts near both ends and that all the packed-bed is not used equally. However, the effective depth was remarkably improved as compared with the usual packed-bed.[8]

The packed-bed electrode was applied to the reduction of iron(III) ion under conditions of limiting current by mass transfer in a solution of 0.02M $FeCl_3$ in 1M HCl. The dependence of total cell current on the potential of probe No. 1 (*vs.* SCE) was examined at different flow rates by using packed-bed electrode of 1.5 cm depth constructed with 14—20 mesh carbon particles (Fig. 6). The cell current depending on flow rate was much larger than that at feeder electrode only. The limiting current appeared clearly at a lower flow rate at more negative potential than 0.3 V. But this became ambiguous with an increase in flow rate. This may be ascribed to the disturbance of flow path in the bed and to the change of potential distribution in the bed due to the increase in cell current. The total cell current is expected to increase when the flow rate becomes large. This was examined at different bed depths (Fig. 6). The total cell current increased with flow rate (Fig. 7). A linear relationship is expected between total cell current and flow rate under conditions of limiting mass transfer from the theory of mass or heat transfer in a packed-bed reactor.[9] However, this was not the case as shown in Fig. 7. This may also be ascribed to the disturbance of flow path in the packed-bed because of its construction.

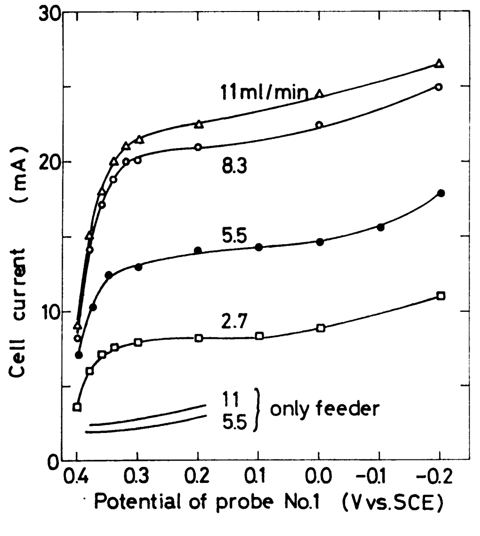

Fig. 6. Current potential relationships on a packed-bed electrode of 1.5 cm depth in 0.02 M $FeCl_3$+1 M HCl at different flow rate.
Potential of probe No. 1 was set *vs.* SCE.

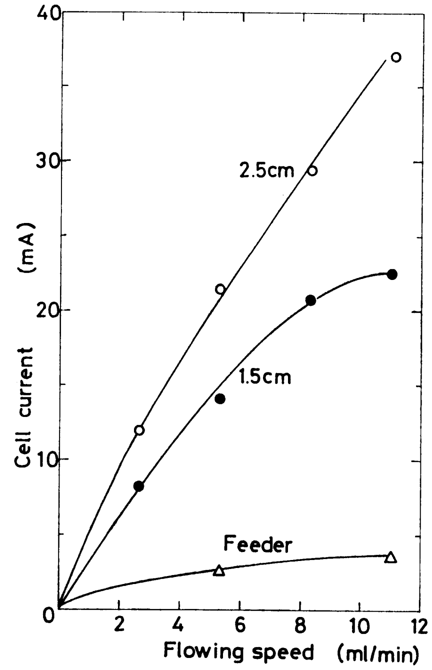

Fig. 7. The dependence of total current on flow rate in 0.02 M $FeCl_3$+1 M HCl.
Potential of probe No. 1 was set at 0.2 V (*vs.* SCE). Bed depth, —●—: 1.5 cm, —○—: 2.5 cm, —△—: feeder electrode only.

The profile of $\Delta\varphi$ was examined under conditions of potentiostatic electrolysis where the potential of probe No.1 was set *vs.* SCE. $\Delta\varphi$ was larger than 0.4 V (Fig. 8), indicating that the particle potential throughout the bed was negative as conditions of limiting current

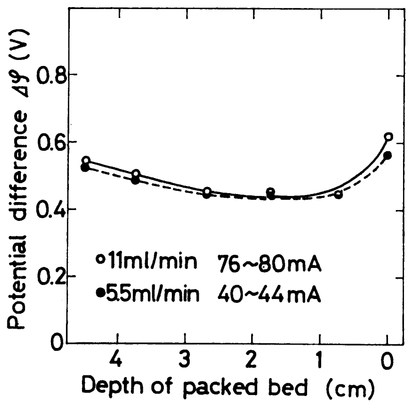

Fig. 8. The change of $\Delta\varphi$ along the bed depth in 0.02 M $FeCl_3$+1 M HCl. The potential of probe No. 1 was set at 0.2 V (*vs.* SCE).
—○—: 11 ml/min, total current 76—80 mA.
—●—: 5.5 ml/min, total current 40—44 mA.

** This value should be proportional to the current. However, we could not observe the proportionality and a reproducible result according to φ_m at zero position. This may be due to the small change in the surface roughness of the feeder electrode and that of film thickness of penetrated electrolyte between feeder electrode and particles.

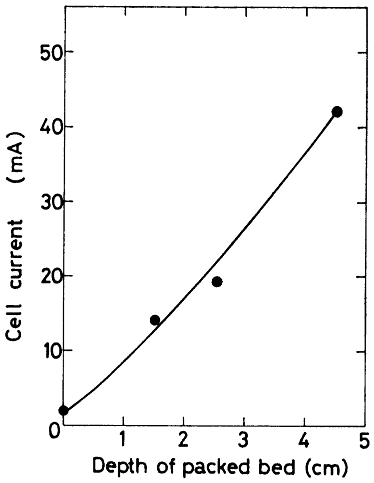

Fig. 9. Dependence of total cell current on bed depth in 0.02 M $FeCl_3$+1 M HCl at flow rate 5.5 ml/min. Potential of probe No. 1 was set at 0.2 V (*vs.* SCE).

were attained. The electrode reaction occurred almost at the same rate in the whole part of packed-bed. All the particles in the packed-bed were used effectively. This was confirmed by an experiment in which the relationship between total cell current and bed depth was examined. Total cell current increases with the bed depth (Fig. 9). The increase of cell current thus can be attained by the increase in bed depth.

The reaction ratio of reactant was small even at a low concentration because of the thinness of the bed. The reaction ratio would increase by using a thicker bed. In this case the potential distribution along the thickness might be taken into consideration. Use of this thicker bed will make this type of electrode more effective for the treatment of waste water containing harmful components in a low concentration. It is easier to control an electrode of this type than a fluidized-bed electrode.

Conclusion

The distribution of particle potential appears in the bed in a packed-bed electrode constructed with particles of moderate resistance. The distribution enables the packed-bed electrode to act in the same manner as the fluidized-bed electrode. The effective depth in the former could be improved as in the latter. As the potential in a bed can not be accurately controlled, the potential region of the desired reaction should be made wide. The electrode can be effectively applied to the solution of a low reactant concentration such as waste water.

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