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Application of a circulating suspended particle-electrode to electrochemical hydrodimerization of acrylonitrile

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A circulating suspended particle-electrode was applied to the electrochemical hydrodimerization of acrylonitrile in order to examine the possibility of scaling up the cell capacity. Total current on a feeder electrode was increased remarkably by an addition of lead particles and the current was proportional to the quantity of lead particles added. Total current was also increased with the increase of circulating speed. The current increased with electrolysis time because the surface oxide was gradually reduced with continuing electrolysis. Contact resistance between a suspended particle and a feeder electrode was not as large as in the Kolbe synthesis on a particulated electrode, and electron transfer between the particle and the feeder electrode at their collision was fast compared with charge transfer on the particle electrode. Current efficiency for adiponitrile formation was less on the suspended electrode than on a plane electrode. However, the rate of adiponitrile formation was markedly increased by the use of the suspended electrode.

1. Introduction

An application of a circulating suspended particle-electrode to the Kolbe electrolysis was reported in a previous paper [1]. In this case, a charge transfer reaction proceeded through an oxide film formed on both the particle and feeder electrodes. The oxide layer became more dense with electrolysis time, and the contact resistance between particle and current feeder increased proportionally with the growth of the oxide layer. Accordingly the current on the feeder electrode decreased with electrolysis time, so that it was difficult to scale up utilizing this type of electrode. In the application of the circulating suspended particle-electrode to cathodic reactions, however, this disadvantage is not experienced; this electrode was applied to the electrochemical hydrodimerization of acrylonitrile which is industrially important in the formation of 6,6-nylon. The possibility of scaling up the cell capacity was examined.

2. Experimental

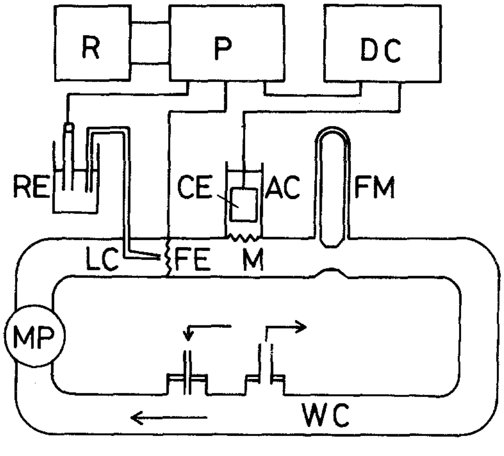

Fig. 1. A schematic diagram of electrolysis system of circulating suspended particle-electrode. WC-cathode compartment; AC-anode compartment; FE-feeder electrode; CE-counter electrode; RE-reference electrode (SCE); FM-flow meter; MP-magnetic pump; R-recorder; M-diaphragm; LC-Luggin capillary; P-potentiostat; DC-stabilized power source.

An electrolysis cell is shown diagramatically in Fig. 1. The cell was constructed from glass pipe and PVC tube or silicone rubber tube and the cathode compartment had a volume of about 500 ml. The anode compartment, in a side tube, was separated from the cathode compartment by an anion exchange membrane. Flow speed was

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measured by an orifice flow meter which was inserted midway along the circulating cathode. Lead net of 15 mesh from a lead battery* was used as the feeder electrode; its working part was a circular disc 11 mm in diameter whose calculated surface area was about 3·0 cm^2. A platinum plate was used as the counter electrode. The potential of the feeder electrode was measured with reference to a saturated calomel electrode (SCE). Lead particles of 60–120 mesh, made of lead powder of 99·9% purity for battery use, were utilized for the suspended electrode. The lead particles were surface oxidized requiring cathode reduction before use. Lead particles from 0–5 g were dispersed in 500 ml catholyte as a fine dispersion. A 50% aqueous solution of tetraethylammonium *p*-toluenesulphonate (TEATS) was used as a catholyte and 1N H_2SO_4 as an anolyte. TEATS was prepared from ethyl *p*-toluenesulphonate and triethylamine [2].

The cathode compartment was first filled with 1 N H_2SO_4 and the feeder electrode was cathodically reduced. Secondly the compartment was washed by distilled water after the 1 N H_2SO_4 had been drained. Thirdly, a 50% TEATS solution was put in the cathode compartment and a given amount of lead particle was added to this. Fourthly, the surface oxide was cathodically reduced for 30 min at 3–5° C in an ice bath with circulation of the electrolyte, then a given amount of acrylonitrile was added. Products were analysed by utilizing a gas chromatographic technique in order to calculate current efficiencies for adiponitrile and propionitrile formations. A Tween 80 column was used. Small amounts of bis-(2-cyanoethyl)-ether and other compounds were also detected on the gas chromatograms.

3. Results

3.1. *Polarization curves by means of potential scanning technique*

It has already been reported by Baizer [3] and Asahara *et al.* [4] that adiponitrile is produced at high current efficiency by cathodic reduction of acrylonitrile on the electrodes such as mercury or lead which have high hydrogen overpotentials in a TEATS solution. Polarization curves were measured by means of a potential scanning technique in order to examine this reaction. In an aqueous solution of 50% TEATS, oxygen was evolved at 1·5 V (versus SCE) and hydrogen at −0·7 V on a platinum electrode. The addition of acrylonitrile to this solution did not cause any significant change. This means that acrylonitrile does not react on a platinum electrode. When a lead plate electrode was used, the addition of acrylonitrile caused a change on the polarization curve as shown in Fig. 2. Curve a in Fig. 2 represents a result obtained without acrylonitrile. This curve shows that hydrogen evolution begins at a more negative potential by about 1·4 V than on a platinum electrode. On the other hand, oxidation of the lead surface takes place at −0·4 V. The addition of acrylontrile gave the curve b in Fig. 2 and a reduction peak appeared at −1·9 V. Increasing the amount of acrylontrile, gave a proportionately higher peak. Adiponitrile was produced at a current efficiency of 70–90% by electrolysis at −1·9 V. This indicates that the peak current corresponds to the formation of adiponitrile. Hydrogen evolved mainly at −2·1 V, so that the potential region for the formation of adiponitrile is narrow and limited between −1·9 V and −2·1 V.

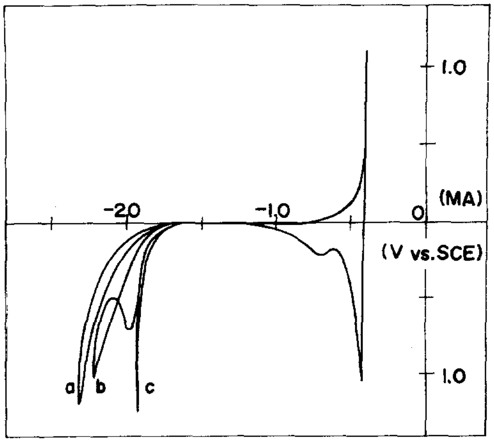

Fig. 2. Cyclic voltammogram on a lead electrode. Electrolyte: 100 ml 50% TEATS solution + acrylonitrile. a: 0 ml; b: 2 ml; c: 5 ml. Scanning rate: 10 s V^{-1}. Direction of sweep: anodic from − 1·0 V (versus SCE), cathodic and then anodic.

3.2. *The effect of suspended lead particles*

Fig. 3 shows the effect of the addition of lead particles on the current–potential relationship

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* [1] Lead was of 99% purity and contains a little antimony.

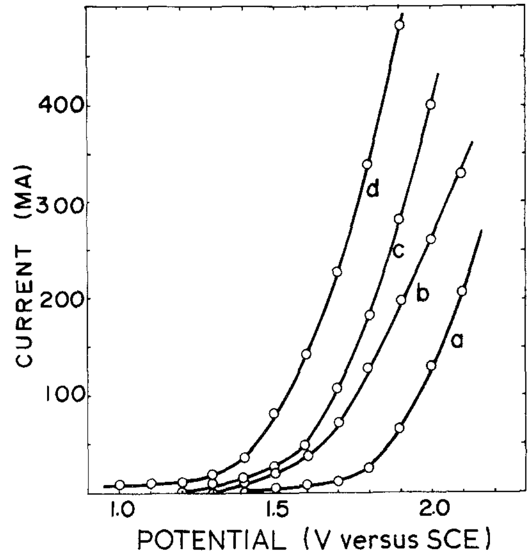

Fig. 3. Current potential relationship in the circulating suspended particle-electrode system. Electrolyte: 400 ml 50% TEATS solution + 100 ml acrylonitrile. Circulation speed: 200 ml s^{-1}. Suspended particles: lead particle a: 0 g; b: 1 g; c: 3 g; d: 5 g (in 500 ml catholyte).

obtained at a circulation speed of 200 ml s^{-1} in the solution which consists of 400 ml 50% TEATS solution + 100 ml acrylonitrile. An addition of 5 g lead particles resulted in an increase of current, to the extent of eight times at $-1{\cdot}9$ V, where acrylonitrile was reduced.

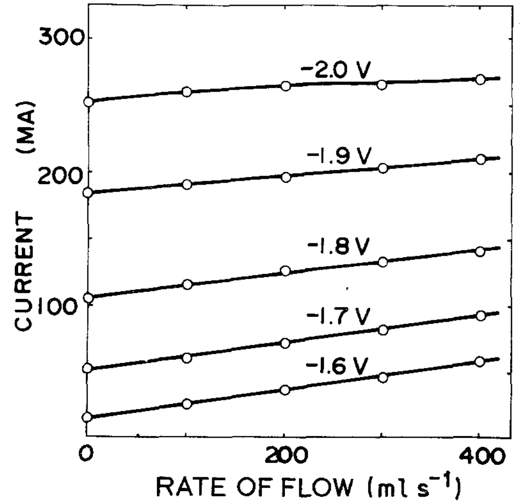

Fig. 4. Effect of circulating speed on current at different potential of feeder electrode. Electrolyte: 400 ml 50% TEATS solution + 100 ml acrylonitrile. Suspended particle: 1 g lead particles in 500 ml catholyte.

3.3. *The effect of circulating speed of electrolyte*

Fig. 4 shows the effect of circulation speed on current investigated at different potentials. Current increased proportionally to circulation speed for the particulate electrode but did not increase without lead powder. This increase was steep at small overpotentials. The same phenomenon was also observed in the application of particulate bed electrodes to the Kolbe electrolysis [1].

3.4. *Time dependence of current*

The surface of a lead particle is oxidized under air and the oxide layer formed is of low conductivity. Using such particles in a particulate electrode for a cathodic reaction, the contact resistance becomes fairly high and makes the electron transfer between a particle and feeder electrode difficult. However, this surface oxide is gradually reduced with continuing electrolysis and the contact resistance becomes less and less. On the other hand, adsorption of products and intermediates might lead to the formation of resistive films on the particles, which increase contact resistance. Fig. 5

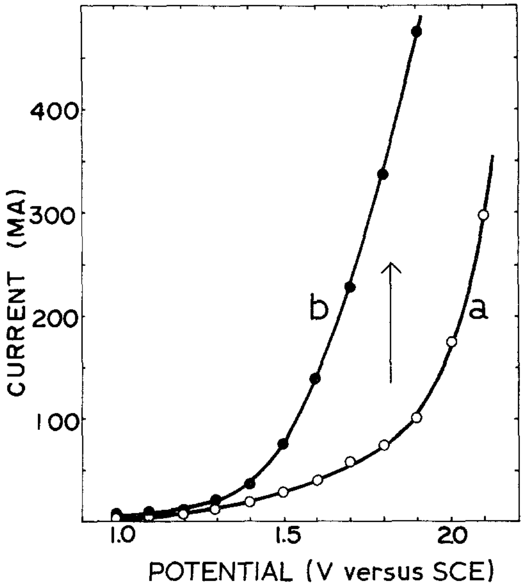

Fig. 5. Effect of electrolysis time. Electrolyte: 400 ml 50% TEATS solution + 100 ml acrylonitrile. Suspended particle: 5 g lead particles in 500 ml catholyte. Circulation speed: 200 ml s^{-1}; curve a: 1 min after beginning of electrolysis; curve b: Particle initially cathodically reduced and the curve is obtained 1 h after beginning of electrolysis.

shows the effect of electrolysis time on the current–potential relationship in the system involving lead particles. Curve a in Fig. 5 represents the relationship obtained at 1 min after an addition of lead particle. Curve b represents the relationship at 1 h after an addition of lead particles which had been electrochemically reduced in 1 N H_2SO_4 prior to the addition. In the case of surface oxidized particles curve a approached curve b after continuing electrolysis for several hours. After reaching curve b there appeared to be no change with electrolysis time. This result indicates that, once the oxide layer has been reduced no further change in activity takes place, so scaling up becomes more reliable.

3.5. *Current efficiency*

The current efficiency for adiponitrile formation was examined at a lead plate electrode. Results are shown in Table 1. Propionitrile was produced as a by-product but its current efficiency is very small and less than 0·1% in accordance with the results of Baizer [3]. A gaseous product, hydrogen, did not evolve either. The current efficiency was 70% at 5 mA cm^{-2}.

The amount of acrylonitrile consumed was also measured and the ratio of adiponitrile produced to acrylonitrile consumed which is designated as product yield from now on, was calculated to be 29·8%. This means that about 70% of acrylonitrile consumed reacted to form some species besides adiponitrile and propionitrile. The fact that the current efficiency for adiponitrile formation was 70% implies the polymerization of acrylonitrile. With electrolysis at current densities of 50 mA cm^{-2} and 2·5 mA cm^{-2}, where adiponitrile was formed at a current efficiency less than 70%, the product yields decreased to 20·7% and 12·0% respectively. In both of the above experiments a yellow polymer was formed. In the case of potentiostatic electrolysis, both current efficiency and product yield for adiponitrile formation were improved compared with the case of constant current electrolysis. Adiponitrile was produced at about 100% current efficiency at −2·0 V. In this experiment the product yield exceeded 80% and 10 ~ 20% of acrylonitrile consumed produced some species other than adiponitrile. The high current efficiency for adiponitrile formation, about 100%, is considered to show the occurrence of acrylonitrile polymerization as a side reaction.

Current efficiencies were examined also on a circulating suspended particle-electrode by electrolysing at the potential where the high current efficiency for adiponitrile formation could be expected. Results are shown in Table 2. Adiponitrile was produced at 35·1% current efficiency by the electrolysis on a lead feeder electrode at −1·95 V (versus SCE) with a circulation speed of 200 ml s^{-1}. The production of propionitrile was below 0·1% but hydrogen evolution was observed. One reason for the low current efficiency is considered to be that the purity of the lead net electrode is lower than that of the lead plate electrode. The yield was very low, 2·2%. This implies that circulation of electrolyte accelerates the polymerization of acrylonitrile.

The effect of addition of hydroquinone as a polymerization inhibitor was examined. The current efficiency and the product yield for adiponitrile formation were improved to 43·7% and 34·5% respectively. The use of a lead net electrode of higher purity, which might cause

Table 1. Dependence of current efficiency on electrolysis conditions at Pb plate electrode

Condition		*Current efficiency*	
Current (mA cm^{-2})	*Potential* *(V versus SCE)*	*Adiponitrile* *(%)*	*Propionitrile* *(%)*
50*	−2·1 ~ −2·2	43·4	trace
5*	−1·9 ~ −2·0	69·9	trace
2·5*	−1·8 ~ −1·9	36·3	trace
20 ~ 25	−2·00†	101·5	trace
1 ~ 2	−1·70†	8·0	trace

* constant current; † constant potential.

Table 2. Dependence of current efficiency on electrolysis conditions at a circulating suspended particle-electrode. Circulation: 200 ml min^{-1}; cell volume: 500 ml; electrolyte: 50% TEATS solution containing 20% acrylonitrile

Condition		*Current efficiency*	
Potential (V versus SCE)	*Electrolysis period (h)*	*Adiponitrile (%)*	*Propionitrile (%)*
Pb feeder			
−1·95*	0 ~ 2	43·7	trace
−1·95	0 ~ 2	35·1	trace
−2·00	0 ~ 2	49·7	trace
−2·10	0 ~ 2	36·6	1·0
+ powder 5 g			
	0 ~ 2	12·7	0·7
−1·9 ~ −2·0*	0 ~ 4	44·5	0·9
	2 ~ 4†	76·3	1·1

* Hydroquinone is added to the electrolyte; † Calculated.

some trouble in the respect of its mechanical strength, would improve the current efficiency. Results obtained on a circulating suspended particle-electrode are also shown in Table 2. It was difficult to set the potential at a given value in this system, so electrolysis was carried at −1·9 ~ −2·0 V. The apparent current efficiency for adiponitrile formation after 2 h of electrolysis was lower than in the system without suspended particles, while the current efficiency for propionitrile formation was 0·7% and higher than in the latter system. The apparent current efficiency for adiponitrile formation was improved with electrolysis time and it approached 44·5% after 4 h electrolysis. From these data, the apparent current efficiency in the region from 2–4 h after the beginning of electrolysis, is calculated to be 76·3%. It is obvious from Fig. 5 that the surface of the lead particle was covered with oxide at the beginning of electrolysis and that this oxide was cathodically reduced with electrolysis time. Accordingly, the low current efficiency during the early period of electrolysis may certainly be ascribed to the consumption of electricity for the reduction of this oxide. The current efficiency in the suspended system is better than that on the feeder electrode alone, because of the higher purity of the suspended particles than that of the feeder electrode.

On the other hand propionitrile was formed increasingly with the passing of electrolysis time. Baizer [3] reported that propionitrile was formed more and more with decrease of acrylonitrile concentration. In our case the change of concentration of acrylonitrile at the electrode surface may have an effect on current efficiency.

4. Discussion

The formation of adiponitrile by the cathodic hydrodimerization of acrylonitrile has been investigated by Baizer [3], Asahara *et al.* [4] and Beck [5] and the following reaction path has been proposed. Acrylonitrile is first reduced through a one electron transfer reaction

$$CH_2 = CHCN + e \rightarrow \cdot CH_2\bar{C}HCN. \qquad (1)$$

An anion radical formed thus is protonated into the radical $\cdot CH_2CH_2CN$ when the proton concentration is high:

$$\cdot CH_2\bar{C}HCN + H^+ \rightarrow \cdot CH_2CH_2CN. \qquad (2)$$

Coupling of this species does not seem to occur because it is not inhibited by radical scavenger and is dependent on the pH of the solution [3]. The anion radical or the radical is considered to further the second one-electron reduction followed by reaction with acrylonitrile to form adiponitrile

$$\begin{aligned} &\cdot CH_2\bar{C}HCN + e \rightarrow \bar{C}H_2\bar{C}HCN \\ &\bar{C}H_2\bar{C}H_2CN + CH_2 = \\ &\quad = CHCN \rightarrow NC\bar{C}HCH_2CH_2\bar{C}HCN \qquad (3) \\ &NC\bar{C}HCH_2CH_2\bar{C}HCN + \end{aligned}$$

$$+ 2H_2O \rightarrow NC(CH_2)_4CN + 2OH^-$$

or

$$\cdot CH_2CH_2CN + e \rightarrow \bar{C}H_2CH_2CN$$

$$\bar{C}H_2CH_2CN + CH_2 =$$

$$= CHCN \rightarrow NCCH_2CH_2CH_2\bar{C}HCN \qquad (4)$$

$$NCCH_2CH_2CH_2\bar{C}HCN +$$

$$+ H_2O \rightarrow NC(CH_2)_4CN + OH^-.$$

The first one-electron transfer described by Equation (1) is rate determining. If the acrylonitrile concentration is not high enough, intermediates such as the anion radical, the dianion and so on, could react with water or a proton and produce propionitrile as a by-product. Some radical or anion intermediate species do not further the next charge transfer or the reaction with water or proton but react with acrylonitrile, and cause the production of acrylonitrile polymer. If this polymerization occurs, much monomer would be consumed. The relative concentrations of acrylonitrile, water and intermediates at the electrode interface determine the current efficiencies for the various products. At a high water concentration, propionitrile tends to be formed and at a high acrylonitrile concentration, polymer tends to be formed. The results described in Tables 1 and 2 show that electrolyte circulation affects the current efficiencies and the product yields. Adiponitrile was optimally produced at −2·0 V and at a more positive potential polymer was liable to be produced, while at more negative potential propionitrile was liable to be produced. These facts indicate that the concentration of intermediate anion radical at the interface is very important for adiponitrile formation. Electrolysis at about −2·0 V on a suspended electrode resulted in the formation of adiponitrile at the current efficiency of about 76%. This current efficiency is lower than that on a plate electrode but fairly good. It is possible on a plate electrode to set the electrode at a given potential. However, on a circulating suspended particle-electrode it is difficult to obtain a uniform given potential because of contact resistance, because contact time is very short, and the potential of a particle gradually changes in the anodic direction between contacts. Thus, the potential of particles changes as shown in Fig. 6. At a more positive potential than −1·8 V, the current efficiency for adiponitrile formation using a pure lead plate was less than 10%. Therefore the potential change sketched in Fig. 6 is not considered to be large, because the current efficiency for adiponitrile formation is high, reaching about 76%. Thus observation indicates that the electricity consumed in the recharging of a particle is not large and the electron transfer at the contact between particle and current feeder is faster than the charge transfer on the particle surface. The small potential change as described in Fig. 6 may be one reason why the current efficiency for adiponitrile formation is not as large on suspended electrodes as on plate electrodes. In the present experiments acrylonitrile was added at the beginning of electrolysis. If the concentration of acrylonitrile at the interface is kept constant by continuous feed of acrylonitrile and continuous separation of products, a higher current efficiency might be obtained on a suspended electrode. On the suspended electrode the current increased with time and the current efficiency for adiponitrile formation was improved. This is because the current for the reduction of the surface oxide of suspended particle-electrode becomes less and less with electrolysis time and because the reduction of surface oxide decreases the contact resistance.

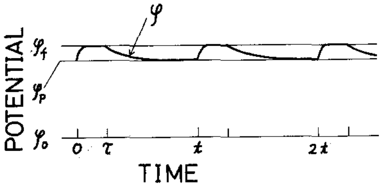

Fig. 6. A model of potential change on a particle. ψ_f: potential of a feeder electrode; ψ_p: potential of a particle just before the collision; ψ_0: supposed equilibrium potential; τ: contacting time with feeder electrode.

A plane disc electrode of the same area as the current feeder would give a current of about 20 mA. This value is about one twenty-fifth of curve d in Fig. 3.

The energy and volume required for recirculation must be considered. The time between one collision and the next collision of particles with the feeder electrode could be shortened by having many current feeders in the cathode compartment. Thus the total current would increase without much further loss of energy and cell volume, and the above disadvantage might be minimized.

5. Conclusion

The following results were obtained in the application of a circulating suspended particle-electrode to the electrochemical hydrodimerization of acrylonitrile.

(1) Adiponitrile was formed at fairly high current efficiency (~76%) on the suspended electrode. This may be improved by using lead of higher purity.

(2) The reaction proceeds 25 times faster on the suspended electrode than on a plane electrode of the same area as the feeder. This scaling up factor may be made larger by having many current feeders in the cathode compartment.

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