Ultrasonic Effects on Electroorganic Processes.[1] Electroreduction of Benzaldehydes on Ultrasound-vibrating Electrodes

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Ultrasound-vibrators (stepped horns) themselves were used as cathodes for electroreduction of benzaldehydes. Current efficiency for the reduction and selectivity for the corresponding hydrodimeric products (HD) were increased with increase in ultrasound-oscillating power.

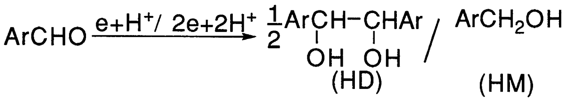
Chemical application of ultrasounds has received much attention in recent years.[2-7] However, the application to electrochemistry, particularly to electroorganic processes, has been rarely studied so far. The first report of ultrasonic effect on an electroorganic process was published in 1990 by Mason *et al.*,[8] who found influence of ultrasonic irradiation on product-selectivity for a Kolbe-electrolysis system, but the influence did not seem to be simple and clear.

Subsequently, in our previous work,[9,10] clearer and more significant effects of the ultrasonic irradiation on product-selectivity control could be demonstrated in electroreduction of benzaldehydes and alkyl halides on lead and tin cathodes, respectively. The former cathode played a role as an electron-transfer electrode to give the corresponding hydromonomeric and hydrodimeric products, while the latter led to formation of the corresponding alkyl tin compounds as a reactive electrode. It was hypothesized that the product-selectivity control on the both ultrasound-irradiated electrodes is rationalized as due to significant promotion of mass transfer across the electrode interface caused by peculier agitation effect of ultrasounds.

In this work, comparatively to the above ultrasound-irradiated electrodes, ultrasonic effects on an electroorganic process was examined using ultrasound-vibrating electrodes (stepped horn ; titanium alloy, Ti:Al:V=90:6:4 atomic ratio).

As shown in Figure 1, three types of electrodes were prepared by insulating different parts of the stepped horn with thermally-shrinking tubes (Cross-linked polyolefin) or a septum cap (Silicone rubber). Loop and node of vibration are located at the tip and root of the stepped horn with 75 mm of length, respectively, since the wave length is about 300 mm at 20 kHz in the titanium alloy. Figures 1 (a), (b) and (c) show tip-section-loop (TSL) (Diameter, 19 mm), lateral-node (LN) (Diameter, 6 mm; length, 15 mm) and lateral-loop (LL) (diameter, 6 mm; length, 15 mm) electrodes, respectively.

The electroreducton of benzaldehydes was used as a model reaction for examining ultrasonic effects of the vibrating electrodes. The reaction gives the corresponding hydrodimers (HM) and hydromonomers (HD) as shown in the following equation, along with hydrogen evoluation.



$$\mathrm{ArCHO} \xrightarrow{e+H^+/\ 2e+2H^+} \tfrac{1}{2}\,\mathrm{Ar}\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{OH}}{\mathrm{CH}}\mathrm{Ar}\ /\ \mathrm{ArCH_2OH}$$
$$\mathrm{(HD)} \qquad \mathrm{(HM)}$$

Ar : C_6H_5, p-$CH_3C_6H_4$, p-CNC_6H_4

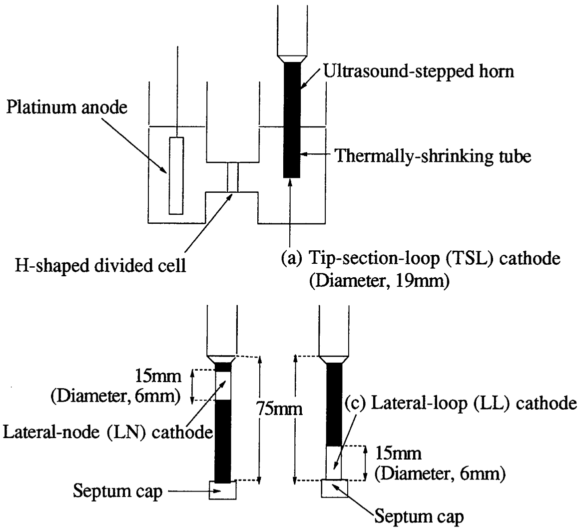


Figure 1. Ultrasound-vibrating electrodes.

An H-shaped divided cell, inserted a stepped horn cathode connected with a PZT oscillator (20 kHz) and equipped with a platinum anode, was used for electroreduction of benzaldehydes (40 mmol) in a 0.25 M H_2SO_4 / 50% CH_3OH catholyte (70 cm^3). The electrolysis was carried out galvanostatically at a variety of current densities by passing 0.2 mol electron mol^{-1} of charge at 20-25 °C. After the electrolysis, the starting benzaldehydes and reaction products (HD and HM) were analyzed by HPLC.

Table 1. Electroreduction of benzaldehydes(ArCHO) at 20 mA cm^{-2} on the tip-section-loop(TSL) cathode of an ultrasound-stepped horn

Ar	Ultrasound-oscillating power / W	Total current efficiency / %	Selectivity for HD / %
C_6H_5	0	5	29
C_6H_5	80	26	36
p-$CH_3C_6H_4$	0	8	65
p-$CH_3C_6H_4$	80	19	75
p-CNC_6H_4	0	10	1
p-CNC_6H_4	80	30	33
p-CNC_6H_4	100	42	40
p-CNC_6H_4	120	48	52

As shown in Table 1, total current efficiencies for HD's and HM's formed in the reduction of unsubstituted, and p-methyl- and p-cyano-substituted benzaldehydes on an ultrasound-vibrating tip-section-loop (TSL) cathode were much larger than those on a still cathode in a catholyte stirred by a magnet bar. Selectivities for HD's were also increased with increase in ultrasound-oscillating power. These ultrasonic effects are quite similar to those observed on ultrasound-irradiated electrodes,[9] and are rationalized as due to promotion of the mass transfer caused by transversal ultrasound waves.

Figure 2 indicates that the total current efficiency for the reduction of p-cyanobenzaldehyde on lateral-node (LN) and lateral-loop (LL) cathodes are increased with increase in the ultrasound-oscillating power. The selectivity for the HD was also increased with increase in the power, as shown in Figure 3. Interestingly, it is noted that the current efficiency and selectivity on the LL cathode are higher than that on the LN cathode, since the surface of the lateral (LN and LL) electrodes vibrates longitudinally. This fact may be rationalized as due to a greater vibration velocity at the loop than at the node.[11]

Decreases in the current efficiency and selectivity with increase in current density have generally been explained on the basis of a mass transfer theory in our previous work.[12] A further theoretical investigation on the ultrasonic effect in the reduction on the ultrasound-vibrating electrodes is in progress.

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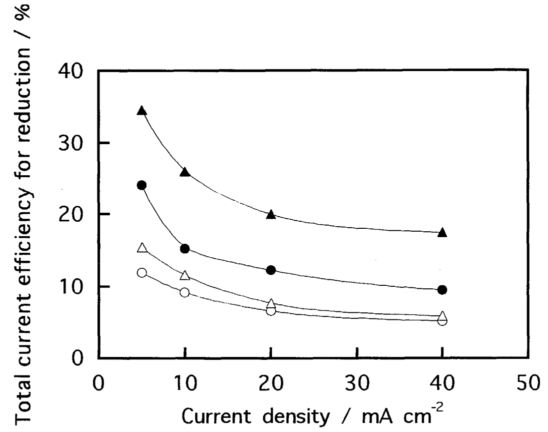

Figure 2. Total current efficiency for the reduction of p-cyanobenzaldehyde on lateral-node (LN) and -loop (LL) cathodes. Ultrasound-oscillating power : ○, 3W (LN) ; △, 3W (LL) ; ●, 6W (LN) ; ▲, 6W (LL).

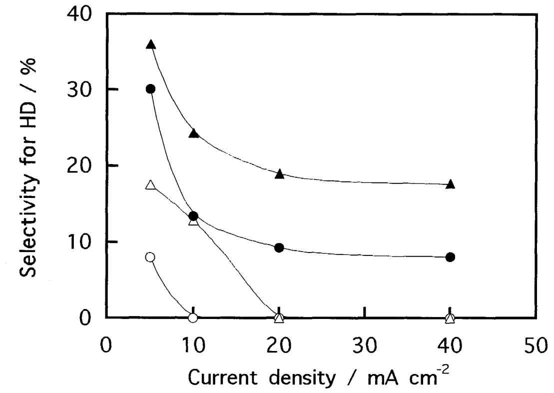

Figure 3. Selectivity for HD in the reduction of p-cyanobenzaldehyde on lateral-node (LN) and -loop (LL) cathodes. Ultrasound oscillating power : ○, 3W (LN) ; △, 3W (LL) ; ●, 6W (LN) ; ▲, 6W (LL).

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