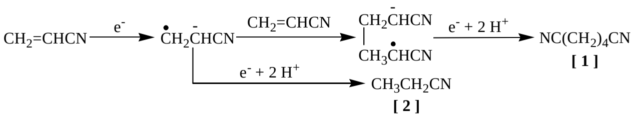
Effect of Ultrasonic Irradiation on Electroreduction of Acrylonitrile at Suspended Particle-electrode

Ryosuke Asami, Mahito Atobe, Toshio Fuchigami
Department of Electronic chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

INTRODUCTION

Suspended particle-electrode can be used to achieve a high space time-yield, since they can play a role as an electron transfer mediator and possess a large surface. Therefore, an application of suspended particle-electrode to electrolyses has been reported by several researchers[1,2]. However, the particle-electrode is usually aggregated during electrolysis in the absence of stabilizer and the total surface area of the electrode is reduced.

Meanwhile, it is well known that aggregated particles in liquid can be dispersed effectively by ultrasonic irradiation. Therefore, ultrasonic dispersion is expected to be useful for suppression of agglomeration of particle-electrode. From this point of view, in the present work, the effect of ultrasonic irradiation on the electrolysis at suspended particle-electrode was examined using a model reaction such as the electroreduction of acrylonitrile at Pb particle-electrode (Scheme 1).



Scheme 1. Mechanism for the electroreduction of acrylonitrile to adiponitrile (**1**) and propionitrile (**2**).

EXPERIMENTAL

A divided H-type glass cell with a glass frit diaphragm in a cooling bath was equipped with Pb feeder cathode (4 mesh, 2 cm^2), a platinum plate anode (3 x 4 cm^2), a rotating magnetic stirrer, and an ultrasonic stepped horn (diameter, 13 mm) connected with a PZT oscillator (20 kHz). The horn was vertically positioned 6.5 cm apart from the cathode surface.

Acrylonitrile (1.0 M) was galvanostatically electrolyzed at 700 mA of current in a 3.0 M tetraethylammonium *p*-toluenesulfonate solution (120 cm^3) in the presence and absence of Pb particle-electrode (1 g, 100 mesh) by passing 7.5 x 10^{-3} F mol^{-1} of charge at 23 ± 2 ^oC at 1000 rpm of stirring speed under ultrasonic irradiation with 30 W of intensity, unless otherwise stated.

RESULTS AND DISCUSSION

Fig. 1 shows linear sweep voltammograms obtained at Pb feeder cathode for the reduction of acrylonitrile. By addition of Pb particle-electrode, the cathodic current for the reduction was increased, and moreover the cathodic current was further increased by ultrasonic irradiation.

Subsequently, we carried out the macro-scale electroreduction of acrylonitrile. Although current efficiency was not affected by addition of Pb particle-electrode and ultrasonic irradiation, the product selectivity for adiponitrile was found to be increased by addition of Pb particle-electrode and further increased by ultrasonic irradiation as shown in Table 1.

It is known that the reactivity of electrolysis at suspended particle-electrode depends on its effective surface area. Therefore, Pb particles before and after electrolysis were observed by microscope (See Fig. 2).

As shown in Fig. 2, the Pb particle-electrode was aggregated during the electrolysis without ultrasonic irradiation but agglomeration during the electrolysis was suppressed under ultrasonic irradiation.

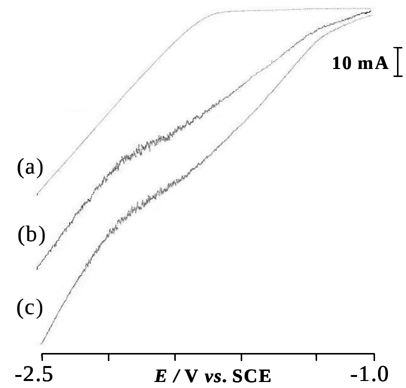


Fig. 1 Linear sweep voltammograms obtained at Pb feeder cathode for electroreduction of 1.0 M acrylonitrile in a 3.0 M tetraethylammonium *p*-toluenesulfonate aqueous solution at 1000 rpm of stirring speed at scan rate of 5 mV s^{-1} (a) without and (b) with 1 g Pb particle in silence, and (c) with 1 g Pb particle under ultrasonic irradiation.

Table 1 Current efficiency (C.E.) and product selectivity ([1] / [2]) in the macro-scale electroreduction of acrylonitrile

Lead powder [g]	Agitation[b]	C.E. (%) [a] [1]	[2]	Total	Selectivity of [1] / [2]
0	Mec	39.7	20.8	60.5	1.91
0	Mec+ US	41.8	21.5	63.3	1.95
0.2	Mec	39.1	21.8	60.9	1.79
0.2	Mec+ US	43.4	19.1	62.5	2.27
0.5	Mec	42.7	19.7	62.4	2.17
0.5	Mec+ US	44.4	16.1	60.5	2.77
1.0	Mec	44.6	17.0	61.7	2.62
1.0	Mec+ US	44.8	12.5	57.2	3.60

a) Determined by GC.
b) US : Ultrasonic irradiation at 30 W cm^{-2}, Mec : Mechanical Stirring at 1000 rpm.

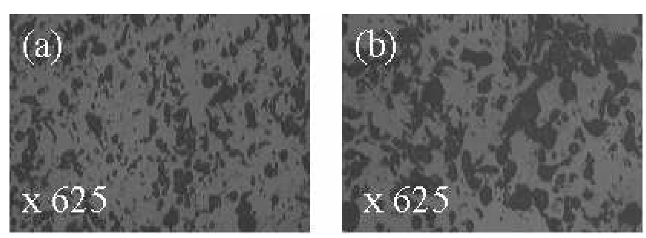


Fig. 2 Microscope photographs of Pb particle-electrode after electrolysis (a) with and (b) without ultrasonic irradiation.

From these facts, ultrasonic effect on the product selectivity can be explained as follows.

As previously mentioned, the effective surface area of the particle electrode is increased by ultrasonic irradiation. An increase in the effective surface area of electrode results in the decrease in the current density. Generally, the electrolysis in low current density promotes formation of the product consuming the smaller number of electrons per substrate. Therefore, the product selectivity for **1** was increased by ultrasonic irradiation in the electroreduction of acrylonitrile at suspended particle-electrode.

References

1) T. Hirai, I. Tari, *Kagakusosetsu* **7**, 111 (1975).
2) Z. Ogumi, *et al*., *J. Appl. Electrochem*. **35,**165 (1976)