Observation of Noise Generation Induced in Ultrasonic Cavitation with Ultramicroelectrode

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Voltammetric measurements at a platinum ultramicroelectrode were performed in the presence of intense ultrasound. Fast Fourier transform (FFT) of the voltammetric data shows that the subharmonics and the second harmonics of the fundamental frequency were generated when the ultrasound intensity exceeded a cavitation threshold.

The effect of intense ultrasound on electrochemical processes is a field which is attracting much attention in both fundamental and applied research recently. When a liquid is irradiated with ultrasound of high intensity, it may be rupture to form bubbles or cavities. The phenomenon is called acoustic cavitation which is accompanied by generating extreme local temperature (~ 5000 K) and pressure (~ 500 atm) on a submicrosecond time scale.[1] In general, ultrasound do not directly induce the chemical reactions, but the cavitation may cause the thermal activation of molecules or generation of radicals which can significantly affect the electrochemical processes. From the results of previous studies, these effects have included the enhanced mass transport,[2] product-selectivity control in electrosynthetic reaction [3,4] and unusual homogeneous solution reactivity.[5]

Cavitation is a very complex physical and chemical phenomena, which is always accompanied by intense noise emission. According to a proposed theoretically model from numerical computing,[6] the noise generation seems to depend on the intensity of ultrasound, and is governed by highly nonlinear equations. In order to get a deeper understanding of the nature of cavitation bubble dynamics, it is necessary to study experimentally of the noise generation process. However, the rare investigation by electrochemical techniques has been involved in this area.

In this work an alternative method for the study of cavitation induced noise with ultramicroelectrodes is presented. Ultramicroelectrodes are essentially suited for the investigation of cavitation events at the solid/liquid interface because they are small enough on comparing with the cavitation bubbles.[7] Moreover, as the currents measured at ultramicroelectrodes are so small that the signals at noise level are easily recorded. Thus, they might be used as a probe for the observation of acoustic cavitation noise.

An ultrasonic cell homogenizer (Taitec Co., Model VP-5S) capable of operating up to 50 W at 20 kHz was used as a supply of ultrasound. Electrochemical experiments were performed using a electrochemical workstation (CH Instruments, USA, Model 660) with three-electrode arrangement. The working microdisk electrode was fabricated by sealing a platinum fiber (12 μm diameter) in a glass tubing and was introduced into a Pyrex cell (20 ml) from the bottom facing a ultrasonic titanium horn tip (2 mm diameter). The distance between the working electrode and the ultrasonic horn tip was adjusted to 4 mm with a XYZ-positioner. The cell was filled with 10 ml of acetonitrile solution containing 1 mM ferrocence and 0.1 M tetraethylammonium perchlorate (TEAP) supporting electrolyte. A platinum counter electrode and a Ag/AgCl (3.3 M KCl) reference electrode were placed near the surface of the solution. In order to reduce the electric noise from the environment, all measurements were performed inside a Faraday cage.

Figure 1 shows the voltammograms at a platinum ultramicroelectrode for oxidation of 1 mM ferrocene with and without sonication. At the relatively low power intensity (5W), ultrasonic irradiation resulted only in a slight increase in oxidation current (Figure 1b), which was very similar to the voltammograms obtained at the rotating disk electrode in absence of ultrasound. This steady-state component is more likely due to the acoustic streaming arising from alternation of sound field within the liquid and results in a pressure gradient and subsequent liquid motion. However, when the power was increased to 15 W, an extreamely enhanced mass-transport-limited current with oscillatory behavior was observed, as shown in Figure 1c. As was also observed by the other authors, [8,9] the significantly enhanced mass transfer can be explained by the effect of microjet streaming occurred when a cavitation bubbles collapsed, and the transient portion is attributed to the individual impacts of the microjets. As the power was further raised, the transient component in the voltammogram was found to be supressed (Figure 1d). In this case, the transient currents might be spatially averaged due to a large number of cavitation bubbles over the electrode surface. On comparison with conventional sized electrode, microelectrode has the advantage for examing the cavitation bubbles by monitoring the transient current. In this experimental system, the threshold power to produce cavitation was assumed to be near 15 W.

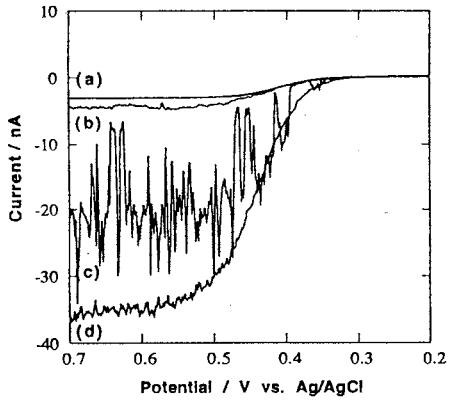

Figure 1. Voltammograms of 1 mM ferrocene at a platinum ultramicroelectrode obtained at the ultrasonic power level of a) 0W, b) 5 W, c) 15 W and d) 30 W.

From the voltammograms in Figure 1, however, there is not any information associated with the acoustic noise. As the measurements with fast scan cyclic voltammetry were typically limited to the millisecond time scale, it should be available for

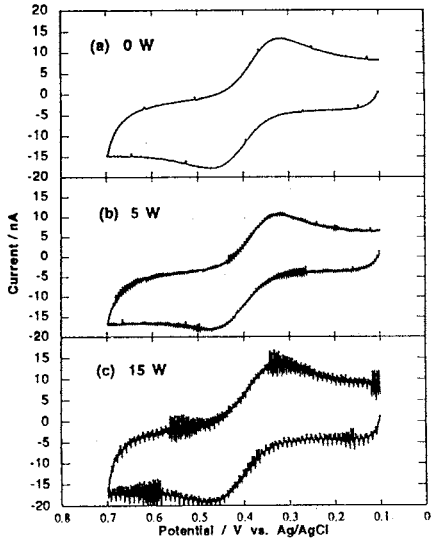

Figure 2. Voltammograms of 1 mM ferrocene at a scan rate of 100 V/s under the ultrasonic output power level of a) 0 W, b) 5 W and c) 15 W.

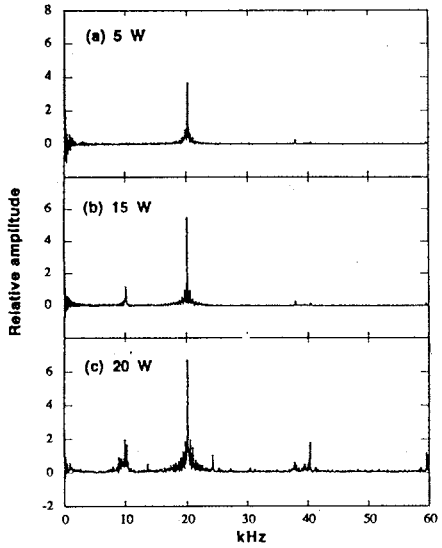

Figure 3. FFT spectra of the noise components from the voltammetric data obtained at the ultrasonic output power level of a) 5 W, b) 15 W and c) 20 W.

recording the alternating current (a.c.) component in a frequency up to 1000 kHz. Figure 2 illustrates the representative cyclic voltammograms of the redox couple of ferrocene/ferrocenium at a scan rate of 100 V/s, obtained in the same system as in Figure 1. In contrast to the results obtained at a lower scan rate, there are no significant peak-shape distortion and current change in the voltammograms even with 20 W ultrasonic irradiation, indicating that the electrode reaction was a diffusion-controlled process. On the other hand, however, the a.c. components was clearly recorded on the voltammograms in the presence of ultrasound.

The noise components were analyzed by fast Fouier transform of the voltammetric data as is shown in Figure 3. The spectra were the results subtracted from their background components in absence of ultrasound. There are several significant vibrational bands could be found in the FFT spectrum. At the relative weak ultrasound intensity (5W), the noise was mainly raised from the fundamental frequency of 20 kHz. However, as the ultrasound intensity exceeded a cavitation threshold, i.e. the output power was raised to 15 W, the half-frequency subharmonic at 10 kHz was identified. When the power was increased to 20 W, the second harmonic at 40 kHz was also observed.

Recently, Lauterborn and Suchla have investigated theoretically the generation of subhamonics, harmonics and white noise in ultrasonic fields from the view point of acoustic chaos.[6,10] The present work experimentally observed the noise in ultrasonic field for the first time with the ultramicroelectrde. It strongly supports the assumption that the cavitation is a non-linear hydrodynamic process which may generate subharmonics and second harmonics. Because of the high spatial resolution of the ultramicroelectrode, further study about the noise distribution around the ultrasound source is now in progress.

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