New Chronoamperometric Technique Using Laser Ablation

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New chronoamperometry, in which a diffusion layer is renewed with laser ablation of an electrode surface, was compared with conventional potential step chronoamperometry. While the two methods gave similar current–time curves obeying the Cottrell equation for oxidation of hexacyanoferrate(II), only the new method gave the well-defined current–time curve for oxidation of ascorbic acid, which has a tendency to foul the electrode surface.

Recently, lasers have been widely used in electrochemistry.[1] However, its usage has mainly aimed to activate an electrode but has not been appreciably concerned with the methodological development. We employed laser irradiation in order to develop new voltammetry as well as to activate the electrode and proposed laser ablation voltammetry (LAV),[2] in which the voltammogram is measured by using an electrode surface periodically renewed through an ablation action caused by a strong laser pulse. Because the ablation action constantly keeps the electrode surface fresh, LAV is very effective for examining electrode reactions fouling the electrode surface. In addition to such a renewal of electrode surface, it is also expected that the ablation action can renew the diffusion layer growing on the electrode during electrolysis. In fact, a steady-state voltammogram like a polarogram obtained with a dropping mercury electrode was observed in LAV, suggesting the renewal of diffusion layer upon the ablation action. In this work, current–time (I–t) curves observed immediately after the laser ablation were closely examined by using model electrode reactions and compared with those obtained by potential step (PS) chronoamperometry.

The experimental setup was similar to that described previously.[3] A Q-switched Nd:YAG laser was used for ablating the electrode surface. The pulse width was nominally 5 ns and the spot size was ca. 6 mm in diameter at the electrode. A power of the laser pulse was measured in atmosphere with a laser power meter (OPHIR, 30A-P-SH and AN/2), and changed from 45 to 130 mJ/pulse by placing several slide glass plates for microscopy in front of the laser head. A digital oscilloscope (Tektronix, 2440) was used for monitoring the I–t curve. The monitoring was started by a Q-switched trigger signal from the laser control electronics. Although there existed a delay time of 3 μs between the Q-switched trigger signal and an output of the laser pulse, that is, a beginning of the laser ablation, the Q-switched trigger signal was taken as $t = 0$ s. A working electrode was prepared by sealing a Pt (Nilaco, 99.98 %) or Au (Nilaco, 99.95 %) wire of 0.50 mm diameter into a glass tube. The working electrode was positioned carefully by using an X-Y-Z stage with a micrometer so that a center of the electrode met that of the laser spot. The Pt and Au electrodes were used for electrooxidation of a hexacyanoferrate(II) ion, $[Fe(CN)_6]^{4-}$ and ascorbic acid (AA), respectively. All potentials in this work were measured with respect to a saturated calomel electrode (SCE) and a Pt spiral served as a counter electrode. All reagents used were of reagent grade, and all solutions were prepared with Milli-Q water (Millipore Ltd.). Before each experiment, the solution was purged with nitrogen gas (99.9%) for at least 20 min, and the electrode surface, which had been polished to a mirror finish with 0.3 μm-alumina-powder slurry, was thoroughly treated by the laser ablation in the solution. All the experiments were carried out at 25 ± 0.1 °C.
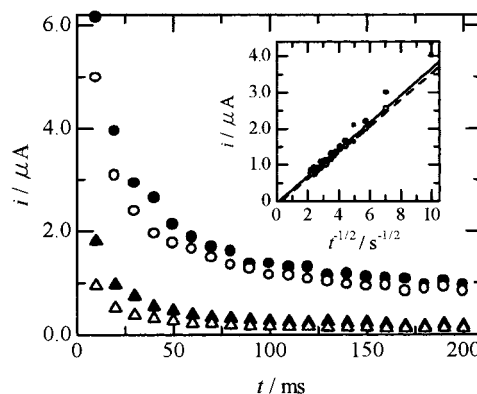

Figure 1. I-t curves and I-$t^{1/2}$ plot (inset). The circle and triangle refer to 1.0 mM $[Fe(CN)_6]^{4-}$ in 1 M KCl (sample) and 1 M KCl (blank). The solid and dotted lines were determined from the LP and PS data in the time range between 60 and 200 ms by using the least-squares method.

Figure 1 shows the I–t curves for oxidation of $[Fe(CN)_6]^{4-}$. The solid and open marks refer to laser pulse (LP) chronoamperometry at a constant potential of 0.500 V with the power of 97 mJ/pulse and PS chronoamperometry from 0 to 0.500 V. Because the cyclic voltammogram showed well-shaped oxidation and reduction waves at 0.26 and 0.18 V, the potential of 0.500 V is positive enough for the oxidation to proceed under a diffusion-controlled condition. The I–t curve obtained from the LP experiment fairly agrees with that from the PS experiment for both the sample and blank solutions in the time range between 60 and 200 ms. The current for the sample corrected by that for the blank was plotted against a reciprocal value of square root of the time, as shown in an inset of Figure 1. The plots display straight lines in the time range between 60 and 200 ms, though not passing through the origin exactly because of uncertainty of the blank correction. The straight lines suggest that the I–t curves obey the Cottrell equation.[4] The I vs $t^{1/2}$ plots at the laser powers other than 97 mJ/pulse will be discussed later. The slopes of the straight lines are in good agreement with each other, and the diffusion coefficients calculated from these slopes and a geometrical area of the electrode were 12.0×10^{-6} for LP and 11.4×10^{-6} cm^2 s^{-1} for PS. If these values are equal to the literature value of 7.8×10^{-6} cm^2 s^{-1},[5] the electrode area is effectively ca. 1.2 times larger than the geometrical one. On the other hand, the current observed in the LP experiment is somewhat larger than that in the PS experiment in the time range below 60 ms and a difference between

the currents increases with shortening time. There are two possible causes of the difference. One is an increase in area of the electrode by the laser ablation. It is, however, unlikely that only one pulse produces a further increase in the area, because the electrode is treated thoroughly by the laser ablation before the experiment. The other is an existence of an additional mass transfer process. It is reasonable that a mechanical shock accompanied by the laser ablation agitates solution around the electrode and results in more efficient mass transfer.

Electrooxidation of AA in 0.5 M (M = mol dm^{-3}) sulfuric acid was also examined with the Au electrode by LP chronoamperometry at 0.4 V and by PS chronoamperometry from 0 to 0.4 V. Figure 2 shows the I–$t^{-1/2}$ plots. While the plots obtained from the LP experiments show straight lines, the plot from the PS experiment extensively bends. Namely, the electrode reaction of AA is expected to be diffusion-controlled at 0.4 V in the LP experiment, but not in the PS experiment. The oxidation of AA is a two-electron reaction in a strong acid medium and has a tendency to foul the electrode surface.[2,3] In fact, although a cyclic voltammogram of AA in 0.5 M sulfuric acid showed a sharp oxidation wave at 0.32 V immediately after the laser ablation treatment of the electrode, broadening of the wave gradually occurred with a negative shift of the peak potential as the electrode was repeatedly used in the sample solution. This is probably because the electrode is fouled by adsorption of AA or its oxidation products. Consequently, the bending of the I–$t^{-1/2}$ plot from the PS experiment is thought to result from the fouling of the electrode surface. The diffusion coefficient of AA was calculated to be 5.0 × 10^{-6} cm^2 s^{-1} by using a slope of the I–$t^{-1/2}$ plot obtained from the LP experiment and the geometrical electrode area. This value is slightly smaller than the literature value, 6.3 × 10^{-6} cm^{2}s^{-1}.[6] Taking account of the fact that the effective electrode area is greater than the geometrical one, the experimental value becomes small further. The smaller value may be associated with a photochemical reaction of AA. Its detail is under study.
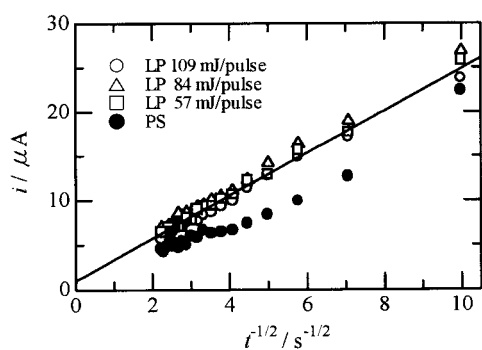

Figure 2. I-$t^{1/2}$ plots obtained by LP (open) and PS (solid) chronoamperometry. The sample solution was 5.0 mM AA in 0.5 M H$_2$SO$_4$. The solid line was determined from the LP chronoamperometric data in the time range between 60 and 200 ms by the least-squares method.

Because the I–$t^{-1/2}$ plot from the LP experiment displayed a straight line at the other laser power, similarly to the I–$t^{-1/2}$ plot shown in the inset of Figure 1, an apparent diffusion coefficient, D_{app}, was calculated at each power. In the calculation, the slope in the time range between 60 and 200 ms and the geometrical electrode area were used. Figure 3 shows a dependence of the apparent diffusion coefficient on the laser power. At the powers below 50 mJ/pulse, the coefficients are nearly zero for both the Pt
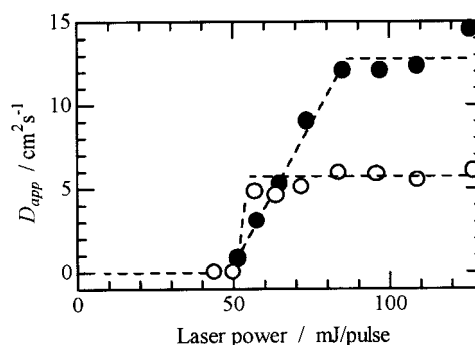

Figure 3. Dependence of the apparent diffusion coefficient on the laser power. The solid and open circles refer to the oxidation of [Fe(CN)$_6$]$^{4-}$ with the Pt electrode and the oxidation of AA with the Au electrode.

(solid) and Au (open) electrodes, indicating that the diffusion layer as well as the electrode surface is never ablated by the laser irradiation at these powers. On the other hand, the coefficient levels off at the powers from 85 to 130 mJ/pulse, which suggests that the diffusion layer can be entirely renewed. The coefficient for the Au electrode shows a jump at 50 mJ/pulse but that for the Pt electrode increases linearly in the power range between 50 and 85 mJ/pulse. It is well known that there exists a threshold in the laser ablation.[7] In the case of the Au electrode, the threshold value is clearly 50 mJ/pulse. However, the threshold is not clear for the Pt electrode because of the linear increase of the coefficient. The difference in threshold between the Au and Pt electrodes and the linear increase for the Pt electrode can be related with physical properties of the electrode material, e.g., a melting point, and durability of a crystal plane against the laser ablation. Namely, the electrode of Au with a low melting point (1064.43 °C)[8] could be entirely ablated at the powers greater than the threshold in spite of a difference in the crystal plane, whereas the electrode of Pt with a high melting point (1772 °C)[8] could be ablated stepwise depending on the durability of the crystal plane.

It has been shown that the laser ablation can renew the diffusion layer as well as the electrode surface. Further it is expected that LP chronoamperometry becomes a promising technique for determining a diffusion coefficient of a substance which and/or whose electrolytic products have a tendency to foul the electrode.

References and Notes
1   R. L. McCreery, in "Electroanalytical Chemistry," ed. by A. J. Bard, Marcel Dekker, New York (1991), Vol. 17, pp. 306–311. R. P. Akkermans, S. L. Roberts, F. Marken, B. A. Coles, S. J. Wilkins, J. A. Cooper, K. E. Woodhouse, and R. G. Compton, *J. Phys. Chem. B*, **103**, 9987 (1999).
2   T. Hinoue, I. Watanabe, and H. Watarai, *Chem. Lett.*, **1996**, 329.
3   T. Hinoue, N. Kuwamoto, and I. Watanabe, *J. Electroanal. Chem.*, **466**, 31 (1999).
4   A. J. Bard and L. R. Faulkner, "Electrochemical Methods, Fundamentals and Applications," John Wiley & Sons, Inc. (1980), p. 143.
5   M. Kakihara, H. Ikeuchi, G. Sato, *J. Electroanal. Chem.*, **117**, 201 (1981).
6   X. Xing, T.-C. Tan, M. Shao, and C.-C. Liu, *Electroanalysis*, **4**, 191 (1992).
7   J. C. Miller and D. B. Geohegan, "Laser Ablation, Mechanisms and Applications-II," AIP Conference Proceedings 288, AIP Press, New York (1994).
8   "Handbook of Chemistry and Physics," ed. by R. C. Weast, CRC Press, Cleveland (1972), p. D-142.