Voltammetry with an Electrode Surface Successively Renewed by Laser-Ablation

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Voltammetric measurement was performed with a solid electrode surface which was renewed every several seconds by laser-ablation. The voltammograms obtained were, in appearance, quite similar to polarograms obtained with a dropping mercury electrode (DME). Oxidation waves of $[Fe(CN)_6]^{4-}$ and *L*-ascorbic acid were examined by this voltammetry.

Recently electrochemists have started to use the laser not only as a light source for spectroelectrochemical studies but also as an energy source for modifying electrode reactions. For example, laser-heating of the electrode can thermally modify various processes in the electrode reaction.[1-5] In addition, laser-ablation, which is usually achieved with a strong laser pulse, activates the electrode surface to improve a kinetic aspect of the electrode reaction.[6,7] We also have remarked such applications of the laser as the energy source and proposed the laser electrochemical detection technique.[5] In this letter, we will briefly report new voltammetry (laser-ablation voltammetry, LAV) in which the electrode surface is successively ablated with a laser pulse.

The laser used was a Q-switched Nd:YAG laser (Quantel, Brilliant ω) with nominal energy of 350 mJ per pulse at 1064 nm. The pulse width was 5 ns and a diameter of the laser beam was *ca.* 5 mm on the electrode surface. The working electrode used was a gold or platinum rod of 2 mm in diameter (Nilaco, 99.95% for gold and 99.98% for platinum) buried in a glass tube with epoxy cement. The rod end was successively polished to a mirror finish with emery paper and 0.3 μm alumina-powder-water slurry. The voltammetric measurements were performed with a potentiostat (Huso, HECS 972) and a potential sweep unit (Huso, HECS 980), which were controlled with a personal computer. In the measurement, the electrode surface was ablated every 2 s while the potential was scanned at 5 mVs^{-1}. A flask (200 cm^{-3}) with four slots served as the electrolytic cell. The working, spiral platinum counter, and saturated calomel reference electrodes were inserted into the sample solution from each slot of the flask. The laser pulse struck the electrode surface through a 5 mm-thick glass wall of the flask and the 3 cm-thick sample solution. When the electrode surface was struck with the laser pulse, various phenomena, such as intense optical emission, sound and heat generation, and generation of fine metal particles and gas bubbles, simultaneously occurred. Although it is likely that such instant and drastic phenomena affect the electrode reaction chemically as well as physically, we have not yet tried to examine the chemical effects of the phenomena. All reagents used were of reagent grade and Milli-Q water was used for preparing all sample solutions. The sample solution was purged with nitrogen gas for 30 min at least before each measurement. The measurements were performed at room temperature (20 - 25 ℃).

Figure 1 shows the LA voltammograms for a 4.90 mM (1M = 1 mol dm^{-3}) $[Fe(CN)_6]^{4-}$ and 1M KCl solution (a) and the blank solution (b). Both LA voltammograms are similar to polarograms obtained with DME. This similarity comes from four prominent features. The first is that the current largely vibrates every laser-ablation, which corresponds to the current vibration observed during a life of one mercury drop at DME. Most of the current in LAV is, however, ascribed to non-faradaic processes caused by the laser-

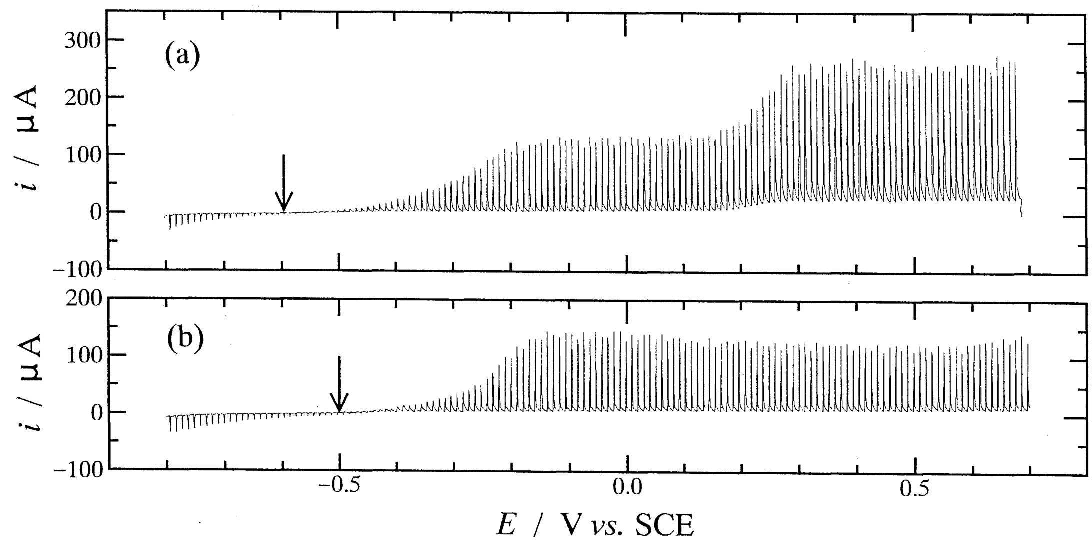

Figure 1. Laser-ablation voltammograms for the $[Fe(CN)_6]^{4-}$ solution (a) and the blank solution (b). electrode, Pt; scan rate, 5 mVs^{-1}; time constant, 0.02 s; ablation interval, 2 s. Each arrow denotes the potential at which the current reverses its direction.

ablation and is different from that in polarography in particular when faradaic processes proceed, because it is not expected that the laser-ablation extends the electrode area. The second is that the upper and lower enveloping current-potential curves which are drawn from the current vibrations look like Nernstian curves. (see Fig. 1(a)) In fact, the log-plot analysis of the lower curve around the inflection point indicated a half-wave potential and a slope to be 0.22 V and 59 mV, respectively. The third is that a limiting current can be observed, which is because the diffusion layer is renewed at each laser-ablation. In Fig. 1(a), the limiting current is seen in the potential range more than 0.3 V, which was proportional to the concentration of $[Fe(CN)_6]^{4-}$. The last is that a potential appears at which the current reverses its direction from cathodic to anodic. It is likely that this potential corresponds to the potential of zero charge (pzc), because if there is any electric charge at the electrode-electrolyte interface, thermal and mechanical agitation of ions at the interface followed by laser-ablation should be compensated with the corresponding charging current under the potential-controlled experiment.

MaCreery *et al.*[6,7] showed that when a carbon electrode was hit with intense laser pulses, the surface was activated, leading to a marked improvement of the oxidation wave for *L*-ascorbic acid. We also observed this fact with a gold electrode. Figure 2 shows a change of the voltammogram for *L*-ascorbic acid with the elapse of time after laser-ablation. The oxidation wave displayed a sharp and single peak immediately after the laser-ablation, but the peak split into two broad peaks and each peak potential shifted to a more positive potential, as the time elapsed. In the study on oxidation of *L*-ascorbic acid with a gold electrode treated electro-chemically in a hydrochloric solution,[8] scanning electron micro-scopic observation indicated that crystallization of the electrode surface by the electrochemical treatment caused the sharp wave. The sharp oxidation wave observed here, therefore, seems to be due to partial crystallization of the electrode surface caused by laser-ablation. Such a chronological change of the voltammogram could not be found for the $[Fe(CN)_6]^{4-}$ solution, however. This change is under further investigation.

Figure 3 shows the LA voltammograms for the 4.01 mM *L*-ascorbic acid and 0.5 M sulfuric acid solution (a) and the blank solution (b). As expected from the above discussion, a Nernstian curve was observed on the electrode successively renewed by laser-ablation, (see the lower enveloping current-potential curve in Fig. 3(a)) though the upper curve showed the complicated structure similar to that for the blank solution. The half-wave potential and the slope were determined to be 0.29 V and 30 mV, respectively. The slope of 30 mV implies that the oxidation of *L*-ascorbic acid proceeds *via* a two-electron transfer process. It is remarkable that the limiting current in the lower enveloping curve was constant over the wide potential range from 0.3 to 0.9 V.

Finally, we summarize advantages and possibilities of LAV. (1) Because the electrode surface is periodically renewed by laser-ablation, a reproducible voltammogram can be readily obtained for any kinds of solid electrodes. (2) The LA voltammogram closely resembles the polarogram in essence as well as in appearance. (3) LAV is very sensitive to the presence of charges on an electrode surface, leading to the determination of pzc.

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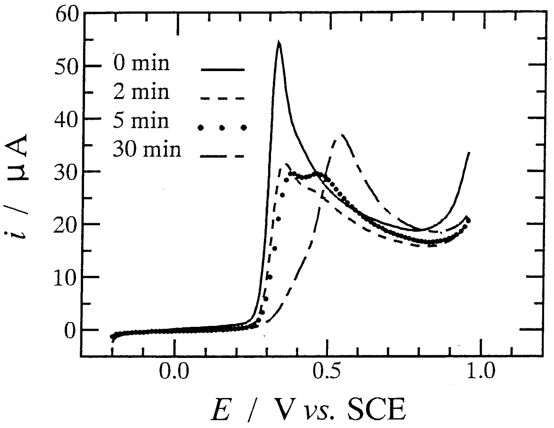

Figure 2. Chronological change of the linear sweep-voltammogram for *L*-ascorbic acid after laser-ablation. Electrode, Au; scan rate, 50 mVs^{-1}.

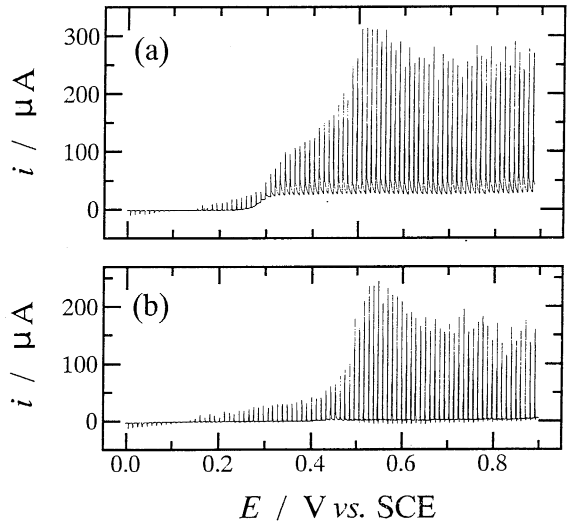

Figure 3. Laser-ablation voltammograms for the *L*-ascorbic acid solution (a) and the blank solution (b). Electrode, Au; scan rate, 5 mVs^{-1}; time constant, 0.02 s; ablation interval, 2 s.

References and Notes

1 B. Miller, *J. Electrochem. Soc.*, **130**, 1639 (1983).
2 J. L. Valdes and B. Miller, *J. Phy. Chem.*, **93**, 7275 (1989).
3 V. A. Benderskii and G. I. Velichko, *J. Electroanal. Chem. Interfacial Electrochem.*, **140,** 1 (1982).
4 J. F. Smalley, C. V. Krishnan, M. Goldman, and S. W. Feldberg, *J. Electroanal. Chem. Interfacial Electrochem.*, **248,** 255 (1988).
5 T. Hinoue, R. Harui, T. Izumi, I. Watanabe, and H. Watarai, *Anal. Sci.*, **11**, 1 (1995).
6 M. Poon, R. L. MaCreery, and R. Engstrom, *Anal. Chem.*, **60**, 1725 (1988).
7 R. J. Rice, R. L. MacCreery, *Anal. Chem.*, **61**, 1637 (1989).
8 T. Izumi, I. Watanabe, and Y. Yokoyama, *J. Electroanal. Chem. Interfacial Electrochem.*, **303**, 151 (1991).