Potential of Zero Charge of a Molybdenum Electrode by Laser Ablation Voltammetry

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(Received June 16, 2000; CL-000593)

We found that a zero-current potential, ZCP, in the laser ablation voltammogram agreed with a potential at which a differential capacitance component showed a minimum in the corresponding phase-selective ac voltammogram at the Mo electrode in phosphate buffer. This fact suggests that the ZCP is identical with the potential of zero charge (pzc). A pH dependence of the ZCP for the Mo electrode is discussed in terms of specific adsorption of a hydroxide ion.

The pzc of a solid electrode is an important parameter in various fields associated with electrochemistry. Thus many methods have been proposed and applied to the measurement of pzc.[1] Among them, the method evaluating a potential of minimum differential capacitance is probably most widely used. However, even in this method, there exist some difficulties, such as reproducing the electrode surface and keeping it clean. In order to overcome such difficulties, Andersen et al.[2–4] proposed an alternative for the pzc measurement and determined the pzc of many metals. In their method, the electrode surface is kept clean, because the surface is periodically scraped with a rotating sapphire bit. On the other hand, remarking that an ablation action caused by irradiation of a strong laser pulse is available for a renewal of the electrode, we have proposed laser ablation voltammetry (LAV) as a new voltammetric technique and showed that LAV is effective for investigation of electrode reactions deactivating the electrode.[5,6] Further, when a top surface of the electrode is peeled off by the laser ablation, that is, the electrode surface is renewed, a diffusion layer growing on the electrode during electrolysis is also renewed simultaneously. Taking advantage of this renewal, we have proposed a new chronoamperometric technique using the laser ablation and proved that diffusion coefficients can be determined even for substances deactivating the electrode.[7] Compton et al.[8] employed LAV in a channel flow cell to determine diffusion coefficients of electro-passivating species such as pyrrole and phenol. In the present work, based on a renewal of an electric double layer, being adjacent to the electrode surface, by the laser ablation, we propose a new method for the pzc measurement[9] and report a pH dependence of the pzc for the Mo electrode in aqueous phosphate buffer.

The experimental setup for LAV was similar to that described previously.[6] 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 determined to be ca. 100 mJ/pulse in atmosphere with a laser power meter (OPHIR, 30A-P-SH and AN/2). We have reported threshold values of Pt and Au for the laser ablation to be between 50 and 85 mJ/pulse in the same experimental setup.[7] Consequently, Mo would be ablated at 100 mJ/pulse. In fact, strong emission confirming the laser ablation was observed even with the naked eye. In order to determine the ZCP, two voltammetric techniques were attempted. One is the conventional technique, in which a current-potential curve was recorded at a scan rate of 5 mVs^{-1} while irradiating the electrode with the laser pulse at regular time intervals of 2 s (Figure 1). The other is the time-resolved technique (Figure 2). A procedure of the technique was as follows: At a given potential, irradiation of the laser pulse was repeated 6 times at intervals of 2 s. Currents induced by each laser ablation were sampled every 50 μs from the irradiation and stored in a personal computer (EPSON, PC-286VG). The 6 currents sampled at the same delay time were averaged and then one current-time curve was completed at the given potential. After the potential was stepped by 10 mV, the similar measurement was repeated. From the current-time curves obtained through such a procedure over a certain potential range, a current-potential curve at each delay time was drawn with the aid of the computer. Voltammograms obtained by the two techniques were compared in terms of reading the ZCP. As the result, the latter technique was chosen for the determination of the ZCP in this work. On the other hand, ac voltammetry was performed with a potentiostat (Huso, HECS 972), a lock-in amplifier (NF, LI-570A), and a potential sweeper (Huso, HECS 980) combined with a function generator (NF, FG-100A). A sine wave with amplitude of 10 mV and a fixed frequency being in a range from 5 Hz to 10 kHz was superimposed onto a lamp wave generated from the potential sweeper by using the function generator. After a phase dial of the lock-in amplifier was calibrated with pure resistance and capacitance, the capacitance component of the electrode-electrolyte interface was selectively measured as a function of the potential. A working electrode was prepared by sealing a Mo (Nilaco, 99.95%) wire of 0.60-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. 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.

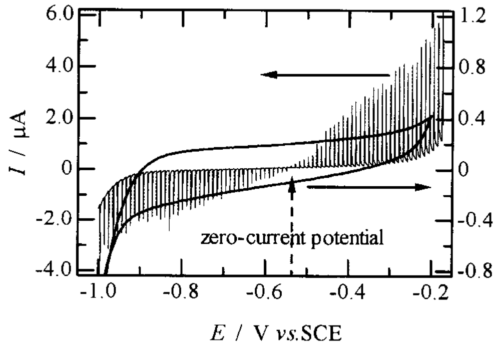

Figure 1. Conventional LA voltammogram and the corresponding cyclic voltammogram of the Mo electrode in phosphate buffer solution (pH 6.97, ionic strength 0.2 mol dm^{-3}). Scan rate, 5 mVs^{-1} for the LAV (-1.0 to -0.15 V) and 50 mVs^{-1} for the CV (-1.0 to -0.2 and -0.2 to -1.0 V), ablation interval, 2 s.

All the experiments were carried out at 25 ± 0.1 °C.

Figure 1 shows a conventional LA voltammogram and the corresponding cyclic voltammogram obtained with the Mo electrode in phosphate buffer solution (pH 6.97). As can be seen in this LA voltammogram, the conventional technique gives voltammograms exhibiting large periodic fluctuations of current caused by the laser ablation. This current fluctuation is mainly due to charging the electrode and its direction depends on the electrode potential. Strictly speaking, the total current, I_t, observed immediately after the laser ablation is expressed as follows:[2]

$$I_t = dq/dt + I_a + I_c$$

Here q is the charge on the electrode, and I_a and I_c are the anodic and cathodic currents coming from faradaic processes, such as oxidation of the electrode and reduction of impurities in the electrolyte solution. Because $I_t = 0$ at ZCP, if no faradaic processes occur, $dq/dt = 0$. This means that no change in the charge occurs during the laser ablation, and hence suggests that there would exist no charges on the electrode before the laser ablation at the ZCP. Namely, the ZCP is considered to be identical with the pzc. The cyclic voltammogram shown in Figure 1 indicates neither oxidation nor reduction waves in the potential region including the ZCP of the LA voltammogram. Consequently, the ZCP, which can be seen at –0.54 V in the conventional LA voltammogram, is expected to be the pzc of the Mo electrode.

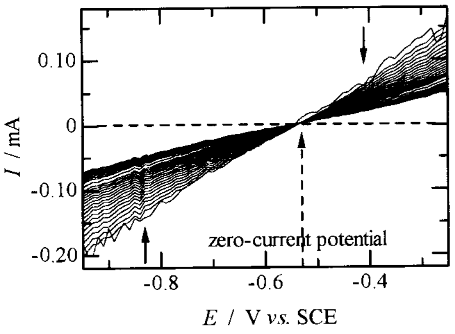

Figure 2. Time-resolved voltammograms of the Mo electrode in phosphate buffer (pH 6.97, ionic strength 0.2 mol dm^{-3}). Delay time, 50 to 1500 μs; time interval, 50 μs. According to the arrows, the delay time becomes longer.

Figure 2 shows the corresponding time-resolved voltammograms obtained according to a procedure described above. All the 30 voltammograms, measured at intervals of 50 μs from the laser irradiation, intersect at a point on the zero-current line. As can be seen from this figure, it is evident that reading the ZCP from the time-resolved voltammograms is easier and preciser than that from the conventional LA voltammogram in Figure 1. Thus, all the ZCP's were determined from time-resolved voltammograms in this work.

Figure 3 shows a pH dependence of the ZCP, E_{zcp} and the minimum capacitance potential, E_{mcp}. The minimum capacitance potentials measured at 1 kHz are representatively shown in this figure. The potentials obtained at the other frequencies were similar to those at 1 kHz. The pH dependence of the ZCP entirely agrees with that of the minimum capacitance potential. This agreement confirms that the ZCP is identical with the pzc. In a pH-potential diagram of Mo,[10] which is shown with dotted lines in Figure 3, the pH dependence of the ZCP does not exist in a region of metal Mo but in the higher oxidation state. From a viewpoint of thermodynamics, this means that the metal Mo should be oxidized to the soluble species with a higher oxidation number, that is, the electrode should be solved into the solution. However, in practice, the cyclic voltammogram showed no oxidation waves in this potential range, as described above. This contradiction is probably attributed to slow kinetics of the oxidation.

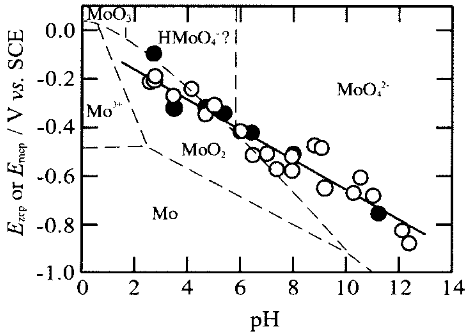

Figure 3. Dependence of the zero-current potential, E_{zcp} (open circle) and the minimum capacitance potential, E_{mcp} (solid circle). The pH-potential diagram is drawn with the dotted lines, where concentrations of the soluble species are 0.01 mol dm^{-3}.[10]

The pH dependence is linear with respect to pH with a slope of –61.9 mV/pH. It is known that specific adsorption of an anion is responsible for a negative shift of the pzc.[11] The pzc shifts to the more negative potential with increasing concentration and enhancing adsorptivity of the anion. In the present case, a hydroxide anion is expected to be specifically adsorbed one because of the negative shift. In addition, a value of 61.9 mV/pH indicates that the hydroxide ion has adsorptivity as strong as bromide and iodide ions.[4] On the other hand, the value seems to be the Nernstian slope, that is, 59 mV at 25 °C. In order to explain the negative shift with the slope similar to the Nernstian one, acid-base dissociation equilibrium on an oxide layer of the Mo electrode may be possible. Because the laser ablation induces high temperature and pressure at the electrode–electrolyte interface during a period as short as the pulse width of 5 ns, the oxide layer may be formed on the electrode. The present measurement, however, gives little information about reactions during the laser ablation because of a long time constant of the experimental apparatus. Further, it seems to be essentially difficult to distinguish a difference between the specific adsorption and the acid–base dissociation on the oxide surface. A systematic measurement of the pzc is under study using various electrode materials.

References and Notes

1 J. O'M. Bockris, S. D. Argade, and E. Gileadi, *Electrochim. Acta*, **14**, 1259 (1969).
2 T. N. Andersen, R. S. Perkins, and H. Eyring, *J. Am. Chem. Soc.*, **86**, 4496 (1964).
3 D. D. Bodé Jr., T. N. Andersen, and H. Eyring, *J. Phys. Chem.*, **71**, 792 (1967).
4 T. N. Andersen , J. L. Anderson, and H. Eyring, *J. Phys. Chem.*, **73**, 3562 (1969).
5 T. Hinoue, I. Watanabe, and H. Watarai, *Chem. Lett.*, **1996**, 329.
6 T. Hinoue, N. Kuwamoto, and I. Watanabe, *J. Electroanal. Chem.*, **466**, 31 (1999).
7 M. Ohno and T. Hinoue, *Chem. Lett.*, **2000**, 752.
8 Q. Fulian and R. G. Compton, *Anal. Chem.*, **72**, 1830 (2000).
9 We have already reported a preliminary study of the pzc measurement using laser ablation at the 74th Annual Meeting of the Chemical Society of Japan, Tanabe-Kyoto, March 28, 1998, Abstr., 353.
10 "Denkikagaku Binran," ed. by Denkikagaku Kyokai, Maruzen, Tokyo (1985), p. 117.
11 For example, A. J. Bard and L. R. Faulkner, "Electrochemical Methods, Fundamentals and Applications," John Wiley & Sons, Inc., New York (1980), p. 513.