

# Ellipso-Microscopic Observation of Titanium Surface under UV-Light Irradiation

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The ellipso-microscopic observation of a titanium surface undergoing anodization in 0.05 mol dm<sup>-3</sup> of H<sub>2</sub>SO<sub>4</sub> was conducted. During irradiation by ultra-violet (UV) light with a wavelength of 325 nm, the titanium surface allowed for the flow of a photo-induced current and showed up as a bright, patch-like image on an ellipso-microscopic view. The brightness and patch-pattern in the image changed with flowing photo-induced current. The changes in the brightness and the image corresponded to the formation and/or degradation of titanium oxide due to the photo-electrochemical reaction of the oxide. An *in situ* monitoring using the ellipso-microscope revealed that the film change was dependent on the irradiation light power, by UV-light increases the anodic current and results in the initiation of pitting at lower potentials as compared with the non-irradiated condition.

**Keywords :** *ellipso-microscopy, UV-light, passivity, titanium, photo-corrosion, non-uniformity*

## 1. Introduction

Titanium is covered with chemically stable oxide film on the surface and shows a superior corrosion resistivity in general. Thus, titanium and titanium alloy are frequently used as materials for bridge and roof in seashores. Titanium oxide has an n-type semiconductive property<sup>1)</sup> and the Schottky-barrier is formed on the oxide surface by anodic polarization of titanium substrate. However, under sunshine condition, the materials are exposed to irradiation with UV and visible lights. It is considered that the photo-induced current is flowed, resulting in photo-induced corrosion. Ohtsuka and Otsuki reported an effect of UV-light irradiation on photo-corrosion of anodic oxide films on titanium in H<sub>2</sub>SO<sub>4</sub><sup>2)</sup>. Electrochemical ellipsometry with UV-light irradiation on the oxide revealed that the irradiation increased anodic current and induced oxide dissolution. They suggested that UV-light irradiation resulted in occurrence of non-uniform corrosion. Recently, the authors developed an electrochemical ellipso-microscope to monitor an electrode surface and reported non-uniform change of anodic oxide film on titanium<sup>3)</sup>. Degradation of oxide film due to bromo-oxide formation as well as growth of the film was observed as a change in optical condition of the ellipso-microscope. In this study, ellipso-microscopic imaging

of the oxide surface on titanium with current measurement was carried out in order to clarify the effect of UV-light irradiation on titanium. By the ellipso-microscopy, we detected heterogeneity of the surface oxide from the brightness of a polarized reflection light depended on the thickness and optical property of the microscopic site.

## 2. Experimental Procedure

### 2.1. Material and electrochemistry

A titanium plate or a titanium wire (Nilaco) with a purity of 99.5 % was used as a specimen. The specimen surface (2 mm x 0.5 mm or 0.5 mm in dia.) was polished with grinding discs (Struers) and burnished with colloidal silica of 0.04 μm in particle size. The surface orientation was identified by an Auger electron spectrometer (AES; JAMP-9500F, JEOL) equipped with an electron backscatter diffraction (EBSD; SC-200, TSL) detector.

The electrolyte used was 0.05 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solution or a solution containing 2 mol dm<sup>-3</sup> KBr deaerated by bubbling with pure Ar gas before measurement. The specimen was set as a working electrode at the bottom of a three-electrode-type electrochemical cell. The cell had three parallel quartz plates for optical windows. A Pt wire was used as a counter electrode. An Ag/AgCl/saturated KCl electrode (SSE) was connected with a Luggin-Haber capillary and used as a reference electrode. The specimen was polarized by using a Solartron potentiostat (SI1287)

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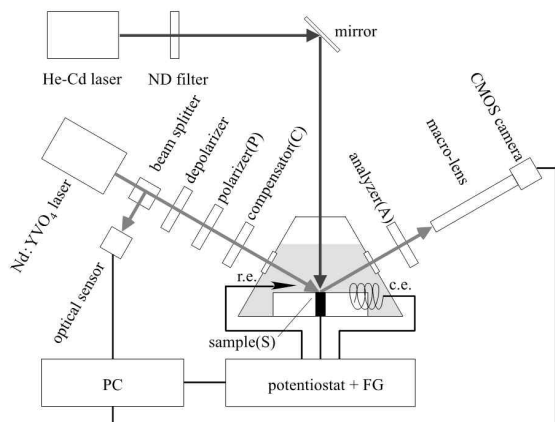


Fig. 1. Schematic diagram of the experimental set-up used.

in an air-conditioned room at 295 K. Potentiodynamic polarization was carried out with a potential sweep rate of  $5 \text{ mVs}^{-1}$  from an open circuit potential to 10 V. Potentiostatic polarization was also carried out after potentiostatic polarization at 4 V for 1.8 ks. After the polarization, the specimen surface was rinsed with Milli-Q water and immediately subjected to AES for surface analysis.

## 2.2. Ellipso-microscopy

A schematic diagram of the ellipso-microscope used in this study is shown in Fig. 1. The most of parts for ellipso-microscopy was similar to the apparatus reported previously<sup>3</sup>. Monochromatic light beam with a wavelength of 532.0 nm passing through a polarizer (P) and compen-

sator (C) was specularly reflected at the specimen (S) surface immersed in solution in the electrochemical cell at an incident angle of  $60.0^\circ$  and guided to an analyzer (A). The null ellipsometric condition of PCSA optical configuration was established by controlling azimuths of P and A with an azimuth of C at  $45.0^\circ$  before polarization of the specimen. The surface change was monitored by light intensity deviated from the initial null condition under the initial azimuths of P, C, and A. The spot light intensity change through the PCSA configuration was measured by a 3.2 M pixels CMOS camera with a macro lens. In addition to above optics for ellipso-microscopy, UV-light emitting from He-Cd laser with a wavelength of 325.0 nm and an output power of 8 mW was irradiated on the sample surface through a mirror and an optical window. The power of the incidence UV light was reduced to 80, 70, and 50 % by neutral density filterers.

## 3. Results and Discussion

### 3.1. Photo-induced anodic current

Anodic polarization of titanium in aqueous solution induces formation of an oxide film on the titanium surface and the oxide film suppresses the anodic current flow. After the potentiostatic polarization of titanium at 4 V(SSE) in  $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ , anodic current was less than  $10^{-5} \text{ A cm}^{-2}$ . Electrochemical ellipsometric measurement<sup>4</sup> revealed that titanium oxide film with an average thickness of 10 nm was formed at 4 V in  $\text{H}_2\text{SO}_4$ . Fig. 2 (a) shows

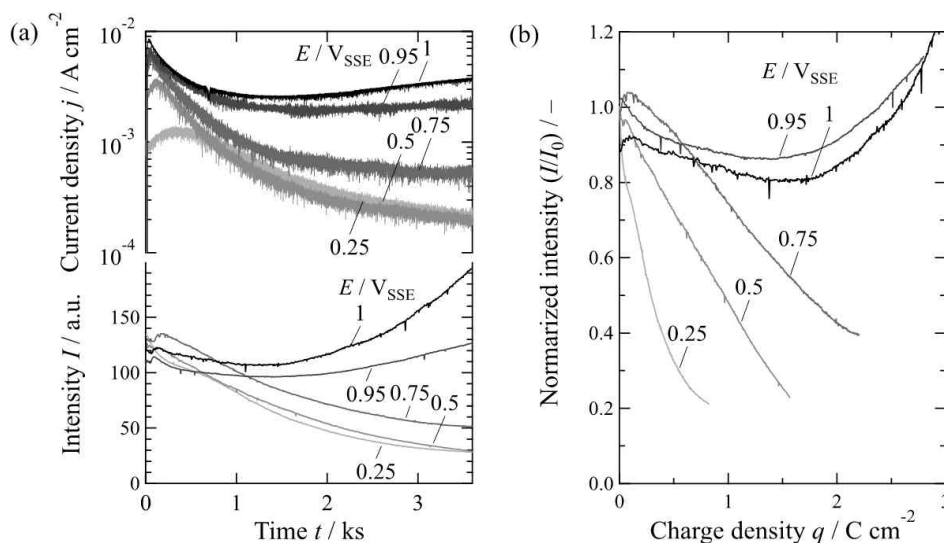
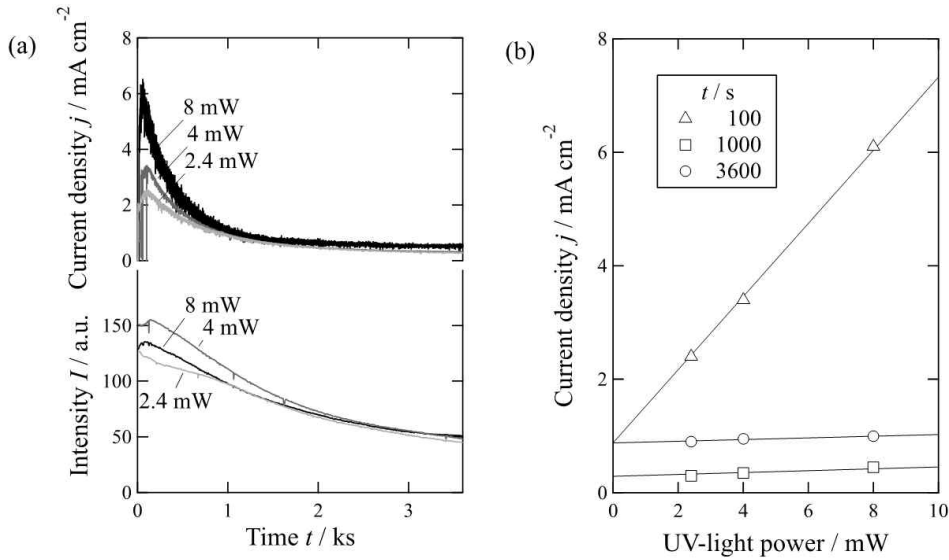


Fig. 2. (a) Time variations of current density and total light intensity of an ellipso-microscopic image during UV-light irradiation of 8 mW and potentiostatic polarization at 0.25, 0.5, 0.75, 0.95 or 1 V(SSE) in  $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Before the UV-light irradiation, titanium was polarized at 4 V(SSE) for 1.8 ks. (b) Relation between total light intensity normalized by the intensity when irradiation of UV-light commenced.

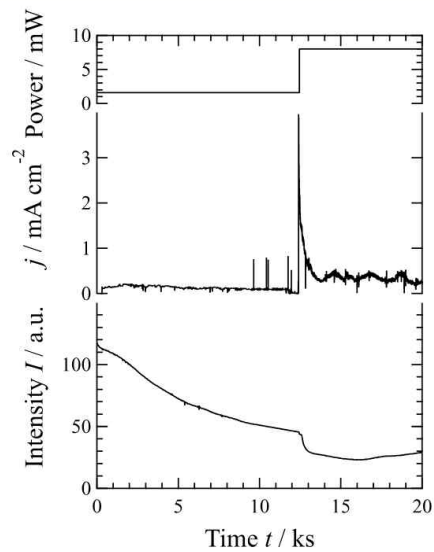


**Fig. 3.** (a) Time variations of current density and total light intensity of an ellipso-microscopic image during UV-light irradiation and potentiostatic polarization when power of UV-light was changed by a ND filter as 2.4, 4 or 8 mW. Before the UV-light irradiation, titanium was polarized at 4 V(SSE) for 1.8 ks. (b) Relation between current density and UV-light power after the irradiation for 0.1, 1 and 3.6 ks.

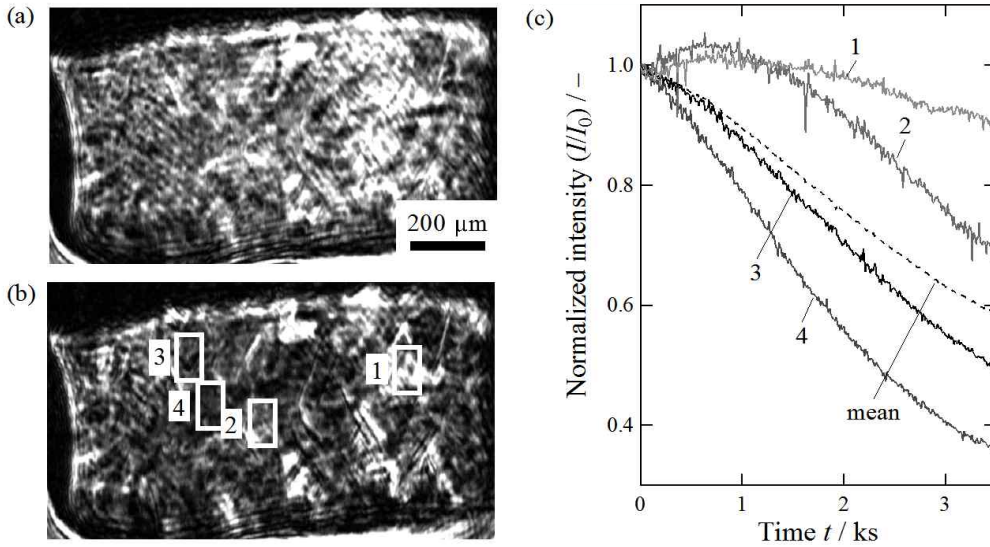
time variations of anodic current density and total light intensity of the ellipso-microscopy during UV-light irradiation under the potentiostatic condition at various potentials in H<sub>2</sub>SO<sub>4</sub> after the potentiostatic polarization at 4 V(SSE). Anodic current initially by UV-light irradiation under potentiostatic polarization at potentials lower than that for oxide film formation and the changes depending on the polarization potential. At the lower potentials lower than 0.75 V, the UV-light induced current decreases gradually by time while it turns to increase after ca. 1 ks at the higher potentials than 0.95 V. The total light intensity of ellipso-microscopic image also changes, indicating that the oxide film changes in thickness and optical property. The change depends on the applied potential. After the commencement of UV-light irradiation, the intensity of some samples slightly increases, although the change of the intensity could be seen to vary with the identity of the sample. The intensity gradually decreases with time at lower potentials but turns to increase at higher potentials. The light intensity normalized by the initial intensity at the commencement of UV-light irradiation has a linear relationship with charge density consumed during the polarization during the UV-light irradiation (Fig. 2 (b)). The negative slope of line means that the oxide film on titanium is degraded or thinned due to the irradiation. The slope is steep at lower potentials but it becomes gentler as the applied potential increases. At the higher potentials, the slope shows a bending point and then turns to be positive, indicating that the oxide film resumes to thicken.

UV-light assisted oxidation might be effective to form a protective oxide film on titanium.

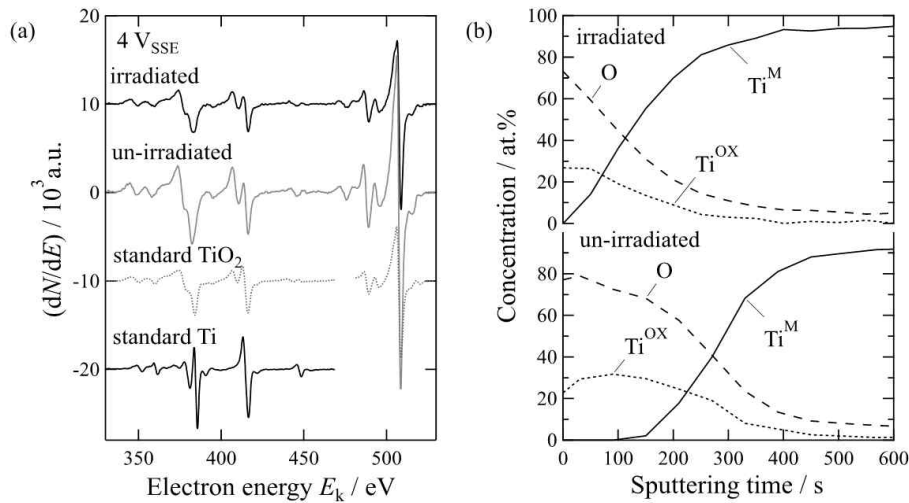
Fig. 3 (a) shows time variations of the induced current and light intensity of ellipso-microscopic image when power of UV-light intensity is decreased using ND filters. Although the photo-induced current increases with increase in UV-light power at the initial period, it is in-



**Fig. 4.** Time variations of (a) power of UV-light irradiated, (b) current density and (c) total intensity of an ellipso-microscopic image when titanium was polarized at 4 V(SSE) and UV-light power is switched from 1.6 mW to 8 mW.



**Fig. 5.** Ellipso-microscopic images of titanium surface polarized at V(SSE) (a) before and (b) after UV-light irradiation with a power of 8 mW. Before the imaging, the surface was polarized at 4 V(SSE) for 1.8 ks. (c) time variation of the mean and partial light intensity of squares 1–4 in (b) normalized by the intensity at UV-light irradiation commencement. EBSD patterning assigned squares 1 and 2 as (XXX0) grain and squares 3 and 4 as (0001) grain, respectively.

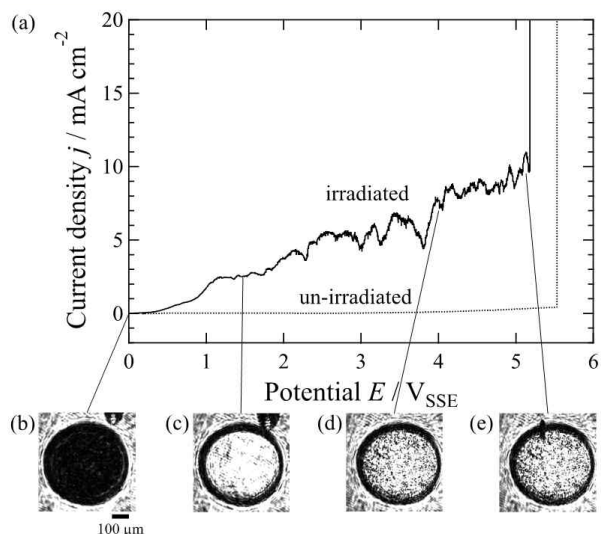


**Fig. 6.** (a) AES differential energy spectra of titanium surface polarized at 4 V(SSE) for 1.8 ks before or after UV-light irradiation with a power of 8 mW and polarization at 1 V for 3.6 ks. (b) Depth profile of titanium surface when the surface was sputtered with Ar<sup>+</sup> ions.

dependent of UV-light power after 1 ks (Fig. 3 (b)). The light intensity decreases with time and photo-induced current. However, the light intensity after 1 ks is independent of UV-light power. It is suggested that photo-induced current is limited and UV-light power more than 2.4 mW is an excess to induce photo-electrochemical reaction.

Fig. 4 shows time variations of current and light intensity of ellipso-microscopic image when the UV-light

power was increased from 1.6 mW to 8 mW. Immediately after the increase in UV-light power, photo-induced current jumps and the light intensity decreases. However, the decrease in light intensity is suspended with decrease in current. No or less change in light intensity occurs, though fluctuation of anodic current is observed. The photo-induced film degradation and the film formation seem to be in a steady state, suggesting that the oxide film is aged in this condition.



**Fig. 7.** (a) Time variations of the current during the dynamic polarization of titanium at  $5 \text{ mVs}^{-1}$  in  $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  containing with  $2 \text{ mol dm}^{-3} \text{ KBr}$  when the titanium surface was irradiated with UV-light with a power of  $8 \text{ mW}$  or not. (b-e) Ellipso-microscopic images of titanium disc electrode during the UV-irradiation and polarization.

### 3.2. Non-uniform degradation

Fig. 5 (a) shows an ellipso-microscopic image of titanium surface before UV-light irradiation. It is clear that the oxide film was formed non-uniformly depending on surface texture, though some moirés are also observed. The non-uniform formation of oxide film on titanium was discussed previously<sup>3</sup>. After the UV-light irradiation for 3.6 ks, the microscopic image becomes more non-uniform and darker (Fig. 5 (b)), indicating that photo-induced oxide degradation is strongly dependent on substrate texture. Although the mean light intensity of whole ellipso-microscopic image is decreased by 40 %, changes in the light intensity by 10 % to 60 % are observed in a time variation of the partial light intensity normalized by area and by that at the commencement of UV-light irradiation (Fig. 5 (c)). EBSD patterning gave us the crystallographic orientation of the titanium substrate. On (XXX0) grains, the normalized light intensity increases slightly during UV-irradiation for ca. 1 ks and decreases with time while it decreases significantly on the (0001) grain. It is suggested that the oxide degradation on the (0001) grain is severer than that on the (XXX0) grain.

Raman spectroscopy of titanium surface polarized at

4 V(SSE) and irradiated UV-light for 3.6 ks was carried out to investigate the crystallinity of oxide film. Although a strong peak could be found at  $415 \text{ cm}^{-1}$  which was assigned to anatase-type of  $\text{TiO}_2$  formation<sup>5</sup>, an effect of UV-light irradiation on the crystallinity was not observed clearly from the comparison with the spectrum of un-irradiated specimen. On the other hand, AES indicates the photo-induced degradation of oxide clearer. Fig. 6 (a) shows AES spectra of titanium surfaces polarized at 4 V(SSE). Peaks at 380, 385, 418 and 503 eV are assigned to Ti-L<sub>3</sub>M<sub>2,3</sub>M<sub>2,3</sub>, Ti-shake-up line, Ti-L<sub>3</sub>M<sub>2,3</sub>V and O-KLL, respectively. Irradiated specimen shows more similar peaks to a standard anatase  $\text{TiO}_2$  rather than un-irradiated specimen. The depth profiles of atomic concentration of titanium surface reveals that a UV-light irradiated specimen is covered with a thinner oxide film less than half of un-irradiated specimen (Fig. 6 (b)). Although the mean thickness is compared here, it is in good agreement of the reported previously<sup>1</sup>.

Bromide ions contained in solution lead to a local breakdown of the anodic oxide film on titanium and to induce pitting corrosion<sup>3</sup>. Fig. 7 (a) shows time variations of current during the potentiodynamic polarization of titanium in  $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  containing  $2 \text{ mol dm}^{-3} \text{ KBr}$ . In un-irradiated condition, a stable current less than  $0.1 \text{ mA cm}^{-2}$  flows but the current abruptly jumps at potentials higher than 5.5 V(SSE) due to pitting propagation. In UV-light irradiation condition, flowing a relatively large and fluctuated current is observed, suggesting that UV-irradiation accelerates anodic current due to photo-induction. The fluctuated current jumps due to pitting propagation at potentials similar to or lower than that in un-irradiated condition. Fig. 7(b) - Fig. 7 (e) show ellipso-microscopic images of titanium disc electrode during the polarization under UV-irradiation. As the potential increases, the image becomes brighter due to film formation (Fig. 7 (c)) but it shows a non-uniform pattern (Fig. 7 (d)). The pattern becomes more significant at higher potentials (Fig. 7 (e)). The pitting initiation occurred at a site where the light intensity in the image was darker than others, indicating that the local breakdown of the oxide film was taken place at the site at which a thinner oxide was covered. The thinner oxide film forms on (0001) grain rather than on(XXX0) and the donor density in the film on (0001) grain is higher than that on (XXX0) grain<sup>6-8</sup>.

#### 4. Summary

Effect of UV-light irradiation on passivity of anodic oxide film formed on titanium in  $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  was investigated by using ellipso-microscopy. UV-light irradiation allowed to flow photo-induced current and to induce non-uniform degradation of the film depending on crystallographic orientation of the titanium substrate. Ellipso-microscopy also revealed that a local breakdown of the thinner film occurred in bromide ions-containing solution.

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#### References

1. J. W. Schultze, U. Stimming and J. Weise, *Ber. Bunsen. Phys. Chem.*, **86**, 276 (1982).
2. T. Ohtsuka and T. Otsuki, *J. Electroanal. Chem.*, **473**, 272 (1999).
3. K. Fushimi, K. Kurauchi, Y. Yamamoto, T. Nakanishi, Y. Hasegawa, and T. Ohtsuka, *Electrochim. Acta*, **144**, 56 (2014).
4. T. Ohtsuka, M. Masuda, and N. Sato, *J. Electrochem. Soc.*, **132**, 787 (1985).
5. T. Ohtsuka, J. Guo, and N. Sato, *J. Electrochem. Soc.*, **133**, 2473 (1986).
6. S. Kudelka, A. Michaelis, and J. W. Schultze, *Electrochim. Acta*, **41**, 863 (1996).
7. S. Kudelka and J. W. Schultze, *Electrochim. Acta*, **42**, 2817 (1997).
8. K. Fushimi, T. Okawa, K. Azumi, and M. Seo, *J. Electrochem. Soc.*, **147**, 524 (2000).