Degradation of Organic Coatings on Steel Investigated by Dynamic Electrochemical Impedance Spectroscopy

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ABSTRACT

Degradation of the organic coatings on steel has been investigated by the dynamic impedance measurements. The electrochemical impedance spectroscopy (EIS) has been used to evaluate the corrosion of steel coated by the organic film. Generally the electrochemical impedance of the coated steel shows complicated behavior, because the degradation of organic coating involves various steps until the steel corrodes under the coating. In the present paper, time variation of electrochemical impedance was measured to investigate the initial stage of coating degradation. The dynamic impedance was displayed on 3-dimension plots, whose axes were real and imaginary components and time. The time variation of the film resistance related to the permeation of water was monitored to discuss the corrosion mechanisms of coated steel.

INTRODUCTION

Many researchers have used the electrochemical impedance method to analyze the degradation of organic coating on metal because the corrosion under the organic film can be determined. [1-15] For example, Walter [1] discriminated between the two time constants in the impedance spectrum of the coated metal and reviewed the availability of the impedance analysis on the degradation of coating and the corrosion of coated metal.

A great number of papers were published concerning the electrochemical impedance to investigate the corrosion under the coating. However, there is no article regarding the impedance behavior during the water permeation into organic film just after the immersion in the electrolyte solution. Since the water permeation process into the organic film progresses abruptly, the time-stability of the electrode system was not satisfied while measuring the electrochemical impedance. In this paper, the degradation mechanism of the coated metal was examined by using the dynamic impedance method to obtain the correct impedance spectrum.

EXPERIMENTAL

Dynamic impedance

The surface of the carbon steel was polished with the emery paper up to the no. 2000 and rinsed by distilled water successively. The working electrode was carbon steel coated with commercial vinyl resin. The thickness of coated film was approximately 40 μm. Drying time was 1 day. The schematic of the electrochemical cell is depicted in Fig. 1(a). The coated steel was fixed in a cylindrical cell with o-ring, and immersed in 0.5 mol/dm^3 NaCl solution. The surface area of the working electrode contacted with the solution was 7 cm^2. The counter electrode was platinum wire, and the reference electrode was a wire of Ag/AgCl. The schematic of the instruments for the impedance measurements is illustrated in Fig. 1(b). Potentiostat (Hokuto, HA-501G) and frequency response analyzer (Solartron SI1254) were used to measure the impedance spectra. The frequency range of impedance was from 10 mHz to 10 kHz, and the frequency of imposed signal was scanned logarithmically at 5 point for each decade from the high frequency region. The amplitude of the sinusoidal current signal was 10 nA. The integration time was 20 at high frequency region and 1 below 1 Hz. Impedance spectrum was continuously measured 20 times, and the instantaneous impedance was decided by the following method. In the present paper, the distortion of the impedance spectrum in the low frequency region of the electrode without time-stability is corrected with 3D complex diagram. The time-stability means that the reaction rate and surface condition don't change during the impedance measurement. The time-stability of the electrode is the necessary condition for the electrochemical impedance measurement generally. Stoynov *et al.* [16] proposed the compensation method with 3D complex diagram in order to correct the distortion of the impedance spectrum in the low frequency region for the electrode without the time-stability. The 3D complex diagram has not only real and imaginary part axes but also a time axis. The impedance spectra were measured successively and plotted on 3D complex diagram. The plots were connected by the spline under tension function at each frequency (Fig. 2(a)). The cross section of 3D impedance shell perpendicular to the time axis gives the instantaneous impedance at an arbitrary time (Fig. 2(b)).

RESULTS AND DISCUSSION

Electrochemical impedance of carbon steel coated with vinyl resin

The electrochemical impedance on the complex diagram, which was measured at first scan after the immersion, of the carbon steel coated with vinyl resin presented in Fig. 3(a). The impedance spectra were measured from the high frequency region to low frequency region. Impedance can be measured in a short time in the high frequency region. Contrary to this, relatively long time is necessary for the measurement in the low frequency region, thus the impedance spectrum in the low frequency region was distorted in the case of the electrode without time-stability. Therefore, an accurate curve-fitting cannot be carried out by the equivalent circuit. In order to visualize the time variation of the impedance spectra, the impedance measured successively was presented on 3D complex diagram (Fig. 3(b)). The value of impedance is large just after the immersion. The value of impedance becomes small with time. The cross section of 3D impedance shell perpendicular to the time axis gives the instantaneous impedance at an arbitrary time. The instantaneous impedance on the complex diagram at 500 s of the carbon steel coated with vinyl resin presented in Fig. 3(c) and the distorted impedance spectrum in the low frequency region was corrected. As the amplitude of imposed ac current was 10 nA and the value of impedance was about 20 MΩ at 500 s after the immersion for

example, the ac potential response is calculated as approximately 0.2 V. Therefore, there is possibility that the linearity of the impedance analysis is not satisfied with large potential amplitude. However, because almost part of the voltage must be applied to organic film and the applied voltage to organic film/metal interface must be very small, the large potential response doesn't violate the linearity at the initial stage of the degradation. With the passage of time, the ac potential response becomes smaller than 10 mV, and the linearity is satisfied sufficiently. The instantaneous impedance of the carbon steel coated with vinyl resin at 500-1900 s was presented in Fig. 4. The instantaneous impedance shows two clear capacitive semicircles. The equivalent circuit with two time constants is assumed to perform the curve-fitting as depicted in Fig. 4. Many researchers employed the similar equivalent circuit. [6-10] On the other hand, there are some reports in which the impedance was analyzed by the other equivalent circuits. [11-15] In the present paper, the equivalent circuit presented in Fig. 4(a) was used, because it was assumed that the electrolyte penetrated in the pore of the coating and that the corrosion under the coating progressed in organic film/metal interface. The equivalent circuit used in the present analysis is composed by two time constants. R_f is film resistance of defect, C_f is capacitance of film, R_{ct} is charge transfer resistance. C_{dl} is double layer capacitance. Generally in the impedance spectrum of the coated metal, the high-frequency semicircle by R_f and C_f is concerned with the coating, and the low-frequency semicircle by R_{ct} and C_{dl} is concerned with the corrosion on metal surface. On the basis of the equivalent circuit in Fig. 4(a), the curve-fittings for the instantaneous impedance were performed by using the commercial software (Solartron, Zview). In this paper, C_f and C_{dl} were replaced with CPE (Constant phase element) and the curve-fitting was carried out for the depressed capacitive semicircles. Admittance Y of CPE is defined by the following expression:

$$Y = Q(j\omega)^\alpha \qquad\qquad (1)$$

where j is the unit of imaginary number, ω is the angular frequency, Q is the CPE constant and α is the CPE exponent. The CPE element is often used as an element that describes the distortion of the semicircle in the curve-fitting. The reason for distortion of the semicircle is mainly the roughness of electrode surface and the current distributions [17, 18]. The time variations of four parameters determined by the curve-fitting are shown in Fig. 5. R_f decreases remarkably until 2000 s after immersion. This result indicates that the electric conductivity in the organic film increases by the diffusion of electrolyte. CPE constant for film capacitance Q_f increases with the immersion time, meaning that the dielectric constant in the coating increases by involving water. R_{ct} decreases with the immersion time, as the corrosion under coating progress. CPE constant for double layer capacitance Q_{dl} increases with the immersion time, because the reactive site increased due to the corrosion at metal/coating interface. The vinyl resin used by this research is deteriorated in a short time, compared with the results by other groups [5-7]. The pre- and after-treatment were not done for organic films in the present experimental because it was expected that the degradation of organic film occured in a relative short time to verify the ability of the present dynamic impedance method.

CONCLUSIONS

Dynamic impedance spectroscopy was applied to the analysis of the degradation process of the organic coated steel. The cross section of 3D impedance shell perpendicular to the time axis gives the instantaneous impedance at an arbitrary time and the impedance spectrum in the low frequency region was corrected. The equivalent circuit was assumed for the obtained

instantaneous impedance spectra, and the curve-fitting was carried out. The deterioration mechanism of the coated metal was examined by the parameters determined by curve-fitting.

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(a)
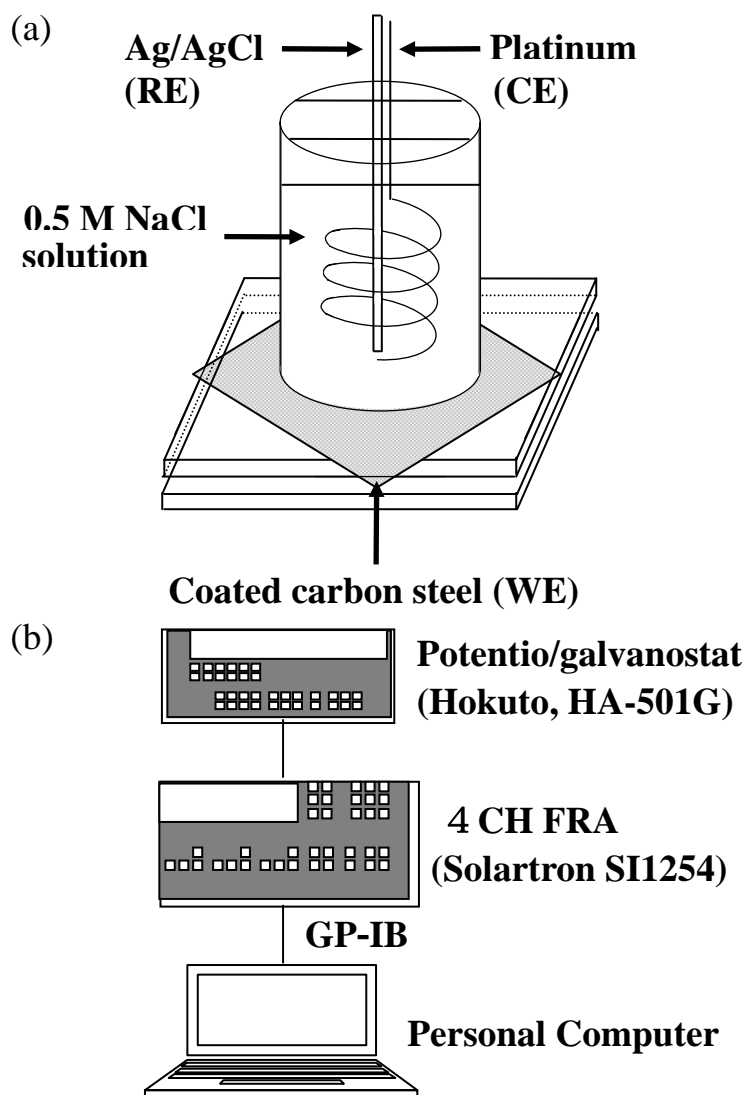
Ag/AgCl → ← Platinum
(RE) (CE)

0.5 M NaCl →
solution

↑
Coated carbon steel (WE)

(b)

Potentio/galvanostat
(Hokuto, HA-501G)

4 CH FRA
(Solartron SI1254)

GP-IB

Personal Computer

Fig. 1 (a) Scheme of the electrochemical three-electrode cell.
(b) Scheme of instruments for impedance measurement.

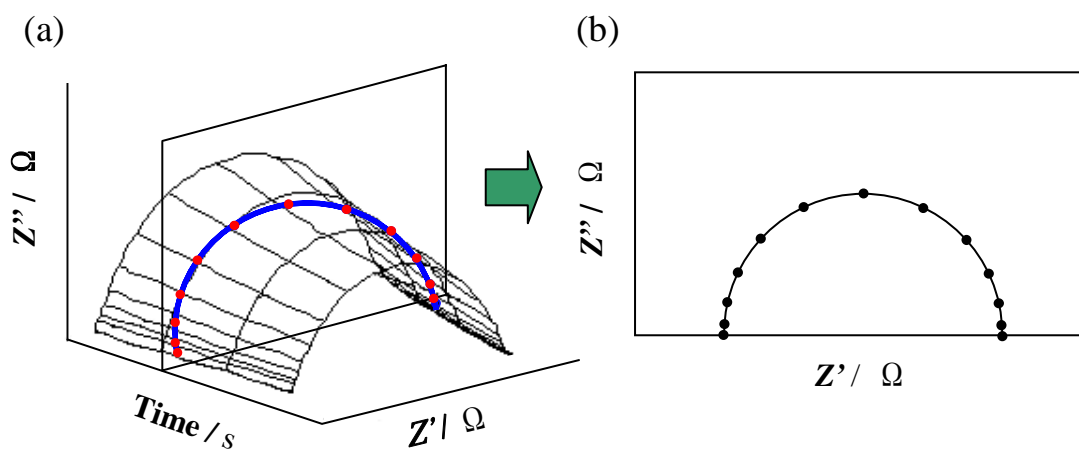(a)   (b)

Z'' / Ω

$Time$ / s Z' / Ω

Z'' / Ω

Z' / Ω

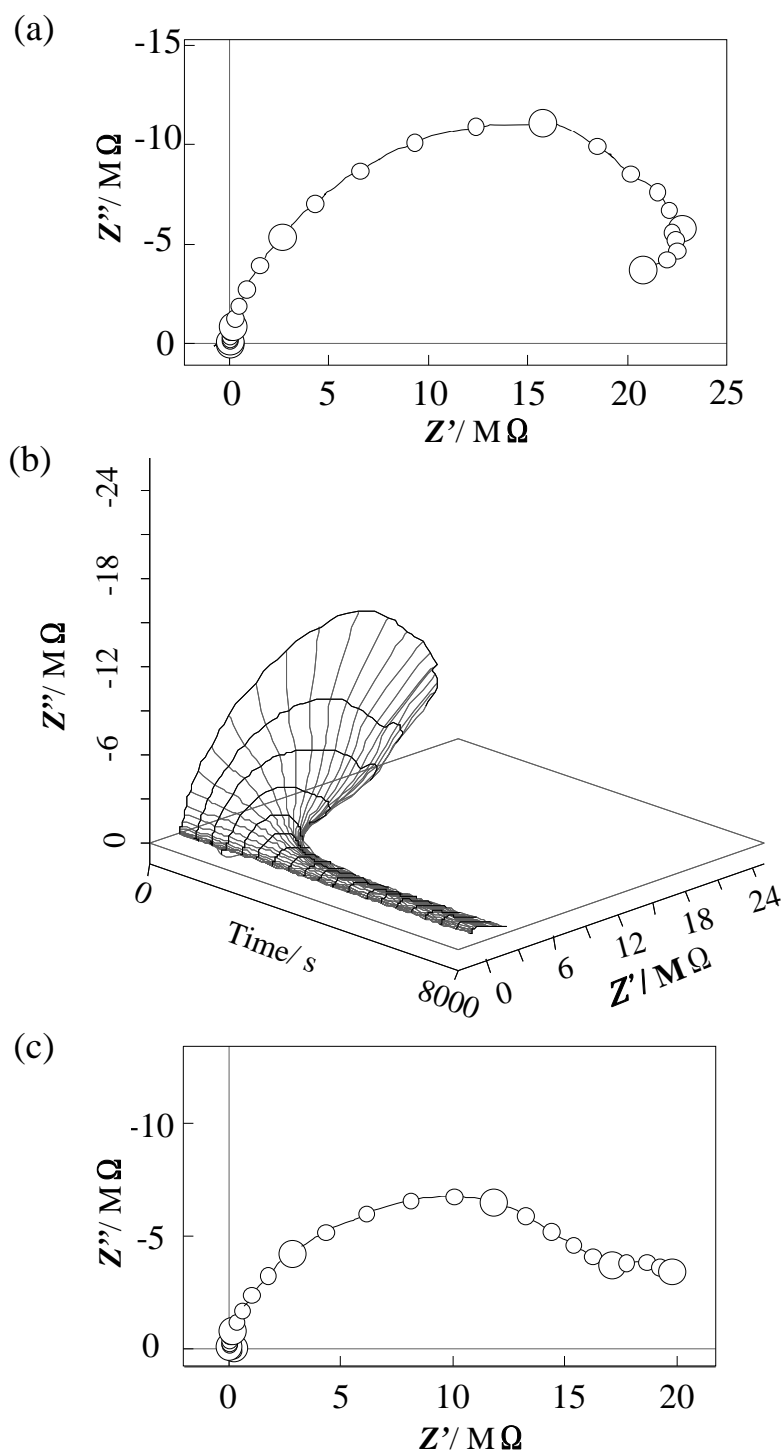**Fig. 2 (a) 3D complex diagram. (b) Instantaneous impedance**

(a)

(b)

(c)

Fig. 3 (a) Experimental result of electrochemical impedance of the carbon steel coated with viniyl resin measured just after immersion. (b) 3D complex diagram of the impedance of impedance spectra of the carbon steel coated with viniyl resin. (c) Instantaneous impedance of the carbon steel coated with viniyl resin at 500 s.
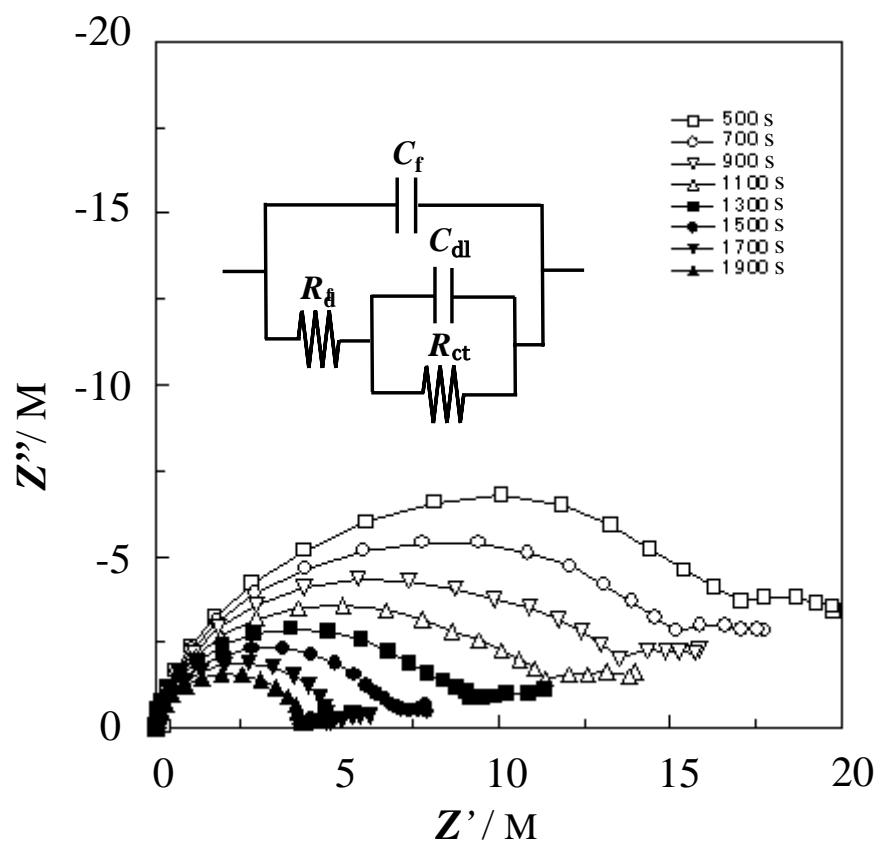
Fig. 4 Variation of Instantaneous impedance of the carbon steel coated with viniyl. Equivalent circuit for the carbon steel coated with viniyl resin. R_f is Film resistance of defect area. C_f is Capacitance of film. R_{ct} is Charge transfer resistance. C_{dl} is double layer capacitance.
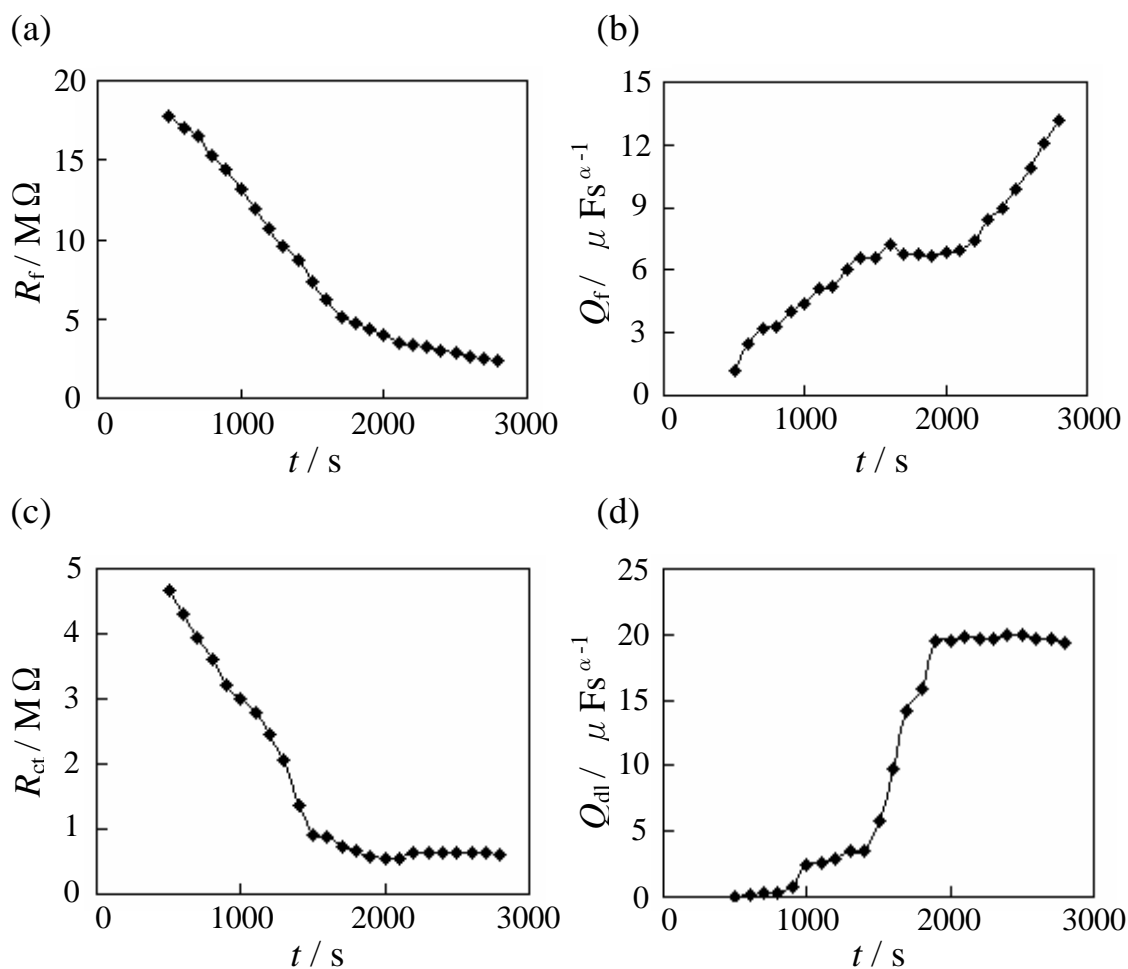
Fig. 5 Change of each parameter with the time determined by the impedance of the carbon steel coated with vinyl resin. (a) Film resistance of defect area. (b) CPE constant for film capacitance. (c) Charged-transfer resistance. (d) CPE constant for double layer capacitance.