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Electrochemical Methods for Corrosion Monitoring: A Survey of Recent Patents

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Abstract: A survey and review of recent patents on electrochemical methods for corrosion monitoring from 1999 to 2009 are presented in this paper. The patents were classified into 4 groups according to different electrochemical theories, which are potential, polarization, electrochemical impedance and electrochemical noise. A future outlook of the development on new research aspects particularly on methods based on electrochemistry is prospected.

Keywords: Corrosion monitoring, electrochemical potential, polarization, electrochemical impedance spectroscopy, electrochemical noise.

1. INTRODUCTION

It is well known for a long time that corrosion exists, and actually was demonstrated with sound scientific and technological foundations. Corrosion results in the deterioration and further destruction of corrodible structures such as piping, tanks, steel soaked in concrete, etc., leading to serious economic problems [1]. Corrosion monitoring techniques have been widely used to inspect and predict the corrosion damage level of these structures [2]. Information depicted has been favored to the development and adoption of effective methods to minimize the loss induced by corrosion. Electrochemical methods are sensitive to the surface state of engineering structures and have been widely used for corrosion monitoring [3]. Several international standards intended to evaluate engineering structures' corrosion state are based on electrochemical methods. In addition, many scientists have been studying electrochemical methods for corrosion detecting and have developed many patents for corrosion monitoring using these methods. This paper provides a survey of new corrosion monitoring patents using electrochemical methods during the period from 1999 to 2009. The patents were classified into 4 groups according to normal electrochemical methods used for corrosion monitoring named open circuit potential, linear polarization curve, electrochemical impedance spectra and electro-chemical noise.

2. ELECTROCHEMICAL METHODS FOR CORROSION MONITORING

2.1 Electrochemical Potential Monitoring

The monitoring method through electrochemical potential for detecting the corrosion activity of metals and their alloys is widely used in many aspects. This was demonstrated in several standards and patents published through this decade.

Lazzari *et al.* [4] developed a patent on monitoring the onset of corrosion on steel reinforcements embodied in reinforced concrete, particularly but not exclusively on pre-stressing cables or steel bars. The invention performs continuous monitoring on localized corrosion conditions of steel cables. The basic corrosion principle applied to the patent is in accordance to those presented by the ASTM C876-91 standard. ASTM C876-91 standard can not be used to detect the potential map of cable. The potential of the small area of the steel reinforcement is detected through the wire electrodes buried in the concrete as reference electrodes. When the corrosion occurred at a certain area, the potential measured shows a more negative value. When the potential is below a certain value, the localized corrosion occurs.

Herts [5] developed a new method and apparatus on detecting corrosion and/or deposit formation in water systems. His invention includes the installation of a cell with a cathode and an anode in the heat control system. Applying a potential between 50mV and 1V on the cell, the corrosion rate and/or deposit formation can be detected through the current between the cathode and the anode.

The components transporting fluid of nuclear reactors are made of various materials which may be susceptible to corrosion and irradiation induced or assisted by stress corrosion cracking. Electrochemical corrosion potential is an effective method for corrosion monitoring and detection of components in a nuclear power plant. On one hand, the electrochemical corrosion potential could provide a guide to determine the amount of an oxidation/reduction reaction which occurs in metal. On the other hand, it could be used to determine whether there are corrosive conditions in the station and whether stress corrosion cracking is likely to

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occur. Mihai *et al.* [6] developed a new patent on detecting the corrosion potential of nuclear fuel rods. This invention provides at least two electrochemical sensors and one of the sensors has a zirconium electrode. Put the sensors in a nuclear reactor. The corrosion potential of a nuclear reactor fuel rod can be calculated by the current induced by the voltage between the sensors.

Thomas *et al.* [7, 8] developed patents to predict the corrosion damage of tanks. Fig. (**1**) is a diagram illustrating potential (E_{corr}) in negative volts (tank potential referenced to the potential of Ag/AgCl half cell) plotted against the cathode surface area of a tank. Take the distribution of sacrificial anodes in a tank is 1.2 sq ft for example; the corrosion state can be learned by comparing the results in Fig. (**1**). It can be learned that a rise in cathodic surface area results in the decrease in protection levels for a typical sacrificial anode system. More precisely, a tank with little coating damage would have potentials near -1.0V, while one with a large coating damage percentage would have potentials nearer to a freely corroding steel potential of -0.7V.

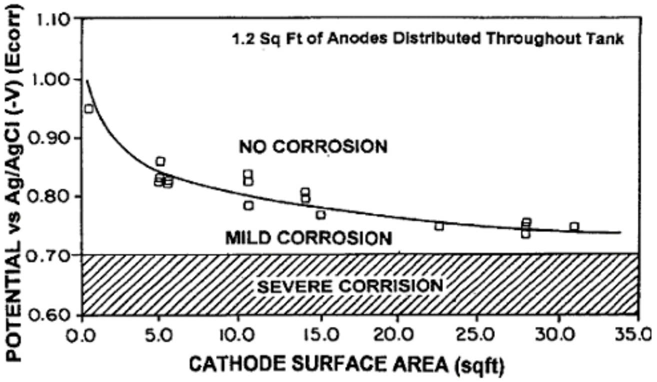


Fig. (1). Corrosion state of the tank determined by the cathode surface area and the potential of the tank. (Cited from US 20050006251).

2.2. Polarization

Polarization method is commonly used for detecting the corrosion rate and the deterioration of coatings. Niblock [9] developed a Linear Polarization Resistance (LPR) sensor device for monitoring the corrosion rate which is shown in Fig. (**2**). This sensor is composed of two electrodes (1 and 2). One or two of the electrodes may have a width (w_1) of about 10-200µm and a length (l) of about 0.1-20mm. The two electrodes are positioned at a distance (d) of 1mm or less. One or two of the electrodes are made of the same material as the metal being monitored. When a small potential drop (ΔE) is applied, a current flow (ΔI) can be obtained. And the corrosion current density (I_{corr}) can be calculated through Equation 1 [10]:

$$\frac{\Delta E}{\Delta I} = R_{p} = \frac{\beta_{a} \times \beta_{b}}{2.303 \times I_{corr} \times (\beta_{a} + \beta_{b})} \tag{Eq. 1}$$

In Equation 1, β_a and β_b are Tafel constants which can be obtained from a well-known Tafel plots for the system under consideration.

The corrosion rate of the structure can be calculated through I_{corr}.

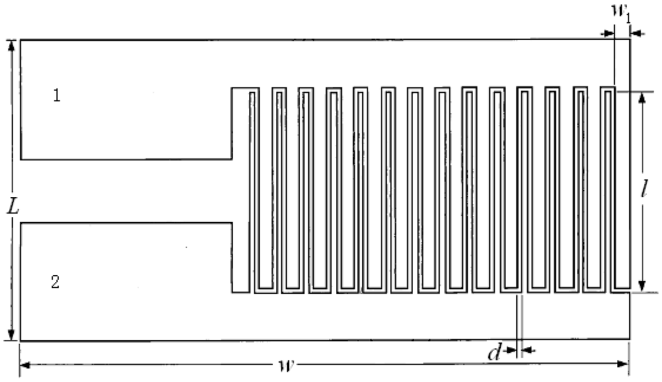


Fig. (2). The schematic diagram of a micro-fabricated linear polarization resistance (LPR) sensor in accordance with the invention. (Cited from US 20060006137).

Martin [11, 12] developed an equipment to control the addition of corrosion inhibitor using linear polarization rate (LPR) to monitor the corrosion rate of a structure. The corrosion rate (*MPY*) can be got through Equation 2 [10]:

$$MPY=K/R_{p} \tag{Eq. 2}$$

where:

K is the Stern-Geary constant.

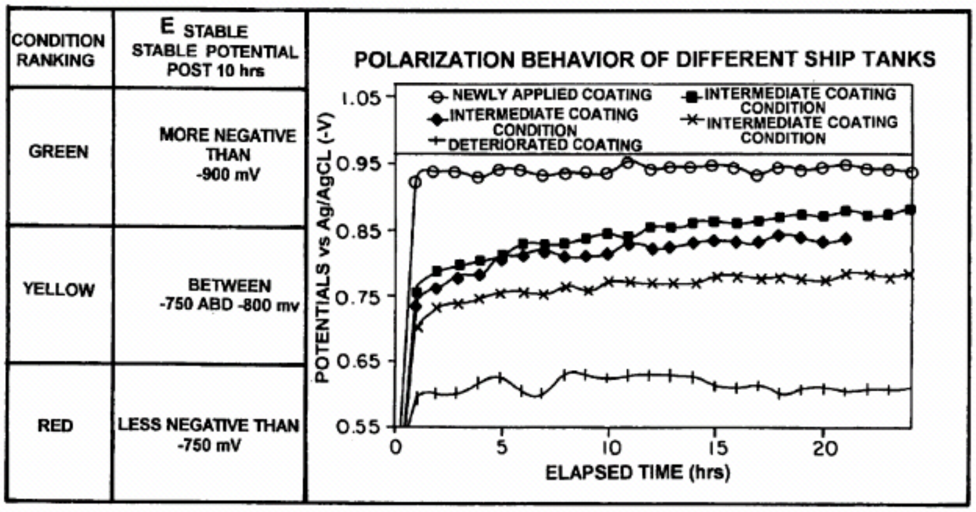
R_p is the polarization resistance.

R_p can be obtained using linear polarization resistance curve electrochemical method [10]. The addition of corrosion inhibitor can be determined according to the corrosion rate calculated from Equation 2.

Thomas *et al.* [7, 8] developed patents to predict the coating deterioration of tanks. The zinc galvanic anode system can polarize the coated steel surface and output protective current. The state of coating deterioration can be predicted using the polarized potential or output current as shown in Figs. (**3**, **4**). The potential and current levels were graded into 3 conditions. “Green” were considered trouble free (more negative than about -900 mV or 75 mA). Tanks which fall in to a “yellow” zone (about -750 mV to -900 mV or about 75 mA to 175 mA) were indicative of increased activity placed on the cathodic protection system and had the requirement of additional current to protect more bare or degrading coating’s area. Tanks with nearly freely corroding conditions, fell into the “red” zone (more positive than about -750 mV or more than 175 mA) and had an unacceptable percentage of corrosion damage.

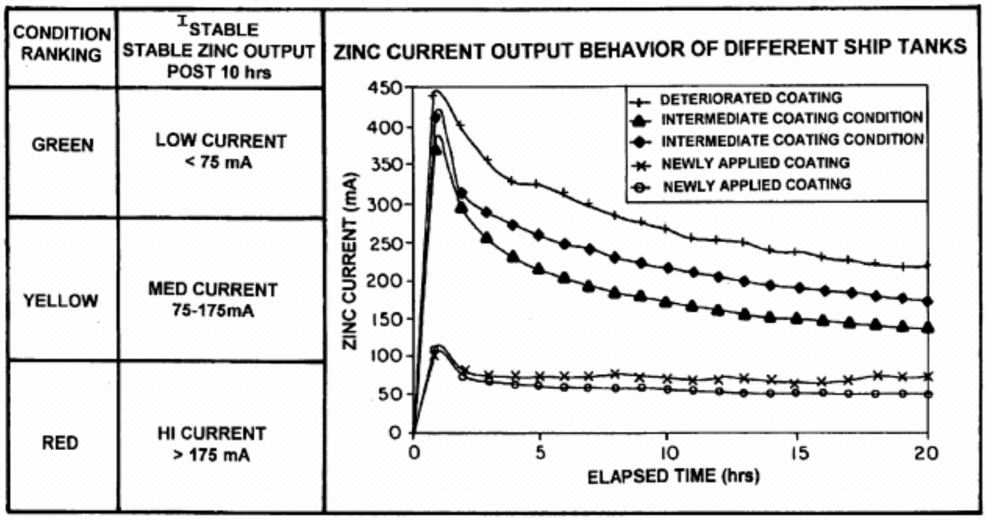
2.3. Electrochemical impedance Spectroscopy (EIS)

The EIS is a method designed to avoid severe deterioration of the exposed surface of the structure studied and was widely used for monitoring the corrosion of a working electrode [11]. This method consists of applying frequencies and low amplitude sinusoidal voltage wave to produce perturbation signals on the working electrode. The corrosion state can be predicted by analyzing the current response of the voltage or the frequencies. In modern practice, the impedance is usually measured with loch-in amplifiers or frequency-response analyzers, which are faster and more convenient than impedance bridges. The job of theory is to interpret the equivalent resistance and capacitance values in terms of interfacial phenomena. EIS is



CONDITION RANKING	E STABLE STABLE POTENTIAL POST 10 hrs
GREEN	MORE NEGATIVE THAN -900 mV
YELLOW	BETWEEN -750 ABD -800 mv
RED	LESS NEGATIVE THAN -750 mV

Fig. (3). The standard between coating deterioration and the polarized potential, and the tank polarization test results for several tanks. (Cited from US 20050006251).



CONDITION RANKING	I STABLE STABLE ZINC OUTPUT POST 10 hrs
GREEN	LOW CURRENT < 75 mA
YELLOW	MED CURRENT 75-175mA
RED	HI CURRENT > 175 mA

Fig. (4). The standard between coating deterioration and the output current, and the tank current output test results for several tanks. (Cited from US 20050006251).

capable of high precision and is frequently used for the evaluation of heterogeneous charge-transfer parameters and for studies of double layer structure. The value of R_p calculated from EIS is more precious and easier than polarization methods. And the Nyquist and Bold graphs obtained from EIS can better reflect the corrosion mechanisms.

Graves and Weerstra [13] developed a device for measuring liquid conductivity and the corrosion rate of metal. The equivalent circuit for the corrosion system was shown in Fig. (**5**). The capacitance and the resistance in the equivalent circuit can be calculated by applying two different frequencies on the electrode. The conductivity of the solution indicates ionic concentration and ion mobility in the water. The polarization resistance, which can imply the corrosion rate of metal, can be calculated through Equation 3 [14]:

$$R_p = (R_L + 1/(2\pi FC))^{1/2} \qquad \text{(Eq. 3)}$$

where R_L is the liquid resistance (solution resistance R_s), F is the frequency in Hz, C is the capacitance in Farads, R_p is the polarization resistance.

R_p is proportional to the reciprocal of the corrosion rate.

As for the metal electrode, the impedance at high frequency can be thought to be the liquid resistance (solution resistance R_s). The impedance at low frequency can be thought to be the sum of liquid resistance and polarization resistance. Eden [15] and Cottis [16, 17] developed methods for calculating the polarization resistance using the impedances at high frequencies and low frequencies, respectively. The polarization resistance can be used to predict uniform corrosion. The pitting corrosion can be predicted using the relationships between the frequencies and the current densities.

Brossia and Dunn [18] developed a method for monitoring the substrate surface protection effectiveness of a coating. The correct application of the method could indicate

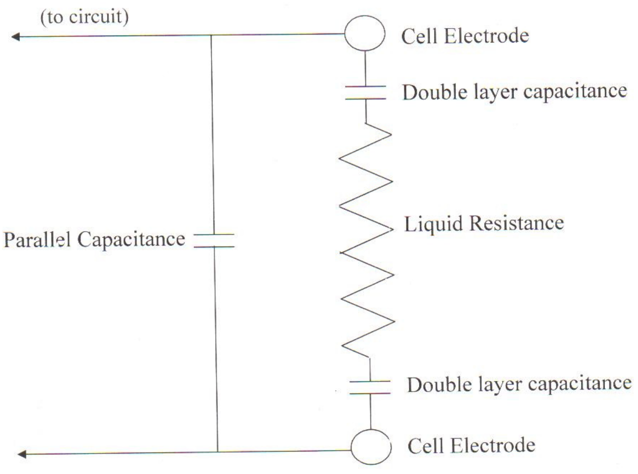


Fig. (5). The electrical schematic representing a conductivity cell with parasitic capacitance. (Cited from US 20070024287).

where the coating adequately protects the surface from corrosion degradation. Two sensor designs are considered in the implementation of the system of the present invention. The first sensor structure consists of a system of pins that can either all be mounted and electrically isolated from the substrate panel or have one of the sensing pins in electrical contact with the substrate panel. The second sensor structure consists of similar components but is much smaller in nature. In this case, it is fabricated using MEMS technology to enable miniaturization of the sensor so that it can be incorporated into the paint itself. The electrodes of the sensors are embodied under the coatings. A normalized parameter N', which is the product of the impedance magnitude and the phase angle, is utilized as a direct indication of the resistance and capacitance characteristics of the coating. This parameter was used as a direct indication of the coating protection effectiveness.

2.4. Electrochemical Noise (EN)

EN technique has been promoted in recent years as a test method for both corrosion science and localized corrosion on engineering alloys monitoring. The basics behind the concept for localized corrosion have foundation in the galvanic current between two nominally identical electrodes, or by monitoring the corrosion potential of a single electrode carefully, thus metastable pitting can be detected by applying a signal to the electrode assembly and obtains a current response of it. The metal corrosion status can be determined by the current response to the noise signal and the harmonic content of the current response.

Eden [19-21] developed methods and apparatus for estimation of general and localized corrosion penetration rates of metallic objects. The invention can also be used to discriminate between general and localized corrosion. The electrodes are made of the same material as the object being monitored and are located in the same corrosive environment of it. The electrochemical harmonic analysis, electrochemical noise signals, and the resulting response are analyzed and compared to discriminate between general and localized corrosion attack and to determine a localized corrosion penetration rate. A low frequency sine wave is applied to the working electrode. Harmonic analysis of the electrode response provides information regarding the general corrosion rate and the Stern-Geary constant. Electrochemical noise analysis of the electrode response and comparison with harmonic data provide a means of determination of localized corrosion penetration rate.

Lin *et al.* [22] and Pope *et al.* [23] designed electrodes for corrosion monitoring using electrochemical noise measurements. The detecting system contains two electrodes which are made of the same material as that of the metal being monitored. Each of the working electrodes has a defined surface roughness. By reducing the surface roughness of one of the pair of working electrodes, the increasing of the sensitivity of the detection signals can predict whether the corrosion will occur while the current noise can be used to accurately measure the general corrosion rate on the unpolished electrode.

Breen [24, 25] developed methods for monitoring the corrosion in furnace boiler tubes by measuring electrochemical noise as they are exposed to combustion products. The perspective view of the embodiment of the probe is shown in Fig. (**6**). The probe to carry out noise monitoring is fixed on the surface of the waterfall of the boiler and connected to a monitoring instrument. The monitor contains a computer and software which determines a corrosion rate from the measured electrochemical noise. The rate is compared to a standard to determine if the rate is within an acceptable limit.

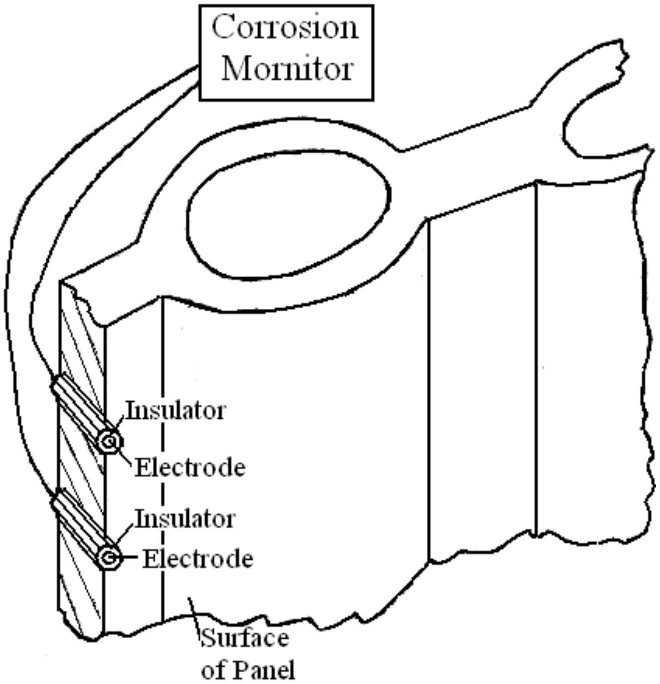


Fig. (6). Perspective view of the embodiment of the probe. (Cited from US 20020117401).

Atherton [26-28] developed new methods for performing electrochemical noise to monitor the metal corrosion condition. The monitoring system contains three electrodes. One is the inner reference electrode. Another is constructed of the material which is to be monitored. The galvanic potentials of those two electrodes can be modified by reducing the DC current to zero. Yet another is constructed of inert material. As corrosion activity occurs on the working

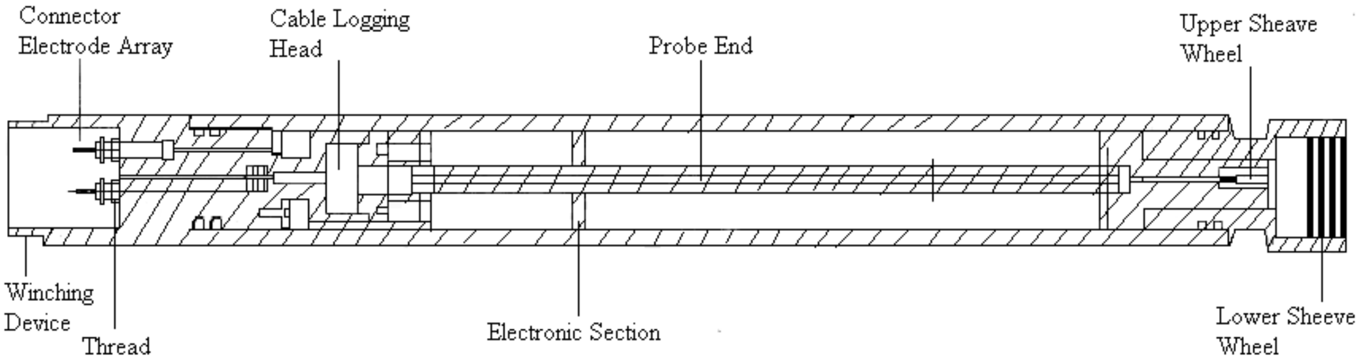


Fig. (7). The downhole corrosion monitoring tool electronics section. (Cited from WO 2006059133).

electrode, both current noise and voltage noise may then be monitored simultaneously.

Martinchek *et al.* [29] developed an apparatus and a method for monitoring localized or pitting corrosion of metal or other materials which are described. The probe contains a working electrode which is made of the material being monitored. The electrochemical noise detected between the working electrode and the other electrodes is processed to provide an indication of the state of localized corrosion of the material being monitored. An anodic bias voltage is applied to the working electrode. This bias voltage accentuates localized corrosion at the working electrode, improving sensitivity and permitting more accurate evaluation of the electrochemical noise signals.

Atherton [30, 31] invented a downhole corrosion monitoring equipment which comprises a sensor head. The downhole corrosion monitoring tool electronics section was shown in Fig. (**7**). The sensor head comprises a plurality of mutually insulated electrical sensors (connector electrode array) and is tied to a cable which is extensible so as to raise or lower the sensor head downhole and has a signal conductor (electronic section) to return data from the sensor head to the surface. The corrosion state can be predicted through analyzing linear polarization curve and electrochemical noise.

3. CURRENT AND FUTURE DEVELOPMENT

Electrochemical methods are effective and economical for corrosion monitoring. In particular, electrochemical impedance method has a great potential for corrosion monitoring. It has advantages of being sensitive to and not destroying the assessed metal surface. As the double layer is not due to pure capacitive conditions and the data cannot be actually analyzed according to partial data of the electrochemical impedance spectroscopy, the corrosion monitoring methods based on electrochemical impedance techniques still need to be improved.

Improving the data analysis and automatic control of electrochemical impedance spectroscopy methodologies is a difficult and important research work aspect. Neural networks may be an effective method as to intend to give response to this problem.

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