

CORROSION PREDICTION IN COMPLEX ENVIRONMENTS USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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Abstract—Rapid corrosion estimation in poorly defined, complex environments is required for making appropriate materials related decisions in the process industries. One problem is that the chemistry of these systems is often impossible to characterize. Using corrosion screening in process waste as an example, this paper examines how electrochemical impedance spectroscopy (EIS) can contribute to screening metal corrosion in these types of environments. Lack of characterization forces the careful use of circuit analogues to model the results. Good agreement between corrosion rates estimated by EIS, *dc* polarization and short term mass loss is used to provide confidence that the circuit models invoked to classify the spectra are reasonable.

Key words: corrosion, electrochemical impedance spectroscopy, rotating cylinder electrode, prediction, steel, circuit analogues, waste streams, chemical process industries.

INTRODUCTION

Generation of the impedance spectrum provides only one part of the required information needed to make full use of Electrochemical Impedance Spectroscopy (EIS). The spectra must still be interpreted. At present, difficulties in data interpretation remain a major obstacle to making *routine*, stand-alone use of this technology for corrosion prediction in poorly characterized complex environments.

EIS can make an important contribution to practical corrosion prediction because it enables rapid estimates of a wide range of corrosion rates, especially low ones[1-3]. Corrosion rates of 2.5×10^{-4} to 250 mm y^{-1} can be estimated in about 24 h of total immersion time. However, making predictions requires some way of deconvoluting the impedance spectrum to extract those corrosion related parameters that can be used to predict the corrosion rate or mechanism. The most satisfying method would be to be able to write the kinetic equations, solve for the predicted impedance spectrum and then show agreement between the predicted and actual spectra. However, the poor characterization of many process streams severely inhibits this approach. Therefore, the most prevalent method is classification by circuit analogues and making predictions from them.

The need for deconvolution has led to a number of algorithms that attempt to model the impedance spectrum in terms of circuit analogues[2, 4-7]. Such analogues allow the corrosion practitioner to bridge the gaps in knowledge so that corrosion rates might be estimated, corrosion mechanisms hypothesized, and materials selections made in these poorly characterized systems. The one major drawback is that more than one analogous circuit model can fit the same data[8]. This observation means that if this approach is taken, at least some of the predictions derived from EIS should be corroborated by independent measurements.

Proper handling of waste streams is important to the process industries. Rapid determination of corrosion in such streams often is required during a materials evaluation. Characterization of such streams is difficult. Thus, corrosion mechanisms are not easily determined. When EIS is used for these evaluations, phenomenological circuit analogues often provide the only way to relate the electrochemical results to corrosion. Agreement among EIS, *dc* polarization and mass loss measured on the same electrode in the same experiment provides confidence and enables EIS to contribute to practical corrosion predictions when few experiments are possible.

EXPERIMENTAL/ANALYSIS

The experimental arrangement and controlling algorithm have been discussed in detail previously[1, 2]. A Hewlett-Packard 9816S microcomputer guided the experiment by controlling the flow of commands. The impedance spectra were generated by a Solartron 1250A Frequency Response Analyzer and a Princeton Applied Research 173D potentiostat with 276 programmable interface. The excitation amplitude was 5 mV.

The solutions were a number of wastes that were "frozen" in various stages of processing. These wastes were from a number of processes and companies. Therefore, there were numerous unknown components. Economic considerations made steel the material of choice. The need for aerating the waste suggested the need to determine if corrosion was sensitive to fluid movement.

A rotating cylinder electrode[9] made from steel (UNSG1018) was used for all of the studies. The impedance spectra were generated after 30 min, 3-5 h and every 24 h after that. The spectra obtained at 3-5 h and every 24 h at 200 rpm were generated to

0.001 Hz. After 24 h, each experiment at 200 rpm was followed by an excursion to 1000 and sometimes 2000 rpm. Each excursion lasted for about 1 h, 0.5 h to reach steady state and another 0.5 h to generate the spectra to 0.01 Hz.

The data were uploaded to an IBM mainframe computer for analysis in terms of the circuit analogues shown in Fig. 1. The four circuits are expected to empirically classify the spectra into four types of corrosion phenomena with a minimum number of circuit elements. The circuits were chosen to model a single charge transfer reaction, an imperfectly covered electrode as might be found with an inhibitor, diffusion through a finite boundary layer[10], and an adsorbed intermediate that might create pseudo-inductance[11].

Corroboration that actual corrosion phenomena and rates were being measured was provided through two independent measures on the same electrode. First, the voltage was varied from the corrosion potential at 0.1 mV s^{-1} to 20 mV in the cathodic (active) and anodic (noble) directions from the corrosion potential. These curves were created after each impedance spectrum was generated to 0.001 Hz at 200 rpm. The points were fit to Wagner-Traud theory in which one anodic and one cathodic reaction were assumed. The procedure has been outlined previously[2, 3]. Second, the mass loss of the elec-

trodes was measured. Corrosion rates estimated from these mass losses were compared to those obtained by time-averaging the rates extracted from the impedance spectra.

RESULTS

Though seven different solutions were examined, the spectra from only two are discussed in some detail. Figure 2 shows the spectrum for solution B at 200 rpm after about 47 h of exposure. The spectra generated at 1000 rpm were similar but had smaller impedance magnitudes. These spectra were analyzed by assuming circuit #1 in Fig. 1 representing one charge transfer process. At 72 h, a second, unresolvable time constant began to appear. Figure 3 shows the spectrum for solution E at 200 rpm after about 72 h of exposure. Spectra generated at 1000 and 2000 rpm showed similar pseudo-inductive behavior. The spectra were modeled using circuit 4 but modified to accept the parameters discussed by Epelboin and Keddam[11] and used successfully in a previous study in which pseudo-inductance was observed[12]. The corrosion potential became constant between 24 and 48 h of exposure suggesting that both systems were stable when the spectra were

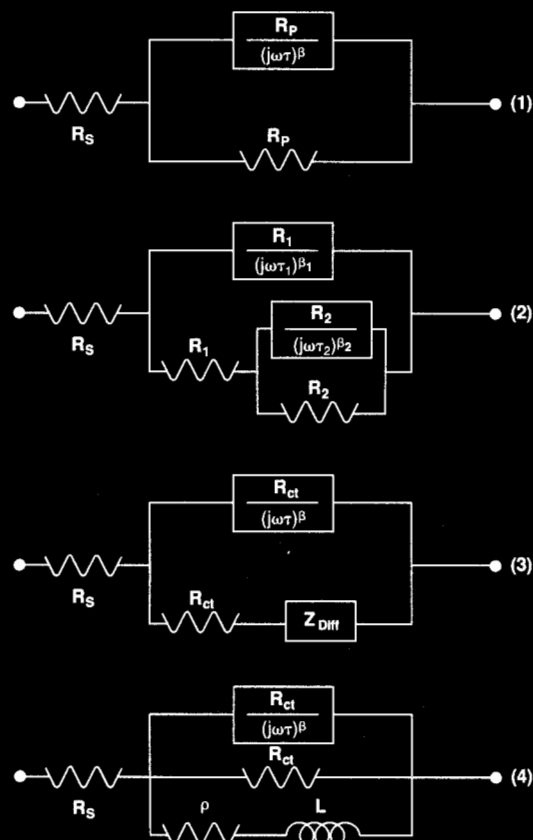


Fig. 1. Circuit models for classifying EIS spectra in complex environments. (1) One relaxation time constant. (2) Two relaxation time constants. (3) One relaxation time constant with extended diffusion. (4) One relaxation time constant with pseudo-inductance.

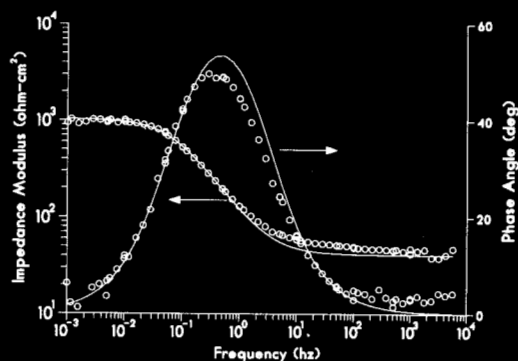


Fig. 2. EIS spectrum of waste solution B at 200 rpm, 47 h. Spectrum modeled by circuit (1). \circ Measured; — calculated.

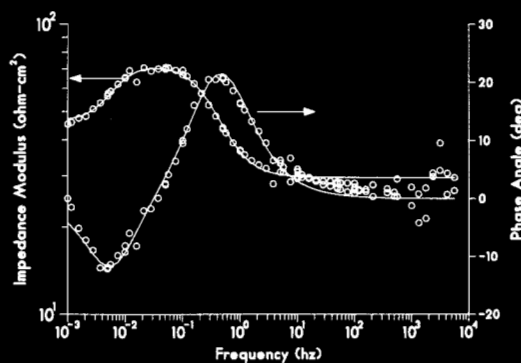


Fig. 3. EIS spectrum of waste solution E at 200 rpm, 70 h. Spectrum modeled by circuit (4). \circ Measured; — calculated.

Table 1. Comparison of resistances: EIS vs. *dc* polarization

Waste solution	Exposure time (h)	Resistance estimate (ohm cm ²)	
		Impedance	<i>dc</i> polarization
Solution B	3-5	960	840
<i>R_s</i> = 40 ohm cm ² 200 rpm (circuit # 1) used as model)	23-25	1170	1060
	46-48	1000	940
	71-73	880	725
Solution E	3-5	46	52
<i>R_s</i> = 20 ohm cm ² 200 rpm (circuit # 4) used as model)	24-26	31	45
	46-48	39	56
	68-70	42	54

generated. The difference in spectra between the two solutions illustrates the diversity of spectra that can be encountered when predicting corrosion in these types of streams.

Table 1 shows the good agreement between the resistances estimated by EIS and those obtained by *dc* polarization. Note that the charge transfer resistance as estimated from the EIS analysis is used for the resistance shown in Table 1 for solution E. This resistance is not necessarily the resistance at zero frequency. Table 2 shows a comparison between the corrosion rates as estimated by time-averaging the resistances extracted from the EIS spectra to the rates obtained by converting the mass loss of the electrode to an average corrosion rate. A value of 0.025 V was used to estimate the corrosion rates from the resistances.

DISCUSSION

The agreement with *dc* polarization and mass loss results shown in Tables 1 and 2 strongly suggests that the analysis of the EIS spectra is providing good estimates for the corrosion rate. This agreement is a good check that the classification is reasonable and actual corrosion phenomena, not experimental artifacts, are being measured. The agreement is important because some of the spectra that demonstrated pseudo-inductance could not be verified to be valid by the methods of, for example, Macdonald[13] because an imaginary contribution still existed at the lowest frequency for a number of the spectra. This low 5 mV amplitude has been shown to prevent non-

linearity between voltage and current in other waste streams demonstrating pseudo-inductance[12].

As shown in Fig. 4, the corrosion rate increased with fluid velocity for solution E. The inverse of the resistances for solution E measured at 48 and 72 h of exposure were regressed together against the rotation rate. The exponent on the rotation rate was 0.47 with a squared correlation coefficient of 0.99. Such agreement suggests mass transfer controlled corrosion. However, if the flow was turbulent, the coefficient would have been 0.7 for the apparatus used[9]. Though the solutions were aqueous, they had a significant amount of solids and some tar-like material. This mixture could have led to altered hydrodynamics, possibly more laminar flow. Other waste solutions showed different dependencies on flow. For example, the resistance of solution R decreased by close to an order of magnitude between 200 and 1000 rpm and by only a factor of 2 between 1000 and 2000 rpm. Spectra for solution R were loosely modeled by circuit 2 which has been used to examine inhibitors. This velocity dependence suggests possible fluid shear affected removal of a loosely bonded, inhibiting surface species present in solution R.

The important point is that combining EIS with the rotating cylinder electrode allowed for a rapid evaluation of the effect of fluid velocity. The results in Tables 1 and 2 indicate that though the models are not perfect, they are adequate to classify the corrosion process in order to make practical corrosion predictions in the absence of characterization of the

Table 2. Time averaged corrosion rate of steel as a function of waste and technique

Waste solution	Time-averaged corrosion rate (mm y ⁻¹)	
	Impedance	Mass loss
Q High tar	0.36	0.30
Q Low tar	0.44	0.38
R Low tar	0.12	0.30
E High tar	8.5	7.4
HV High tar	1.6	1.8
J High tar	0.15	0.19
B High tar	0.30	0.43

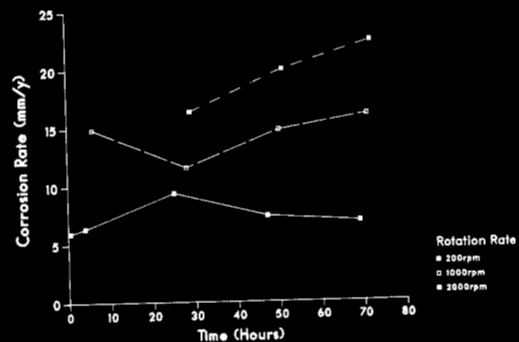


Fig. 4. Corrosion rate as a function of time and rotation rate for solution E.

environment. The practical recommendation is that steel not be used in this application.

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