

Potential Pulse Measurements as an Alternative Way to Identify Controlling Mechanisms for Corrosion

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ABSTRACT

In this work, a potentiostatic pulse measurement is adopted to monitor the current transient, which provides an alternative estimate of corrosion rate as a function of temperature and information on electrochemical processes on the metal substrate. This is an interesting idea when coupled with the electrochemical impedance spectroscopy (EIS) technique in order to determine the intrinsic system resistance, and hence to extract activation energies from this data. The results show that the kinetics of the cathodic reaction beneath the paint are more visible and might be controlling the corrosion rate.

1. INTRODUCTION

In a previous work [1], two different coated mild steels were exposed at 50°C and measured with electrochemical impedance spectroscopy (EIS) across a range of temperatures (25°C–50°C). The resulting impedance data was fitted to a model circuit and changes in the coating resistance and charge transfer resistance with temperature were determined to deduce activation energies for the processes involved. The results showed that the activation energies determined for ion conduction were lower than the values for the corrosion process, which raises the question of whether ion conduction could be controlling the corrosion rate.

In the potentiostatic pulse measurement (PPT), potentials were applied in a series of steps (anodic or cathodic) on top of the free corrosion potential. Correction of the potential was necessary to compensate for ohmic potential drop due to the high resistance of the coating, so that corrected polarization curves could be plotted. Potentiostatic pulse measurement can be used to measure responses of current under a transient state, but in this work, it was used to determine the steady currents after a fixed time of polarization (Figure 1) and to minimize interference from charging of the coating capacitance. The resulting currents at different potentials were then used to plot polarization curves for reactions beneath the coating.

2. EXPERIMENTAL DETAILS

2.1 Materials and Impedance Test

In this work, a commercial epoxy-phenolic paint with 150 μm thickness was tested. Coatings were applied by air spraying to grit-blasted mild steel panels. The edges were protected with a thick high-performance epoxy coating. The electrochemical measurements were made using a three-electrode cell. The working electrode had a working area of 40 cm^2 , the reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a platinized titanium electrode with an area of 9 cm^2 . The sample was placed vertically in hot 3 wt% sodium chloride solution (800 cm^3), made from analytical grade NaCl and deionized water, held at constant temperature in a water bath (or slowly cooled in an insulated box).

The impedance measurements were taken with a Gill AC computer-controlled potentiostat with a high-impedance paint buffer system (ACM Instruments). Tests were carried out at the free corrosion potential for temperatures from 50°C down to ambient (25°C) with 20 mV signal amplitude over a frequency range from 0.1 Hz to 30 kHz. The EIS spectra were analyzed with a non-linear least squares fitting software (ZSimWin) to a $R[Q[R[QR]]]$ model circuit as illustrated in Figure 2 [Q=constant phase element]. This model circuit is a realistic representation of a coated metal, where the coating resistance is considered to be short-circuited by the lower resistance, R_p e.g. pore. The combination of R_{ct} and C_{dl} represents the behavior at the base of the pore.

2.2 Potentiostatic Pulse Measurements

The rest potentials of the epoxy-phenolic coated metal were measured at the beginning of the test. Then a series of potential steps (typically 100-600mV) were applied from the rest potential. The resulting current was measured every second for a period of 300s to allow the current to stabilize, before applying another potential step. Before each measurement, the impedance tests with EIS were conducted to determine the coating resistance that is necessary for iR -correction.

3. RESULTS AND DISCUSSIONS

3.1 Impedance Measurements

In the impedance measurement, the result is expressed as a Nyquist plot at various immersion temperatures. Figure 3 shows impedance spectra recorded from the epoxy-phenolic coated panel before the anodic and cathodic potentiostatic pulse measurements. Notice the effect of temperature is more apparent on the low frequency semicircle. To obtain the coating resistance, the impedance spectra were fitted using the ZSimpWin software with the model $R[Q[R[QR]]]$. The fitted parameters are listed in Table 1. The logarithm of coating and charge transfer resistance is plotted against the reciprocal of temperature, and the plots show linear behavior (Figure 4).

TABLE1:Parameters for Epoxy-Phenolic Coating from Fitting of EIS before PPT

T (°C)	Q_c (Fcm^{-2}) ⁿ	n	R_p (Ωcm^2)	Q_{dl} (Fcm^{-2}) ⁿ	n	R_{ct} (Ωcm^2)
20	1.75E-09	0.80	7.00E+05	1.86E-06	0.57	2.20E+06
30	2.24E-09	0.79	6.06E+05	2.26E-06	0.53	1.14E+06
40	2.67E-09	0.78	4.61E+05	2.41E-06	0.49	8.87E+05
50	3.24E-09	0.77	3.44E+05	2.08E-06	0.48	5.66E+05

The linear dependence logarithm of coating resistance plotted against the reciprocal temperature was first noted by Mayne and Mills [4], and from the slope, the ‘activation energy of ion transport’ was calculated, with a lower value (20-45 kJmol⁻¹) for D type films. This dependence has been also observed by other workers [5, 6].

The activation energy determined for ion transport (calculated from R_p) is 19kJmol⁻¹ and 34kJmol⁻¹ for the corrosion process (calculated from R_{ct}). These finding are similar to the results gathered in the previous work by the same author [1, 3], where the E_A for the corrosion process is significantly higher than E_A for ion transport.

3.2 Potentiostatic Pulse Measurements

3.2.1 Determination of iR-correction

The effect of uncompensated resistance is particularly important in transient studies, since the current/voltage curves are further distorted by alteration of the perturbation function. For instance, in potential step studies, the actual potential drop across the interface may vary with time, even though the applied potential is constant, since the product iR is also a function of time (Figure 5). The corrected polarization curves are plotted on a potential versus log current scale in Figure 6, which shows a more linear behavior than the measured data. Extrapolation of the linear Tafel region E_{corr} would give i_{corr} .

3.2.2 Effect of Temperature

Figure 7 represents current transients at various temperatures when potential steps were applied. For both, i_{steady} is higher at high temperatures. The effect of temperature on the anodic and cathodic polarization for epoxy-phenolic coating after iR correction is presented in Figure 8. It can be seen that the anodic curve is not strongly affected by the temperature changes (Figure 8a). The influence of temperature changes is more evident on the cathodic curve (Figure 8b) where the cathodic current density becomes larger as the temperature rises. Therefore, data from the cathodic curves was analyzed further for generation of activation energy from the corrosion current density. The current density for each temperature was determined from the cathodic Tafel line at a fixed potential ($E=-650mV$).

The logarithm of current density was then plotted against the reciprocal of temperature and the straight line indicates that the current obeys the Arrhenius Law (Figure 9). The activation energy calculated from this plot is 66 ± 2 kJmol⁻¹. This is much higher than E_A value for the film resistance and higher than for the corrosion reaction from the charge transfer resistance. The

increase in the cathodic current generates a smaller increase in i_{corr} because of the need to polarize the anode.

A summary of activation energies for epoxy-phenolic coating calculated from the EIS and PPT test is presented in Table 2. Notice that E_A values determined from EIS tests for the corrosion process (from R_{ct}) and from PPT tests are higher than the E_A value determined for ion transport (from R_p).

TABLE 2: Activation Energy Determined from EIS and PPT Test

Coating	EIS		PPT
	E_A from R_p (kJmol^{-1})	E_A from R_{ct} (kJmol^{-1})	$E_{A, \text{from } i_{\text{corr}}}$ (kJmol^{-1})
Epoxy-phenolic	19	34	66 ^a

^afrom i_{cathode}

4. CONCLUSION

The potential pulse method offers an alternative possibility to impedance measurement in identifying a corrosion controlling mechanism whereby the kinetics of the cathode reaction on the electrode could be controlling the corrosion rate, rather than the film resistance. Potentiostatic pulse measurements on epoxy-phenolic coating have shown that the anode is less affected by the temperature changes than the cathode is. The activation energy value generated for the cathode reaction is higher than that for ion transport from R_p in paint on steel, but more than for a change in R_{ct} . However, previous work on epoxy-phenolic free films shows that for un-degraded coating, higher activation energy for ion transport is observed (73-76 kJmol^{-1}) [3]. This indicates that if the corrosion current returns through un-degraded areas of coating of higher resistance, higher activation energy will be observed for R_{ct} . This also means that the lower resistance that is being measured here does not indicate whether the coating is still protective or not.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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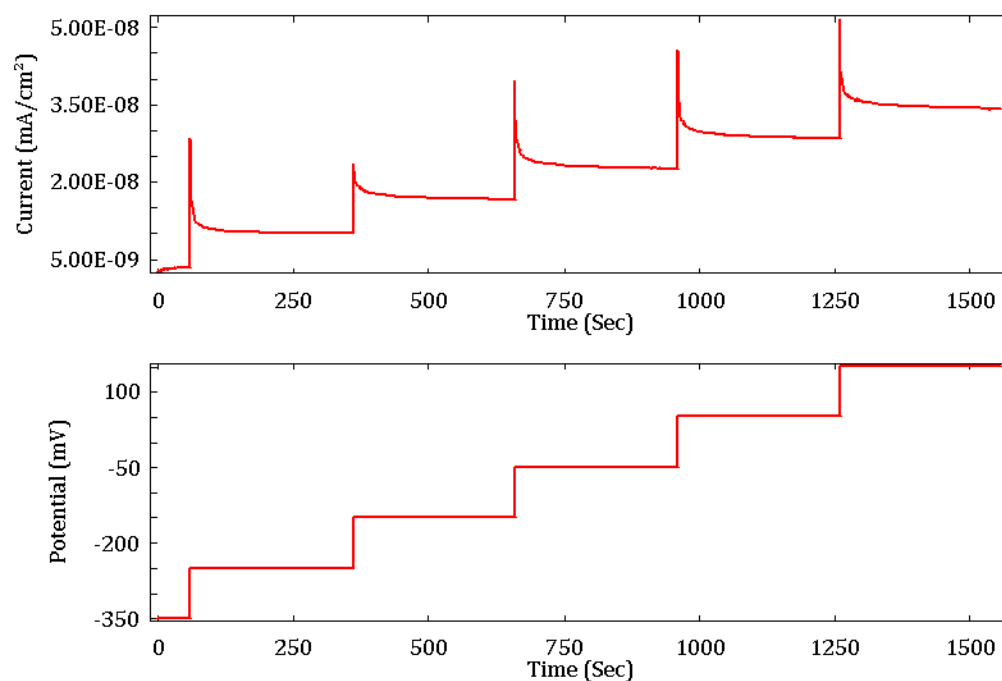


Figure 1: Results of current transient (top) compared to potential pulse measurement (bottom).

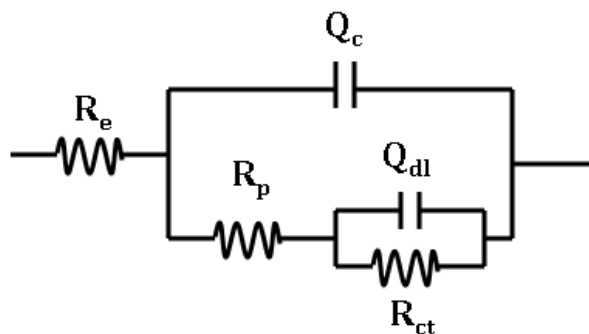


Figure 2: Model circuit for coated metal.

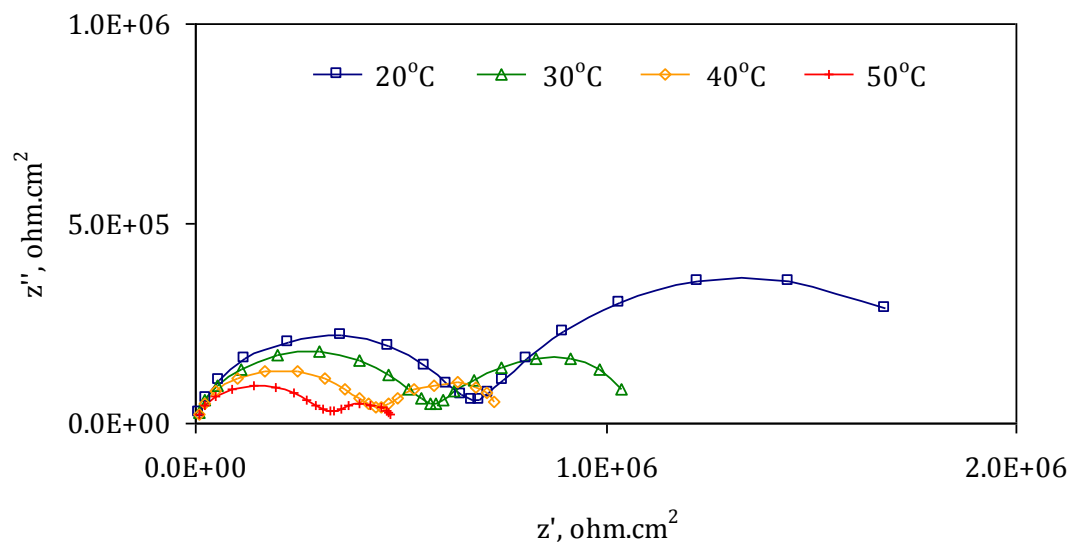


Figure 3: Nyquist plots at various temperatures for epoxy-phenolic coating before PPT.

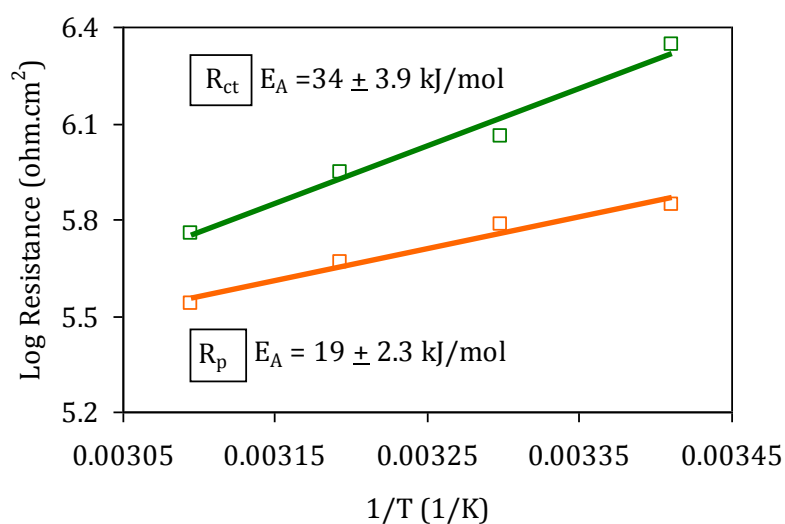


Figure 4: Arrhenius plots of R_p and R_{ct} for epoxy-phenolic coating before PPT.

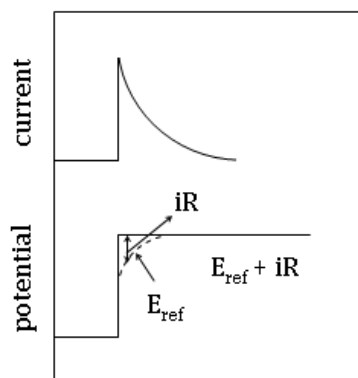


Figure 5: Schematic representation of the effect of uncompensated resistance upon the potential/time profile of an electrode under potentiostatic control [2].

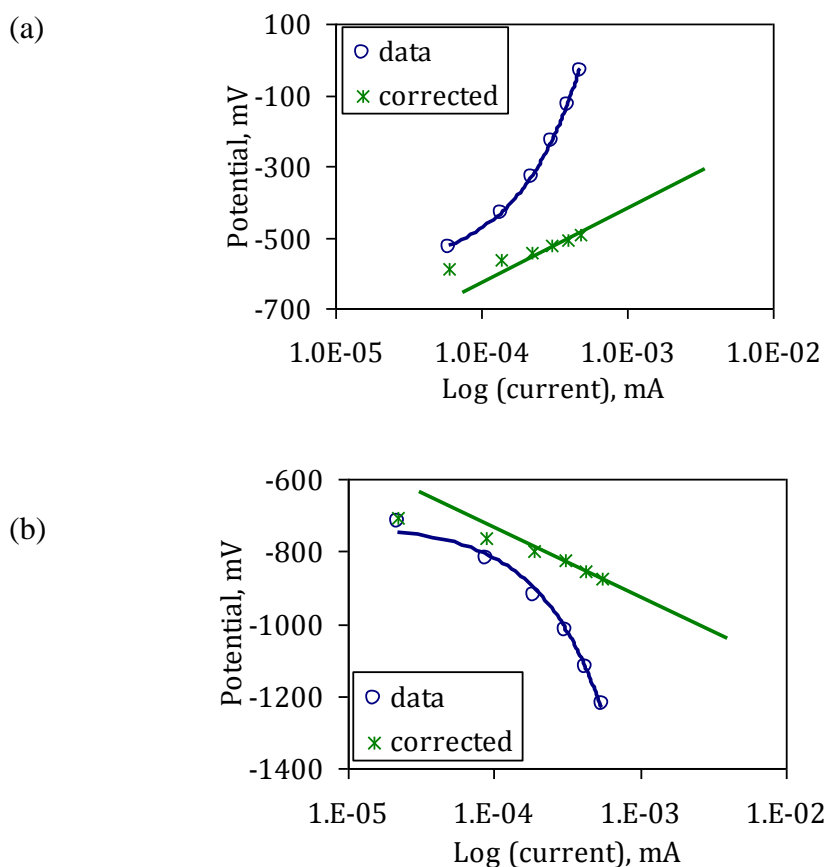


Figure 6: Measured data and corrected potential-current transient for (a) anodic polarization (b) cathodic polarization.

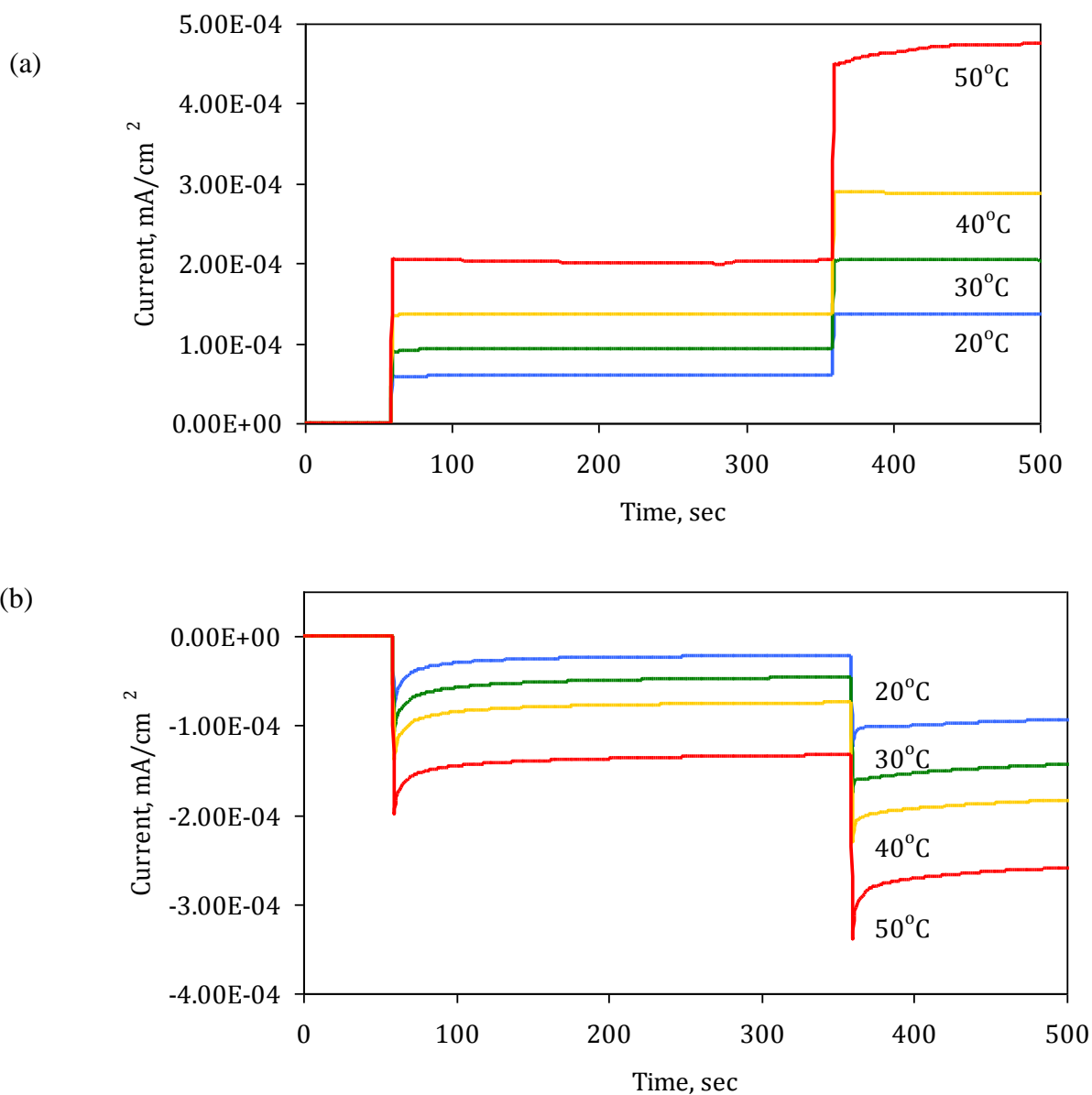


Figure 7: The influence of temperature on current transient during
(a) anodic polarization (b) cathodic polarization.

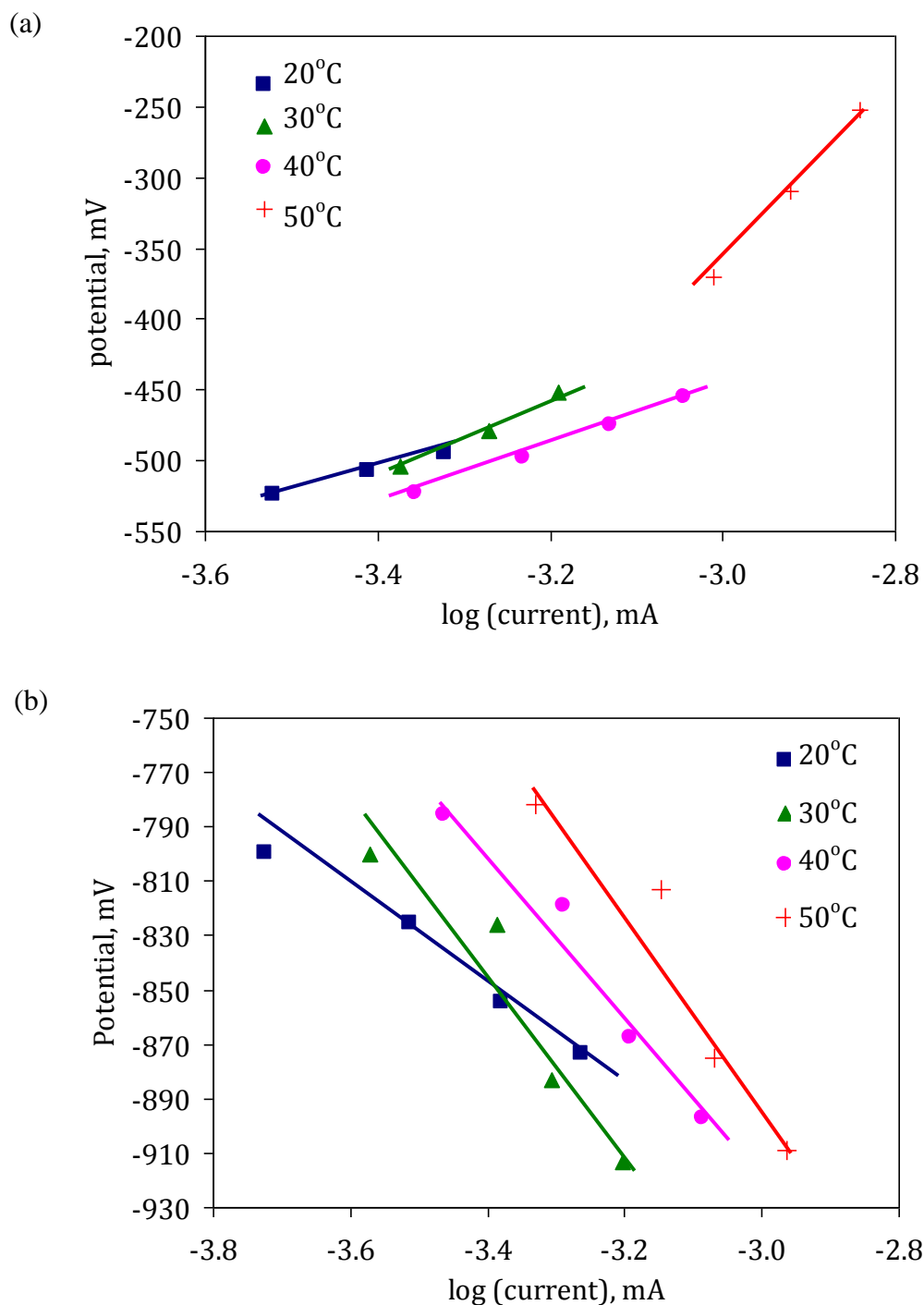


Figure 8: Effect of temperature changes on (a) anodic curves of epoxy phenolic coating (b) cathodic curves of epoxy phenolic coating.

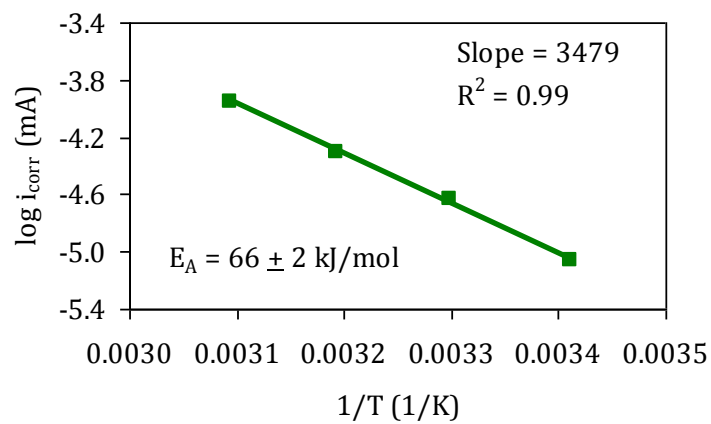


Figure 9: Arrhenius plot calculated from cathodic Tafel lines.