

Electrochemical Frequency Modulation

Comparison of EFM to LPR, EIS, and Tafel Plot for the Measurement of the Corrosion Rate of Iron in Sulfuric Acid

One of the nicer features of the annual Corrosion Short Course at Penn State University is the extensive laboratory experiments that are designed for the course. The students are exposed to a wide range of electrochemical techniques for real, hands-on experience. For most of these experiments, the sample is iron and the electrolyte is 0.5 N sulfuric acid. The iron is cast in epoxy and polished to a mirror finish.

At the 2004 edition of the course, we took the opportunity to compare **Electrochemical Frequency Modulation**, a new technique for corrosion rate measurement, to the more-accepted electrochemical techniques of Polarization Resistance, Tafel Plots, and Electrochemical Impedance Spectroscopy. The results are shown in the table below.

Technique	Corrosion Rate (milli-inches per year)
EFM	64.3
LPR	61.9
Tafel Plot	66.9
EIS	55.7

Most corrosion scientists would agree that the reproducibility of the corrosion rate from these techniques is impressive, suggesting that EFM may be confidently considered as a reliable tool for corrosion rate measurements.

Each technique used a Density of 7.87 and an Equivalent Weight of 27.92. Comments on each measurement follow.

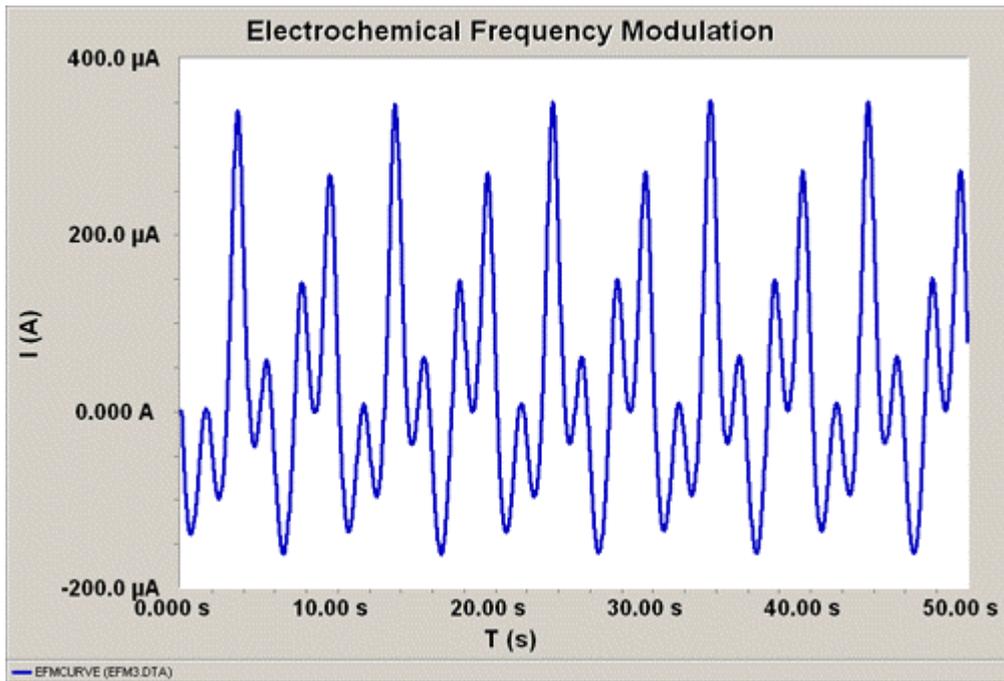
Electrochemical Frequency Modulation

EFM was run with a 10 mV amplitude, 4 cycles, and frequencies of 0.2 and 0.5 Hz. The EFM data acquisition plot is shown below. The results were:

Corrosion Rate 64.24 mpy
Anodic Tafel Constant 52.5 mV/decade
Cathodic Tafel Constant 132.7 mV/decade
Causality Factory (2) 1.943
Causality Factor (3) 3.060

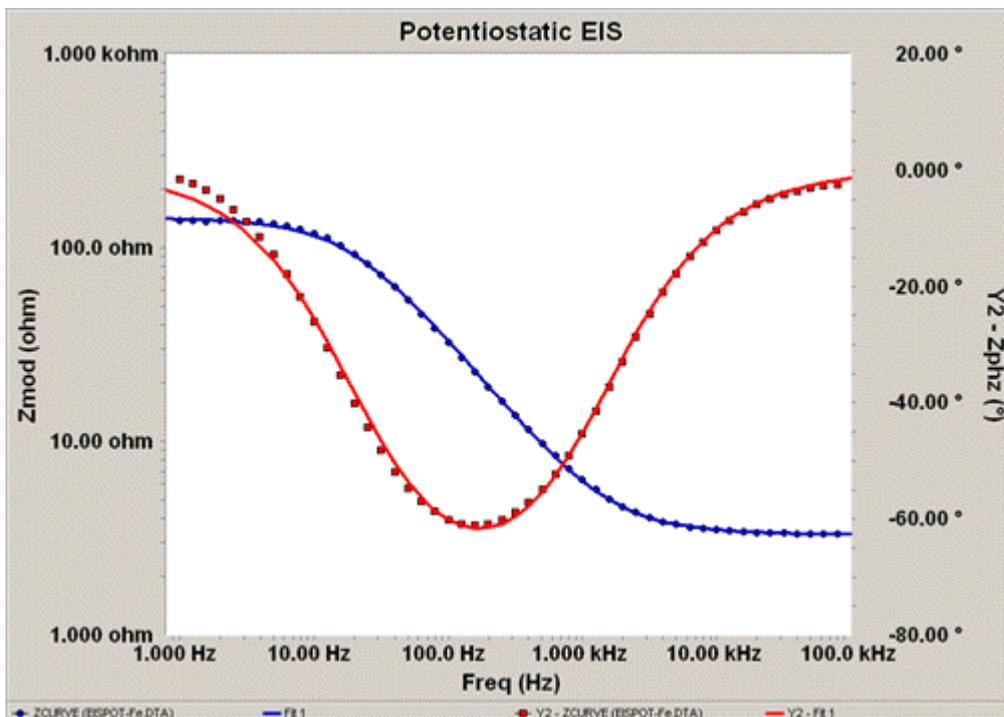
The Causality Factors are very close to the theoretical values of 2 and 3, suggesting that the reaction is accurately described by the Butler-Volmer equation and the data is valid. We will use the Anodic and Cathodic Tafel Constants with LPR and EIS and compare the values obtained with the Tafel Plot.





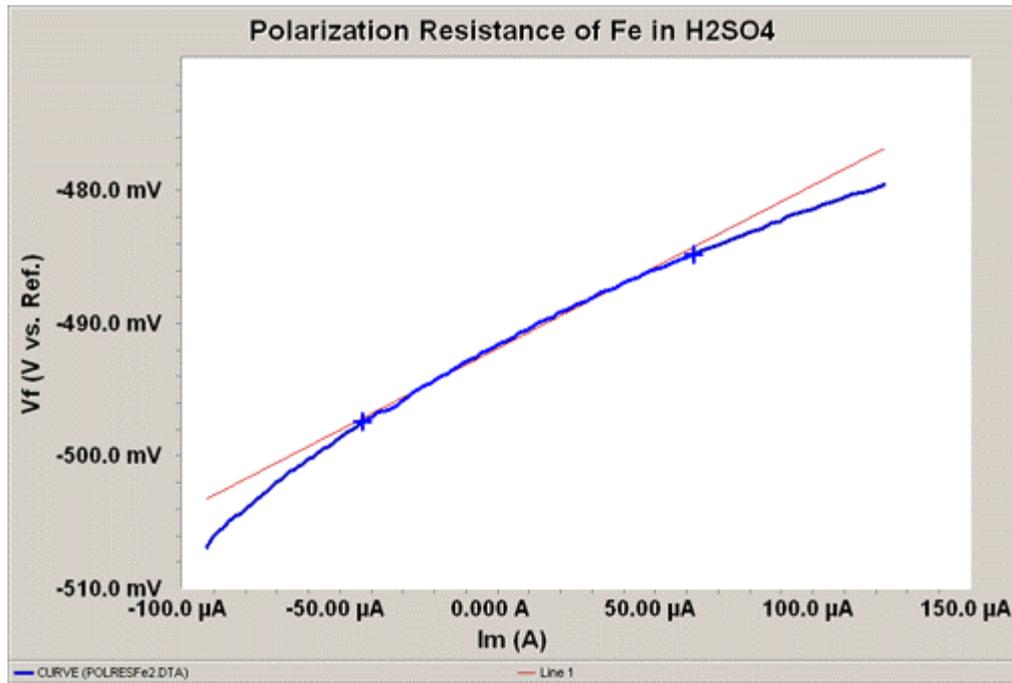
Electrochemical Impedance Spectroscopy

The EIS curve is shown below. The data was fit with a Randles-like circuit that incorporated a CPE instead of a capacitor. The R_p was 136.4 ohms. The Anodic and Cathodic Tafel Constants from the EFM experiment were used to calculate the Corrosion Rate of 55.7 mpy.



Polarization Resistance

The Linear Polarization plot is below. The Scan Rate was 0.125 mV/sec. The Anodic and Cathodic Tafel Constants from the EFM experiment were used to calculate the Corrosion Rate of 61.9 mpy. The blue X's mark the data region used to calculate the slope and the red line is the fit to that data region.



Tafel Plot

The Tafel Plot was run at a Scan Rate of 1 mV/sec because of time constraints. Iron is characterized by a cathodic Tafel Region that can only be described as stunningly gorgeous! The red line on the curve below is the fit of the Gamry DC105 Corrosion Techniques Software to the Butler-Volmer equation. The calculated corrosion rate is 66.9. The calculated Cathodic Tafel Constant is 0.139 V/decade, in excellent agreement with 0.133 from EFM. The Tafel Plot was run last in this series, since the more-extensive polarization was likely to alter the electrode surface.

