Effect of Formic Acid on Iron Corrosion in an Anhydrous Methanol Solution*

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Such a protic acid as formic acid is possible to react with anhydrous methanol. Effect of the formic acid reaction with methanol on the corrosion rate of iron in an anhydrous methanol solution of 0.1M NaClO₄ was investigated by cyclic voltammetry and impedance measurement. The corrosion rate was lowered as the concentration of formic acid decreased with an increase in the immersion time. The formation of methyl formate and water by the reaction complicates the process of iron corrosion in the methanol solution.

Key words: iron corrosion, formic acid, anhydrous methanol, cyclic voltammetry, impedance measurement, esterification.

1. Introduction

Many investigations on corrosion of iron in methanol solutions have dealt with effects of additives or contaminants like water, protic acid, oxygen, and chloride ion on active corrosion and passivity of iron. The content of water is of major importance to the iron passivity in a so-called 'anhydrous' methanol solution. It has been described that water of less than 500ppm in methanol is insufficient to form a stable passive film on the iron surface. Neither water nor methanol plays an important role in the cathodic reaction of iron corrosion in a methanol solution containing less than 460ppm of water. However, the authors have revealed that iron corrosion occurs in an anhydrous methanol solution of 0.1 M(mol dm⁻³) LiClO₄(<150ppm of water) and the corrosion rate decreases with an increase in the immersion time because a protective layer of ferrous methoxide forms on the iron surface. Dissolution of the methoxide layer by the formation of a soluble chelate complex into the solution results in stimulation of the anodic reaction.

Effects of inorganic and organic acids on active corrosion of iron and iron-based alloys in methanol solutions at various concentrations of water have been investigated by number of authors. Some studies have been performed in anhydrous methanol solutions of protic acids. A polarization study on iron corrosion in anhydrous methanol solutions containing HCl plus LiCl has demonstrated that cathodic and anodic processes are closely related to concentrations of proton and chloride ion, respectively. Bellucci et al. have investigated polarization curves for iron in anhydrous methanol solutions of 0.1M LiClO₄ plus H₂SO₄ (<50 mgdm⁻³ of water). However, protic corrosive species like HCl and H₂SO₄ may be reactive with anhydrous methanol as

\[ \text{HCl} + \text{CH₃OH} \rightarrow \text{CH₃Cl} + \text{H₂O} \quad (1) \]
\[ \text{H₂SO₄} + \text{CH₃OH} \rightarrow \text{CH₃SO₃H} + \text{H₂O} \quad (2) \]

In these papers, it has not been described whether the reactions of protic acids with methanol occur or not. It should be noticed that water formed in these reactions may affect corrosion and passivity of metals.

Hronsky has examined corrosion of iron in 0.5M HCl—anhydrous methanol solution at 20° C for 3h and detected no reaction product after corrosion tests. However, occurrences of reactions between corrosive agents and methanol have been pointed out by some researchers. This investigation was undertaken to confirm...
the effect of a reaction between formic acid and methanol,

$$\text{HCOOH} + \text{CH}_3\text{OH} \rightarrow \text{HCOOCH}_3 + \text{H}_2\text{O}$$ (3)
on the corrosion rate of iron in an anhydrous methanol solution of 0.1M NaClO$_4$ plus 0.05M HCOOH. Formic acid is often used as a corrosive species in hydrous methanol since the acid can be formed by oxidation of methanol. Occurrences of iron corrosion in the presence of formic acid and methyl formate were examined by cyclic voltammetry. The corrosion rate of iron in the methanol solution of formic acid was monitored by an impedance technique and discussed using the acid concentration obtained by titration.

2. Experimental
2.1 Materials
An electrode was a 99.99% iron rod (Johnson Matthey Chemicals, 5mmØ) embedded in a Teflon holder. The electrode surface was polished with emery papers and with 1.0 µm alumina abrasive, and then ultrasonically cleaned in methanol. Anhydrous methanol (Merck, for high pressure liquid chromatography, <100ppm of water) was used without further purification. An analytical-grade reagent of NaClO$_4$ was dried with molecular sieves and used as an electrolyte. A reagent of 98% formic acid was dehydrated by stirring with anhydrous boric acid for 1d and then formic acid was distilled under a reduced pressure of nitrogen gas. A high-grade reagent of methyl formate (Merck, for high pressure liquid chromatography, <100ppm of water) was used without further purification. A solution was prepared by diluting 0.1M NaClO$_4$ and 0.05M formic acid with anhydrous methanol under a dry nitrogen atmosphere immediately before measurements. The water content of a fresh solution was maintained below 200ppm, determined by the Karl-Fischer method. Formic acid and methyl formate solutions of 0.1M NaClO$_4$ were also prepared under a dry nitrogen atmosphere.

2.2 Electrochemical measurements
Cyclic voltammograms for the iron electrode in formic acid and methyl formate solutions of 0.1M NaClO$_4$ and an anhydrous methanol solution of 0.1M NaClO$_4$ plus 0.05M formic acid were measured at the sweep rate of 0.1Vs$^{-1}$ under a dry nitrogen atmosphere. The potential was referred to an electrode consisting of Ag/AgCl/methanol saturated with LiCl.

The impedance for the iron electrode in the methanol solution of formic acid was measured at the free corrosion potential $E_{corr}$ under a dry nitrogen atmosphere. The temperature of the solution was maintained at 30±0.1°C. In a cell equipped with a platinum counter and the reference electrode, the impedance measurement for the iron electrode was carried out using a potentiostat, a frequency response analyzer and a computer, Sinusoidal voltages (5mVrms) between 10kHz and 100mHz were superimposed on the potential. The measurement was automatically controlled with the aid of computer programs.

3. Results and Discussion
Cyclic voltammograms for the iron electrode in a formic acid solution of 0.1M NaClO$_4$ and in a methanol solution of 0.1M NaClO$_4$ plus 0.05M formic acid are shown in Fig.1(a) and (b), respectively. Occurrences of iron corrosion were evidently observed in both voltammmograms. The corrosion rate of iron in the former solution was higher than that in the latter solution. Fig. 1(c) shows a voltammogram for iron in a methyl formate solution of 0.1M NaClO$_4$. Since methyl formate is an aprotic solvent, the cathodic process did not occur and the anodic process was far slower in the methyl formate solution than that in the formic acid solution. However, iron can corrode in the formate solution if the cathodic process is stimulated by contamination of a protic species such as acid or water.

On the assumption that a circuit of a parallel capacitor and resistor combination is equivalent to the metal-solution interface, the charge transfer resistance $R_t$ was determined by fitting a semi-circle to the Nyquist diagram in which a well-defined capacitive loop appeared. The corrosion rate was evaluated from the faradaic conductance $K_f$ defined by a reciprocal of $R_t$ at $E_{corr}$ (4). Fig. 2 shows a change in the logarithm of $K_f$ at $E_{corr}$ with the immersion time $t_i$ for the iron electrode in an anhydrous methanol solution of 0.1M NaClO$_4$ at 30°C under a dry nitrogen atmosphere. The curve indicates a decrease of the corrosion rate with increasing $t_i$.

Along with the impedance measurement, the concentration of formic acid $c_f$ was monitored by titration of the sampled methanol solution. The value of log $c_f$ linearly decreased with increasing $t_i$, as also shown in Fig.2. The linear decrease of log $c_f$ with increasing $t_i$ indicates the first order reaction with respect to $c_f$. 


for esterification of the acid in a methanol solution, as

\[ \text{HCOOH} + \text{CH}_3\text{OH} \rightarrow \text{HCOOCH}_3 + \text{H}_2\text{O} \]  \hspace{1cm} (4)

The rate constant of the reaction was $1.20 \times 10^{-2}$ h$^{-1}$. Because this reaction is reversible, the reaction rate should gradually be decreased with the time.

In order to confirm the occurrence of reaction between formic acid and methanol, the reaction product at ambient temperature for more than 75h was analyzed by $^1$H NMR measurement of a methanol solution containing formic acid (3.78 µL in 1 mL of the solution). Because a signal of methyl formate appears near a signal of formic acid, deuterated methanol CD$_3$OH was used in this experiment. The occurrence of esterification was verified from an appearance of HCOOCD$_3$ in the $^1$H NMR spectrum.

The decrease of the corrosion rate can be attributed to the decrease of $c_\text{f}$ and increases in concentrations of methyl formate and water produced through the esterification. Rates of both cathodic and anodic processes for iron in acetonitrile solutions of carboxylic acids have been reported to be lowered with decreasing $c_\text{f}$\textsuperscript{15). It has been demonstrated that the anodic reaction of iron corrosion is markedly stimulated in an anhydrous methanol solution containing a protic complexing agent whereas the cathodic process is independent of the presence of the agent\textsuperscript{16}. Water afforded by the reaction may affect passivity of iron. Although the corrosion rate may be lower than that in a methanol solution of formic acid, iron can corrode in the solution of methyl formate plus water.

The steep decrease of log $K_\text{f}$ in the initial region of $t_1$ corresponds to the decrease of log $c_\text{f}$, because the concentrations of proton and formate...
ion may closely be related to rates of the cathodic and anodic processes\textsuperscript{25, 10}. At $t_1 = 46\text{h}$, for example, the concentration of water generated by the esterification was 0.022M, being equivalent to about 400 ppm. If the content of water in the fresh solution is assumed to be 100 ppm, there was 500 ppm of water in the methanol solution at that time. Hence, the iron surface might partly be passivated with water, resulting in a decrease of the corrosion rate. On the other hand, since the dissociation of formic acid in methanol is enhanced in the presence of water, the corrosion is accelerated with water afforded by the reaction. Methyl formate may also affect the corrosion rate. The change of the corrosion rate in the methanol solution of formic acid with the time must thus be associated with these effects of species formed by the reaction between formic acid and methanol.

In general, formic acid is used as a corrosive substance for metals in a methanol solution containing more than a few percent of water. Since a protic corrosive species like formic acid can react with anhydrous methanol even at ambient temperature, the effects of the reaction products may complicate behavior of metallic corrosion in a methanol solution. A special attention should be paid to use of a protic acid for studying corrosion of metals in the anhydrous methanol solution.

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References