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Effects of water additions on the passivity of iron in dimethoxyethane solutions

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Abstract

The effects of trace water additions on the passive behavior of iron in an otherwise anhydrous dimethoxyethane/0.5 M LiAsF₆ solution have been studied by electrochemical and surface analytical techniques. The results indicate that the passivity observed in the anhydrous solvent is maintained when small (less than 2000 ppm) concentrations of water are present as a contaminant. Passive current densities increase slightly, but water does not cause any catastrophic interference with the various passivation mechanisms. Water, when present at these levels, actually helps to extend the passive range of iron by several hundred millivolts in this system. This behavior is the result of a complex interplay between iron dissolution and solvent electropolymerization at increasingly anodic potentials. Water is believed to be the component responsible for the localized acidification of areas of active dissolution, which then results in optimal conditions for polymer film formation. This behavior is peculiar to the system of iron in dimethoxyethane/LiAsF₆.

Keywords: Iron passivity; Water; Dimethoxyethane solutions

1. Introduction

Historically, research efforts aimed at understanding the corrosion and passivity of metallic materials in liquid environments have focused on water as the primary, if not the sole, component in that phase. This is justifiable in view of the ubiquitous nature of water in our environment. Organic solvents, on the other hand, have typically been treated as benign phases which do not threaten the integrity of metal structures. Indeed, the common view of organic solvents as non-aggressive species had led some researchers to use these solvents as a medium in which to isolate and study the effects of water on passivity without undue interference [1]. Recently the behavior of metals and alloys in non-aqueous organic solvents has begun to receive more attention [2]. With this increased attention the notion that organic solvents do not pose any serious corrosion problems has been largely disproved. Results from our work and from that of others have demonstrated that metals and alloys in various non-aqueous solvents have exhibited behavior ranging from active dissolution to extensive stable passivity [3-9].

This paper presents a follow-up to studies performed on high purity iron in anhydrous dimethoxyethane (DME) with 0.5 M LiAsF₆ as the supporting electrolyte [3]. Water concentrations in the solutions in that study were intentionally minimized so that the behavior of iron in an isolated organic solution could be studied. Successful isolation of the organic solvent allowed for interpretation of the results without any significant interference by water contamination. Among the observations from that study were the following: (i) an inability of the native oxide film to provide adequate protection at increasingly anodic potentials, and (ii) a large stable passive region which relies on solvent chemisorption at lower potentials and formation of a polymer film at higher potentials. Chemisorption of the DME solvent is possible only at potentials below the DME oxidation potential (DME_{ox}). Below DME_{ox}, chemisorption of DME precludes formation of the polymer film. The polymer film formation was not observed when salts other than LiAsF₆ were used, and the range of passivity was reduced accordingly. While the results obtained from that study were necessary for a fundamental understanding of the passive behavior in this system, the conditions studied do not provide an accurate representation of the true service conditions because the removal of water to the low levels of that

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study is generally not achieved in practice. Even in the case of lithium batteries, contamination by water in secondary cells typically exceeds the levels used in our research.

This study aims to provide a qualitative, if not mechanistic, explanation for the polymer film formation as well as other observed behavior by intentionally adding trace amounts of water and studying the effects. Among the questions to be addressed are:

(i) What roles do water and LiAsF_6 play in the polymer film formation?

(ii) Why does the polymer film form only on bared iron surfaces?

(iii) Why is there no polymer film formation at lower potentials?

These and other questions regarding the unusual passive nature of iron in DME/LiAsF_6 will be discussed.

2. Experimental

Solutions of 0.5 M LiAsF_6 in DME were prepared from chemicals of the highest purity commercially available. The 1,2-dimethoxyethane (Burdick and Jackson) contained a maximum of 120 ppm water. The lithium hexafluoroarsenate (Lithium Corporation of America) contained a maximum water content of 100 ppm. The solution was mixed in a round bottom flask under nitrogen atmosphere in a glove bag. Type 4A molecular sieves were added to the flask prior to sealing with rubber septa. A more detailed discussion of solution preparation and handling has been presented elsewhere [3]. This solution preparation method enabled us to obtain nominally non-aqueous solutions containing less than 100 ppm water. For experiments in which small concentrations of water were added as a contaminant, Millipore water was injected from a microliter syringe directly into the electrochemical cell through the rubber septum.

The working electrode was constructed by press fitting a high purity iron rod (99.9985% Fe, 5 mm diameter from Johnson-Matthey) into a Teflon cylinder, yielding a surface area of 0.2 cm². The iron working electrode was polished to an 800 grit finish, rinsed with Millipore water, and finally rinsed in acetone and methanol before being dried in warm air. Platinum gauze was used as the counter electrode. Prior to use, the platinum was immersed in nitric acid, rinsed in the sequence described above, then flamed to red-hot in an alcohol flame to remove any organic impurities.

Electrochemical measurements were performed with a PAR model 342 corrosion measurement system that incorporated a PAR model 273 potentiostat/galvanostat. The specifics of the electrochemical techniques have been presented in a previous paper [3]. An aqueous saturated calomel electrode (SCE) with Vycor tip was

used as the reference electrode in all experiments. All potentiodynamic scans were run at a rate of 0.5 mV/s and were *IR* corrected via automatic current interruption. Experiments were conducted at room temperature ($25 \pm 2^\circ\text{C}$) after allowing the working electrode to reach a steady open-circuit potential. This typically was achieved in 2 to 3 hours. The electrochemical cell had separate compartments for working, reference and counter electrodes. At the conclusion of each experiment, the specimen was removed from solution while still under potentiostatic control, rinsed in pure DME and dried in warm air. Scanning electron microscopy (SEM) was performed on a JEOL JSM-6100 SEM with a Kevex Delta Class energy-dispersive X-ray microanalyzer. X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer PHI 5100 ESCA system.

3. Results

Before the effects of trace additions of water on the passive behavior of iron in $\text{DME}/0.5\text{ M LiAsF}_6$ can be presented, it is beneficial to review the results obtained for iron in dry $\text{DME}/0.5\text{ M LiAsF}_6$ [3]. The driest solutions prepared contained less than 100 ppm water, which is sufficiently low to limit most of the interfering effects of water. This issue will be addressed in more detail later. In $\text{DME}/0.5\text{ M LiAsF}_6$ solutions in the absence of water, iron displays a stable passive region which extends from the open-circuit potential of iron to approximately 1350 mV (SCE). Above 1350 mV (SCE) any and all passivating films are breached and localized corrosion ensues. In the passive region two different mechanisms are responsible for repassivation of the iron surface following removal of the air-formed oxide film by mechanical abrasion. Below DME_{ox} the surface is passivated by chemical adsorption of the DME solvent molecules. Above DME_{ox} , where the solvent oxidizes upon contact with the iron surface, passivation is by a thin polymer film up to about 1300 mV (SCE) and by a much thicker polymer film in a narrow range of potentials above 1300 mV (SCE). Each of these mechanisms has a characteristic repassivation rate as well as a unique visual appearance of the film when it forms in the scratched areas. It should be noted that throughout this passive region, the possibility exists that more than one passivation mechanism may be operative at a given potential. However, the fact that passivation is secured by the mechanism which is most favorable and occurs with the greatest facility makes it experimentally impossible to define the exact limits of the region over which a specific passivation mechanism is operative. For iron in $\text{DME}/0.5\text{ M LiClO}_4$, neither a polymer film nor a salt film forms and breakdown occurs at DME_{ox} . Passivity below this potential is provided by chemical adsorption of DME acting in concert

with the air-formed film. Polymer film formation is thus unique to the system of iron in DME/LiAsF₆.

3.2. Iron in DME/0.5 M LiClO₄ solutions with trace water additions

The effects of trace water additions on the passive behavior of iron in DME solutions were investigated by injecting various amounts of water, from 50 to 2000 ppm, by microliter syringe into otherwise anhydrous solutions of DME (base water content of 100 ppm). The expected result based on the previous work of Kelly et al. [5] and Agladze et al. [9], was a uniform activation of the surface. This would be manifested by an increase in the passive current density owing to competitive adsorption between molecules of DME and water [1]. This type of behavior was observed for iron in DME/0.5 M LiClO₄ solutions. Fig. 1 shows the effect of adding 750 ppm of water to an anhydrous DME/0.5 M LiClO₄ solution. The current densities for the solution with the added water are increased by almost an order of magnitude over the entire passive region. However, the breakdown potentials for the two curves are nearly identical. Therefore, small water additions affect the maintenance of the passive state, but not its eventual breakdown.

3.3. Iron in DME/0.5 M LiAsF₆ with trace water additions

The situation is quite different for iron in DME/0.5 M LiAsF₆ solutions. Again, water additions ranging from 50 to 2000 ppm were added to anhydrous solutions of DME with 0.5 M LiAsF₆. Figs. 2 and 3 show the results of these experiments. There are several observations to be made regarding the consequences of contamination by water in this system. One is that there is a shift in the open-circuit potential by several hundred

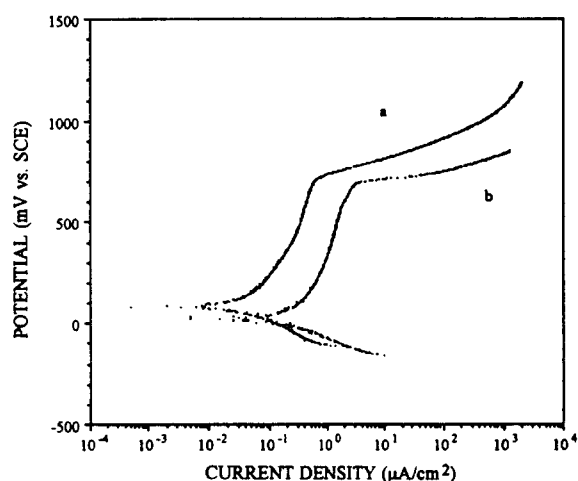


Fig. 1. Effect of adding trace amounts of water to DME/0.5 M LiClO₄: (a) dry, and (b) 750 ppm.

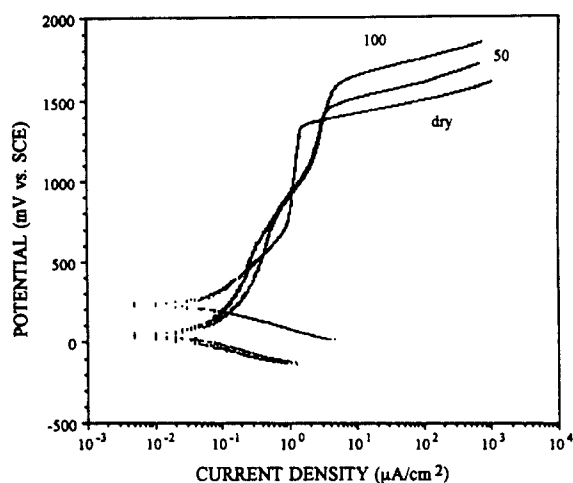


Fig. 2. Polarization scans of iron in DME/0.5 M LiAsF₆ with different amounts of added water measured in ppm.

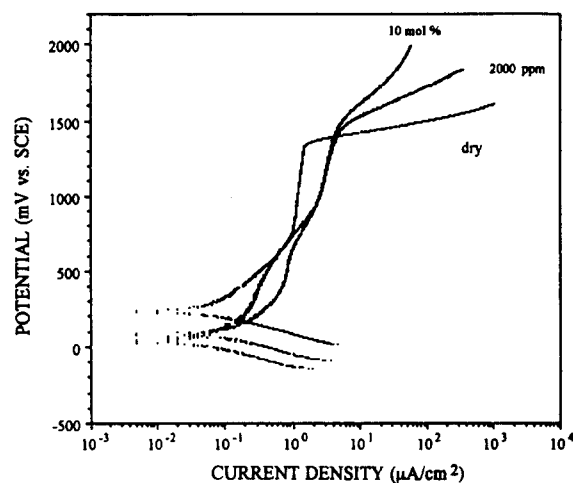


Fig. 3. Polarization scans of iron in DME/0.5 M LiAsF₆ with different amounts of added water.

millivolts in the active direction. Another is that there appears to be no uniform activation over the passive range. The current density is slightly lower below 900 mV (SCE), then crosses over the anhydrous curve and becomes slightly greater at more positive potentials. This behavior is counter intuitive and is not well understood.

The most peculiar observation from this data is that of the behavior at the breakdown potential. The nature of the curves near the breakdown potential has three notable features. The most obvious is an increase in the breakdown potential for solutions containing greater water concentrations. This behavior seems to be limited in the positive direction since, eventually, incremental additions of water have no further effect. The fact the water is an aggressive species in DME solutions makes the increase in the breakdown potential with increasing water content difficult to understand. However, when the peculiarities of the solution chemistry in the presence of the LiAsF₆ salt are considered, these observations

can be rationalized. In addition to the breakdown potential becoming more positive with increasing contamination by water, two other effects are observed: (i) the increase in the current at the breakdown becomes more gradual, and (ii) the Tafel slope following breakdown becomes greater. Clearly the behavior under anhydrous conditions is more typical of a passive film breakdown 'event', where the breakdown is very sharp (occurring over a range of perhaps 10 mV) and large increases in the current density owing to the pitting process occur almost independently of potential once pitting is initiated.

Water does not appear to have a significant effect on the repassivation process at lower potentials. Hold-and-scratch experiments at 700 and 900 mV (SCE) show nearly identical behavior to those performed in the anhydrous solutions. However, at higher potentials water does have an effect on repassivation. Fig. 4 is a plot of charge passed during repassivation (corrected for scratched area) versus applied potential for hold-and-scratch experiments performed on iron in DME/0.5 M LiAsF₆ with 100 ppm water added. This amount of water results in a breakdown potential just above 1600 mV (SCE). Scratching experiments were limited to potentials below this value, since above the breakdown potential not only does pitting occur, but removal of the air-formed film by scratching leads to general dissolution in the scratch. The plot shows that the amount of charge passed increases tremendously at higher potentials. The reasons for this will be explained in the discussion section.

The change in Tafel slopes and the gradual change in current density after the breakdown potentials suggest that something other than a classic breakdown phenomenon is occurring [10]. A cyclic polarization scan was performed in DME/0.5 M LiAsF₆ with 100 ppm added water to observe the effect of a reversal of

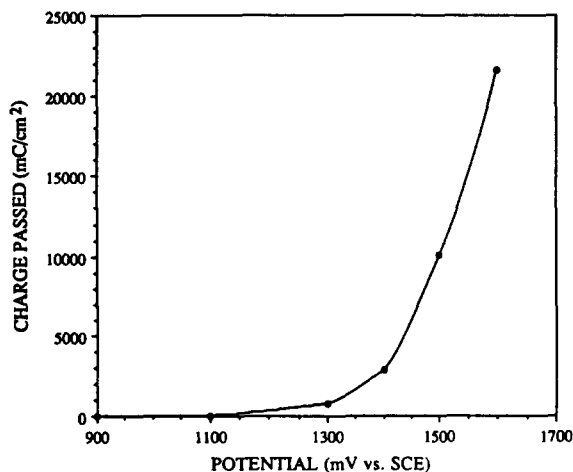


Fig. 4. Charge passed during repassivation vs. applied potential for hold-and-scratch experiments performed on iron in DME/0.5 M LiAsF₆ with 100 ppm added water.

potentials after breakdown had been initiated (Fig. 5). The expected result would be a continued increase in current density until the potential had dropped to a level where one of the repassivation mechanisms was operative, whereupon the current would then decrease to low passive levels. This was not observed during the scan. Rather, the increasing current was halted almost immediately and a decrease in current was observed well before the potential had dropped below the breakdown potential.

3.3. Iron in DME/0.5 M LiAsF₆ with trace additions of acetic acid

It has been suggested that trace water additions in neutral organic solutions act in a somewhat acidic manner [1]. To explore whether the added water was, in fact, exhibiting proton-donor characteristics, polarization scans and hold-and-scratch experiments were performed in DME/0.5 M LiAsF₆ with various amounts of acetic acid added in the ppm range. Acetic acid is an organic acid that is very weak in aqueous solutions. It is expected that it is also a weak acid in organic solutions. The passive behavior of iron in the DME/0.5 M LiAsF₆ solution with added acetic acid is nearly identical to the behavior with added water. This observation lends credence to the suggestion that water can act in an acidic manner in neutral organic solutions.

Fig. 6 shows another interesting aspect of the polymer film formation. This photomicrograph shows a pit which formed while the specimen was held above the breakdown potential, and which subsequently repassivated by the polymer film when the potential was dropped into the range where electropolymerization takes place. There is no evidence of a thick polymer film having formed in surrounding regions. This provides evidence that the polymer film forms only on bare metal surfaces and not in any of the surrounding areas. The metal

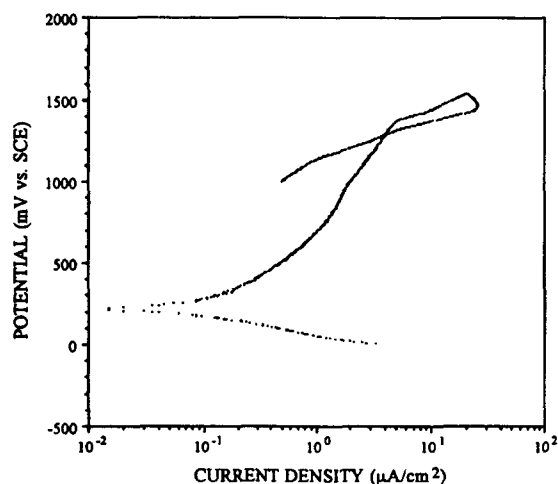


Fig. 5. Cyclic polarization scan of iron in DME/0.5 M LiAsF₆ with 100 ppm added water.

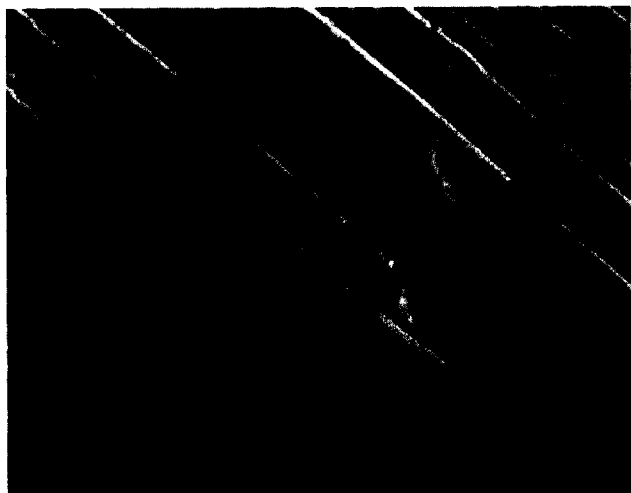


Fig. 6. SEM photomicrographs of pits which formed above the breakdown potential and were repassivated by the polymer film upon subsequently lowering the potential.

surface may be exposed by mechanical removal of the native oxide film or by a localized chemical attack leading to pitting. This observation also proves that a high potential is not sufficient, in and of itself, to promote the polymerization reaction. The reasons for this will be explained in section 4.

4. Discussion

Given the data and observations for the system of iron in DME/0.5 M LiAsF₆ and the cited literature on polymerization [11–15], the presumed series of steps leading to repassivation by electropolymerization is as follows. Near 1300 mV (SCE) in DME/0.5 M LiAsF₆, iron lacks any of the traditional passivation mechanisms outlined by Agladze et al. [9]. The air-formed oxide film has defects and pores, DME oxidizes on contact with the metal surface, and the salt film is too soluble or unprotective. The result of this condition is that the iron surface pits (or, if the air-formed film is scratched off, general corrosion occurs). Ferric or ferrous ions are thus produced from the pitting process and they are subsequently hydrolyzed by the trace water in solution. (Recall that even the driest solutions studied contained about 100 ppm water.) Oxidation of free water can also take place on the metal surface at these high potentials, thereby increasing the supply of hydrogen ions in solution. This production of hydrogen ions is a very localized event, occurring only where the underlying metal surface has been exposed. The acidification of the solution near the exposed iron leads to a further dissociation of AsF₆⁻ to form AsF₅. This promotes further acidification of the solution and the process continues in an autocatalytic fashion. The result of these chemical and electrochemical reactions is a

localized region adjacent to the exposed iron surface which consists of a relatively high concentration of AsF₅ (a strong Lewis acid) and hydrogen ions in the DME solvent. This represents the ideal conditions for cationic polymerization of either the DME ether solvent or its oxidation product. Cationic polymerization is a type of polymerization reaction known to occur to some organic molecules in the presence of strong Lewis acids and a source of protons [15]. Further, the presence of AsF₅ in electrolytes is known to polymerize some ether solvents [12]. The absence of a strong Lewis acid in the DME/LiClO₄ solutions precludes the formation of a polymer film for that system.

The generation of hydrogen ions by either hydrolysis or oxidation of water emphasizes the importance of the bare metal surface for the initiation point of the polymer formation. Also, the initiation of the polymerization reaction is clearly not dependent only on potential since initiation would be expected to proceed from the moment the potential was stepped from open circuit to 1300 mV (SCE). Initiation does not occur until the passive layer is disrupted by a chemical breakdown or by a mechanical process. This mechanism also makes clear the reason why the polymer film will form only in the presence of water or some other proton donor. The role of water as proton donor was verified by the experiments in which water was replaced by acetic acid. The two species were shown to act in equivalent roles in the initiation of the polymerization.

As more water is introduced into solution, the potential range where polymer film growth is possible expands to higher potentials. Conversely, as the amount of water in solution is reduced, the range of potentials over which the polymer film forms is also reduced. Though practically unattainable, a DME/LiAsF₆ solution containing no water whatsoever would be expected to have a breakdown potential coincident with the DME oxidation potential.

A distinction is made between the thick polymer film that forms above 1300 mV (SCE) and a thin film of identical composition that forms between 850 and 1300 mV (SCE), still above DME_{ox}. There are a number of possible explanations for why the polymer film does not form as thick a layer at these lower potentials. One explanation may be that at lower potentials the driving force for dissolution is not as great. A thin polymer film which forms quickly and seals off the bared surface will limit the amount of proton production. This, in turn, shuts down any subsequent polymer formation by reducing a key component of the reaction. Likewise, the reason that the polymer does not form at potentials below DME_{ox} on iron is that the bare metal surface is quickly covered by a chemisorbed passive layer which removes the necessary conditions for polymer growth.

One of the more interesting aspects of the passivation by polymer film formation is the affect of trace water additions on the shape and position of the potentiodynamic scans near the breakdown potential. In dry solutions (100 ppm water) breakdown occurs just above 1300 mV (SCE) and there is a very narrow potential range in which scratching results in long passivation times and formation of the thick polymer film. When breakdown occurs, it is fairly sudden and complete. When trace water (50 to 2000 ppm) is added to the solution, the breakdown potential increases slightly, the transition from the passive to the active state becomes much more gradual, and the Tafel slope increases somewhat. All of these observations can be explained if the dual effects of both water and potential are considered simultaneously. Additions of water and increases in potential are both beneficial and detrimental. Additions of water to the anhydrous solution enhance proton production by hydrolysis or water oxidation. This makes the conditions for subsequent solvent polymerization more favorable. However, water additions also make the solution more corrosive. On the other hand, increasing potential helps drive the polymerization reaction by breaking down other passive films and introducing more metal ions into solution, but it also increases the driving force for the dissolution which can undermine the polymer film.

The polarization scans show that although breakdown is initiated, pitting does not go unchecked. As the pitting process begins, it promotes the ideal conditions for growth of the polymer film. The character of the curves can thus be explained in terms of a dynamic equilibrium between dissolution and polymer film growth. For solutions with trace water additions, potentiostatic holds above the breakdown potential bear this out. In these holds currents were high but stable potentials for more than 100 mV above what was assumed to be the breakdown potential. The charge passed during repassivation for hold-and-scratch experiments (Fig. 4) is further evidence that, at higher potentials, the polymer film has a difficult time keeping the surface passivated under a large driving force for dissolution, so repassivation is exceedingly slow. Eventually, at high enough potentials, the driving force for dissolution overcomes the driving force for polymerization and the iron pits without passivating. The advantageous effect of water lessens at higher concentrations and consequently there appears to be an optimum water concentration for promoting passivity by polymer film growth. The curve for 10 mol% water shows the optimum passive behavior of all the water concentrations tested.

In these systems the manner in which the different mechanisms act in concert to passivate the metal surface is quite remarkable. The native oxide film is the first line of defense. If it has defect or is somehow removed

in service, solvent chemisorption is the next most efficient passive layer. When it is no longer able to function owing to its own electrochemical oxidation, minor dissolution of the metal surface may cause precipitation of some sparingly soluble salt. If the salt film is too soluble or unprotective then a polymer film may form. If not, then pitting or even general corrosion finally occurs. In these neutral organic solutions, as many as three and sometimes four types of films can act in sequence to provide protection against corrosion. Also, the easiest and most efficient mechanisms tend to predominate, and can preclude the formation of less efficient films. The manner in which these passive films tend to be self-healing is also remarkable, in that they can, in effect, search out the active dissolution sites and seal them off.

5. Conclusions

The effects of trace water additions on the passive behavior of iron in DME solutions have been studied. For iron in DME/0.5 M LiClO₄, trace amounts of water increase passive current densities by interfering with the chemisorbed DME film. There is no effect on the passive film breakdown potential in that system. For iron in DME/0.5 M LiAsF₆, water has little effect on the passive state below DME_{ox}. Above DME_{ox}, water additions extend the passive range by several hundred millivolts. This is the result of the creation of ideal conditions in solution for the polymerization of the DME solvent. The polymer film formation requires three conditions: a bare iron surface, a source of protons, and a strong Lewis acid. The bare iron surface provides iron ions which subsequently hydrolyze in the presence of trace amounts of water (the source of protons). The LiAsF₆ supplies the strong Lewis acid. If any of these conditions is not satisfied the polymer film does not form and the passive range is reduced accordingly.

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