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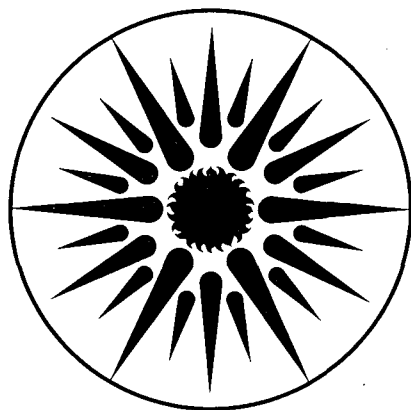## UNIVERSITY OF CALIFORNIA

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Corrosion, Passivity and Breakdown of Alloys
Used in High Energy Density Batteries

J. Kruger

January 1990

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# CORROSION, PASSIVITY AND BREAKDOWN OF ALLOYS

# USED IN HIGH ENERGY DENSITY BATTERIES

Final Report

January 1990

by

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for

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# 1 Introduction

The role of passive films in aqueous solutions has been studied extensively [1], yet the passivity of metals and alloys in non-aqueous solutions has received comparatively little attention despite its importance to such technologies as lithium batteries, chemical processing, and fuel processing [2-4]. In an extensive review of the corrosion of metals and alloys in organic solvents in 1974 [5], Heitz stated at the time "there have been no relevant results published on the nature and structure of passive layer in organic solvents." With increasing demands on lithium cells, the long term integrity of the container and structural components become increasingly important. Corrosion problems in lithium batteries are well documented [6-9]. Long term integrity depends on the protective ability of the passive film in the non-aqueous electrolytes employed. By understanding the nature of passivity in non-aqueous solvents, and factors which cause its breakdown, improvements in the corrosive behavior of structural alloys and electrode materials in lithium batteries and other commercial applications in non-aqueous solutions can be made.

The overall objective of this work is to enhance the understanding of the major processes affecting corrosion in non-aqueous solvents: passivity and breakdown of passivity. Since passive layers control corrosion, the achievement of such an understanding especially in regards to how alloy composition affects these layers is crucial to the development of alloys more corrosion resistant in non-aqueous solvents. This research addresses the following fundamental questions: (1)Are the films found in organic solvents different from those produced in aqueous environments ? (2)Can passive layers form on bare metals in the absence of water, and if they can, what is their nature ? (3)What are the kinetics of passive film formation, breakdown and repassivation? This report presents the findings and pertinent conclusions for Year III of this program (August 1,1988 to July 31,1989).

During Year III, work that has tried to answer some of the questions about the passivity and breakdown of 99.9985% iron and 1018 carbon steel in anhydrous PC solutions with 0.5M LiAsF$_6$ or 0.5M LiClO$_4$. Tests of 1018 carbon steel in solutions of anhydrous high purity PC/0.5M LiAsF$_6$ with 100 ppm to 2000 ppm added water were also conducted. Electrochemical tests involving 1018 carbon steel, nickel 200, and 304 stainless steel in solutions of technical grade propylene carbonate(PC) with lithium perchlorate or lithium hexafluoroarsenate as the electrolyte were also conducted. Water additions to technical PC from 30 mole% to 70 mole% have been studied as well as totally aqueous solutions.

# 2 The Passivity of Iron and 1018 Carbon Steel in Anhydrous PC Solutions

## 2.1 Experimental

Some work performed during Year III has been involved with the corrosion behavior of high purity (99.9985%) iron and 1018 carbon steel in anhydrous PC/LiClO$_4$ and PC/LiAsF$_6$ solutions. The pure iron rod (5 mm dia.) sample (99.9985% Fe, obtained from Johnson-Matthey) was mounted in a Teflon cylinder. The 1018 carbon steel samples were available in 5/8" dia. disks from Metal Samples (Munford, Alabama) and were mounted in a Teflon test holder. The 99.9985% Fe and 1018 carbon steel samples were polished to an 800 grit finish, rinsed with water purified from a Millipore system, followed by rinsing in acetone and methanol before being dried in warm air.

Propylene carbonate from Burdick and Jackson was received with a water content of 140ppm. LiClO$_4$ (anhydrous 99.5%) was obtained from Johnson-Matthey and LiAsF$_6$ (99.5% min.) was obtained from Lithium Corporation of America (Gastonia, North Carolina).and was used without further purification.

Preparation of anhydrous PC solutions containing either 0.5 M LiClO$_4$ or 0.5 M LiAsF$_6$ were handled in a glove bag. To reduce water impurities in the PC solutions to the ppm range, a vacuum line technique, as used earlier by Kelly et al [10], was applied. The apparatus is shown in Figure 1. It consists of 7 parts: (1) a vacuum pump and associated traps, (2) a UHP N$_2$ (99.999%) source which feeds into a Supelco gas purifying system which reduces water and oxygen content in the N$_2$ gas to less than 0.1 ppm each (the purified gas is referred to as VUHP N$_2$ throughout to remainder of the paper), (3) a 3-port manifold with Teflon valves which allows independent control of vacuum and VUHP N$_2$ distribution, (4) a storage vessel for the PC solutions, (5) a deoxygenation stage and associated PC trap, (6) a vacuum fraction cutter for measuring solution volume, and (7) an electrochemical cell. The solutions analyzed were found to have a water content of between 50-100 ppm (approximately 20 ppm can be considered due to exposure with the air during transfer). Cyclic voltammetry was conducted on Pt in both perchlorate and hexafluoroarsenate solutions prior to many of the tests. Calculations based upon the cyclic voltammetry results and diffusion coefficient data by Atanasoski et al [11] show the water contents of either solution to be about 10 ppm.
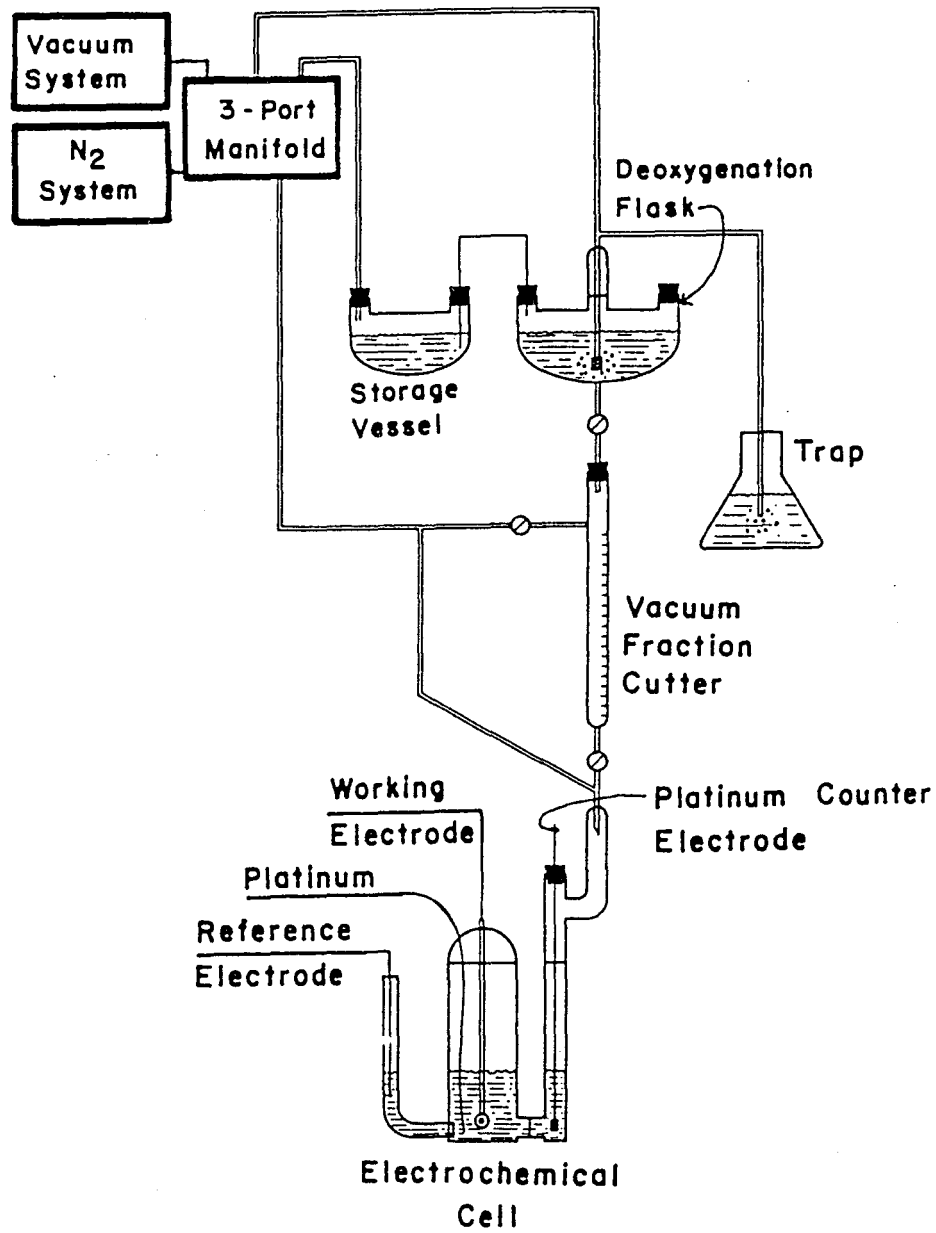
**Figure 1:** Experimental apparatus for purification, handling, and test scans of anhydrous PC. See text for details.

The reference electrode used was $Ag/AgClO_4$(20 mM in PC) as developed by Kirona-Eisner and Gileadi for electrochemical studies in PC [12]. This electrode, referred to as the SSP, was chosen for its reproducibility, insensitivity to small amounts of water, lack of contaminating ions and its very small liquid junction potential. This electrode was found to be at +3.1 V versus $Li^+/Li$.

Electrochemical measurements were performed with a PAR Model 342 Corrosion Measurement System. All experiments were conducted at room temperature (25 ± 2°C) after allowing the electrodes to come to a steady state open circuit potential (generally about 2 hours). In some experiments, part of the Fe electrode surface was bared by scratching in-situ by means of a glass rod ground to a sharp tip. The slow scan rate used for all potentiodynamic scans was 0.5 mV/sec and was IR-corrected via automatic current interruption. The experimental range during potentiodynamic scans was generally -250 mV versus $E_{corr}$ to +2300 mV versus SSP. A number of constant potential experiments were conducted at specific potentials of interest to assure the steady state behavior (i.e. passivity or corrosion).

## 2.2 Results and Discussion

### 2.2.1 99.9985% Fe with Air-formed Film Intact

The possible passivation mechanisms available to anhydrous organic solvents are: (a) air-formed film, (b) salt film and (c) chemisorption of the solvent molecules. High purity iron and 1018 carbon steel in neutral anhydrous solutions of PC/0.5M $LiClO_4$ or PC/0.5M $LiAsF_6$ has demonstrated that each of these three mechanisms have a region of dominance. However these regions may be influenced by such factors as the cleanliness of the metal surface or the physical and chemical properties of the electrolytes.

Figure 2 shows the behavior of 99.9985% Fe with its air-formed film in place in neutral anhydrous solutions of PC/0.5M $LiClO_4$ and of PC/0.5M $LiAsF_6$. In both solutions no active/passive transition is observed, although a cathodic reaction may disguise it, as is the case with Cr in aqueous solutions [13]. A slight increase in the current density occurs at potentials just above $PC_{OX}$ (ca. 0.6-0.7 V(SSP)), due to PC oxidation as observed on platinum. At potentials above around +1.4 V(SSP) in perchlorate solutions, pitting of the iron surface is observed. Pitting is verified by optical microscopy. This pitting is believed to be due to the oxidation of the perchlorate anion and its influence on the air-formed film. In constant potential holds of at least 4000 seconds duration on high purity Fe in perchlorate solutions, the air-formed film is protective for any potential from $E_{corr}$ up to the perchlorate anion oxidation potential.
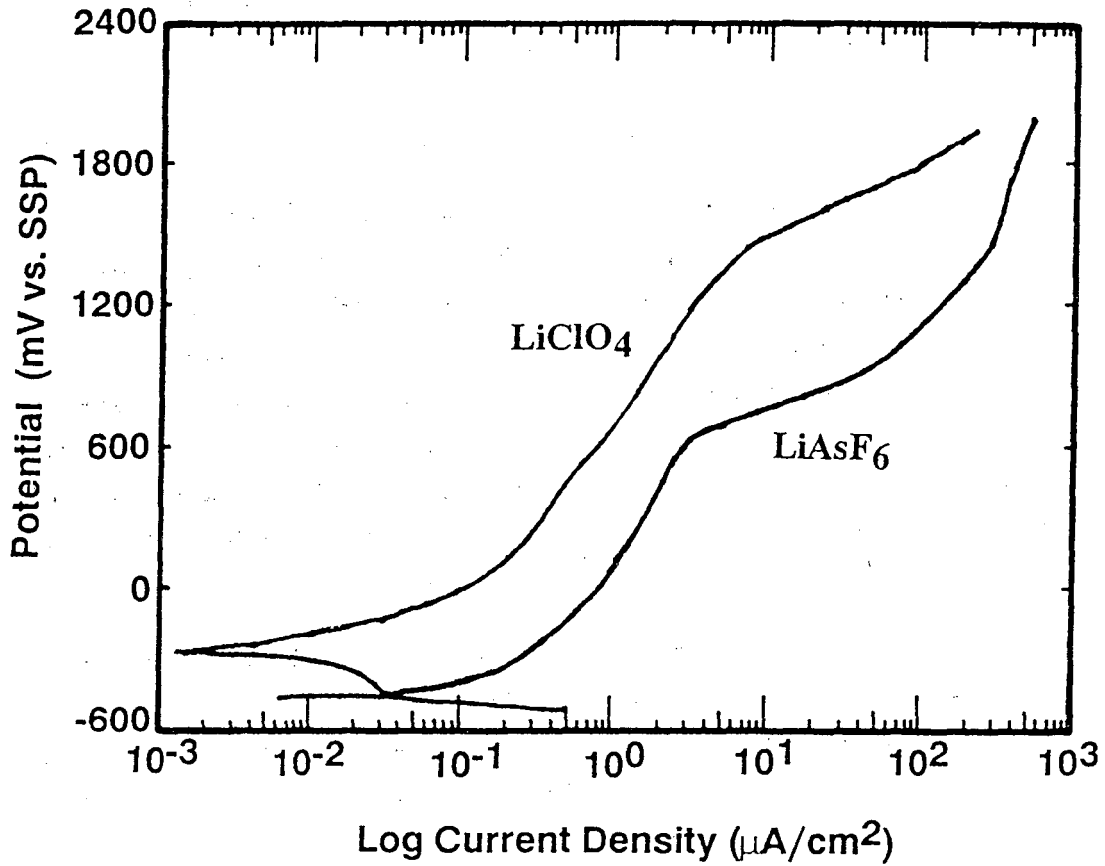
**Figure 2:** Slow scans on 99.9985% Fe in PC containing 0.5 M $LiAsF_6$ or 0.5M $LiClO_4$. Below $PC_{ox}$, the currents are low in both scans ; above $PC_{ox}$ the $Fe/LiAsF_6$ scan shows currents an order of magnitude higher than the $Fe/LiClO_4$ scan up to $ClO_4^-$ oxidation.

In the case of 99.9985% Fe in PC/0.5M LiClO$_4$ solutions during Year II and our subsequent studies in Year III have shown that the air-formed film on Fe remains intact and provides protection over a wide potential range. Since no source of oxygen is available in anhydrous organic solutions, the passive behavior is not caused by oxide film growth; in addition, the low current densities observed are insufficient to precipitate a salt film. Chemisorption of the solvent may occur over the air-formed film and contribute to the overall passive behavior of the metal.

In 0.5M LiAsF$_6$ solutions, the current density remains low until potentials of approximately +0.6-0.7 V(SSP) are reached during slow scans which show a "breakdown" above which a relatively rapid increase in the current density occurs. The current density observed below PC$_{OX}$ during slow scans with high purity iron in PC/0.5M LiAsF$_6$ solutions is an order of magnitude higher than in perchlorate solutions and is likely the result of the increased ionic conductivity of the surface film in hexafluoroarsenate solutions [14]. The passivity of the air-formed film on iron in 0.5M LiAsF$_6$ solutions deteriorates at potentials slightly above PC$_{OX}$ and the anodic currents increase with time. The possible higher solubility of the probable Fe(AsF$_6$)$_2$ salt, requires higher iron dissolution rates to precipitate a salt film on the iron surface.

In constant potential holds below PC$_{OX}$, high purity iron in 0.5 M LiAsF$_6$ solutions displays stable passivity during our 4000 second tests. Unlike the results in perchlorate solutions, potentiostatic holds above PC$_{OX}$ in hexafluoroarsenate solutions reveal a loss of passivity on the iron surface. The anodic currents increase with time. This is shown in Figure 3 at a constant hold of +1.0 V(SSP). Pitting of the iron surface is observed after potentiostatic holds above PC$_{OX}$ in 0.5M LiAsF$_6$ solutions. This differs from the results in perchlorate solutions, where pitting is not observed on iron until oxidation of the perchlorate anion occurs.

## 2.2.2 1018 Carbon Steel with Air-formed Film Intact

The polarization behavior of 1018 carbon steel with its air-formed film intact in neutral anhydrous solutions of PC/0.5M LiClO$_4$ and PC/0.5M LiAsF$_6$ is shown in Figure 4. Anodic polarization exhibits low current densities in both perchlorate and hexafluoroarsenate solutions up to about +0.4-0.5 V(SSP) where PC begins to oxidize. Above PC$_{OX}$ in perchlorate solutions, the current density of the carbon steel increases slightly to levels similar to high purity iron in perchlorate. Above +1.4 V(SSP), the oxidation of the perchlorate anion occurs and pitting of the carbon steel is also observed as it was for iron in 0.5M LiAsF$_6$ solutions.

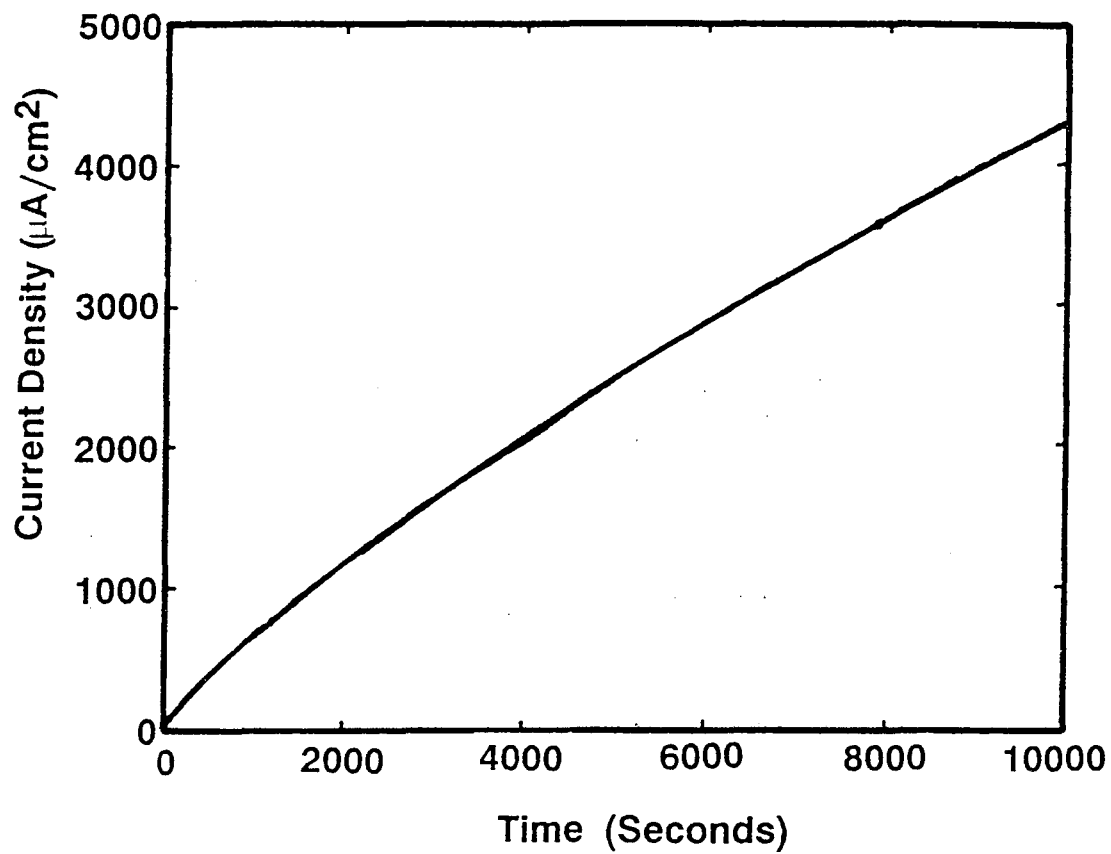**Figure 3:** Potentiostatic hold of 99.9985% Fe at + 1 V(SSP) in PC/0.5M LiAsF$_6$. Unlike in the perchlorate solutions, the anodic currents increase with time.

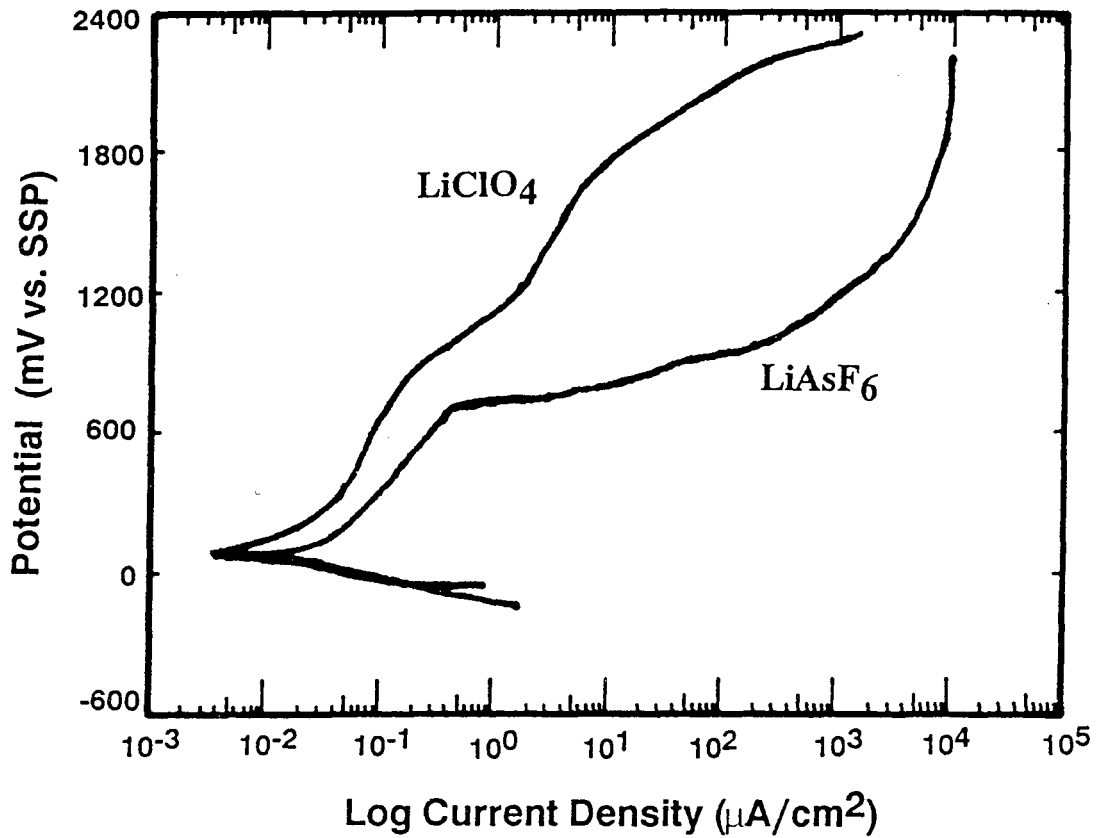**Figure 4:** Slow scans on 1018 carbon steel in PC. 0.5M LiAsF$_6$ vs. 0.5M LiClO$_4$. Below PC$_{ox}$ the scans are similar; above PC$_{ox}$ the corrosion currents in the PC/LiAsF$_6$ solutions rise to levels an order of magnitude higher than in PC/LiClO$_4$.

The carbon steel samples in either solution shows deterioration of the adsorbed PC/air-formed passive film at about 100-200 mV negative to that observed in high purity iron when PC begins to oxidize. Pitting is observed in carbon steel tests run above $PC_{OX}$ in either electrolyte. This is believed to be caused by the presence of sulfide surface inclusions. The sulfide inclusions are highly conductive and can act as sites which catalyze the cathodic reactions and raise the corrosion potential and increase the anodic corrosion currents, which is responsible for pitting at sites adjacent to the inclusions, as seen in aqueous solutions [23,24]. Hydrolysis of the PC may also produce a local acidic environment which could attack the inclusions and the surrounding metal.

At constant potentials below $PC_{OX}$, the passivity of the air-formed film on the 1018 carbon steel is stable for at least 4000 seconds. At potentials above $PC_{OX}$, the air-formed film is not stable. Figure 5 shows a hold at +1.0 V(SSP) in a perchlorate solution. When the potential is first applied rapid dissolution of the steel occurs; no apparent induction time is observed prior to the current rise. The anodic current density reaches a maximum of about 1 $mA/cm^2$ in about 4 minutes at which time a salt film develops which gradually blocks the surface from the bulk solution and reduces the current density to approximately 200 $\mu A/cm^2$ after 1.5 hours. In hexafluoroarsenate solutions, constant potential tests above $PC_{OX}$ result in rapid current density increases as shown in Figure 6. These high currents increase until a limiting current density of about 10 $mA/cm^2$ is reached. When a passivated surface is exposed to an environment that can attack the metal substrate rapidly while only slowly attacking the passive layer, film disruption and undermining can occur at any incidental breaks in this film [28].

In 0.5M $LiAsF_6$ solutions, potentials above $PC_{OX}$ lead to sharply increased current densities until a limiting process at about 10 $mA/cm^2$ begins. In this limiting region, a brown salt film, presumably $Fe(AsF_6)_2$, is formed on the metal surface, although this salt film does not adequately protect iron or steel. The behavior of the steel above $PC_{OX}$ is related to the apparent solubility of the salts formed in their respective electrolyte solutions. Pitting of carbon steel is observed by optical microscopy on specimens scanned above $PC_{OX}$ in 0.5M solutions of $LiClO_4$ or $LiAsF_6$. The pit density on steel is higher in the hexafluoroarsenate solutions. Air-formed oxide films generally have defects over such areas as mechanical imperfections, second phase particles, grain boundaries, etc. where pitting can initiate [28]. While the air-formed film passivity remains stable during scans and potentiostatic holds above $PC_{OX}$ for iron in perchlorate solutions, constant potential holds above $PC_{OX}$ for carbon steel in perchlorate solutions result in deterioration of the air-formed film, at or near the sulfide inclusions.
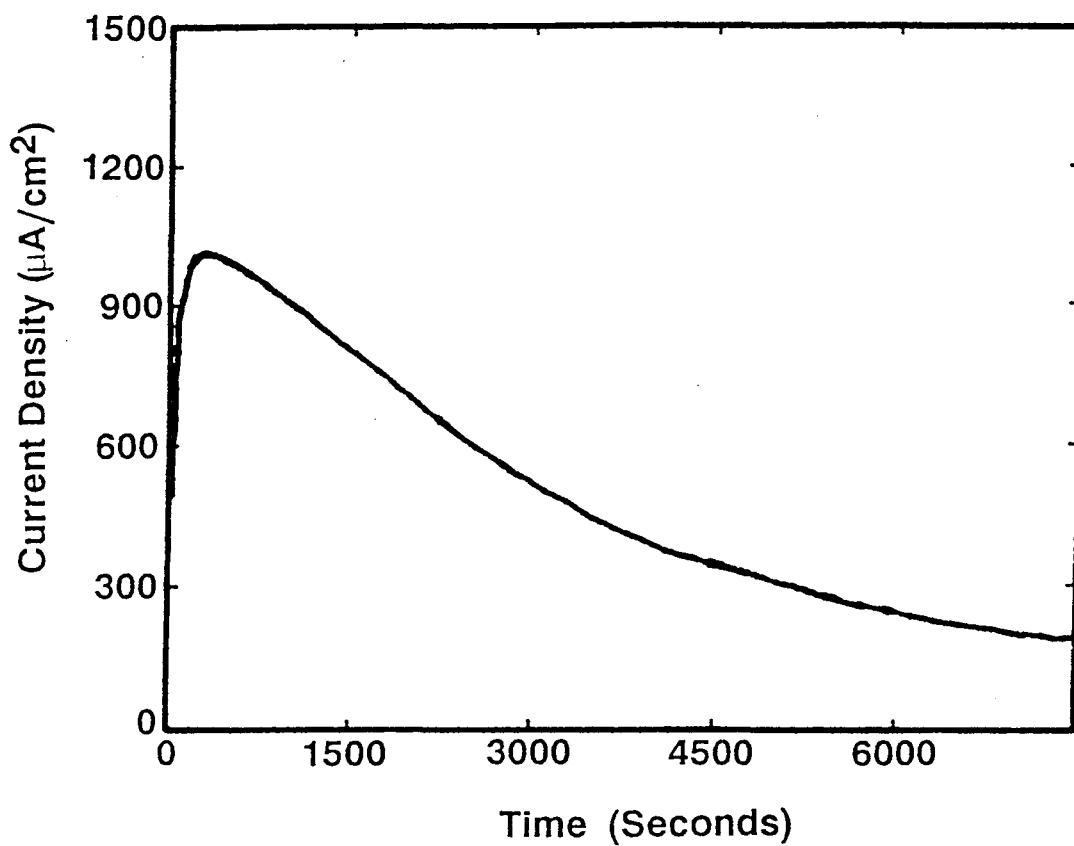
**Figure 5:** Potentiostatic hold of 1018 carbon steel at +1 V(SSP) in PC/0.5M LiClO$_4$. The anodic current density rises rapidly to about 1 mA/cm$^2$ then settles at about 200 μA/cm$^2$ after 1.5 hours.
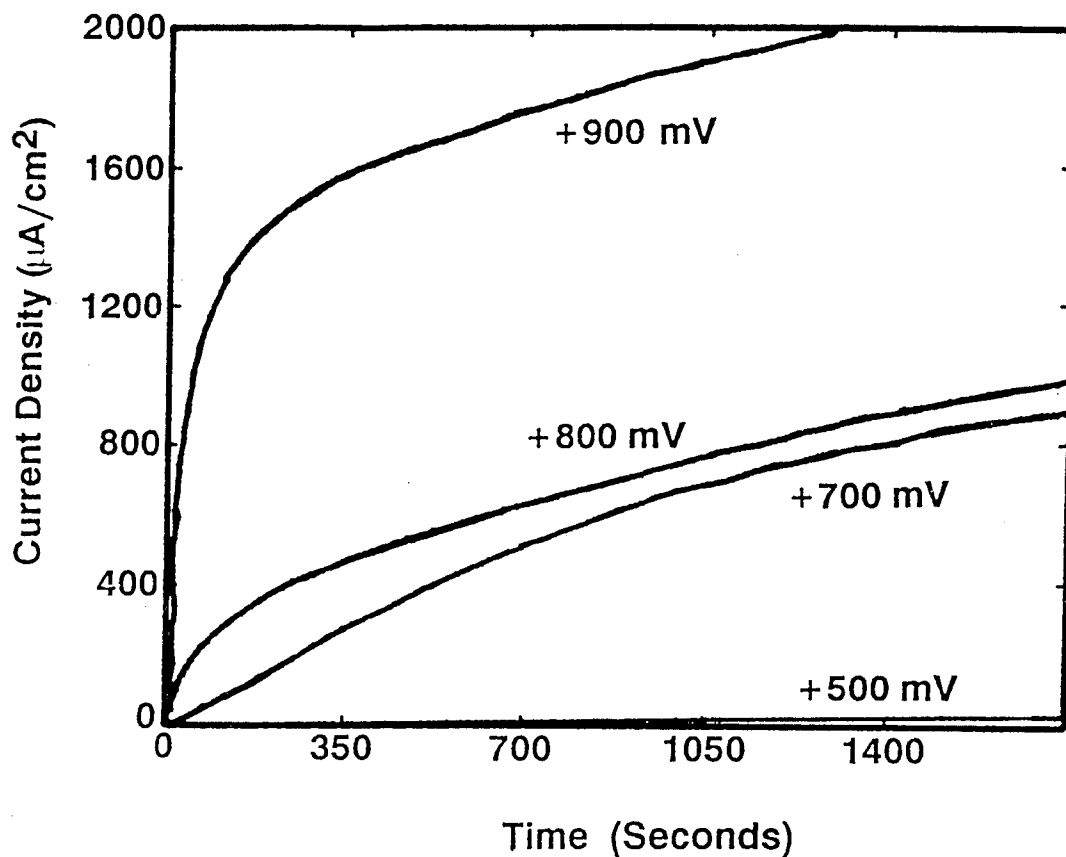
**Figure 6:** Potentiostatic holds of 1018 carbon steel at several potentials above $PC_{OX}$ in PC/0.5M $LiAsF_6$. The potentials are versus the SSP reference electrode. Note that the anodic current slopes increase as the potentials are raised above $PC_{OX}$.

Slow scans and potentiostatic holds for iron or carbon steel in hexafluoroarsenate solutions result in high current increases above $PC_{OX}$ that continue until a limiting current density of about $10 \, mA/cm^2$ is reached. When a passivated surface is exposed to an environment that can attack the metal substrate rapidly while only slowly attacking the passive layer, film disruption and undermining can occur at any incidental breaks in this film [28]. It is believed that the air-formed film may be undermined in hexafluoroarsenate solutions since its current density at steady state above $PC_{OX}$ is at least an order of magnitude larger than in perchlorate solutions. More pits were also found on either iron or steel surfaces in $LiAsF_6$ solutions than in $LiClO_4$ solutions subjected to potentials above $PC_{OX}$. The slope of the current increments is steeper for the carbon steel samples which appears to confirm that there is a greater surface defect concentration present on the 1018 carbon steel surface than on iron. Salt film formation is the only mechanism operative in this potential region, but the high solubility of the expected $Fe(AsF_6)_2$ salt does not passivate the surface. Also this salt film conductivity or its porosity may allow easier ion transport through the film than in the perchlorate salt film. The perchlorate salt film forms more easily because of its lower solubility and its lower conductivity, which provides a greater barrier to ion movement, blocks the surface and passivates the metal substrate.

## 2.2.3 Air-formed Film versus Bare Metal

To determine the effects of the air-formed film on the passivity of high purity iron and 1018 carbon steel, a sequence of experiments were conducted in which the electrode surface was scratched in situ. Kelly et al [10] found that a scratch on 99.9985% Fe surfaces prior to a slow scan in anhydrous perchlorate solutions resulted in no appreciable difference in the passive behavior of the bare metal versus air-formed film protected Fe at potentials below $PC_{OX}$. However, above $PC_{OX}$ the current density increased rapidly until a limiting current density of about $1 \, mA/cm^2$ was reached. Currents thereafter resumed to the passive levels seen before the scratch. Examination revealed a scratch filled with a precipitated salt of $Fe(ClO_4)_2$.

In slow scans of carbon steel in perchlorate solutions, the potential-current plot is similar to iron when the air-formed film is intact. However, as stated earlier, during a potentiostatic hold above $PC_{OX}$ (+1.0 V(SSP)), the passivity of the air-formed film on carbon steel in perchlorate solutions deteriorates until an average current density of about $1 \, mA/cm^2$ is reached before returning to a steady state current of approximately $200 \, \mu A/cm^2$. This suggests that the air-formed film on carbon steel is not, in itself, totally protective above $PC_{OX}$. The perchlorate salt film does not form its partially protective barrier on the steel surface until significant corrosion

has taken place. Pitting is found on the steel surface after potentiostatic holds above $PC_{OX}$ in either electrolyte. Scratching the steel surface in perchlorate solutions below $PC_{OX}$ leads to rapid repassivation of the steel before damage is observed. At potentials above $PC_{OX}$, scratching the steel surface in perchlorate solutions results in a huge anodic spike and a slow return of about 3500 seconds to the 200 $\mu A/cm^2$ pre-scratch condition as shown in Figure 7. The rate of salt film reformation in steel is about three times slower than iron under similar conditions. Seemingly, with all other conditions the same, it appears that the sulfide inclusions on the steel surface participate in retarding salt film formation over the bared steel surface. When the air-formed film is removed one of the other two passivation mechanisms must be operative to repassivate the bare metal. At potentials below $PC_{OX}$, a scratched surface repassivates quickly (ca. 2 sec.) without dissolution inside the scratch and with no observation of a salt film formed. The only possible mechanism remaining, the oxidative chemisorption of the PC molecules occurs and renders the iron surface or the steel passive below $PC_{OX}$.

In PC/0.5M $LiAsF_6$ solutions, the air-formed film is stable below $PC_{OX}$ and is rapidly repassivated by PC adsorption after scratching both iron and steel specimens. In both metals, the air-formed film is not stable at potentials above $PC_{OX}$ in hexafluoroarsenate solutions. The anodic currents increase rapidly in both metals. The current increments are 2-3 times steeper on the carbon steel than on iron. Baring either metal at potentials above $PC_{OX}$ only shifts the currents to even higher anodic values.

In order to verify the potentials at which the salt film can form and evaluate its protective capability, potentiostatic holds followed by scratching while maintaining the potential were conducted. At holds below $PC_{OX}$, Kelly et al [10] reported a scratch on 99.9985% Fe in perchlorate solutions resulted in an anodic spike and rapid repassivation. The charge passed until passivation of the surface thought to be caused by a monolayer of PC molecules occurred. In perchlorate solutions the steel also repassivates quickly (ca. 2-3 seconds). Figure 8 shows the hold and scratch of 1018 carbon steel in 0.5 M $LiAsF_6$ solutions below $PC_{OX}$. The scratch causes a sharp anodic transient with a relatively fast (ca. 10 seconds) recovery to the same current level prior to scratching. The charge passed before repassivation is about 7 $mC/cm^2$ (correcting for the scratch area) indicating that some dissolution may have occurred. Inspection of the carbon steel surface revealed no apparent electrochemical dissolution in the scratch. Since the air-formed oxide film has been removed and cannot reform in anhydrous organic solutions, and since no salt film is observed, passivation occurred by the chemisorption of PC molecules. The passivity of iron and carbon steel, promoted by this adsorption, is stable below $PC_{OX}$.

1500

1200

900

600

300

0

Current Density (μA/cm²)

Scratch of 1018 Carbon Steel
Above $PC_{OX}$

Repassivation ~ 3500 sec

7000    8000    9000    10000    11000

Time (Seconds)
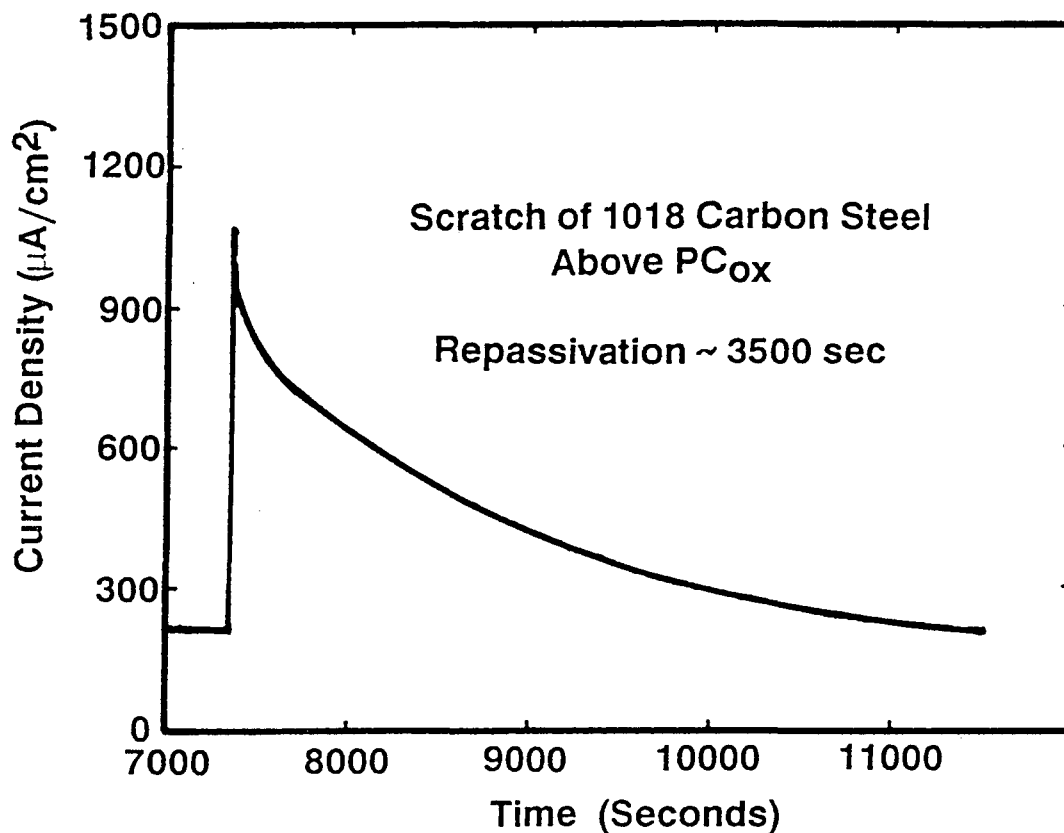
**Figure 7:** Potentiostatic hold of 1018 carbon steel in PC/0.5M $LiClO_4$ above $PC_{OX}$ followed by a scratch of the surface to remove the air-formed film. A anodic spike upon scratching is followed by slow repassivation of the damaged surface through salt film precipitation.
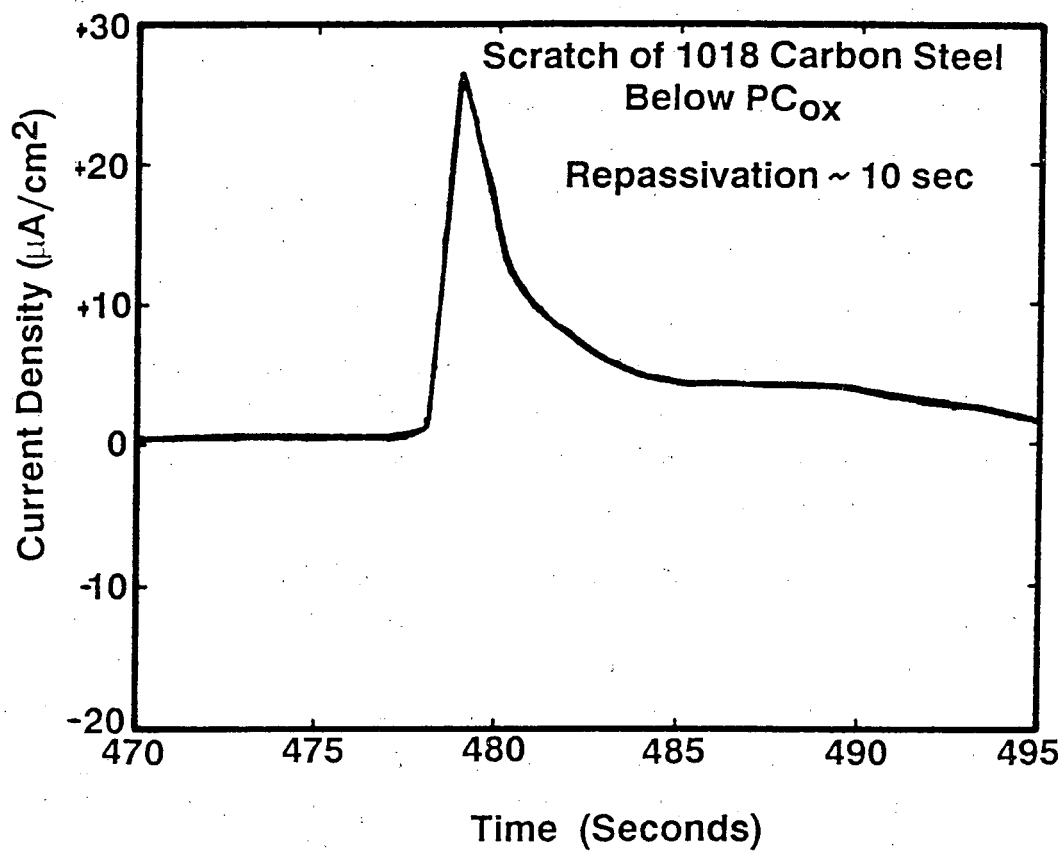
**Figure 8:** Potentiostatic hold of 1018 carbon steel in PC/0.5M LiAsF$_6$ below the oxidation potential of PC followed by a scratch of the surface to remove the air-formed film. The anodic spike upon scratching is followed by rapid repassivation by PC adsorption.

In hexafluoroarsenate solutions, scratching either ferrous specimen during holds above $PC_{ox}$ will cause huge anodic spikes relative to the magnitude of the pre-scratch current. At potentials above $PC_{ox}$ where the current density is typically 6-7 $mA/cm^2$ at steady state, scratching through the salt film and the air-formed layer causes about a 200-400 $mA/cm^2$ anodic transient in the scratched area which does not return to the pre-scratch condition even after 2000 seconds. Though the salt film does form, the high solubility of ferrous hexafluoroarsenate, $Fe(AsF_6)_2$, precludes adequate protection of either the iron or carbon steel. Pitting and dissolution within the scratch occurs on Fe in PC/0.5M $LiAsF_6$ held above $PC_{ox}$.

When the salt layer of $Fe(ClO_4)_2$ precipitates it protects the previously bared surfaces by ohmic blocking. These salt layers remain stable and passivates either specimen surface up to the potential where the perchlorate anion begins to oxidize. At potentials above perchlorate oxidation, none of the mechanisms provide passivity; pitting is observed on high purity iron because of the formation of highly reactive radicals.

Repassivation times are longer in the hexafluoroarsenate solutions (ca. 10 sec.) than in the perchlorate solutions. This may be caused by the higher ionic conductivity of the film in $LiAsF_6$ [14] or by a greater porosity of the adsorbed PC molecules from the larger hexafluoroarsenate anions [18] competing for adsorption sites. Both metals display higher current densities in hexafluoroarsenate solutions, sometimes by an order of magnitude, than their counterparts in perchlorate solutions which also support competitive adsorption. Studies by Borkowska and Fawcett on mercury [19] and Valette [20] on silver surfaces have shown that $ClO_4^-$ anions are more highly adsorbed than $PF_6^-$ anions in PC solutions. The hexafluorophosphate anion has similar properties to the hexafluoroarsenate anion [21]. The adsorption capability of the hexafluoroarsenate anion is presumed to be less than the perchlorate anion in PC. In aqueous environments, perchlorate is used as an inhibiting salt for iron to repress pitting [22]. Its inhibition effectiveness is less than nitrates or sulfates and this corresponds to its decreased adsorption on iron.

The carbon steel specimens require a longer time to repassivate by salt film formation than iron specimens in the same solutions. In aqueous environments it has been established that manganese sulfide inclusions are more susceptible to attack than iron sulfide inclusions. In acid solutions, MnS and FeS inclusions dissolve with the formation of $H_2S$ molecules. In the presence of $H_2S$ the anodic and cathodic reactions were accelerated [25] by the adsorption of

HS⁻ anions on the metal surface. Adsorption of $H_2S$ molecules or HS⁻ anions impede the formation of passive films. Reviews by Janik-Czachor [26] and Szklarska-Smialowska [27] discuss factors such as surfaces inclusions that lead to pit initiation.

## 2.2.4 Metallographic Examinations

Metallographic examinations of both 99.9985% Fe and 1018 carbon steel were conducted. After polishing, etching and staining with a solution that identifies sulfides [16], the high purity iron reveals an absence of non-metallic inclusions on the surface though the surface is not homogeneous. The 1018 carbon steel surface shows many surface inclusions after staining. These inclusions were confirmed by XRM (X-ray Dispersive Analysis) to consist of sulfides as shown in Figure 9. By calculating the volume percentage of sulfides by methods described under ASTM standard E-562 [17], a close correlation between the sulfide inclusion concentration and the pit density was observed on carbon steel exposed to perchlorate solutions. In hexafluoroarsenate solutions, sulfide inclusions provide pit initiation sites. With time rapid dissolution at these sites undercuts the remaining air-formed film and in the absence of a protective salt film leads to a higher concentration of pits on carbon steel.

## 2.3 Conclusions

Below $PC_{OX}$, the air-formed film and adsorption of the PC molecules provide stable passivity on both iron and carbon steel samples with neutral anhydrous solutions of $PC/LiClO_4$ or $PC/LiAsF_6$. Hexafluoroarsenate interferes with PC adsorption to a degree since its solutions display slightly higher anodic currents. Removal of the air-formed film is quickly repaired and repassivated by adsorption of the PC molecules for either material.

With its air-formed film intact, iron is not passive in $PC/LiAsF_6$ solutions above $PC_{OX}$. Deterioration of the passive air-formed film occurs at defects in the oxide film and is not repaired or repassivated by a salt film of $Fe(AsF_6)_2$ since it requires huge currents (10 mA/cm²) before it is formed. This is consistent with the higher solubility of the $Fe(AsF_6)_2$ salt. This is in contrast to the passive behavior observed for iron in perchlorate solutions which repassivates the defects in the air-formed film before considerable damage to the underlying iron has developed.

Above $PC_{OX}$, adsorption of PC molecules can no longer provide protection since it is being oxidized. With its air-formed film intact, iron is passive in $PC/LiClO_4$ solutions up to the
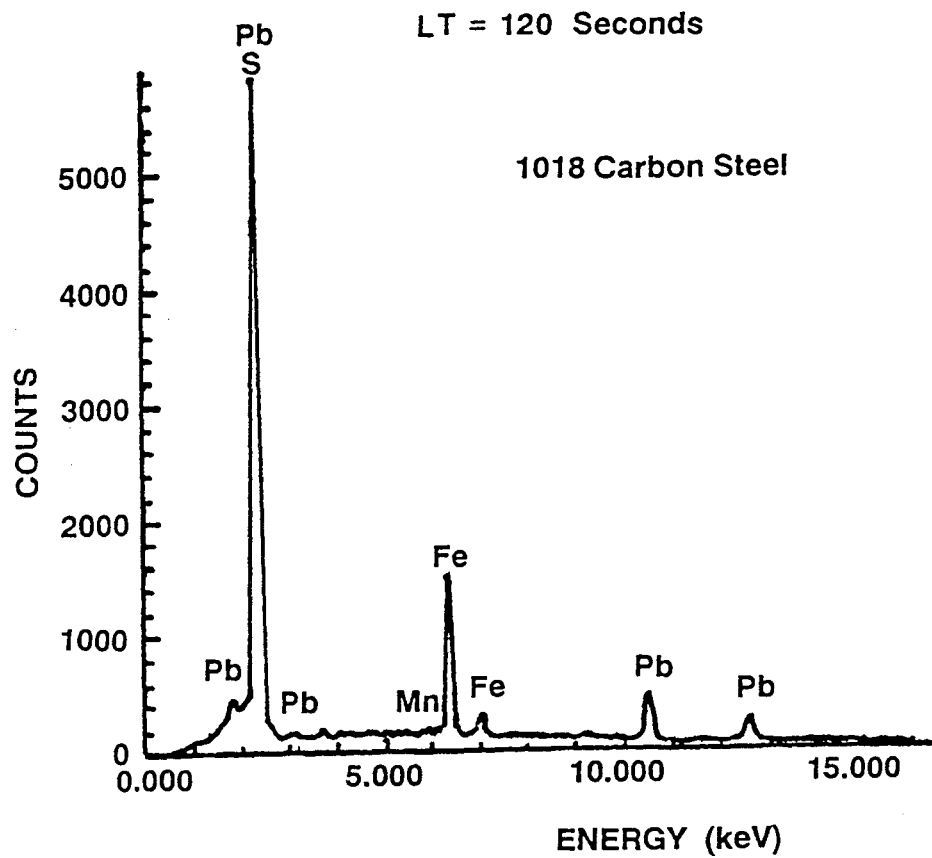
**Figure 9:** XRM spectrum within a typical inclusion on the carbon steel surface confirms that sulfides are present. The presence of the lead is due to sample staining with a thiosulfate/lead acetate solution prior to the scan.

perchlorate anion oxidation. Bare Fe passivates by the formation of a salt film of $Fe(ClO_4)_2$ above $PC_{ox}$. At potentials above $(ClO_4^-)_{ox}$ pitting has been observed on the iron surface since the salt film is no longer stable.

With its air-formed film intact, 1018 carbon steel is not stable above $PC_{ox}$ in either electrolyte solution. Deterioration of the film is associated with sulfide surface inclusions. Pits initiate and grow at the sulfide inclusions sites. The sulfides also appear to impede repassivation by salt film formation. In perchlorate solutions, the formation of a salt film of $Fe(ClO_4)_2$ does provide limited protection, but currents approaching $1 \, mA/cm^2$ were reached before it formed. For $PC/LiAsF_6$ solutions, no passivity is observed. The dominant passivating mechanism above $PC_{ox}$, salt film formation, is negated by the high $Fe(AsF_6)_2$ salt solubility. Steady state current densities of $10 \, mA/cm^2$ are maintained by the $Fe(AsF_6)_2$ salt film above $PC_{ox}$ on either the iron or 1018 carbon steel specimens. When salt film formation is the dominant passivation mechanism above $PC_{ox}$, the solubility and the chemical properties of the salt determine whether this mechanism will actually passivate the underlying metal.

# 3 1018 Carbon Steel in Propylene Carbonate and Small Additions of Water

## 3.1 Results and Discussion

During Year III, the passivation of 1018 carbon steel was investigated in neutral pH anhydrous PC/0.5 M $LiAsF_6$ with small amounts of water (up to 2000 ppm) added. Prior to adding the anhydrous PC to the electrochemical cell, prescribed amounts of water were injected into the cell. The effect of small water (up to 2000 ppm) additions on the polarization behavior of 1018 carbon steel in PC/0.5 M $LiAsF_6$ is shown in Figures 10 and 11. Additions of 100 ppm or 200 ppm water to the PC/$LiAsF_6$ solutions introduce surface activation and increasing current densities below $PC_{ox}$ (ca. +0.4-0.5 V(SSP)) from the competitive absorption of PC and water. Water vies with PC for adsorption sites on the steel surface. This is possibly caused by the formation of a porous film as was found on lithium by Geronov et al [14] in PC/$LiAsF_6$ solutions containing varying amounts of water. The 500 ppm $H_2O$ scan shows similar current densities below $PC_{ox}$ as compared to the 200 ppm $H_2O$ scan. The PC solution containing 1000 ppm water causes qualitatively different behavior below $PC_{ox}$. The slope decreases at about 0 V(SSP) and then returns to the prior anodic slope at about +0.1 V(SSP). The scans of all the solutions show an abrupt change in the E vs log i slope at about +400 to 450 mV(SSP) where PC oxidizes. The 1000 and 2000 ppm scans each show another reaction occurring at +0.65 V(SSP) which is likely the oxidation of water.

Above $PC_{ox}$ the addition of water appears to decrease the limiting currents slightly. The slow scans with 0 to 200 ppm added water show a limiting current of about 10 mA/cm². The 500 ppm, 1000 ppm, and 2000 ppm slow scans exhibit limiting currents of about 8, 6, and 4.5 mA/cm² ,respectively, at potentials above $PC_{ox}$.

With water additions of 500 ppm and above, the slow scans shown in Figure 11 indicate that the passivity of the carbon steel below $PC_{ox}$ is affected as more water becomes available for adsorption on the steel surface. Above $PC_{ox}$ the adsorption of PC molecules can no longer provide protection since they are being oxidized. Above $PC_{ox}$ the limiting current densities decrease at water contents above 500 ppm. It appears that sufficient water is present at the metal surface to contribute to the formation of a less soluble, probably hydrated salt film of $Fe(AsF_6)_2$. The solubility of $LiAsF_6$ is less soluble in water than in PC (910 vs 640 g/liter) [29]. This would suggest that water replaces the absorbed PC once it oxidizes and absorbs on the steel surface. The air-formed film has been found to be unstable above $PC_{ox}$ in perchlorate solutions with water concentrations above
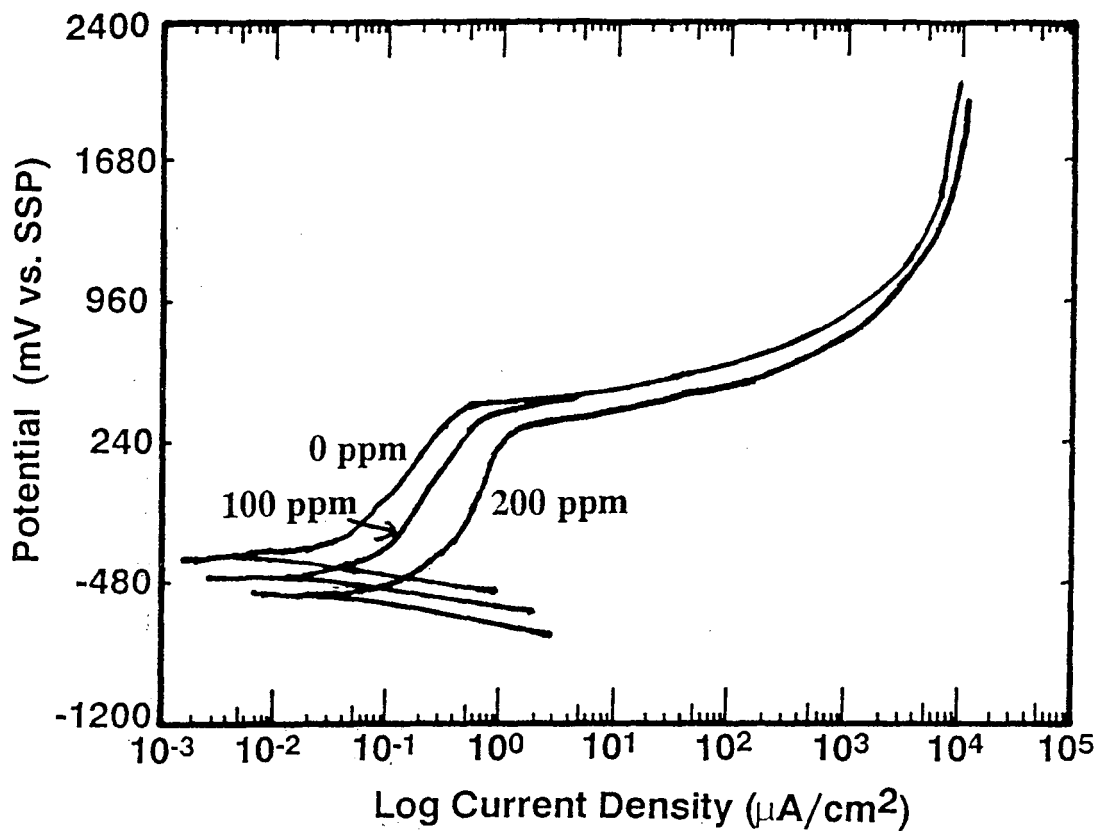
**Figure 10:** Slow scans of 1018 carbon steel in PC/0.5M LiAsF$_6$ with water additions of 0, 100, 200 ppm. The 100 and 200 ppm addition causes surface activation and increasing currents below PC$_{ox}$.
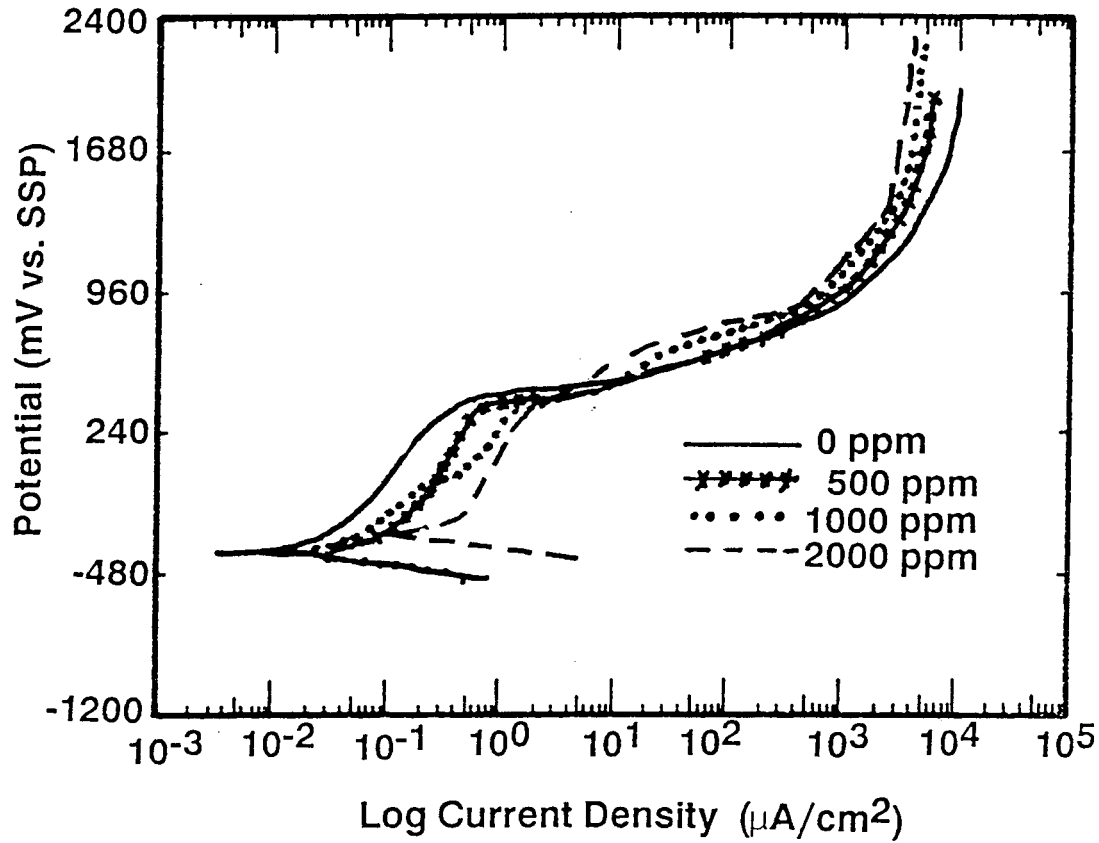
**Figure 11:** Slow scans of 1018 carbon steel in PC/0.5M LiAsF$_6$ with water additions of 0, 500, 1000, and 2000 ppm. The additions activate the steel surface with the 500 scan similar to 200 ppm. The 1000 ppm and 2000 ppm scans show qualitatively different behavior below PC$_{ox}$ and lower limiting currents above PC$_{ox}$.

500 ppm [10] and unstable in anhydrous hexafluoroarsenate solutions [30]. The only possible passivation mechanism available at potentials above $PC_{ox}$ in organic solvents is the formation of a salt film on the metal surface.

## 3.2 Conclusions

The addition of as little as 100 ppm water to anhydrous PC/LiAsF$_6$ solutions activates and interferes with the passive film present on the 1018 carbon steel surface. With additions of more than 500 ppm water, local acidic conditions found at sulfide inclusions cause instability of the air-formed film below $PC_{ox}$. The water further depresses the oxidation potential of PC from its anhydrous value on carbon steel by lowering the activation energy for PC hydrolysis. Additions of water in excess of 200 ppm to PC/LiAsF$_6$ solutions decrease the limiting current densities above $PC_{ox}$. This is due to the lower solubility of the $Fe(AsF_6)_2$ salt or its hydrated form in water. The salt only offers minimal protection as the limiting current density in 2000 ppm water solutions is still 4.5 mA/cm$^2$. The presence of sulfide inclusions on the steel surface prevents stable passivity above $PC_{ox}$.

# 4 Carbon Steel 1018, Nickel 200, and 304 Stainless Steel in Technical Grade PC and Binary Mixtures of PC-$H_2O$

## 4.1 Experimental

During Year III, the polarization behavior of 1018 carbon steel, nickel 200, and 304 stainless steel samples in technical grade PC solutions containing 0.5M $LiAsF_6$ or 0.5M $LiClO_4$ was investigated. These samples were each available in 5/8" diameter disks from Metal Samples (Mumford, Alabama) and were mounted in a Teflon test holder which exposed 0.7 $cm^2$ of the specimen to the electrolyte. Each experimental sample was polished to an 800 grit finish, rinsed with water purified from a Millipore system, followed by rinsing in acetone and methanol before being dried in warm air.

The technical grade PC (99%) obtained from Alfa Products (Danvers, Massachusetts) may contain impurity levels that may approach 10000 ppm (by weight). After solution preparation and the addition of 4A molecular sieves, the actual water contents of the technical grade (or simply technical) PC solutions were estimated to be about 50-150 ppm. Mixtures of PC and water incorporating $LiAsF_6$ or $LiClO_4$ were prepared prior to conducting the experiments. All tests were performed at room temperature (25± 2°C) using a saturated calomel (SCE) reference electrode. The SCE is -0.4 V versus the SSP electrode. The slow scan rate in all potentiodynamic experiments was 0.5 mV/sec and all scans were IR-corrected via automatic current interruption. The potential limits during the slow scans were generally -250 mV vs. $E_{corr}$ to at least +1.6 V(SCE).

Prior to conducting an experiment, all solutions were deoxygenated with pre-purified $N_2$ gas (99.9%) for at least 100 minutes in an electrochemical cell containing 150 ml of solution or for at least 4 hours when 500 ml of solution was used. Purging with pre-purified $N_2$ continued throughout the experiments.

## 4.2 Solution Electrochemistry in Technical PC

A slow potentiodynamic scan was conducted on Pt to assess the stability of the technical grade PC/$LiAsF_6$ solution over a potential range of -0.1 to 2.3 V(SCE). The anodic slopes of each solution are similar until a potential of +0.5 V(SCE) is reached. In the technical PC, an anodic reaction occurs at +0.5 V(SCE) during which the anodic currents abruptly increase. This is likely due to the oxidation of PC molecules, that through the synergistic effects of impurities such as propylene glycol and water, cause hydrolysis and oxidation of PC far below the $PC_{ox}$ observed in anhydrous propylene

carbonate (ca. +0.9 V(SCE)). The anodic reaction at +0.5 V(SCE) may also occur because of an impurity such as water or propylene glycol oxidizing itself. Above +0.5 V(SCE) the anodic currents in technical PC are 1 to 2 orders of magnitude higher than in anhydrous PC. A second anodic reaction occurs at approximately +1.7 V(SCE) from the oxidation of the hexafluoroarsenate anion. This is about 400 mV negative of the $AsF_6^-$ oxidation potential found in anhydrous PC and probably triggered by the same impurities or the impurities actually oxidizing.

## 4.3 1018 Carbon Steel Scans in Technical PC and PC-H$_2$O Mixtures

### 4.3.1 Results and Discussion

Slow scans of 1018 carbon steel in technical PC-H$_2$O/0.5M LiClO$_4$ mixtures were conducted with 0, 50, and 100 mole% water. Carbon steel scans in technical PC-H$_2$O/0.5M LiAsF$_6$ mixtures and containing 0, 10, 30, 50, 70, or 100 mole% water are reported here. Results from the slow scans of 1018 carbon steel in 100 mole% technical PC with 0.5M LiAsF$_6$ are shown in Figure 12. The scans show that the air-formed film is "relatively stable" up to the oxidation potential of PC (ca. +0.9 V(SCE)) although the passive currents were 1-2 orders of magnitude higher than reported earlier in scans of anhydrous PC/0.5M LiAsF$_6$. The level of impurities in technical PC (up to 10000 ppm) has caused activation of the carbon steel surface. Several, but not all, of the scans show a decrease in the slope from a anodic reaction occurring at +0.24 V(SCE) and a second anodic reaction at +0.9 V(SCE) where PC oxidizes. The first anodic reaction is likely from the oxidation of water or other impurity such as propylene glycol, a hydrolysis product of PC.

The slow scan of 1018 carbon steel in technical PC/0.5M LiClO$_4$ is shown in Figure 13 and compared to the technical PC/0.5M LiAsF$_6$ scans. The reaction at +0.24 V(SCE) is not observed in the perchlorate scans. Decreases in the slope at about +0.9 V(SCE) and at +2.1 V(SCE) result from the oxidation of the PC molecules and perchlorate anions, respectively, as discussed earlier. In the slow scans stopped below the oxidation potentials of the perchlorate or hexafluoroarsenate anions, no pitting was observed. The scans stopped above the oxidation potentials of the respective anions revealed pitting on the steel surface. The oxidation of the anions interferes with the air-formed film on the carbon steel. No other passivation mechanisms available to organic solutions (adsorption of solvent molecules and salt film precipitation) are stable above the oxidation potentials of the perchlorate or the hexafluoroarsenate anions. High
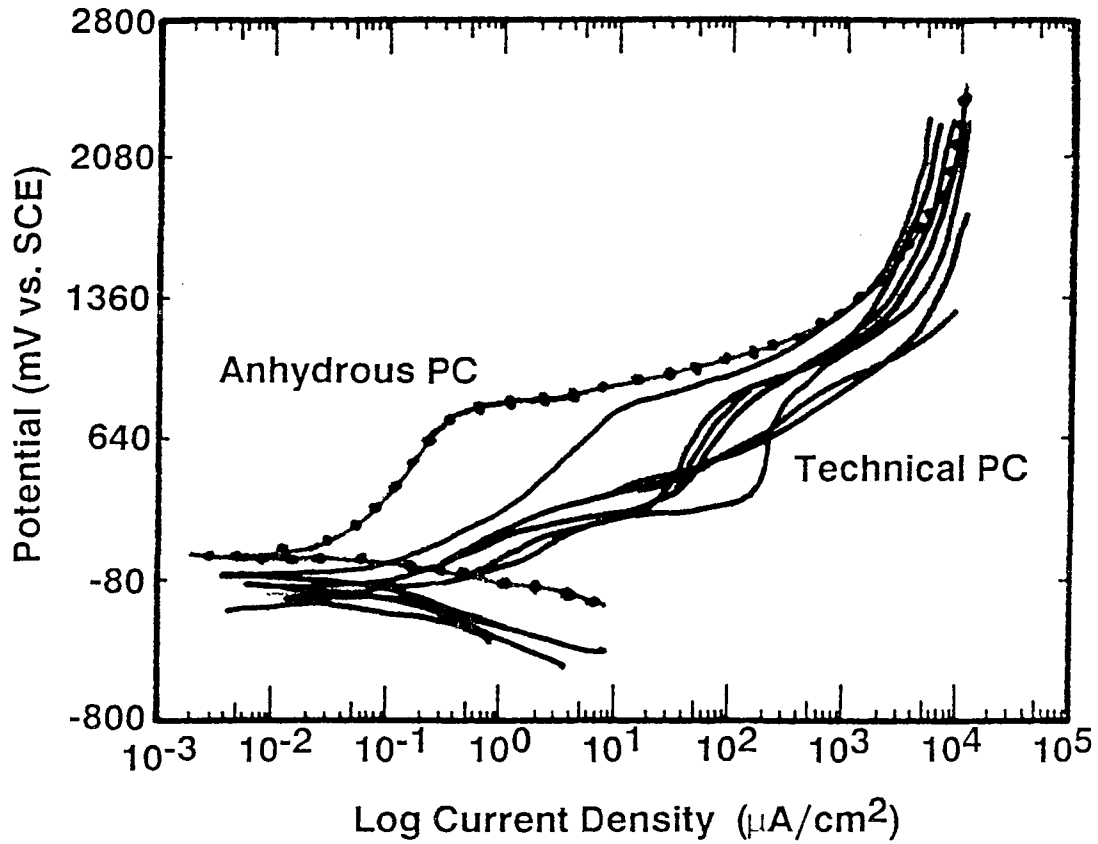
**Figure 12:** Slow scans of 1018 carbon steel in 100 mole% technical PC containing 0.5M $LiAsF_6$. The current densities of the steel in technical PC are 1-2 orders of magnitude higher than in anhydrous PC at potentials below $PC_{ox}$. Most scans have a limiting current density of $10^4 \mu A/cm$ above $PC_{ox}$.
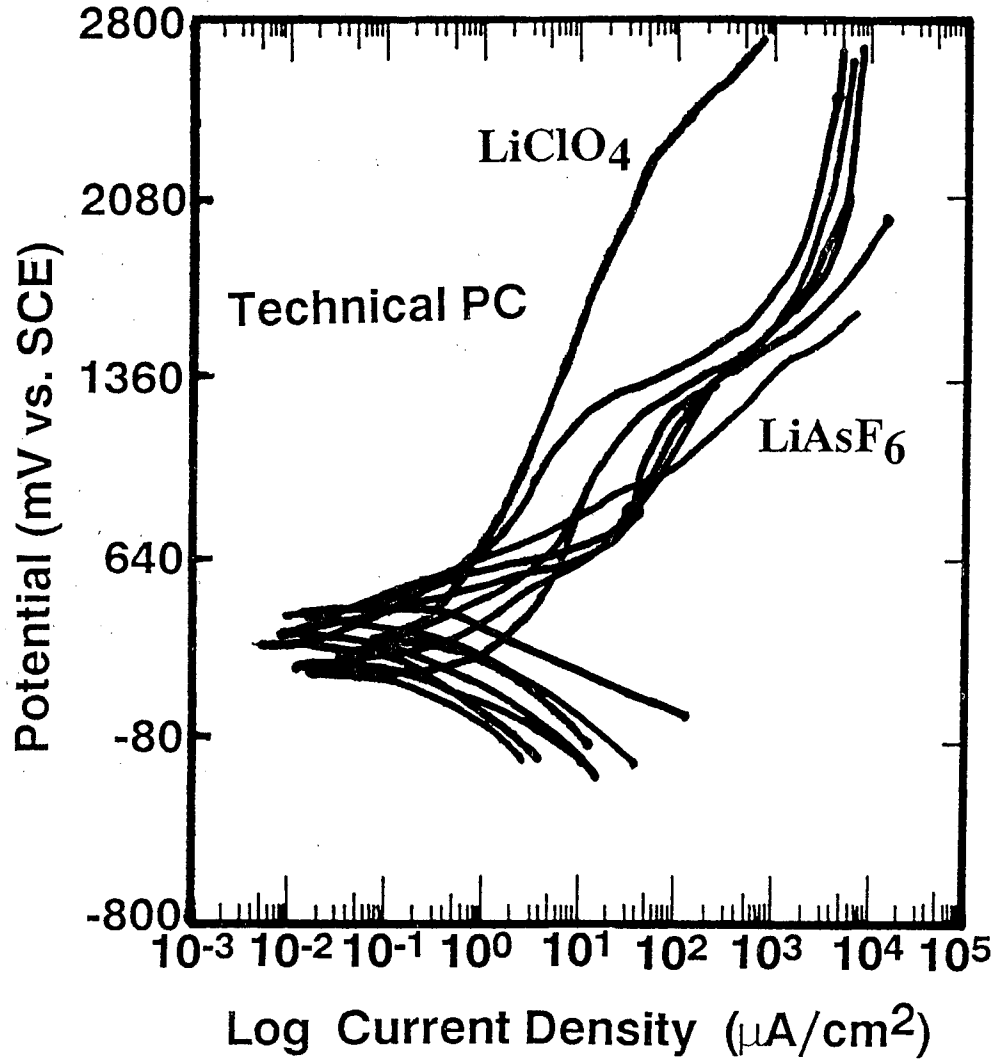
**Figure 13:** Slow scan of 1018 carbon steel in 100 mole% technical PC/0.5M LiClO$_4$ is compared to technical PC/0.5M LiAsF$_6$ scans. The current density on the carbon steel is lower at all anodic potentials in the technical PC/perchlorate solution than in the technical PC/hexafluoroarsenate solution.

impurity levels present in the technical PC activates the steel surface and causes unstable passivity of the air-formed film at potentials above $PC_{OX}$ in neutral PC, as discussed by Kelly et al [10,31] and in the previous anhydrous section.

A potentiostatic hold below $PC_{OX}$, at +785 mV(SCE), was conducted in a technical PC/LiAsF$_6$ solution (Figure 14). After an initial attempt to maintain passivity, the initial current density of 10 $\mu$A/cm$^2$ begins to rise after 350 seconds. After 1800 seconds the current density increases more rapidly. After 4000 seconds when the constant potential hold was terminated, the final current density is 240 $\mu$A/cm$^2$. No visible pitting was observed after the hold. This behavior was not seen in anhydrous PC at this potential. However, the apparent induction period required for the current density on the steel surface to increase suggests that a breakdown process such as local acidification is dissolving or penetrating the air-formed film and hindering adsorption of the PC molecules. This acidification is assisted by sulfides present on the steel surface and the higher levels of impurities such as propylene glycol and water present in technical PC. In a technical PC/0.5M LiAsF$_6$ solution, a potentiostatic hold above $PC_{OX}$ (+1.3 V(SCE)) shows unstable passivity of the air-formed film (Figure 15). A rapid rise in the current density from about 1 $\mu$A/cm$^2$ initially to about 1300 $\mu$A/cm$^2$ after 4000 seconds is observed. No induction period was observed. Subsequent inspection of the steel surface by XRM after the potentiostatic hold above $PC_{OX}$ revealed that the pits contained a salt containing arsenic and fluorine as shown in Figure 16. Scattered particles of the hexafluoroarsenate salt were found within the pits where the current densities are the highest. No salt particles are found outside the pitted regions. Locally high corrosion currents are sufficient to precipitate a salt film of $Fe(AsF_6)_2$. Since high currents are required to precipitate and maintain the salt film, the steel surface is not adequately protected.

The polarization curves of 1018 carbon steel in hexafluoroarsenate solutions of different mole fractions of technical PC with water are shown in Figure 17. In all the curves (10-70 mole% H$_2$O), an active/passive transition is observed after a significant region of active dissolution. This transition is followed by a region of apparent passivity where the current density is essentially independent of potential, which is in turn bounded by a breakdown potential, above which large current densities up to 10 mA/cm$^2$ are observed. In totally aqueous solutions, pitting of the surface is accompanied by oxygen evolution as observed in earlier studies [10,32]. In solutions of lower water content, oxygen evolution decreases to the point where it is difficult to tell if oxygen is being evolved from the surface. Post-test examinations of the steel surface revealed pitting occurred in all mixed PC-H$_2$O cases. The 70 mole% PC scan produced
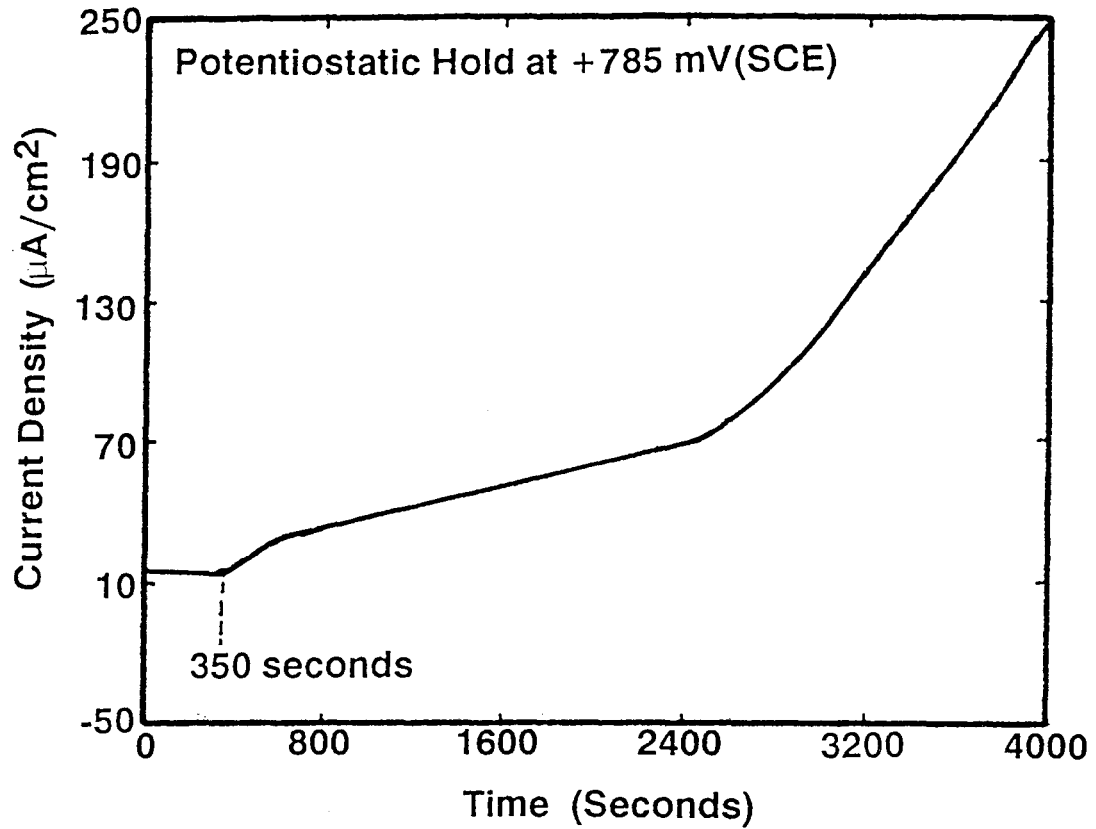
**Figure 14:** Potentiostatic hold of 1018 carbon steel at in technical PC/0.5M LiAsF$_6$ at +785mV (SCE). After an initial attempt to maintain passivity, the current density subsequently increases after 350 seconds.

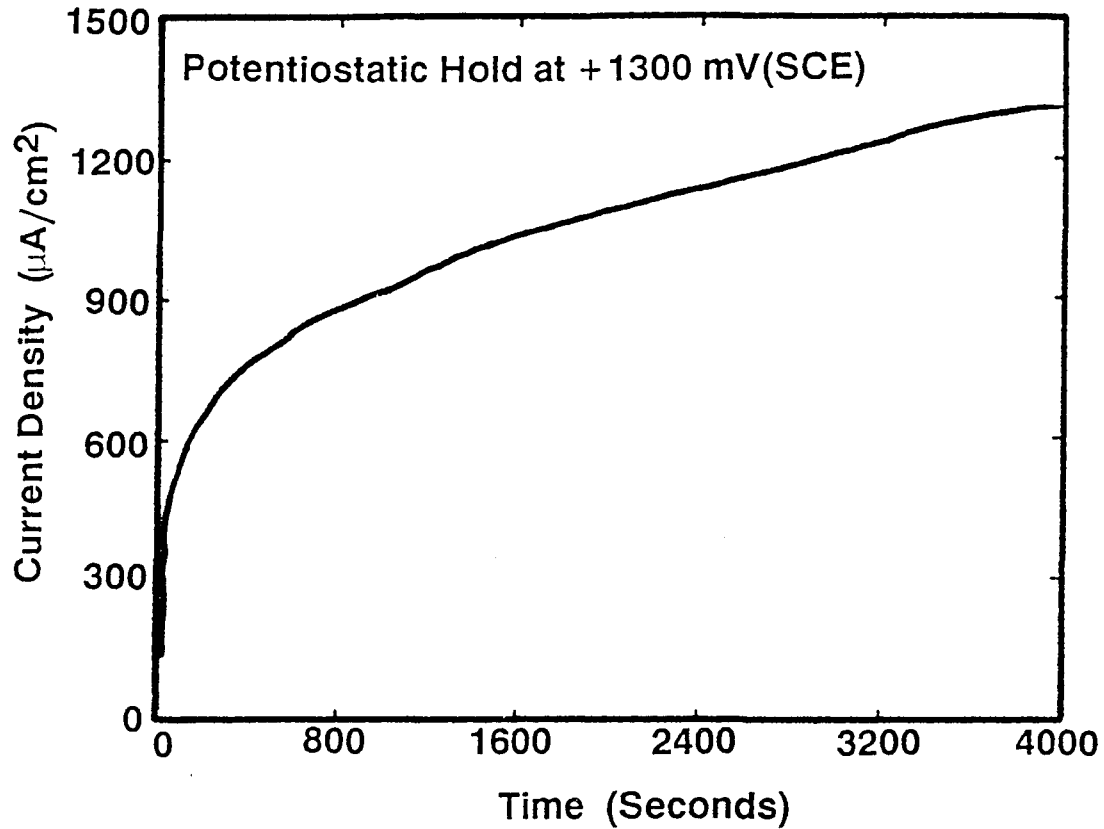**Figure 15:** Potentiostatic hold of 1018 carbon steel above $PC_{ox}$ (+1.3V(SCE)) is technical $PC/0.5M$ $LiAsF_6$ shows unstable passivity of the air-formed film. The current density rises until $40\mu A/cm^2$ to $1300\mu A/cm^2$ after 4000 sec.
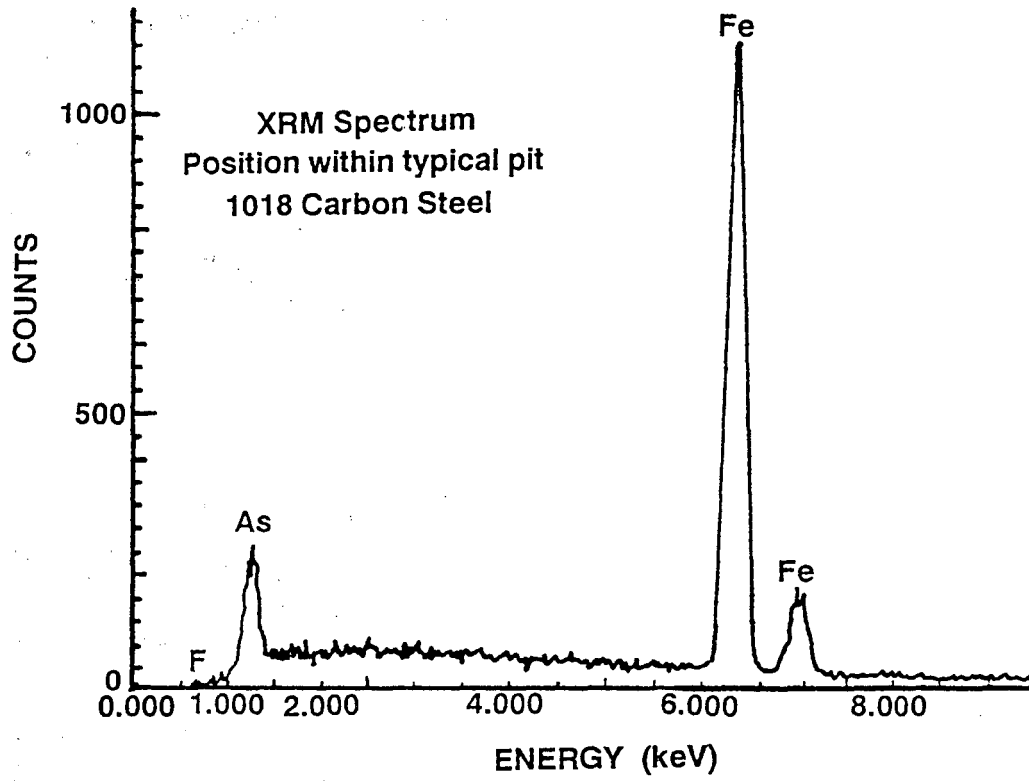
**Figure 16:** XRM spectrum within a typical pit on the carbon steel surface shows the presence of arsenic.
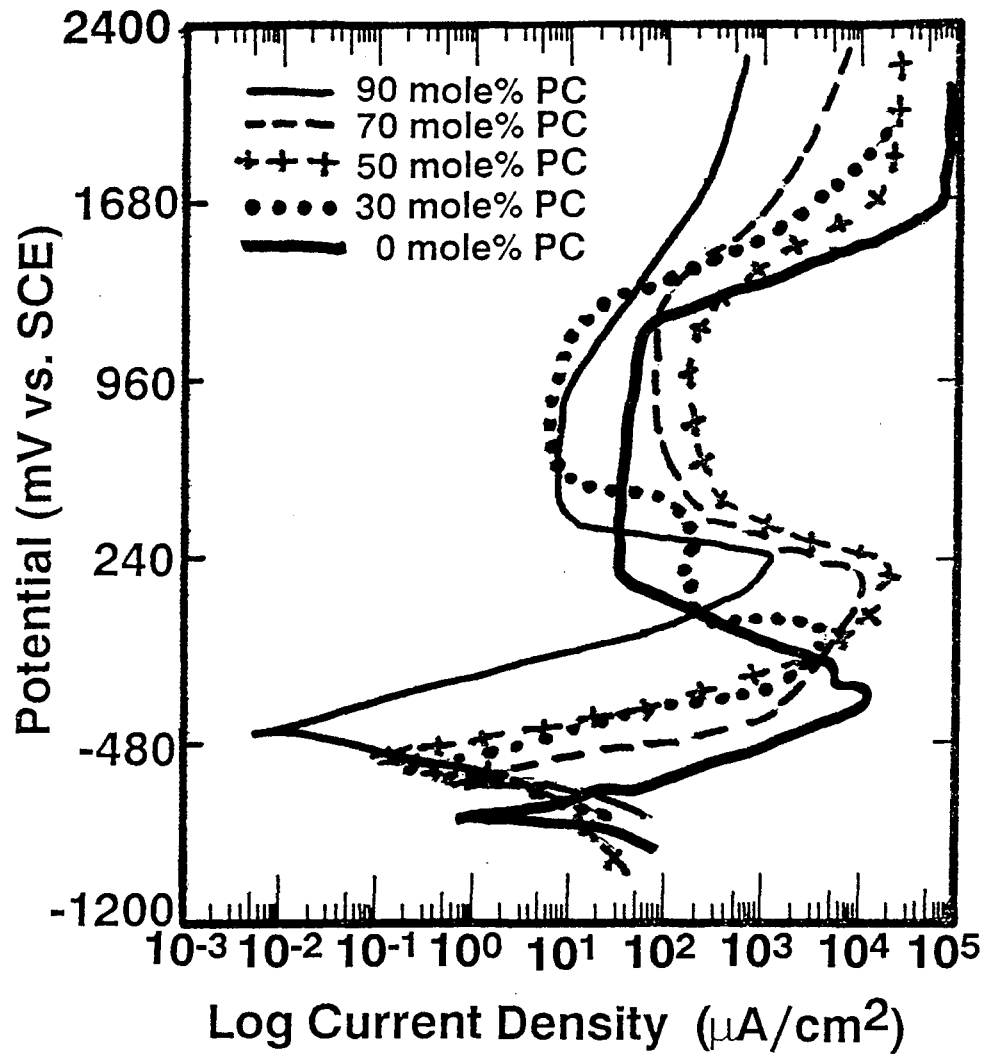
**Figure 17:** Slow scans of 1018 carbon steel in technical PC/$H_2O$ mixture containing 0.5M LiAsF$_6$. The $H_2O$ mole fraction range from 10-70 mole% $H_2O$. In all the scans an active/passive transition is observed after a significant region of active dissolution.

numerous small to medium sized pits and virtually no salt film, while the carbon steel surface after a slow scan in 30 mole% PC, reveals a dark brown surface from precipitation of a salt film $(Fe(AsF_6)_2$ which started to form below $PC_{ox}$. Since corrosion and pitting are observed after this experiment, this suggests that the film is not protective above the breakdown where the oxygen evolution reaction begins. It is interesting that both of the scans had a passive current density of about $10\,\mu A/cm^2$. In the 70 mole% $PC/H_2O$ solution passivity is observed during a slow scan up to $PC_{ox}$, while in the 30 mole% $PC/H_2O$ solution a slow scan shows passive behavior up to $+1.2$ V(SCE) where $O_2$ evolves. This suggests that the principal passivation mechanism in 30 mole% PC is by oxyhydroxide/oxide formation. PC adsorption is the predominant passivation mechanism in 70 mole% PC though the passivity is unstable. The removal of the adsorbed PC film or the removal of the oxide film leads to pitting and corrosion. The salt film does not protect the surface. With increasing mole% PC, the passivation potential, $E_{pp}$, increases from $-300$ mV(SCE) in totally aqueous solutions to $+30$ mV(SCE) in the 30 mole% $PC-H_2O$ mixture and $+240$ mV(SCE) in the remaining $PC-H_2O$ solutions.

While all the slow anodic polarization curves exhibited a region of apparent passivity in $PC-H_2O$ mixtures, it was found that this passivity was unstable with time. This instability manifests itself by an increase in the current density with time which subsequently led to localized attack of the steel. Figure 18 shows a partial polarization curve for carbon steel in 50 mole % $PC/H_2O$ with 0.5M $LiAsF_6$. After scanning from $E_{corr}$ to $+0.75$ V(SCE) which is within the "passive" region during slow scans; the specimen is held at this potential for 1 hour. The dashed line represents the polarization behavior obtained for a full scan in previous experiments. The time dependence of the passive current density is shown by the horizontal line at $+0.75$ V (SCE). After an incubation period, the passive current density gradually increases by an order of magnitude as compared to the values (ca. $25\text{-}40\mu A/cm^2$) obtained during the slow scans. Examination of the 1018 carbon steel surface after the test showed widespread pitting as would be expected from the prolonged high current densities.

Like high purity iron in perchlorate solutions, the aqueous solutions of hexafluoroarsenate on 1018 carbon steel produce a protective oxide film over the entire surface and renders it passive and stable. In totally anhydrous solutions of PC/0.5M $LiAsF_6$, passivation of the carbon steel surface has been shown [30] to be stable up to $PC_{ox}$. Above this potential (ca. $+0.9$ V(SCE)) the current density rises and a non-protective salt film of $Fe(AsF_6)_2$ is formed only after considerable corrosion has occurred. In 100 mole% technical grade PC/0.5M $LiAsF_6$ solutions on 1018 carbon steel, the high impurities levels (up to 10000 ppm by weight) caused the current
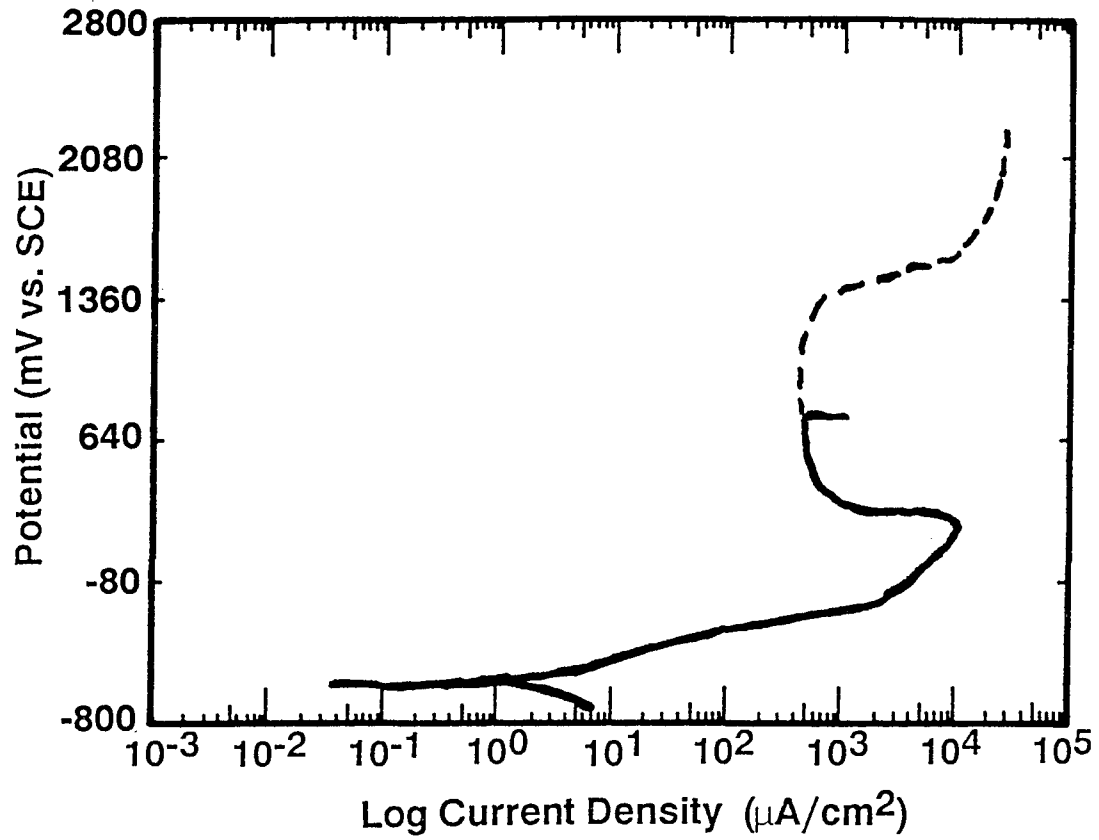
**Figure 18:** A slow scan and subsequent potentiostatic hold @ +750mV(SCE) shows unstable passivity in the "passive" range. The passive current density increases by an order of magnitude during the 1 hour hold. Widespread pitting was found afterwards.

density to increase at potentials 100 mV to 150 mV negative to $PC_{ox}$ after an incubation period. The presence of sulfide surface inclusions aid in the initiation of corrosion by catalyzing the cathodic reactions and increasing the corrosion potential and its anodic currents. An active/passive transition during slow scans on carbon steel is observed with the additions of 10 mole% water or more to the technical PC. Competition between the passivation mechanisms involving oxide film formation (supported by water) and solvent adsorption (supported by anhydrous PC) occurs if the air-formed film is damaged. At potentials within this passive region and below $PC_{ox}$, competition between these mechanisms is incompatible in mixed solutions containing 1000 ppm to 70 mole% $H_2O$ and leads ultimately to a lack of protection and attack of the carbon steel. Kelly et al [31] found that between 35 mM (500 ppm) and 17 M (70 mole %) water and PC caused competition between these two incompatible passivation mechanisms and unstable passivity and subsequent pitting.

## 4.3.2 Conclusions

Slow scans of 1018 carbon steel specimens in technical grade PC solutions with either 0.5M $LiAsF_6$ or 0.5M $LiClO_4$ show currents that are 1-3 orders of magnitude higher than in anhydrous PC and PC solutions containing up to 2000 ppm water. The higher levels of impurities (ca. 10000 ppm) interferes with the PC adsorption film and the air-formed film. At a constant potential in a technical PC/$LiAsF_6$ solution about 100 mV negative of $PC_{ox}$, the passive currents on the steel surface increased (after an incubation period) to a current density over an order of magnitude higher after 4000 seconds. It was suggested that PC impurities and sulfide inclusions on the steel surface caused deterioration of the air-formed film by local acidification which hinders PC adsorption and dissolves the oxide film. Incompatible passivation mechanisms lead to this unstable passivity. This was not observed in anhydrous PC solutions at the same potential.

The air-formed film is not stable above $PC_{ox}$. At constant potentials above $PC_{ox}$, there is no induction period and the current density rises rapidly to a final current of about $1300 \mu A/cm^2$ after an hour in hexafluoroarsenate solutions.

Like high purity iron in perchlorate solutions, the aqueous solutions of hexafluoroarsenate show an active/passive transition on 1018 carbon steel which produces a protective oxide film over the entire surface in the passive region. In totally aqueous solutions, corrosion of the surface is accompanied by oxygen evolution. The polarization curves of 1018 carbon steel in hexafluoroarsenate solutions of different mole fractions of PC and water (10-70 mole% $H_2O$), exhibited active/passive transitions. Pitting was observed in the mixed PC/$H_2O$ solutions after each slow

scan. At constant potentials below $PC_{ox}$ in the "passive" region of the $PC/H_2O$ solution scans, the passivity was found to be unstable with time. Extensive corrosion and pitting were observed on the steel surface after a short time.

The competition between the passivation mechanisms involving oxide film formation (supported by water) and solvent adsorption (supported by anhydrous PC) occurs if the air-formed film is damaged. At potentials in the passive region and below $PC_{ox}$, competition between these mechanism is incompatible in mixed solutions containing 1000 ppm to 70 mole% $H_2O$ and leads ultimately to a lack of protection and attack of the carbon steel.

## 4.4 Nickel 200 in PC - $H_2O$ Solutions

### 4.4.1 Results and Discussion

The nickel specimens were investigated by potentiodynamic slow scans in neutral 100 mole% technical PC solutions, 50 mole% technical PC-$H_2O$ mixed solutions and aqueous solutions with 0.5M $LiAsF_6$. Slow anodic polarization scans of nickel 200 in perchlorate solutions of technical PC and deionized water were also conducted. The scans were conducted with an air-formed film on the nickel 200 intact.

The polarization curves of Ni 200 in technical PC/0.5M $LiAsF_6$ and anhydrous PC/0.5M $LiAsF_6$ are presented in Figure 19. In anhydrous PC the currents are an order of magnitude smaller than in the technical PC slow scans. The nickel is passive in both PC solutions and undergoes slow anodic dissolution when anodically polarized without any active/passive behavior. The higher impurity levels in the technical grade PC activates the surface but does not cause deterioration of the air-formed film. In all scans, including in anhydrous PC, a "breakdown" potential is observed at potentials of about +1.4 to +1.6 V(SCE). This is above the oxidation potential of anhydrous PC on Pt or carbon (ca. +0.9 V(SCE)) and well below the oxidation of the hexafluoroarsenate anion on Pt in anhydrous PC solutions (ca. +2.1 V(SCE)).

Nickel 200 in 100 mole% technical PC/0.5M $LiClO_4$ solutions exhibits no active-passive transition during anodic polarization and anodic currents are greater by 1-2 orders of magnitude than observed in the hexafluoroarsenate scans (see Figure 20). The potentials where the slope exhibits a sharp decrease occurs between +1.15 to +1.35 V(SCE) which is at least 100 mV negative to the slow scan results found in the $LiAsF_6$ solution. Pitting was observed only in
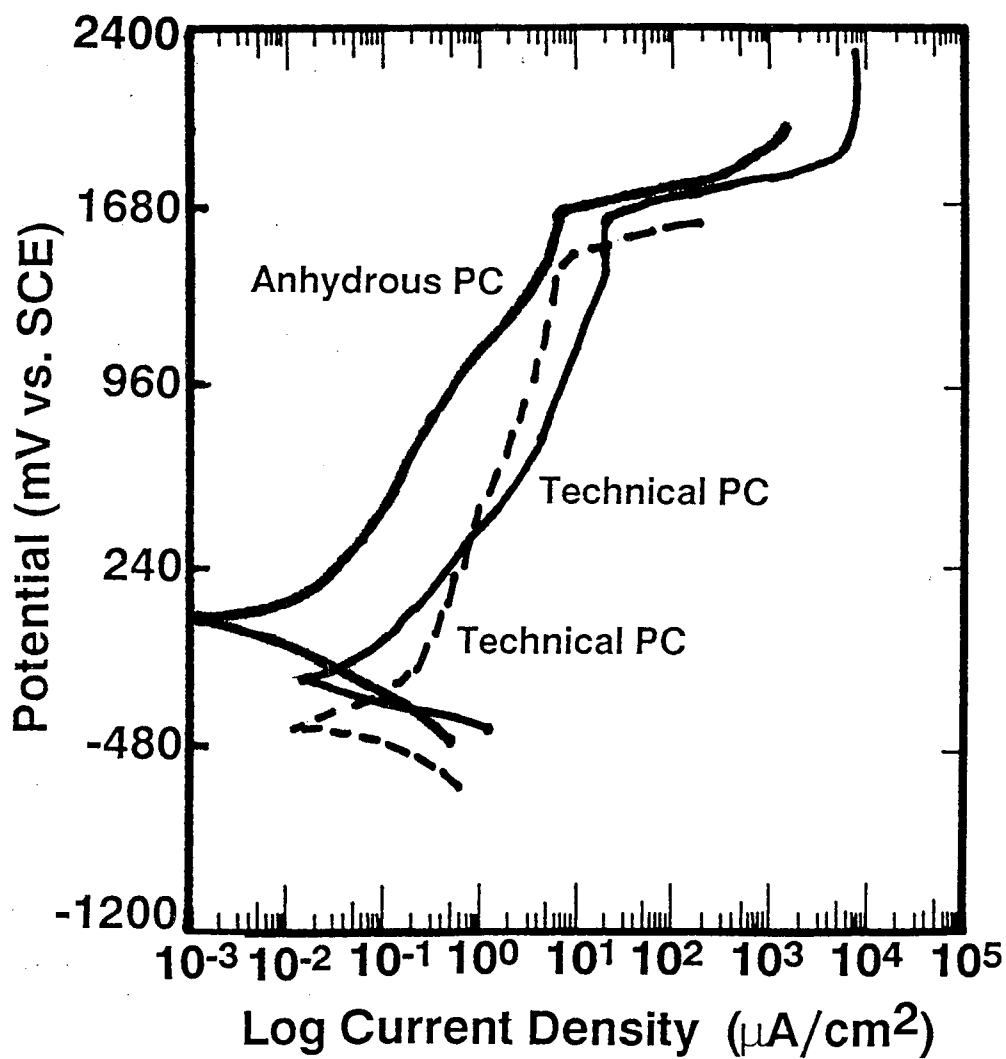
**Figure 19:** Slow scans of Ni 200 in technical PC/0.5M LiAsF$_6$ compared to a single scan in anhydrous PC. The nickel undergoes slow anodic dissolution when polarized without displaying any active/passive behavior though it may be masked.
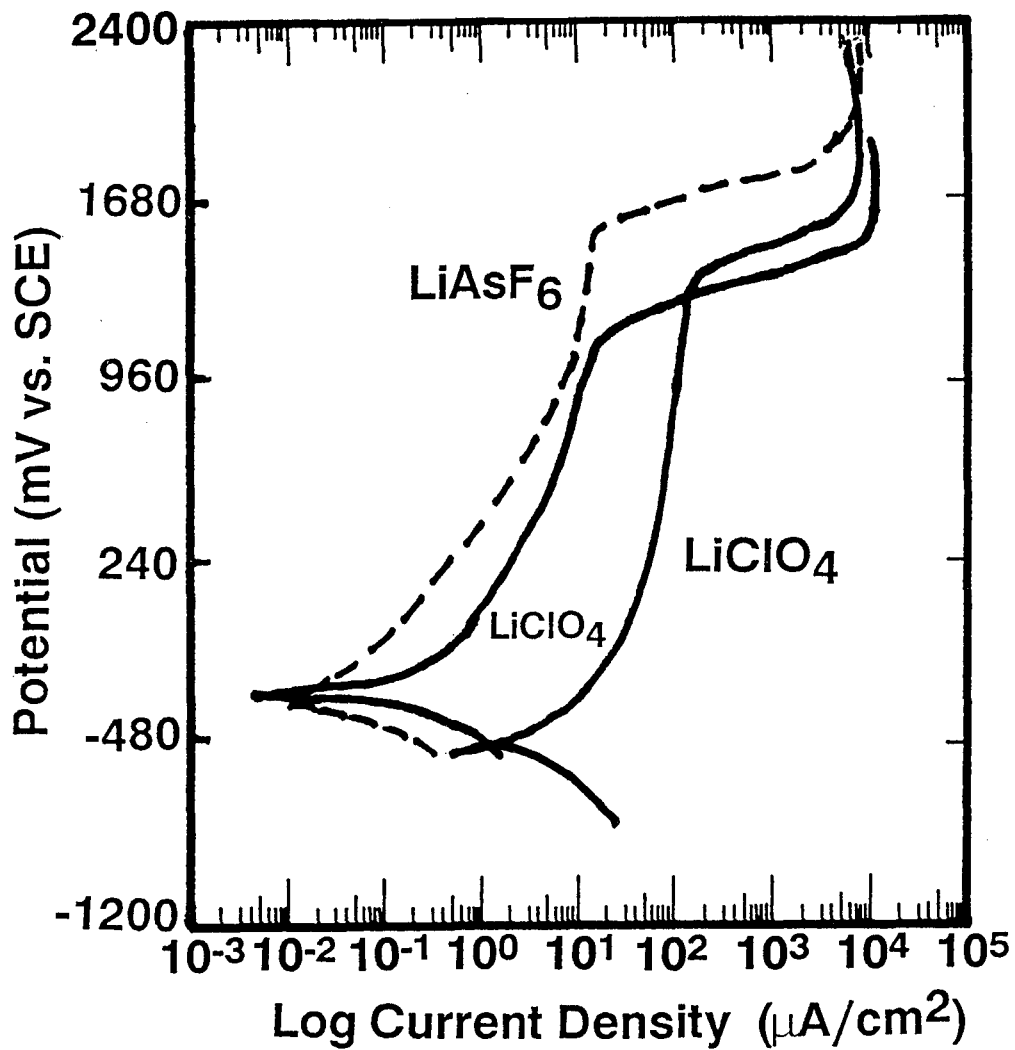
**Figure 20:** Slow scans of Ni 200 in technical PC/0.5M LiClO₄ compared to an anhydrous PC/0.5M LiAsF₆. No active/passive transition during anodic polarization. The anodic currents in LiClO₄ solution are greater by 1-2 orders of magnitude than the anhydrous PC/0.5M LiAsF₆.

scans where the potential exceeded the respective oxidation potentials of the electrolytes. The observed passivity may be due to experimental conditions. The oxidation of PC (ca. +0.9 V(SCE)) removes a passivating layer, leaving only the air-formed film intact. The PC breakdown products discussed by Kelly et al [10] or the electrolyte anions could be absorbed on the surface. The breakdown potential could be the result of an accumulated induction period before breakdown at local defects in the passive layer are observed. Abrashkina et al [33] observed that chloride ions and water molecules lead to stronger surface activities of nickel in dimethyl sulfoxide. They also form surface active complexes [34]. The higher "breakdown" potential observed in the Nickel 200 slow scans compared to similar carbon steel and pure iron scans suggest that the oxide film is more protective and has less defects in its air-formed film. Several inclusions are found on the polished and etched Nickel 200 surface, but staining [16] revealed no sulfides in these inclusions. The pit morphology of the nickel specimens after a slow scan in anhydrous PC exhibits pits about 1-5 μm in diameter which tend to be aligned along the scratch lines.

The polarization curves on Nickel 200 in 50 mole% PC-$H_2O$/0.5M $LiAsF_6$ binary solutions are shown in Figure 21. The nickel 200 sample undergoes anodic dissolution without an active/passive transition when anodically polarized although the transition may be masked by the cathodic reaction. Since iron and carbon steel have demonstrated incompatible passivation mechanisms in mixed PC-$H_2O$ solutions, the observed behavior or nickel indicates that the oxide film may be more stable and less prone to attack.

The polarization behavior of Nickel 200 in totally aqueous solutions containing 0.5M $LiAsF_6$ or 0.5M $LiClO_4$ electrolyte is shown in Figure 22. In either case passivation of nickel occurs without an active/passive transition although it may be masked by the cathodic reaction, as is the case with Cr in aqueous solutions [13]. The anodic currents of the perchlorate scan are about 1-3 order of magnitude higher than observed in the $LiAsF_6$ solutions. This is possibly due to the greater adsorption capability of perchlorate anion relative to hexafluoroarsenate anion. The perchlorate anion may adsorb on the passive film and form surface active complexes as found by Abrashkima et al [34]. All the scans show a sharp decrease in the current slope at +1.2 V (SCE) where oxygen begins to evolve from the nickel surface. While the hexafluoroarsenate scan exhibited small post-test pits on the nickel, the highly activated perchlorate scan revealed deep pitting at the termination of the test. Passivity of the air-formed film on nickel is destroyed when the potential enters into the transpassive region.
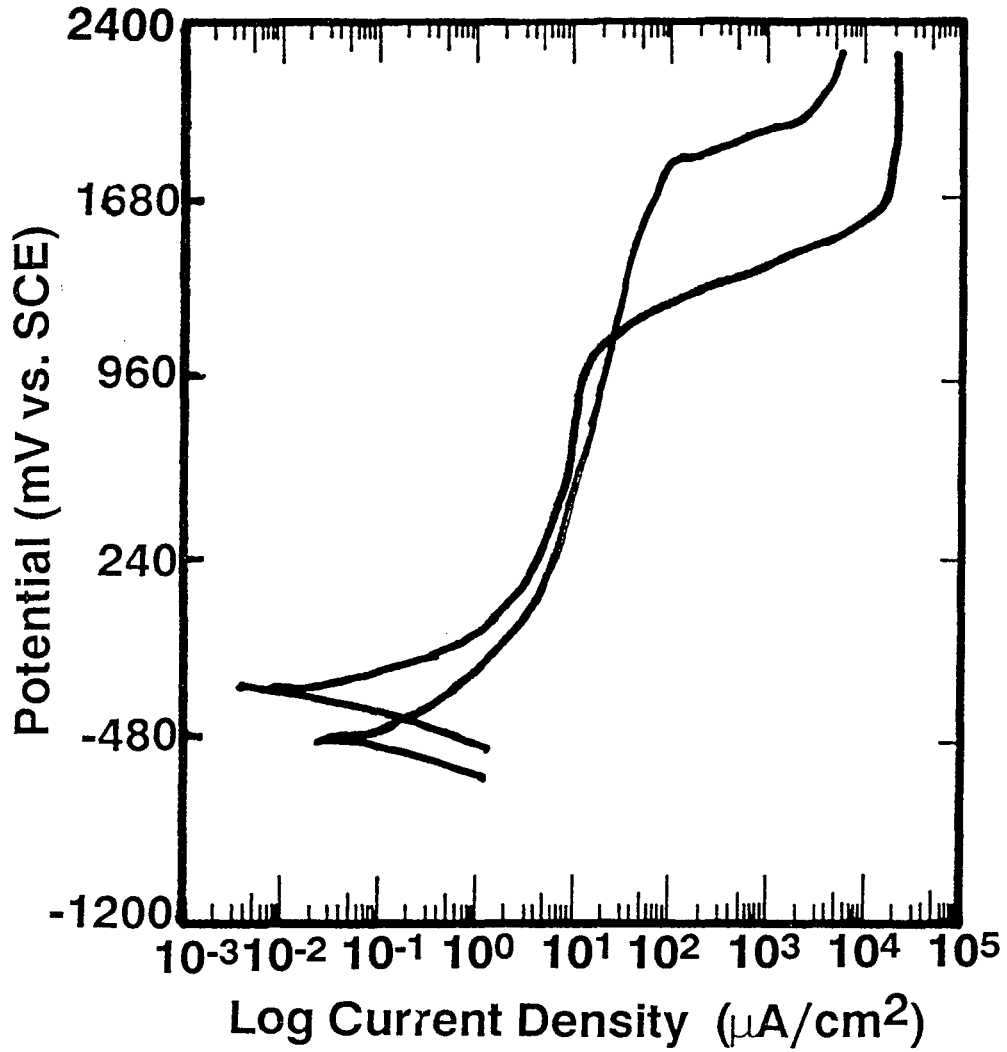
2400
1680
960
240
-480
-1200
Potential (mV vs. SCE)
10-3
10-2
10-1
100
101
102
103
104
105
Log Current Density (μA/cm2)

**Figure 21:** Slow scan on nickel 200 in 50 mole% PC-$H_2O$ solution containing 0.5M $LiAsF_6$ and 0.5M $LiClO_4$. No active/passive behavior is noted on the nickel. The currents are low until the oxygen evolution reaction occurs at +1.1 V(SCE).
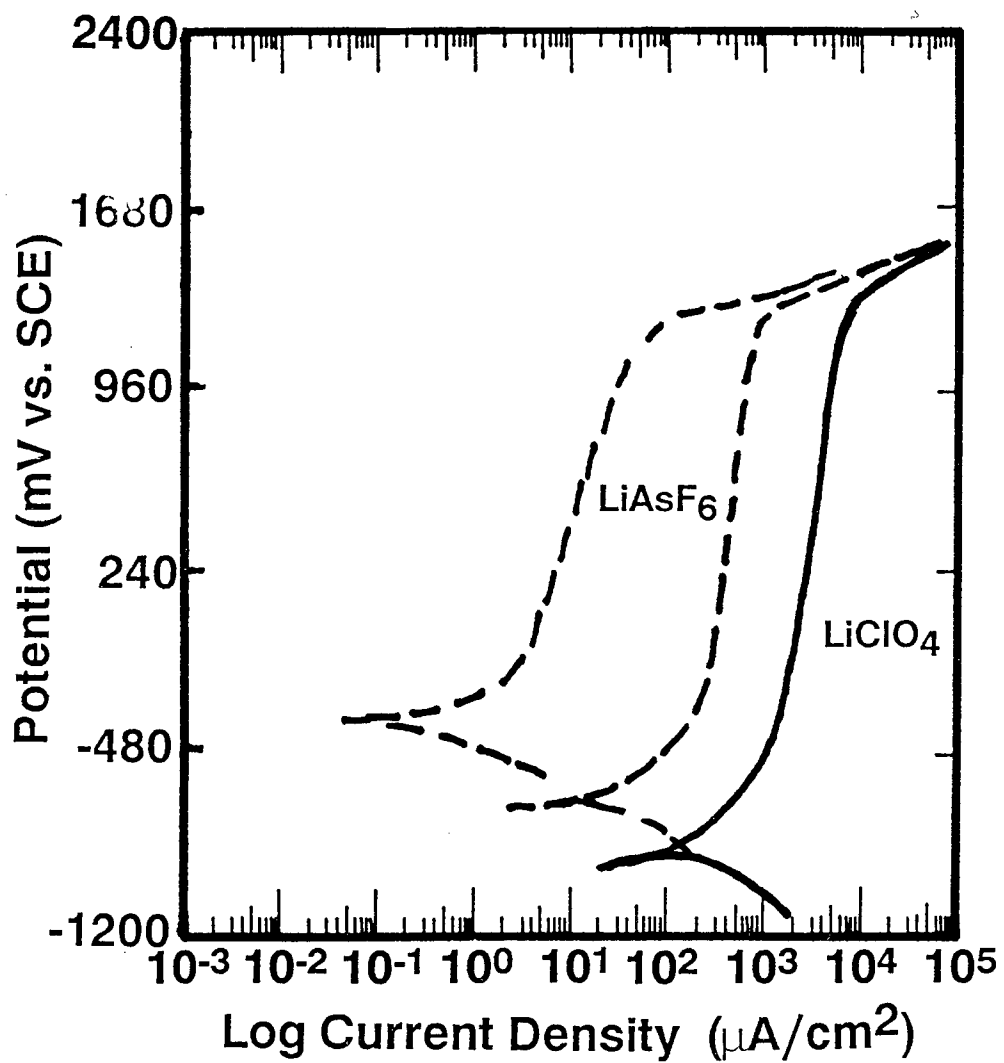
**Figure 22:** Slow scans of nickel 200 in aqueous solutions containing 0.5M LiAsF₆ and 0.5M LiClO₄. The perchlorate scan has anodic currents 1-3 orders of magnitude higher than observed in the hexafluoroarsenate solutions.

## 4.4.2 Conclusions

Nickel 200 showed no active/passive behavior when anodically polarized in hexafluoroarsenate or perchlorate solutions of technical PC, PC-$H_2O$ binary mixtures, and water. In both anhydrous and technical PC/0.5M LiAsF$_6$ solutions, Nickel 200 is passive up to about 700 mV positive of the PC$_{ox}$ observed on iron. Impurities in technical PC activate the nickel surface but, do not cause premature deterioration of the air-formed film. In technical PC/0.5M LiClO$_4$ solutions nickel was passive up to about 500 mV positive of PC$_{ox}$ on iron. Above these potentials nickel was susceptible to pitting. The current increases that are observed at these "breakdown" potentials is speculated to be caused by the oxidation of PC or possibly by the catalyzed oxidation of the electrolytes by nickel. This has not been clarified.

The air-formed film on nickel is more stable than the air-formed films on iron or carbon steel. The higher critical potential observed on nickel in PC solutions suggests that, under the experimental conditions inherent in slow scans, a much longer induction period is required at potentials above PC$_{ox}$ (+0.9 V(SCE)) to initiate pitting by local acidification by PC hydrolysis products.

In mixed PC-$H_2O$ and aqueous solutions with either 0.5M LiAsF$_6$ or 0.5M LiClO$_4$, nickel is passive up to about +1.2 V(SCE) where $O_2$ begins to evolve. The nickel is more highly activated in perchlorate solutions than in hexafluoroarsenate solutions. This is possibly due to the greater adsorptive capability of the perchlorate anion which forms surface active complexes in the passive layer. Passivity of the air-formed film is destroyed when the potential applied to nickel is in the transpassive region. Pitting was observed on the nickel surfaces after the slow scans.

## 4.5 304 Stainless Steel in PC-$H_2O$ Solutions

## 4.5.1 Results and Discussion

The polarization curves of 304 stainless steel in technical PC/0.5 M LiAsF$_6$ is shown in Figure 23 and compared to a slow scan in an anhydrous PC/0.5 M LiAsF$_6$ solution. In the anhydrous scan the stainless steel is passive up to the oxidation potential of the hexafluoroarsenate anion (ca +1.75 V(SCE)). Pitting occurs at potentials above that where the hexafluoroarsenate anion oxidizes. In scans involving technical grade PC the critical potential where breakdown occurs is between +1.2 V and +1.4 V(SCE). This implies that the impurities present in the
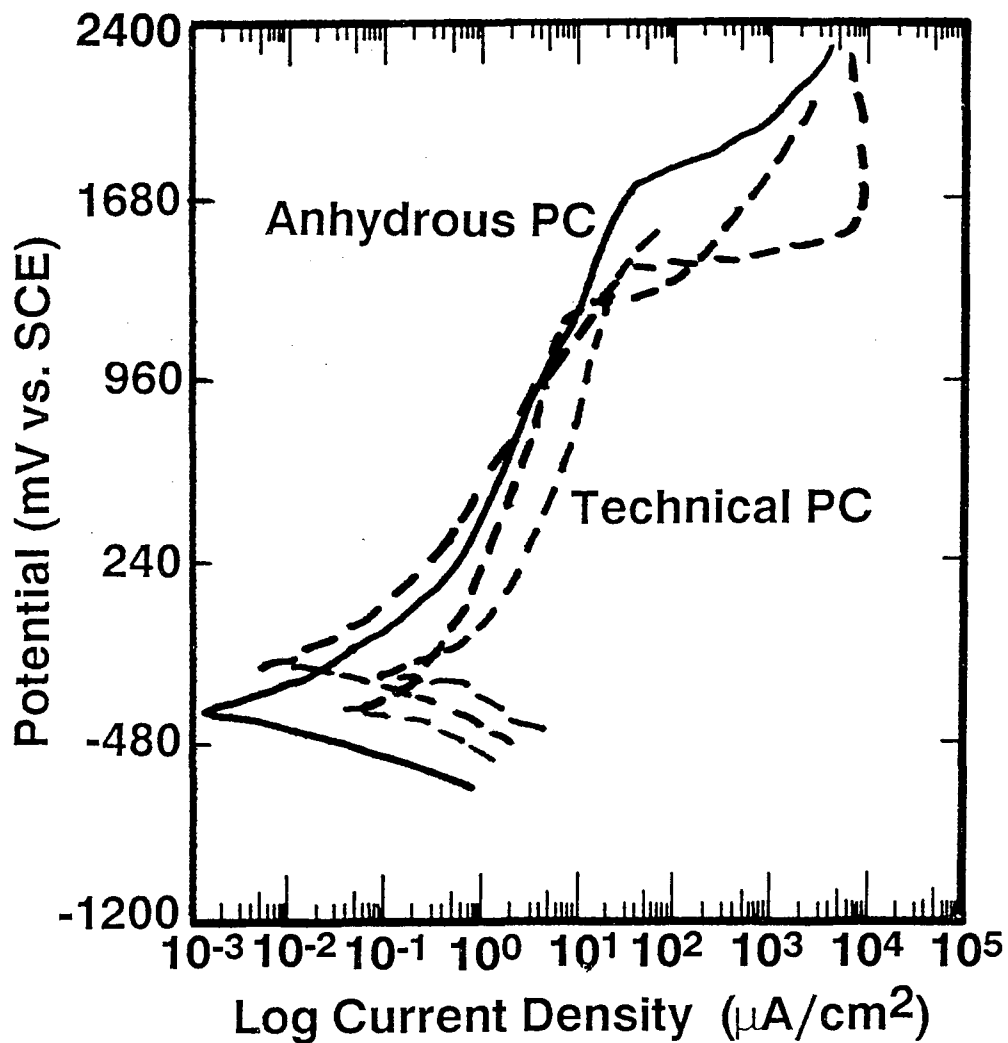
**Figure 23:** Polarization curves of 304 stainless steel in technical PC/0.5M LiAsF$_6$ and anhydrous PC/0.5M LiAsF$_6$ solutions. The anodic currents are similar until + 1.2-1.4 V(SCE) where impurities cause premature deterioration of the passive film. In anhydrous PC the 304 SS is stable up to (AsF$_6^-$)$_{ox}$.

technical PC such as water and propylene glycol are capable of attacking the air-formed film. After slow scans in technical grade PC/LiClO$_4$ solutions that reached a final potential above +2.0 V(SCE), attack also occurred on the stainless steel surface, causing uniform corrosion and small pits aligned along the scratch lines.

The polished and etched stainless steel surface is not homogeneous and displays a multi-crystalline structure with numerous surface inclusions, with some aligned in the rolling direction. Staining of the surface [16] to disclose any sulfide type inclusions revealed none visible up to 400X magnification with an optical microscope. Oxide, silicates, or mixed sulfide-silicate or sulfide-oxide inclusions may be present. Post-test examination of the stainless steel surface after the slow scan in anhydrous PC shows numerous pits generally aligned along the scratch lines. The pit density is approximately equal to the inclusion density. The combination of scratches and inclusions causes weak sites where pitting can occur. The combination of surface scratches and surface inclusions cause weak spots in the oxide film which act as initiation sites for pitting .

The slow scan of 304 stainless steel in 50 mole% technical PC-50 mole% H$_2$O/0.5M LiAsF$_6$ is shown in Figure 24. The 304 steel dissolves anodically without an active/passive transition. No apparent activation of the 304 surface from the 50 mole% PC-H$_2$O solution was observed when compared to the technical grade PC solutions. No dissolution of the 304 surface was observed during the test and post-test examinations. The 304 exhibited no attack or pitting of the stainless steel. It is believed that the water levels are sufficient to support oxide formation, and that the intact air-formed film is protective at potentials where other passivation mechanisms are competing and could be incompatible.

In neutral aqueous solutions of perchlorate or hexafluoroarsenate the 304 stainless steel anodically polarizes at a slope virtually independent of potential and without an active-passive transition [See Figure 25]. At about +1.25 V(SCE) the slope decreases because of oxygen evolution. Inspection of the 304 surfaces after the experiments shows no attack because the chromium incorporated in the oxide film protects the underlying metal.

## 4.5.2 Conclusions

The air-formed film on 304 SS is stable in anhydrous PC up to the oxidation potential of the AsF$_6^-$ electrolyte (ca.+1.7 V(SCE)). Impurities in technical PC attacks the air-formed film and causes deterioration of the film at potentials 200-300 mV negative of that found in
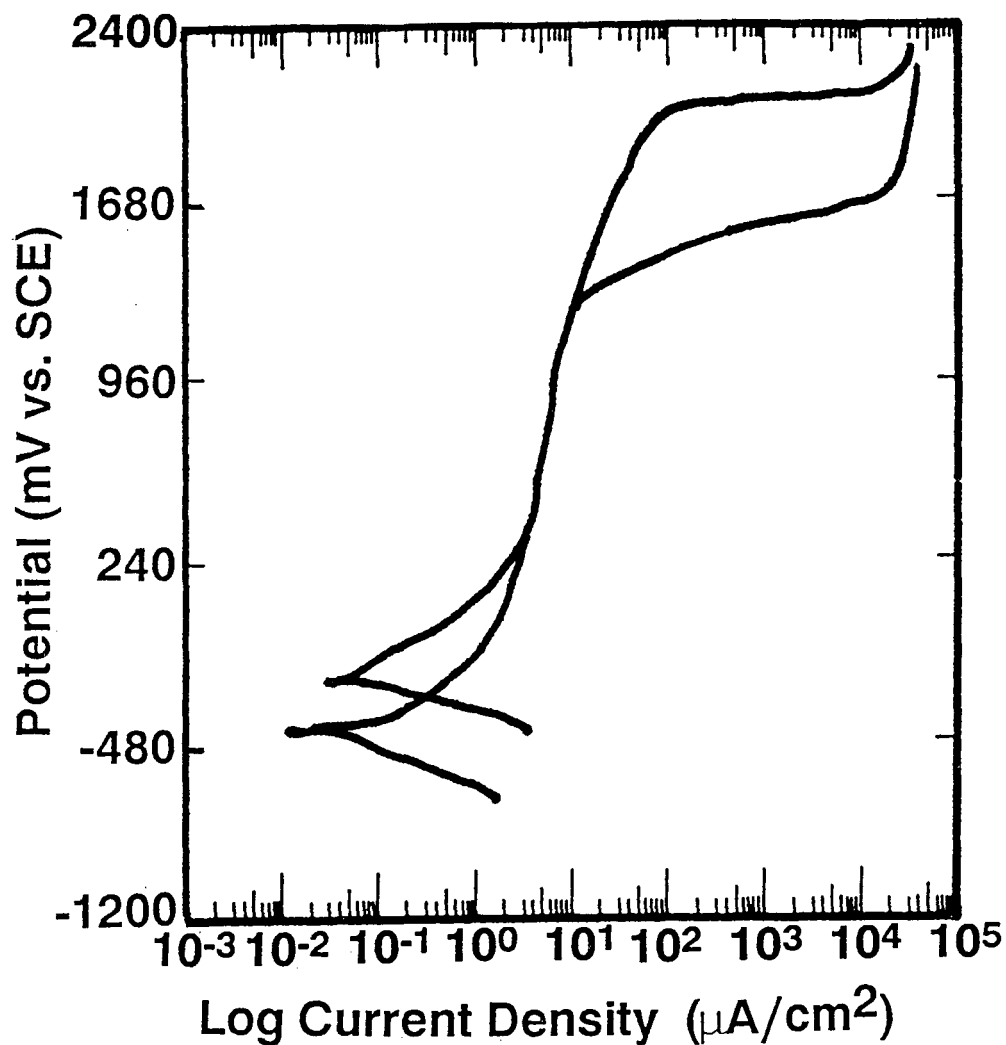
**Figure 24:** Slow scans of 304 stainless steel in 50 mole% $H_2O$/0.5M $LiAsF_6$. The 304 SS dissolves anodically without an active/passive transition. A decrease in the current slope occurs at + 1.25 V(SCE) where $O_2$ evolves and at a hexafluoroarsenate oxidation potential.
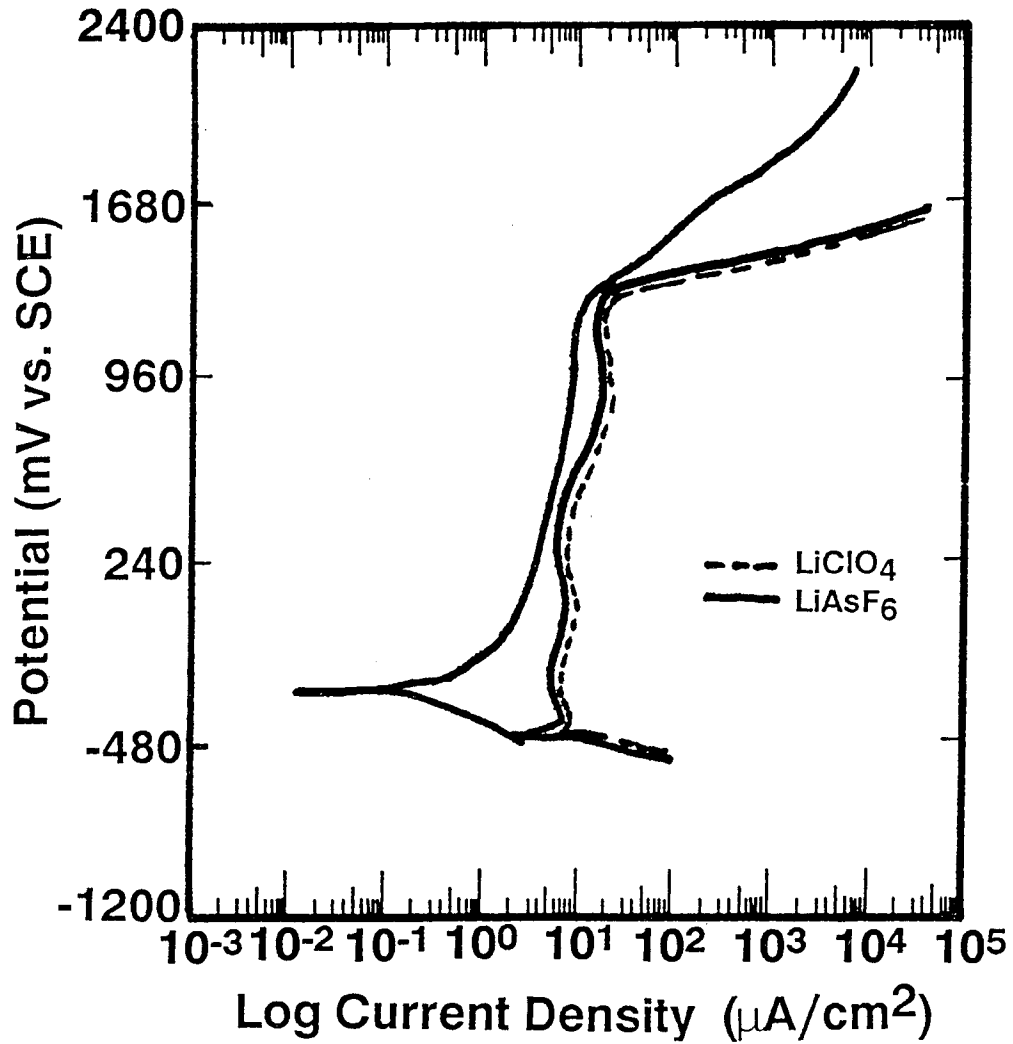
**Figure 25:** Slow scans of 304 stainless in aqueous solution containing 0.5M LiClO$_4$ and 0.5M LiAsF$_6$ are virtually identical. The currents increase at the oxygen evolution potential (+1.25 VSCE)).

anhydrous PC. At potentials far above the oxidation of the hexafluoroarsenate anion, crystal-lographic attack occurred in areas not protected by a salt film. At this potential none of the passivating mechanisms is generally operable. The salt film still present in other areas of the sample protects the stainless from further attack. It acts as a resistor which effectively lowers the potential below the hexafluoroarsenate anion oxidation potential.

The air-formed film on 304SS is stable in PC-$H_2O$ and aqueous solutions. The polarization behavior of 304 SS does not display an active/passive transition although it may be masked by the cathodic reaction. The current slopes decrease at about $+1.2$-$1.3$ V(SCE) when the oxygen evolution begins. It is believed that the water concentrations are high enough to support oxide formation, and that the intact air-formed film is protective at potentials where other passivation mechanisms are competing and incompatible. No pitting is observed in mixed PC-$H_2O$ and aqueous solutions.

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