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The Effect of Ferric Chloride on Charge Injection into Polyethylene

By

Adam Philip Tornheim

A dissertation submitted in partial satisfaction of the requirement for the degree of

Doctor of Philosophy

in

Engineering – Materials Science & Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Thomas M. Devine, Chair
Professor Fiona Doyle
Professor Richard White

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Abstract

The Effect of Ferric Chloride on Charge Injection into Polyethylene

by

Adam Philip Tornheim

Doctor of Philosophy in Engineering - Materials Science and Engineering

University of California, Berkeley

Professor Thomas Devine, Chair

DC charge injection from aqueous electrolytes into low density polyethylene was investigated. Among the electrolytes surveyed, it was found that much higher current densities were recorded when solutions containing both ferric ions and chloride ions were electrochemically oxidized at the polyethylene interface. It was found that exposure to ferric chloride solutions both with and without applied voltage rendered the polyethylene susceptible to charge injection from other solutions that did not contain ferric and chloride ions. Characterization with electrochemical impedance spectroscopy of polyethylene after the application of voltage in the presence of ferric chloride electrolytes did not reveal significant changes, but oxidation products on the exposed surface of polyethylene were detected by both fluorescence spectroscopy and X-ray photoelectron spectroscopy. The effect of oxidation of the surface of polyethylene on charge injection is investigated.

A mechanism of the action of the ferric chloride solutions is proposed by which complexes of ferric ions and chloride ions catalyze the oxidation of a component in the electrolyte. The electron produced by this oxidation reaction is injected into a surface state in the polyethylene. The identity of the complex in ferric chloride solutions responsible for this catalytic behavior is believed to be FeCl₄⁻. The presence of atmospheric oxygen in the electrolyte is thought to be necessary for the production of the oxidation groups on the surface of polyethylene that lead to enhanced charge injection with other electrolytes.
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Introduction

Polyethylene

Polyethylene, a polymer consisting of repeating CH$_2$ monomers, is an extremely common material produced in large quantities for a variety of applications. Some of its desirable properties include very low chemical reactivity and very high electrical resistivity.

As a result of its properties, polyethylene is often found worldwide as electrical insulation of high voltage power cables in underground transmission and distribution settings. A cross-section of a cable is shown in Figure 1, with the different components of the cable described. The cable shown in Figure 1 does not contain polyethylene insulation, but in discussing the different components of distribution cables, the cable shown in Figure 1 is analogous to one with polyethylene insulation.

Starting from the interior of the cable, the central conductor is composed of braided metal wires, either aluminum or copper. The number of braids determines the electrical load that can be connected to the cable. Immediately outside these wires is a layer called the “semi-con” which can be polyethylene with some carbon black mixed in the melt. This layer has a high permittivity, which can mitigate any large electric fields that occur as a result of burrs or other defects in the central conductor. The next layer is the polymeric insulation, which is responsible for insulating the central conductor from ground (the cables are buried underground, and insulation has to be used to prevent electrical leakage and shorts). Depending on the application, it can be a few mm to a few cm thick. Outside this is another semi-con layer, followed by a jacket, which is made out of another rubbery material. Concentric neutrals are either imbedded in this jacket or surrounding it as another layer. The role of concentric neutrals is to carry return current from the electric loads in the case that loads in the system are not balanced.

In practice, low density polyethylene, which is synthesized by a radical-generating polymerization reaction, was used in some electrical insulation applications, but was unable to withstand the same temperatures as other insulation materials, a shortcoming which limited the electrical loads that could be connected to it. However, cross-linking, a process in which different polymer chains are tethered together by carbon-carbon bonds, improved the mechanical properties of the polyethylene cables at elevated temperatures. Shortly after its advent in 1963, cross-linked polyethylene (XLPE) cable quickly gained popularity as a cheaper, lower maintenance, and more environmentally friendly alternative to paper-insulated, lead sheath covered cables, which had been the standard. Unfortunately, these XLPE cables failed in service well before reaching their expected lifetime, resulting in blackouts and underground electrical fires, requiring
costly, unscheduled replacements. While a significant amount of installed cables are from the 60s and 70s, cables made from the same polymer melt that did not fail were not replaced even though they may be susceptible to the same failure mechanism as the cables that did fail. The failure of these cables was initiated at a defect now known as water-trees.

**Water-trees**

Water-trees were first documented in a paper published within a decade of the invention of XLPE (Miyashita, 1969). Since then, a large body of research on the water-treeing phenomenon has been established. Water-trees are collections of water-filled microvoids in the cable insulation that are assembled in tree-like or bush-like patterns. While the water-trees themselves do not necessarily lead to cable failure, they have been shown to act as sites for the initiation of electrical trees, a defect that directly leads to cable failure by providing a current path to ground.

Additionally, there is a significant interest in developing a diagnostic technique that can determine when cables need to be replaced. Current diagnostic techniques are roughly half the cost of simply installing new cable, and produce a significant amount of false positives, requiring costly reinstallation of cable that is not at imminent risk of failure. Part of the reason these diagnostic techniques are so ineffective is that the mechanism of water-tree growth and propagation is not well understood.

This research has, however, identified key elements necessary for water-tree formation, specifically the presence of an AC field and exposure to aqueous electrolyte over time, though the specific influence of these factors is unknown. To this point, numerous studies have been conducted investigating the effects of field strength, temperature, and frequency, as well as chemical characterization of the water-treed area. This work has resulted in two dominant yet incomplete theories for the mechanism of water-treeing.

The first major theory is that water-tree degradation progresses through an electrochemical mechanism. According to this theory, water-treeing is initiated by hydroxyl radical formed either by a discharged hydroxide ion or a split hydrogen peroxide molecule. This hydroxyl radical removes a hydrogen atom from the polymer, creating a carbon radical and leading to a hydrophilic element on the polymer backbone. This process results in a phase separation of the hydrophilic and hydrophobic parts and subsequent water condensation at the hydrophilic boundary. The limitations of this electrochemical theory are that it only includes the influence of an AC field through empirical correlation, and that it does not adequately explain the correlation of water-tree propagation with AC frequency
The second main theory indicates that electromechanical fatigue triggers water-treeing. Osmotic pressure causes water to condense around impurities and inclusions in the polyethylene insulation. The water particles are then deformed in the AC electric field by dielectrophoresis. This cyclic force then initiates bond scission through a fatigue mechanism, extending the water-filled voids in the insulation. While this theory does tie water-tree propagation to frequency of an AC field, it explains neither the effect of free radical scavengers in limiting the propagation rate of water-trees, nor the effect of certain salt solutions in accelerating the propagation rate of water-trees.

The incompleteness of these two dominant theories indicates that additional factors in the mechanism of water-treeing have not been identified. One potential such factor is the composition of the electrolyte environment of the buried power cables. Polyethylene cables are either direct-buried, or buried in conduits. Previous research investigating DC charge injection into anthracene crystals from aqueous solution indicates that certain solutions injected charge into anthracene at much higher rates than had been seen with metal electrodes. If aqueous solutions are able to inject charge into anthracene, could the solution chemistry in the underground infrastructure be an important factor in the mechanism of charge injection and water-treeing in polyethylene cables?

Scope of research

For the case of polyethylene, there is very little research, if any, on the influence of the electrode contact material in DC conduction, while aqueous electrolytes are one of the components that have been found to be necessary for the development of water-trees.

The scientific question this work aims to address is, what role can aqueous electrolytes play in charge introduction, conduction, and subsequent breakdown of polyethylene film under DC voltages? Other authors have developed the theory describing the behavior of insulators under electrical stress with metal contacts in the 1950s and 1960s, and there is no need to revisit that work. The present work deals solely with changes from developed theories brought about by aqueous electrolytes as the electrical contacts to the polyethylene.
Experimental Procedures

One of the objectives of the present work was to determine the effect of electrical contact material on DC charge injection into polyethylene. Most research with polyethylene has used sputtered electrodes (and thereby keeping the electrode area constant), using aqueous electrolytes in this work presented some new difficulties. First, the electrolytes must be kept in contact with the polyethylene throughout the experiment, and secondly, the electrode area cannot change from one test to another. To accomplish these two aims, an apparatus was designed that consisted of two L-shaped glass tubes that were clamped around the polyethylene film such that the film was kept in a vertical orientation throughout the test. The electrode area (area of the electrolyte in contact with the polyethylene film) is determined by the size of the opening of the L-shaped tubes. With the polyethylene aligned vertically, the electrolytes were kept in constant contact with the polyethylene sample.

Test Cell Preparation

Borosilicate glass test cells were manufactured by Adams and Chittendon (Berkeley, CA), who specialize in scientific glassware manufacturing. The test cell consists of two L-shaped glass tubes of about 3 cm on a side. The two legs of the L are different; one leg with a straight tube with an I.D. of 5 mm, and the other leg with a fluted opening that expands to an I.D. of 1 cm. This edge of this fluted opening has a circular indentation approximately 1 mm deep.

To form a test sample, a square of polyethylene film at least 25 μm thick is placed between the two L-shaped glass tubes with the fluted openings on either side. For all tests unless otherwise specified, the polyethylene used has a thickness of 25 μm. On one side of the polyethylene (typically the side in contact with 1M NaCl) an O-ring (20 mm diameter) is placed in the groove of the fluted opening. The two glass tubes are then brought together, sandwiching the polyethylene film. The two glass tubes are subsequently clamped together, with the pressure against the O-ring on both sides creating a watertight seal. Platinum wires are then inserted into the open tops of each of the L-shaped glass tubes. The test cell is shown schematically in Figure 2.

Approximately 5 mL of electrolyte is pipetted into each side. During the pipetting, the apparatus was tilted at approximately 45 degrees to allow the solution to cover the entirety of the exposed polyethylene at the tube opening, otherwise an air bubble would form at the top of the electrolyte – polyethylene interface, which would change the electrolyte contact area.
High Voltage Setup

High voltage tests were necessary in order to determine the effect of the electrolytes on DC charge injection into polyethylene. Tests were performed in which high voltages (up to 6 kV) were applied across the polyethylene and the circuit current recorded. The experimental procedure is described below.

The schematic for the high voltage circuit is shown in Figure 3. The voltage source is a HYPOT III 3770 (Associated Research) and is capable of applying 6 kV DC. The high voltage lead from the HYPOT III is connected to one of the platinum wires immersed in one of the electrolytes in the test cell. If the ground lead from the voltage source is connected to the 1M NaCl electrolyte, then the setup is referred to as "forward bias". If the high voltage lead is connected to the 1M NaCl electrolyte, then the setup is referred to as "reverse" bias. The platinum wire immersed in the second electrolyte is connected by alligator clip to one side of a 300 MΩ resistor, with the opposite side of the resistor connected to the input of the picoammeter (model 6485, Keithley) capable 10 fA resolution, with the output of the picoammeter connected to the ground of the voltage source. This setup is designed to provide a voltage stress to a polyethylene sample, record current, and if the polyethylene breaks down the subsequent voltage and current are limited by the 300 MΩ resistor, preventing damage to the picoammeter. This entire setup is contained within a copper mesh Faraday cage within an insulating box. The Faraday cage is connected to ground and the interlock of the voltage source is connected to the lid of the insulating box.

High Voltage Tests

One of the main parts of this work was to determine the effect of electrolytes on the DC charge injection into polyethylene. However, once voltage is applied current sharply increases and then decays non-linearly to a roughly constant value. This is due to a combination of effects in the polyethylene as well as charging of the electrolyte solutions. To avoid these effects as much as possible, the current was recorded at the end of a voltage step, 19 seconds after voltage was applied.

In this section two different tests are discussed. The ‘standard’ test indicates a polyethylene sample that is subjected to only one current-voltage test – it has not been subjected to any experimental stress before the test. A ‘pretreatment’ test involves a test with a polyethylene sample that has been previously subjected to some experimental conditions (each pretreatment test will describe specifically the exposing conditions).

For both of these tests, both the application of voltage and recording of data are automated by a LabView program. With this program, the user inputs the starting voltage, ending voltage, and the dwell time at each voltage step. Once started, the program controls the voltage source with a serial connection and the
picoammeter with a GPIB interface. Through this program, the applied voltage and measured current are automatically recorded into an Excel spreadsheet. The recorded current is divided by the contact area between the electrolyte and polyethylene sample (1.7 cm$^2$) to obtain the current density. These two tests are described below.

**Standard test**

A standard test begins with 100 V applied across the platinum wires immersed in the two sides of the test cell. Nineteen seconds after the application of voltage, the picoammeter takes a measure of current. The voltage is increased by 100 V for another 20 seconds with current measured 19 seconds in. This step is then repeated until the final voltage step of 6 kV is applied and the current is measured.

**Pretreatment test**

To perform a pretreatment, a test cell is prepared with the pretreating electrolyte on one side of the polyethylene and 1M NaCl on the opposite side. In this work, pretreating electrolytes are 1M FeCl$_3$ + 1M H$_2$SO$_4$, 0.23M K$_2$Cr$_2$O$_7$ + 15M H$_2$SO$_4$, deoxygenated 0.66M FeCl$_3$ + 2M KCl, and 1M NaCl. Pretreatments consisted either of a voltage ramp in the presence of the pretreating electrolyte or a timed exposure with no applied voltage. For the pretreatments involving a voltage ramp, the sample is subjected to an abbreviated reverse bias standard high voltage test (see preceding paragraph) in which the normal procedure for a standard test (described above) is followed, but the pretreatment is stopped once 20 seconds have elapsed at 2 kV or 0.5 kV. At this time the test cell is removed from the high voltage setup, and the pretreating electrolyte is poured out of the glass tube. The empty glass tube is then rinsed with deionized water four times, and a new electrolyte is added. This test cell is then reconnected to the high voltage setup and subjected to a standard test. A “forward bias” pretreatment test connects the opposite leads to the platinum wires once the new electrolyte is added, while for a “reverse bias” pretreatment test the polyethylene is polarized in the same direction. For the timed exposure pretreatment tests, the test cell is prepared with the pretreating electrolyte in contact with the polyethylene. After the appropriate amount of time has elapsed, the pretreating electrolyte is poured out and replaced with 1M NaCl.

**pH measurements**

pH measurements were performed with an Accumet AB15 pH meter. Fresh buffer solutions at pH 2.00 and 4.00 were used to calibrate the electrode
immediately before the pH measurements. Calibrations were performed iteratively until the pH measured was within 0.01 of the pH of the buffer.

To measure the pH of the different electrolytes, a test tube was filled halfway with the electrolyte, and the pH meter was immersed approximately 2 cm. Once the reading on the meter stabilized (usually approximately 1 minute), the value was recorded. After each test, the electrode was rinsed with distilled water.

**Galinstan**

Galinstan (Alfa Aesar) is a liquid metal alloy with a melting point of 10.7°C, composed of gallium, indium and tin. It is commonly used as substitute for mercury when a less toxic liquid metal is desired. It was used in this work as a comparison between electrolyte and metal electrodes. As a liquid, it could be used in the same test cell as the electrolytes.

**Deoxygenation**

For the tests that required deoxygenation of one of the electrolytes, a specific procedure is followed to ensure most/all atmospheric oxygen is removed. First, for at least 24 hours before any tests are run with a ‘deoxygenated’ electrolyte, nitrogen is bubbled through the stock solution at a rate of 0.1 L/min. Before electrolyte is transferred from the solution to the apparatus, an additional line of nitrogen is placed in the empty L-shaped tube where the deoxygenated solution will go. The deoxygenated solution is transferred either with a peristaltic pump (Fisher Scientific) or with a narrow syringe. A small flow of nitrogen (low enough to prevent spilling the electrolyte) is bubbled through the electrolyte in the L-shaped glass tube throughout the test to prevent reoxygenation. Deoxygenated electrolytes were used in both a standard test with 1M FeCl\(_3\) + 1M H\(_2\)SO\(_4\) as well as during pretreatment with 0.66M FeCl\(_3\) + 2M KCl as the pretreating electrolyte (only the pretreating electrolyte was deoxygenated, the subsequent test in 1M NaCl was open to the atmosphere).

**Electrochemical tests**

**Corrosion potential**

The redox potentials of the electrolytes were determined by measuring the rest potential of platinum immersed in the solutions. To measure the rest potential of platinum in a solution, a standard calomel electrode and platinum wire were placed in the solution. Once the voltage between the calomel electrode and the platinum wire stabilized, it was recorded. The voltage was measured with a multimeter.
Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) was performed on polyethylene samples in the presence of 1M FeCl₃ + 1M H₂SO₄ on one side and 1M NaCl on the other both before and after the application of a voltage of 2 kV and 2.5 kV. For each test, a 10 mV amplitude oscillating potential was applied between two platinum wires from a frequency range of 65 kHz to 0.95 mHz, with 6 data points collected per decade. The applied potential was controlled by a Gamry potentiostat.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra were acquired in collaboration with Mr. Gerry Hammer at the National ESCA and Surface Analysis Center for Biomedical Problems, located at the University of Washington. His procedure is given below:

XPS spectra were taken on a Surface Science Instruments S-probe spectrometer. This instrument has a monochromatized Al Ka X-ray source and a low energy electron flood gun for charge neutralization of nonconducting samples. The sample was fastened to the sample holder with double-sided tape and run as an insulator. X-ray spot size for these acquisitions was approximately 800 mm. Pressure in the analytical chamber during spectral acquisition was less than 5 x 10⁻⁹ Torr. The pass energy for survey scans was 150 eV, and the pass energy for high resolution scans was 50 eV. The take-off angle (the angle between the sample normal and the input axis of the energy analyzer) was ~55° (55° take-off angle @ 50 Å sampling depth). Service Physics Hawk Data Analysis 7 Software was used to calculate surface atomic concentrations using peak areas above a linear background and elemental sensitivity factors, and to peak fit high resolution spectra. The binding energy scales were calibrated by assigning the most intense C1s high-resolution peak a binding energy of 285.0 eV.

Two spots were analyzed, one untreated control and one from the etched area.

Fluorescence spectroscopy

Fluorescence spectroscopy of both etched and unetched areas of polyethylene were performed by Mr. Jamie Kulp at the University of California, Berkeley. The procedure followed is given below:

Calibration of surface density of aldehyde groups was done using a standard commercial slide purchased from Schott Glass. These glass slides have known
density of aldehyde groups on the surface and were used to calibrate the fluorescent signal vs. a known number of labeled aldehyde groups. Each slide was treated with a mixture of Texas Red Hydrazide and Fluorescein Hydrazide dyes. The ratio of each dye in solution controlled the number of each dye molecule immobilized onto the surface of the slide. The ratio was varied to generate a calibration curve. A non-labeled slide was also included as a background signal for the Schott slide.

Each fluorescent dye used is functionalized with a hydrazide reactive group which is specifically reactive towards carbonyl groups. The stock dyes were 50mM in dimethyl sulfoxide (DMSO). These were diluted to 50uM in 2-(N-morpholino)ethanesulfonic acid (MES) buffer at pH 5.5 to facilitate the labeling reaction. Samples were incubated overnight at 37°C on a rotating platform to promote mixing. The dye solution was then removed and the samples rinsed well with DMSO before incubating overnight again in DMSO to remove any non-specifically bound dye molecules from the surface. Prior to reading of the fluorescent signal each sample was rinsed with 0.1M phosphate buffered saline pH 7.4 buffer. In addition to labeling carbonyl groups via the hydrazide – carbonyl reaction, carboxyl groups were also labeled via 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) mediated reaction. EDC allows for the specific labeling of carboxylic acid groups by each dye. Each sample was analyzed using a Typhoon scanning fluorimeter. Signal profiles were then generated showing the 2 dimensional distribution of carbonyl and carboxyl groups on the exposed polyethylene samples vs. unexposed polyethylene samples.
Results

Introduction to experimental results

In this section, a large amount of data will be presented, the bulk of which pertains to the current density through a cell that is contacted by different electrolytes. Below, Table 1 shows information that may be helpful in direct comparisons of the behavior of different electrolytes for many of the electrolytes used. The specific action of these electrolytes is to transport charge through the solution and/or inject charge into polyethylene.

Table 1. Electrolytes used in current-voltage tests

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Ionic strength</th>
<th>Rest potential of platinum vs. SCE</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M FeCl$_3$ + 1M H$_2$SO$_4$</td>
<td>10</td>
<td>0.527</td>
<td></td>
</tr>
<tr>
<td>1M CuSO$_4$</td>
<td>4</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>1M KMnO$_4$</td>
<td>1</td>
<td>0.957</td>
<td></td>
</tr>
<tr>
<td>0.04M FeCl$_3$ + 1M H$_2$SO$_4$</td>
<td>4.24</td>
<td>0.527</td>
<td></td>
</tr>
<tr>
<td>0.5M FeCl$_3$ + 1M H$_2$SO$_4$</td>
<td>7</td>
<td>0.527</td>
<td></td>
</tr>
<tr>
<td>1M FeCl$_3$</td>
<td>5</td>
<td>0.514</td>
<td>0.73</td>
</tr>
<tr>
<td>0.5M Fe$_2$(SO$_4$)$_3$</td>
<td>5.25</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>1M Fe(NO$_3$)$_3$</td>
<td>5</td>
<td>0.69</td>
<td>0.06</td>
</tr>
<tr>
<td>0.66M FeCl$_3$ + 2M KCl</td>
<td>4</td>
<td>1.17</td>
<td></td>
</tr>
</tbody>
</table>

The terms “injection” and “extraction” are used in the context of electrochemical reactions at the interface of the polyethylene. This work deals with negative charges, so charge injection and electron injection are synonymous. “Electron extraction” may be used instead of positive charge injection.

In order for an electron to move from the solution to the polyethylene, a component in the electrolyte must be oxidized, i.e. lose an electron, and the electron enters a surface state of the polyethylene. This entire process is what is meant by the term “charge injection” or “electron injection”. The term “injecting species” refers to the component in the electrolyte that is undergoing electrochemical oxidation at the surface of the polyethylene, with the electron lost in this oxidation process moving to a state in the polyethylene surface. At the opposite surface of the polyethylene, electrons are “extracted” from the polyethylene, so in a similar fashion, a component in the electrolyte undergoes electrochemical reduction as an electron moves from the polyethylene surface to the reducible component.
Electrochemical results

The current as a function of time for a sample of polyethylene film sandwiched between two L-shaped glass tubes with 1M FeCl$_3$ + 1M H$_2$SO$_4$ on one side and 1M NaCl on the other side is shown in Figure 4. The convention used in this work is that ‘forward bias’ denotes the applied potential when the ground electrode is immersed in the 1M NaCl electrolyte, and ‘reverse bias’ is where the high voltage electrode is immersed in the 1M NaCl electrolyte. For this experiment, the initial applied voltage was 100 V and the voltage was increased 100 V every 20 seconds to a maximum of 6 kV.

At this point it is necessary to define the parameters of the current density measurements presented in this section. In Figure 4, it is easy to see each distinct voltage step – for each increase in voltage, there is a large increase in current, followed by a fast current decay, then for the remainder of the voltage step the current density behavior depends on both the electrolyte and electric field. Upon closer inspection, it can be seen that this current decay at each step has two distinct parts. The initial spike and quick decay of current density is due to static charging of the electrolyte by the platinum wire; immediately after the application of voltage, there is a potential difference between the platinum electrode and the electrolyte, leading to a short current flow to equalize the potentials. This assertion was tested by recording current density vs. voltage with the high voltage leads immersed in separate and electrically unconnected beakers. With no effective electrical path between the two electrodes (an open circuit), there is still a brief current spike. The behavior of the current density after the initial spike can be attributed to different effects at the interface of the polymer, and will be addressed in a later section.

Ideally, the current at a particular voltage would be measured once the steady state current was reached, however these experiments would take an exorbitant amount of time (at 300 V the current had not reached steady-state after 72 hours). Thus, for the sake of comparing one test to another, the current density after 19 seconds of a voltage step is used to define the current-voltage relationship. This allowed a single current density to be attributed to a voltage step, instead of a range of current densities, and allowed quantitative comparison of the behavior of different electrolytes. The specific factors that influence the current density vs. time at a particular voltage step and the conclusions that can be drawn are discussed in greater detail in the appendix.

For the initial tests, a 20 second delay at each voltage step was chosen so as not to exceed the size of the data buffer of the picoammeter. The picoammeter can record up to 2500 data points, which were recorded in approximately 800 seconds at the slowest, most accurate measurement rate. Preliminary experiments indicated breakdown voltages with 1M FeCl$_3$ + 1M H$_2$SO$_4$ were approximately 3 kV, so a 20 second delay at each voltage step meant that the experiment would terminate at approximately 4 kV. However, once the measurement system was automated,
20 second delay at each voltage step was kept for consistency between data sets, although with the automation, current density data could be collected up to a maximum applied voltage of 6 kV. This choreographed voltage protocol (100 V initial applied potential, increasing 100 V every 20 seconds in a stepwise manner) is referred to as a ‘standard test’.

**Adjusted Data**

The current density as a function of applied cell voltage of both polarities for a test cell with 1M FeCl\textsubscript{3} + 1M H\textsubscript{2}SO\textsubscript{4} as one electrolyte and 1M NaCl as the other electrolyte is shown in Figure 5. At first glance, two trends are very noticeable. First, for both reverse bias and forward bias, the current density rise is not linear with applied voltage throughout the test – indicating Ohmic conduction is not the dominant conduction mechanism (this will be discussed in a later section). Second, as the applied voltage increases, there is a clear discrepancy in current density with respect to the polarity of the applied voltage. This is to say that when the positive voltage lead from the power supply is immersed in the 1M NaCl electrolyte, more current flows than when it is immersed in the 1M FeCl\textsubscript{3} + 1M H\textsubscript{2}SO\textsubscript{4} electrolyte.

The current-voltage behavior of the 1M FeCl\textsubscript{3} + 1M H\textsubscript{2}SO\textsubscript{4} can be compared to Figure 6, which shows the current density as a function of applied cell voltage for a test cell with 1M NaCl as both contacting electrolytes. Looking at the current densities at an applied potential of 3 kV, the cell with ferric chloride in reverse polarity has a current density of 75 nA/cm\textsuperscript{2}, whereas with 1M NaCl as both contacting electrolytes the current density is 3 nA/cm\textsuperscript{2}. These experiments indicate that this oxidizing electrolyte injects charge at a faster rate than 1M NaCl.

1M FeCl\textsubscript{3} + 1M H\textsubscript{2}SO\textsubscript{4} is an oxidizing electrolyte, so to determine if its charge injection ability was due to its oxidizing nature, additional electrolytes were investigated in similar tests. In Figure 7, the influence of applied voltage on cell current density is presented for a test cell with 1M CuSO\textsubscript{4} on one side and 1M NaCl on the other. 1M CuSO\textsubscript{4} is also an oxidizing electrolyte, but does not show a bias-dependent current density that the 1M FeCl\textsubscript{3} + 1M H\textsubscript{2}SO\textsubscript{4} electrolyte shows. Also, the current density with 1M CuSO\textsubscript{4} is much lower than the current density with 1M FeCl\textsubscript{3} + 1M H\textsubscript{2}SO\textsubscript{4} in reverse bias for the higher applied voltages. In fact, the current density with 1M CuSO\textsubscript{4} as an injecting electrolyte is almost equal to the current density with 1M NaCl on both sides, indicating that 1M CuSO\textsubscript{4} does not seem to change the rate of charge injection into the polyethylene.

Additionally, aqueous 1M KMnO\textsubscript{4}, another oxidizing electrolyte, was investigated in a similar way to the aqueous 1M CuSO\textsubscript{4}, with the results of this current-voltage test presented in Figure 8. For tests with 1M KMnO\textsubscript{4}, a trend opposite to that of 1M FeCl\textsubscript{3} + 1M H\textsubscript{2}SO\textsubscript{4} is shown. For tests with 1M FeCl\textsubscript{3} + 1M H\textsubscript{2}SO\textsubscript{4}, the reverse bias current density was higher than forward bias current density. For 1M KMnO\textsubscript{4}, the current density in forward bias is higher than reverse
Unlike 1M FeCl$_3$ + 1M H$_2$SO$_4$, KMnO$_4$ behaves better at "extracting" electrons than it does injecting electrons. However, the forward bias of 1M KMnO$_4$ at 13 nA/cm$^2$ at 3 kV is much lower than the 75 nA/cm$^2$ seen with 1M FeCl$_3$ + 1M H$_2$SO$_4$ in reverse bias.

Noting that 1M KMnO$_4$ is better at extracting electrons from the polyethylene with an applied voltage, some tests were performed with 1M FeCl$_3$ + 1M H$_2$SO$_4$ as one electrolyte and 1M KMnO$_4$ as the second electrolyte, with the positive voltage lead immersed in the 1M KMnO$_4$ electrolyte. In this orientation, both electrolytes were performing in the highest current density configuration – 1M FeCl$_3$ + 1M H$_2$SO$_4$ injecting electrons and 1M KMnO$_4$ extracting them. The results of this test are shown in Figure 9, with a plot of 1M FeCl$_3$ + 1M H$_2$SO$_4$ shown on the same graph for reference. The (1M FeCl$_3$ + 1M H$_2$SO$_4$)/(1M KMnO$_4$) current is larger than that of 1M FeCl$_3$ + 1M H$_2$SO$_4$, as would be expected when using an electrolyte that extracts electrons at a higher rate than 1M NaCl.

The conclusion can be drawn from the experiments with 1M CuSO$_4$ and 1M KMnO$_4$ that it is not only the oxidizing nature of the electrolyte that leads to high electron injection rates with polyethylene, but rather some other property of the 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte.

Once it was determined that some other trait of 1M FeCl$_3$ + 1M H$_2$SO$_4$ other than its oxidizing power was responsible for high rates of charge injection, further experiments were conducted with changes to the original electrolyte composition. The aqueous FeCl$_3$ electrolyte is a two solute solution, with H$_2$SO$_4$ as well as FeCl$_3$. Tests were conducted for an electrolyte with a decreased H$_2$SO$_4$ concentration to determine if H$_2$SO$_4$ concentration was partially responsible for the charge injection seen with the FeCl$_3$ electrolytes. For this test, the H$_2$SO$_4$ concentration was decreased from 1M to 0.1M, and the current density at 3 kV applied voltage (shown in Figure 10) decreased from 75 nA/cm$^2$ to 60 nA/cm$^2$ (albeit with large standard deviations, so the decrease may not be too significant), but still much higher than the current density seen with 1M NaCl electrolyte on both sides.

With H$_2$SO$_4$ largely not responsible for the high rate of charge injection, the FeCl$_3$ concentration of the 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte needs to be examined. In Figure 11 the results of experiments in electrolytes that were 1M in H$_2$SO$_4$ but with varying concentrations of FeCl$_3$ are presented. The concentrations of FeCl$_3$ used for these tests were .04M, .5M, and 1M, with only reverse polarity data presented. Looking at an applied voltage of 3 kV, the current density for these FeCl$_3$ concentrations is 9, 27, and 75 nA/cm$^2$. While the current density increases with increasing concentration of FeCl$_3$, the increase is not linear, even when removing a "baseline" of the current density for an oxygen redox system like NaCl. Regardless, the correlation of current density to FeCl$_3$ concentration is established. All of the ferric chloride solutions were made with 1M H$_2$SO$_4$, yet the current density varies with the FeCl$_3$ concentration.
Concentration of FeCl₃ | Current density at 3 kV (nA/cm²)
---|---
1 | 75
0.5 | 27
0.04 | 9

Standard tests with 1M FeCl₃ + 1M H₂SO₄ were also performed on low density polyethylene films that were 76 μm thick. The current density as a function of applied voltage for these films with 1M FeCl₃ + 1M H₂SO₄ in reverse bias is shown in Figure 12, with the same tests with a 25 μm sample shown as reference. As would be expected, the current density for the thicker polyethylene film is lower. However, if the x-axis in Figure 12 is changed to electric field instead of electric potential, a different plot, Figure 13 is produced. On this figure, the current density for both film thicknesses (25 μm and 75 μm) are shown as a function of electric field, and the values are quite similar for each point.

**Galinstan Tests**

Traditionally, the electrical properties of insulators and semiconductors are investigated with use of metal electrodes. The metal electrodes are either pressed into contact with the polyethylene or sputtered on the surface, allowing for careful dimensional control of the metal electrode area. To compare the literature data on resistivity of polyethylene to the data presented in this work (aqueous electrolytes used as contacts), it was necessary to perform analogous experiments with a metal as the contact to the polyethylene. In order for the comparison to be valid, it was necessary to perform the experiments with metal contacts with same test cell and parameters as the tests with aqueous electrolytes. The test cell used for tests with aqueous electrolytes is designed for use with liquids, so a liquid metal, Galinstan, was used.

Galinstan is a eutectic alloy of gallium, indium, and tin (62:22:16 by weight). It melts at 10.7°C, has a density of 6.359 g/mL, and is non-toxic. Tests with Galinstan contacts instead of the electrolytes were performed in the same cell that the previous tests were done. The current density vs. applied voltage for a polyethylene sample contacted on both sides by Galinstan is shown in Figure 14. At 3 kV, the current density for a Galinstan-polyethylene-Galinstan cell is 9 nA/cm². Recall that for 1M FeCl₃ + 1M H₂SO₄-polyethylene-1M NaCl in reverse bias, the current density is 75 nA/cm². This result indicates that Galinstan (and by extension, most metals that are electronically similar) does not lead to the high current densities seen with 1M FeCl₃ + 1M H₂SO₄ in reverse bias. However, a test cell with 1M FeCl₃ + 1M H₂SO₄ on one side and Galinstan on the other shows high current densities when the 1M FeCl₃ + 1M H₂SO₄ is injecting electrons.
Contribution of the ferric/ferrous system

The contribution of chloride ions in an acidic medium to charge injection into polyethylene was evaluated with I-V tests with an electrolyte composed of 1M HCl + 3M NaCl on one side and 1M NaCl on the other. This data, shown in Figure 15, indicates that free chloride ions are not responsible for the charge injection behavior seen with the ferric chloride solutions.

To determine the effect of different iron ion species on current density under an applied voltage, different iron-containing electrolytes were investigated under reverse bias polarity. These electrolytes include one ferrous salt, FeSO₄, three ferric salts – FeCl₃, Fe₂(SO₄)₃, Fe(NO₃)₃, and one mix of ferric and ferrous, with half the ferrous and half ferric ions as a mixture of FeSO₄ and Fe₂(SO₄)₃. These solutions were created to deconvolute the effect of chloride ion concentration from the charge injection behavior of ferric chloride solutions. All these solutions were 1M with respect to iron and were made without the addition of H₂SO₄. The reverse bias data is shown in Figures 16 (ferric salts) and 17 (iron sulfates). From the data, it is clear that both FeCl₃ and Fe(NO₃)₃ have a high rate of charge injection, all of the iron sulfate solutions do not. The redox potentials of the aqueous iron sulfate and iron chloride solutions were characterized by measurement of platinum’s open-circuit potential, shown in Table 1. For the ferric solutions investigated with the open circuit potential of platinum, the measured potential indicated both ferric and ferrous ions were present in the electrolyte immediately adjacent to the platinum electrode. However, the significant influence of platinum’s open circuit potential of these electrolytes on current density indicates that it is not only the ferric/ferrous redox system in the ferric chloride electrolyte that is necessary for charge injection into polyethylene, but rather some combination of iron and chloride

Complexing

Electrolytes were prepared by combining Fe₂(SO₄)₃, FeCl₃, NaCl and HCl to produce new solutions with different amounts and ratios of iron and chloride. These new electrolyte solutions were 1M Fe³⁺ 1.5M Cl⁻; 0.16M Fe³⁺ 3.33M Cl⁻. The reverse bias current density vs. applied voltage for these new electrolytes is shown in Figure 18 with the reverse bias plot of 0.5M FeCl₃ + 1M H₂SO₄ superimposed. These new solutions had concentrations of ferric and chloride ions such that the ratio of chloride to iron was varied significantly around the stoichiometric ratio of FeCl₃. For the solutions tested, the ratio of chloride to iron ranged from 1.5 to 20. Different ratios of chloride to iron were chosen to promote the formation of different iron chloride complexes in different solutions. These solutions are shown below with compositional information, along with the current density at 3 kV (the H⁺ corresponds to concentration of the additional acid, either as H₂SO₄ or HCl).

<table>
<thead>
<tr>
<th>Ferric</th>
<th>Sulfate</th>
<th>Chloride</th>
<th>H⁺</th>
<th>Chloride/</th>
<th>Current density at 3kV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

15
<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>0.75</th>
<th>1</th>
<th>0.24</th>
<th>Ferric (nA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.5</td>
<td>0.5</td>
<td>3.33</td>
<td>75</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>1.5</td>
<td>1</td>
<td>0.8</td>
<td>27</td>
</tr>
<tr>
<td>0.16</td>
<td>0.24</td>
<td>3.33</td>
<td>0.8</td>
<td>20</td>
<td>51</td>
</tr>
</tbody>
</table>

Note that there is no significant difference in the I-V curves measured in 0.5M FeCl₃ + 1M H₂SO₄ and 0.5M FeCl₃ + 0.5M Fe₂(SO₄)₃. Again, free (uncomplexed) chloride ions are not an active redox system responsible for charge injection in the 1M FeCl₃ + 1M H₂SO₄ solutions (3M NaCl + 1M HCl does not have high current density), so would not directly participate in a redox reaction. This data shows that by doubling the concentration of the only redox system not present in the NaCl electrolyte (Fe³⁺/Fe²⁺) without increasing the ratio of iron to chloride, there is no significant increase in current density. Additionally, if the concentration of the Fe³⁺ is decreased to 0.16M, the reverse bias current density is even higher than the current density measured in 0.5M FeCl₃, as long as there is a larger amount of Cl⁻ present in the solution (3.33M). Figure 19 shows the results of two extreme cases of an iron chloride system, with 1M FeCl₃ superimposed. The two extremes are electrolytes with either no iron (1M HCl + 3M NaCl) and no chloride (0.5M Fe₂(SO₄)₃), which both show much lower rates of charge injection than 1M FeCl₃ + 1M H₂SO₄. Therefore, the charge injection behavior of 1M FeCl₃ + 1M H₂SO₄ is likely due to a synergistic effect of the iron and chloride in solution. The charge injection behavior of 1M FeCl₃ also indicates that the addition of acid is not necessary for high rates of charge injection.

Previous research performed by Magini and Radnai (Magini and Radnai 1979) investigated the structure of the iron atoms in ferric chloride solutions, both with and without added HCl. In the FeCl₃ solutions, the iron and chloride existed as a Fe₂Cl₆ dimer, FeCl₄⁻, or FeCl₂⁺. This research provides a rationale to the behavior of the electrolytes with varying amounts of iron and chloride, in that through a combination of iron and chloride, a complex forms that is directly or indirectly responsible for the increased rate of charge injection into polyethylene. Additionally, the fact that solutions with a high chloride to iron ratio have the highest rates of charge injection (1M FeCl₃, 0.16M Fe³⁺ + 3.33M Cl⁻) indicates that the component responsible for the charge injection is not the dominant component of the 1M FeCl₃ solutions, and is a component with a larger molar fraction at higher chloride/ferric ratios. FeCl₄⁻ as a component fits these requirements.

**Interface Effect**

The fact that the magnitude of the current density is dependent on voltage polarity indicates that the effect of the ferric chloride, i.e., the large charge injection rate, is not due to a bulk change in conductivity of the polyethylene, but rather the result of a change at the polymer-electrolyte interface. The source of this interfacial change could be due either to chemistry – reactions with the polymer surface that
render it more susceptible to charge injection or specific species in solution that are extraordinarily adept at injecting charge OR due to electron energy – the electrons in the electrolyte have an energy level that is matched to a band in the polyethylene or have an energy that is suited to an injection mechanism. For the latter, tests were conducted with 1M KMnO$_4$, an electrolyte that had shown, according to the data in Figure 8, the opposite polarity response as 1M FeCl$_3$ + 1M H$_2$SO$_4$. In these tests, the forward bias current density was higher than the reverse bias current density. To determine if high reverse bias cell current was due to the electron energy level of the injecting electrolyte, first the electron energy of both 1M FeCl$_3$ + 1M H$_2$SO$_4$ and 1M KMnO$_4$ were measured.

The redox potential of the 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte (i.e., the open circuit potential of platinum) was 0.527 V with respect to SCE, while the redox potential of the 1M KMnO$_4$ electrolyte was 0.957 V with respect to SCE. To adjust the redox potential of 1M KMnO$_4$, solid NaOH was added, which lowered the redox potential to 0.547 V with respect to SCE, much closer to the redox potential of the 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte.

The current density vs. applied voltage data for both the standard KMnO$_4$ (redox potential 0.957 V) and alkalized KMnO$_4$ (redox potential 0.549 V) electrolytes are shown in Figures 20 and 21. For the alkalized 1M KMnO$_4$ electrolyte, the current density is slightly less than that of the standard 1M KMnO$_4$ electrolyte for both polarities. For the alkalized KMnO$_4$ electrolyte, the current density at 3 kV for reverse bias is 6.3, compared to 3.8 nA/cm$^2$ for 1M KMnO$_4$, with the forward bias current density at 3 kV 12.2 and 5.1 nA/cm$^2$, respectively. This indicates that the redox potential for an electrolyte is not the sole determining factor in charge injection rate.

**Pretreatment**

The aqueous 1M FeCl$_3$ + 1M H$_2$SO$_4$ solutions lead to high current densities through polyethylene. This effect could be due to either an electrochemical oxidation reaction at the electrolyte-polyethylene interface that is much more efficient at charge injection or to a change in the surface of the polyethylene interface that renders it more susceptible to charge injection from previously less active electrolytes. To test the latter option, an experiment was designed to determine permanent effects of exposure to 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte. This “pretreatment” had to involve exposure to 1M FeCl$_3$ + 1M H$_2$SO$_4$ in combination with an applied potential, yet had to be mild enough so that most polyethylene films would not break down as a result of the pretreatment. With 1M FeCl$_3$ + 1M H$_2$SO$_4$ in reverse bias, it was observed that the average voltage for polyethylene breakdown was 3 kV. For this reason, the pretreatment experiments were abbreviated standard tests, with the final voltage step at 2 kV instead of 6 kV, conducted with 1M FeCl$_3$ + 1M H$_2$SO$_4$ in reverse bias.
Pretreatment tests were performed with four electrolytes after exposure to 1M FeCl$_3$ + 1M H$_2$SO$_4$, with the second part of the test (after the pretreatment step) done in both reverse and forward bias (the pretreatment was always reverse bias, but for the following test the applied voltage was switched). The following 8 figures (Figures 22-29) show current density for both forward and reverse bias as a function of voltage for each electrolyte after the pretreatment step. These data are consolidated into Figure 30, which shows the current density for each of these electrolytes at an applied voltage of 3 kV. For each of the electrolytes, 1M FeCl$_3$ + 1M H$_2$SO$_4$ in reverse bias, the pretreatment results in a higher current density for the equivalent bias. This indicates that the exposure to the voltage test with 1M FeCl$_3$ + 1M H$_2$SO$_4$ leads to a change in the polyethylene that makes other electrolytes more efficient at injecting charge, and this change persists after the 1M FeCl$_3$ + 1M H$_2$SO$_4$ is removed from direct contact with the polyethylene. The only electrolyte for which this was not the case is 1M FeCl$_3$ + 1M H$_2$SO$_4$ in reverse bias, which is the same test configuration as the pretreatment.

To indicate that these changes could not be caused by exposure to a voltage test with any electrolyte, the pretreatment experiments were run with 1M NaCl as the pretreating electrolyte instead of 1M FeCl$_3$ + 1M H$_2$SO$_4$. In Figure 31 we show the current density at 3 kV for three separate 1M NaCl-polyethylene-1M NaCl tests. In one we show data for tests where there was no pretreatment; in the second we show the tests where the pretreating electrolyte is 1M FeCl$_3$ + 1M H$_2$SO$_4$, and in the third, the pretreating electrolyte is 1M NaCl. These data indicate that while exposure to 1M FeCl$_3$ + 1M H$_2$SO$_4$ in a pretreatment test leads to high rates of electron injection, pretreating with 1M NaCl does not.

Additional pretreatment tests were done, with a slight change in the exposure parameters. With the pretreatment tests described previously, the polyethylene was subjected to a combination of exposure as well as applied voltage in the presence of 1M FeCl$_3$ + 1M H$_2$SO$_4$. The data in Figures 32 and 33 show the influence of exposure for varying amounts of time and different peak voltages.

For Figure 32, exposure to 1M FeCl$_3$ + 1M H$_2$SO$_4$ was ended at a maximum voltage of 500 V instead of 2 kV and was followed by tests with NaCl as the second electrolyte. It shows the current density vs. voltage for NaCl-polyethylene-NaCl exposed to the different maximum voltages in the 1M FeCl$_3$ + 1M H$_2$SO$_4$ pretreatment step.

Additionally, other pretreatment tests were done in which no voltage was applied during the pretreatment, which consisted of only a timed exposure to the 1M FeCl$_3$ + 1M H$_2$SO$_4$ solution. For these tests, timed exposure of 1 minute and 10 minutes were used instead of the normal pretreatment step. Figure 33 shows the current density vs. voltage for polyethylene contacted by 1M NaCl on both sides and subjected to a standard test after being subjected to exposure to 1M FeCl$_3$ + 1M H$_2$SO$_4$. Longer exposures to 1M FeCl$_3$ + 1M H$_2$SO$_4$, even without applied voltage, led to higher currents in subsequent voltage tests with 1M NaCl. However, as shown in
Figure 34, comparing the current density at the 3 kV voltage step for a standard test with 1M NaCl for a polyethylene sample exposed to the normal parameters for a pretreatment test (2 kV maximum voltage for a voltage ramp) to the current density at 3 kV for a standard test with 1M NaCl that was exposed to 1M FeCl$_3$ + 1M H$_2$SO$_4$ for 10 minutes with no applied voltage, shows that the voltage ramp pretreatment leads to higher current densities in subsequent tests with 1M NaCl. The normal pretreatment of polyethylene led to a higher current density on the subsequent tests with 1M NaCl, although the time that polyethylene was exposed to the 1M FeCl$_3$ + 1M H$_2$SO$_4$ solution during a normal test was less than seven minutes, not counting some experimental setup time, which is likely less than two minutes. These data (Figure 34) indicate that application of voltage to the pretreatment with 1M FeCl$_3$ + 1M H$_2$SO$_4$ increases the effect of the pretreatment on subsequent charge injection rates with 1M NaCl electrolyte.

**Oxidation groups at the polyethylene surface**

Previous research performed by Briggs et al. (Briggs et al., 2003) investigated the changes to the surface of polyethylene brought about by exposure to various oxidizing agents, including corona, ozone, and “electrochemical”, which was done with 0.23M K$_2$Cr$_2$O$_7$ + 15M H$_2$SO$_4$. For the experiments performed by Briggs, polyethylene was immersed in a bath of 0.23M K$_2$Cr$_2$O$_7$ + 15M H$_2$SO$_4$ and kept at 70°C for 30 minutes. The samples were then investigated with XPS (X-ray photoelectron spectroscopy) to determine the state of the carbon bonds on the surface of the polyethylene. The resultant XPS data indicated that some oxidation of the polyethylene had occurred and generated carbonyl and carboxylate groups on the surface of the polyethylene.

Oxidation on the surface of polyethylene from chromate exposure was also reported by Rasmussen et al. (Rasmussen et al., 1977) using fluorescence microscopy. They found oxidation in the form of carbonyl and carboxylate groups, with very few alcohol groups reported. Based on the results of Briggs et al. and Rasmussen et al., it was hypothesized that 1M FeCl$_3$ + 1M H$_2$SO$_4$ was oxidizing the surface of polyethylene, and that this oxidation was one of the reasons the 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte was able to inject charge at a high rate. To test this hypothesis, a potassium dichromate solution similar to that used by Briggs was used as an electrolyte in the standard voltage ramp tests (Figure 35). These results indicate that 0.23M K$_2$Cr$_2$O$_7$ + 15M H$_2$SO$_4$ shows the same relative behavior as 1M FeCl$_3$ + 1M H$_2$SO$_4$, in that it injects electrons more easily than it extracts them at the surface of polyethylene. This indicates that 1M FeCl$_3$ + 1M H$_2$SO$_4$ may have a similar effect of introducing oxidation groups on the surface of the polyethylene as 0.23M K$_2$Cr$_2$O$_7$ + 15M H$_2$SO$_4$ which is what leads to the high current densities seen on the second test of the pretreatment experiments (Figure 22).

Additionally, if the carbonyl and carboxyl groups introduced by the exposure of polyethylene to 0.23M K$_2$Cr$_2$O$_7$ + 15M H$_2$SO$_4$ electrolyte are at least partially
Mechanism of Oxidation

One hypothesis to explain the introduction of oxygen to the polyethylene surface is a mechanism by which atmospheric oxygen reacts with the surface of the polyethylene in a process catalyzed by the ferric chloride electrolyte. The atmospheric oxygen has an oxidation state of 0 and is therefore more oxidizing than the oxygen of water, which is in an oxidation state of -2. To test this hypothesis, standard tests in a deoxygenated 1M FeCl₃ + 1M H₂SO₄ electrolyte were conducted.

A cell was prepared with a sample of polyethylene and only one of the L-shaped glass tubes filled with 1M NaCl electrolyte and the glass tube on the other side empty. Nitrogen gas was bubbled through water at a rate of 0.1L/min in order to add humidity and prevent evaporation of the solvent in the electrolyte solution. The humidified gas was then bubbled through the stock 1M FeCl₃ + 1M H₂SO₄ electrolyte for at least 24 hours at a rate of 0.1L/min. An additional nitrogen bubbler was inserted into the unfilled tube of the test cell to displace the air in that tube. After a few minutes, the nitrogen bubbler was removed from the test cell and a pump (Fisher Scientific) was then used to transport the deoxygenated 1M FeCl₃ + 1M H₂SO₄ solution from the stock flask into the test cell. Once the pump had filled the test cell, the nitrogen bubbler that had previously de-aerated the unfilled tube was replaced into the tube now filled with 1M FeCl₃ + 1M H₂SO₄ solution to continue deoxygenating the solution while a standard test was being run. In this manner, the 1M FeCl₃ + 1M H₂SO₄ solution was deoxygenated before and after it moved to the test cell.

Figure 37 shows the results of 3 standard tests with the deoxygenated 1M FeCl₃ + 1M H₂SO₄ electrolyte. From Figure 5, the current density at 2.8 kV in the presence of oxygenated 1M FeCl₃ + 1M H₂SO₄ is 64 nA/cm², compared to 48 nA/cm² for deoxygenated 1M FeCl₃ + 1M H₂SO₄. From these data, it is clear that both aerated (oxygenated) and deoxygenated 1M FeCl₃ + 1M H₂SO₄ lead to high current densities through polyethylene. This suggests that the presence of atmospheric oxygen is not necessary for the action of 1M FeCl₃ + 1M H₂SO₄ as seen in the effect of pretreatment. This was confirmed by exposing polyethylene samples to deoxygenated solutions of 0.66M FeCl₃ + 2M KCl for 20 minutes before standard tests with 1M NaCl on both sides. The results of these tests, shown in Figure 38, indicated that oxygen is not required for the pretreatment effect of ferric chloride solutions on the current density vs. voltage of 1M NaCl.
Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy was done on polyethylene samples that had been subjected to different preparation procedures. The different samples consisted of polyethylene films that were exposed to a voltage (2 kV and 2.5 kV) in the presence of 1M FeCl$_3$ + 1M H$_2$SO$_4$. EIS spectra were taken of both samples before and after the application of voltage. This test was performed with the counter and reference electrodes connected to platinum wire immersed in the 1M NaCl electrolyte, and the working electrode connected to platinum wire in the 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte. These spectra are shown in Figures 39-42. From these figures, there is no discernible difference between the before and after EIS spectra of polyethylene that was exposed to 2.5 kV while in contact with 1M FeCl$_3$ + 1M H$_2$SO$_4$ (capacitance changes from 264 pF to 267.5 pF) while there is a small difference in the spectra of polyethylene that was exposed to 2 kV while in contact with 1M FeCl$_3$ + 1M H$_2$SO$_4$ (capacitance changes from 252.5 pF to 314 pF). All spectra show behavior consistent with a thin insulator, namely that the low frequency impedance is extremely high, and at higher frequencies the phase angle is $-90^\circ$, and log modulus/log frequency $> 0.99$. From the fact that higher applied voltages do not lead to a change in the EIS spectra, it follows that 1M FeCl$_3$ + 1M H$_2$SO$_4$ does not influence the bulk impedance of the polyethylene, otherwise exposure to 1M FeCl$_3$ + 1M H$_2$SO$_4$ would lead to more significant changes in the EIS plots of both tests. Thus, the nature of effect of exposure of polyethylene to 1M FeCl$_3$ + 1M H$_2$SO$_4$ is not accompanied by significant changes in the polyethylene impedance spectrum.

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), the same method used by Briggs et al. to determine the nature of oxidation on polyethylene, is one of the methods used in this work to look at the changes brought about in polyethylene by exposure to 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte. This work was performed at BIO-NESAC at The University of Washington.

The test sample for this work was exposed to 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte for one month before the 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte was rinsed out, replaced with 1M NaCl electrolyte, and then subjected to a standard test. This long time was used to achieve a larger effect on the sample in order to give the greatest chance for detection through the surface characterization methods.

XPS was performed at two locations on the sample, one contained in the exposed region and the other outside the exposed region on the same sample (as control). For each location, a low-resolution elemental scan and two high-resolution
(C1s and O1s) scans were performed, with a scan size of 0.8 mm², with sensitivity to a depth of a few nm.

The data for the low-resolution tests are shown in Figures 43 and 44. The data show the relative atomic concentrations of different elements on the two points surveyed. The concentrations of different elements are calculated from the absorbance peak area for the appropriate energy level. The main carbon peak is found at 285.0 eV, a value which was used to calibrate the peak location for the high-resolution atomic scans of C1s. The measured surface composition from the low-resolution atomic scan is shown in Table 2.

Table 2. XPS results of a low-resolution scan showing elemental composition

<table>
<thead>
<tr>
<th></th>
<th>C1s</th>
<th>O1s</th>
<th>Fe 3p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>95.0</td>
<td>5.0</td>
<td>Not detected</td>
</tr>
<tr>
<td>Etched</td>
<td>72.1</td>
<td>22.8</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Comparing the oxygen concentration of the surface from the low-resolution scan, the exposed region has a much higher oxygen concentration, 22.8% to 5%. Of the 22.8% oxygen for the exposed region, 80% is found in carbonyl groups.

**Fluorescence spectroscopy**

Polyethylene samples that were exposed to 1M FeCl₃ + 1M H₂SO₄ electrolyte for one month were investigated with fluorescence spectroscopy. Two fluorescent dye schemes were used; one was sensitive to carbonyl groups and the other was sensitive to carbonyl and carboxylate groups (indicated by + EDC). For each scheme, two sections of the sample were analyzed from areas that were exposed to 1M FeCl₃ + 1M H₂SO₄ (oxidized) and not exposed (unoxidized). These results are shown in Table 3.

Table 3. Fluorescence intensities of both schemes from the surface of polyethylene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average intensity (a.u.)</th>
<th>Std Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidized 1</td>
<td>3588.673</td>
<td>115.995</td>
</tr>
<tr>
<td>Oxidized 2</td>
<td>2282.460</td>
<td>750.116</td>
</tr>
<tr>
<td>Unoxidized 1</td>
<td>1380.336</td>
<td>229.710</td>
</tr>
<tr>
<td>Unoxidized 2</td>
<td>1618.356</td>
<td>357.523</td>
</tr>
<tr>
<td>Oxidized 1 + EDC</td>
<td>4510.950</td>
<td>460.173</td>
</tr>
<tr>
<td>Oxidized 2 + EDC</td>
<td>4098.738</td>
<td>343.771</td>
</tr>
<tr>
<td>Unoxidized 1 + EDC</td>
<td>852.755</td>
<td>400.650</td>
</tr>
<tr>
<td>Unoxidized 2 + EDC</td>
<td>1597.513</td>
<td>346.369</td>
</tr>
</tbody>
</table>
In Table 3, the fluorescence intensity of the oxidized areas in both schemes is higher than the unoxidized areas, indicating a higher concentration of carbonyl and carboxylate products on the surface of the polyethylene after exposure to 1M FeCl$_3$ + 1M H$_2$SO$_4$. 
Discussion

Charge injection

This work investigates charge injection from electrolytes into polyethylene under an applied potential. To approach this phenomenon, it is helpful to understand some of the classical treatments of both charge injection and electronic properties of insulators and polymers. Starting with the simplest concept, charge injection from metals into a vacuum is discussed, followed by injection from a metal into a wide band-gap semiconductor as well as the maximum allowable current from an injecting electrode. It also is necessary to discuss the morphology of polymers, including the electronic states and dominant conduction mechanisms, as well as the electronic properties of an electrolyte/insulator interface.

Much of this section explains and elucidates two of the trends in the data. Specifically, the current density at a particular applied potential for polyethylene films is higher when ferric chloride electrolytes are injecting electrons into the polyethylene, and exposure to ferric chloride electrolytes leads to subsequent higher current densities when the polyethylene is contacted by other electrolytes.

Electron emission from metals

The nature of electron emission from a metal lattice into a vacuum is rooted in the fundamentals of electrostatics. In this theoretical treatment, for an electron to leave the metal and enter the vacuum, it must have sufficient energy to exist classically in the vacuum. For a metal with a Fermi energy $E_F$, the probability of an electron having sufficient energy to exist in the vacuum ($E = 0$) is

$$P = e^{-\Phi_m/kT} \quad \{1\}$$

where $\Phi_m$ is the work function of the metal, $k$ is the Boltzmann constant, and $T$ is temperature. For some common electrode metals, such as aluminum, copper, and gold, the Fermi energy is 4-5 eV below vacuum (Xiao et al.), thus, at normal temperatures very few electrons have enough energy to be emitted into vacuum.

A detailed analysis of emission mechanisms is presented in Dissado and Fothergill’s book, Electrical Degradation and Breakdown of Polymers (Dissado and Fothergill, 1988) and is summarized in the following section.

If an electron leaves the surface of the metal, the electric field it creates will induce charges at the metal surface, such that all electric field lines are perpendicular to the surface of the metal. This creates what is called an “image charge”, which is electrostatically equivalent to an equal charge of the opposite
sign inside the metal, at an equal distance from the metal surface as the electron, which was shown in a derivation performed by Walter Schottky in the early 20th century. The force exerted on the electron by the image charge in the metal at a distance $x$ outside the metal is

$$ F(x) = \frac{-e^2}{4\pi \varepsilon_0 \varepsilon_r (2x)^2} \quad \{2\} $$

where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the relative dielectric constant (equal to 1 in vacuum), and $e$ is the charge of an electron. Integrating the force to obtain the energy, we obtain

$$ V(x) = -\frac{e^2}{16\pi \varepsilon_0 \varepsilon_r x} \quad \{3\} $$

This expression for energy breaks down as $x$ approaches 0: from equation {3}, $V(x)$ approaches negative infinity. When $x = 0$, the energy of the electron should be the same as the negative of the work function of the metal divided by the charge of an electron. To indicate this in the plot of $V(x)$, we use

$$ V(x) = -\frac{e^2}{16\pi \varepsilon_0 \varepsilon_r x + e^2/\Phi_m} \quad \{4\} $$

where $\Phi_m$ is the work function of the injecting metal. To obtain the shape of the energy curve with an applied electric field, the image charge potential is superimposed on the energy of an electron of an applied field, $V(x) = -eEx$, where $e$ is the charge of an electron, $E$ is the electric field strength, and $x$ is distance from the metal electrode. This combination yields an energy of the form

$$ V(x) = -\frac{e^2}{16\pi \varepsilon_0 \varepsilon_r x + e^2/\Phi_m} - eEx \quad \{5\} $$

The shape of this curve is shown in Figure 45, with 4.5 eV used as the work function of the metal, and an electric field of $1.2 \times 10^8$ V/m applied. Both the individual components of the total energy are shown, as well as the superposition.

As can be seen from Figure 45, the total energy of an electron increases rapidly with distance outside the metal until it reaches a peak, then decreases monotonically, such that there is an energy barrier separating two regions of low energy. On the left side of the barrier, the energy of the electron is lowered by the image charge of the metal. On the right side of the barrier, at a sufficient distance from the metal, the applied electric field causes the vacuum level energy to decrease to an energy equal to the Fermi level of the metal. Both the height and width of this potential barrier depend on the applied electric field. The barrier height can be
found by taking the derivative of the energy with respect to $x$ and setting it to zero, which yields the distance of the barrier maximum:

$$x_{max} = \left(\frac{e}{16\pi\varepsilon_0\varepsilon_r E}\right)^{1/2} \quad \{6\}$$

and the barrier height

$$V_{max} = -\frac{e}{2}\left(\frac{eE}{\pi\varepsilon_0\varepsilon_r}\right)^{1/2} \quad \{7\}$$

From equation \{7\} for $V_{max}$, we can see that the maximum potential energy that electrons experience is actually less than zero (vacuum level), and dependent on applied electric field and work function. Once the potential difference between the Fermi level of the metal and the energy of an electron in a vacuum in the presence of an electric field is determined, we can find the effective barrier height that the electron must overcome to escape the metal and be emitted into the vacuum:

$$\Phi_{eff} = \Phi_m - \frac{e}{2}\left(\frac{eE}{\pi\varepsilon_0\varepsilon_r}\right)^{1/2} \quad \{8\}$$

This indicates that the barrier height is now a function of the applied electric field. Thus, as the applied electric field increases, the potential barrier opposing the ejection of electrons from the metal into the vacuum becomes smaller. The smaller barrier means that more electrons have sufficient thermal excitation to overcome the potential barrier and be successfully emitted from the metal into the vacuum, a phenomenon known as Schottky emission. It is important to note that the origin of the reduced barrier height is the image charge, defined as a potential effect present in the vacuum due to forces that originate from effects in the metal. In the absence of the image charge force, an electric field would not decrease the barrier height.

**Electron injection into a dielectric**

The equations governing electron injection from metals into crystalline polymers are slightly different from those equations for injection into vacuum. If dielectrics are assumed to be large band gap semiconductors with a valence band and a conduction band, electrons that are injected into the conduction band are free to move through the dielectric at a drift velocity that is determined by the electric field and the time between lattice collisions (Lewis, 2002). Adapting the derivation of the potential barrier for the injection of electrons from metal contacts into a form that is sufficient for insulators, the energy of this empty conduction band in the insulator is used instead of the energy of vacuum, and $\varepsilon_r$ is the relative dielectric constant of the insulator. This results in a potential curve that is qualitatively unchanged from that of a metal injecting charges into a vacuum, in that there is an
energy barrier with an applied field-dependent height that separates two regions where the electron can exist classically at the Fermi level of the injecting electrode.

For an ideal dielectric with no thermally generated carriers, the number of injected electrons and the mobility of the carriers govern charge flow. Thus, at low fields, the current-voltage behavior is given by Ohm’s law,

\[ J = \frac{n \mu V}{d} \]  

where \( n \) is the number of electrons in the carrier band, \( \mu \) is the mobility of the carriers, and \( d \) is the thickness of the insulator. For an ideal dielectric with no energy states between the valence and conduction bands, the injected charges exist in the delocalized conduction band and contribute to the current as expressed by equation \{9\}.

**Space-charge limited current**

For an insulator with an Ohmic contact (i.e., an infinite supply of electrons that can be injected), electrons will be injected into the surface of the dielectric until the electric field due to charges at the surface of the dielectric is equal and opposite that of the injecting field. While this derivation is discussed in more depth in a later section, suffice it to say that the derivation results from an electric field set to zero at the injecting interface and a current flow through the insulator that is limited by the speed at which electrons can diffuse away from the interface in the absence of a local electric field. For a film of a given material, the derived current density is a function only of the applied voltage, film thickness, film permittivity, and electron mobility in the bulk material (Rose, 1954). However, with electrolytes, there may be charge transfer processes or diffusion processes that restrict the number of electrons available at the surface, thus presenting a situation in which the current that flows is limited by an interfacial process (Lohmann and Mehl, 1975). The fact that different electrolytes lead to different current densities when using polyethylene (the insulator investigated in the current work) indicates that the current is not limited by the bulk properties of the insulator, but rather by the charge transfer process at the interface. These are the effects that this work intends to analyze.

**Electronic states in polymers**

Polymeric dielectrics are known to have both highly ordered crystalline regions as well as amorphous regions due to the presence of side chains, impurities and chain misalignments, which lead to irregularities in crystal packing (Lewis, 2002). These amorphous regions have localized energy states in the forbidden region between the valence and conduction band and are referred to as traps. If these energy states are vacant, an injected charge may subsequently be bound to the
state until it is able to leave by a variety of different mechanisms (discussed later). For polyethylene, the number density and energy levels of these traps have been researched by multiple researchers (Meunier and Quirke, 2000, Kumar and Perlman, 1991, Lewis, 1984). The effects of these traps is to reduce the percentage of injected electrons in the conduction band and to contribute to the charge flow at low fields. For an insulator with a single, discrete trap with an energy $E_t$ below the conduction band, the number of carriers in the conduction band is determined by the number of available states at the trap energy level, the number of available states in the conduction band, and the energy difference between the trap level and the bottom of the conduction band.

**Trap-modulated hopping conduction**

As stated previously, polyethylene contains a distribution of energy states near the bottom of the conduction band in the forbidden region. These localized energy states are thought to change the energy of an electron in the area around the trap. Similar to the energy of an electron in a metal at the boundary with a vacuum, the interaction of electrons with these traps is modeled as a Coulombic attraction. However, these energy states have a finite energy level, so a constant is added to the energy term, similar to equation {4}, in which, instead of work function, the added term is the decrease in electron energy for electrons in the trap as compared with the electron energy in the conduction band. Electrons caught in these potential wells can escape either by thermionic emission over the potential barrier or tunneling through the barrier to another trap. Electrons caught in traps have a residence time determined by the depth of the trap and the temperature. Meunier and Quirke (Meunier and Quirke, 2002) have catalogued residence times for thermal excitation over the potential barriers and found residence times to vary from 0.36 ps for a trap depth of 0.1 eV to 472 seconds for a trap depth of 1 eV. Lewis (Lewis, 1984) has calculated residence times for a tunneling mechanism from one trap to another; for representative values for polyethylene, the author calculated residence times of 1 ns for a trap depth of 0.2 eV and 6 h for a trap depth of 1 eV. Dissado (Dissado and Forthergill, 1988) states that hopping conduction likely comes through as a mechanism of thermally-assisted tunneling, in which an electron in a trap is thermally excited such that its energy is equal to the energy of a neighboring trap, which leads to a higher probability of tunneling, and hence increased conductivity.

In the presence of an electric field, electron energy levels inside an insulator are shifted. In a similar treatment to that of a metal injecting electrons into a vacuum, the energy of traps and the barrier to emission are influenced by the applied field, as shown in Figure 46:

In Figure 46, the curve “Energy from traps” indicates the electron energy due to two neighboring traps in the absence of an applied field in which electrons experience a Coulombic attraction to the center of the trap. The curve “Energy from
applied electric field” shows the energy due to an electric field, and the “Total energy profile” curve shows the shift of energy of an electron in the presence of an applied field, a superposition of the two individual contributions to the energy profile.

As with Schottky emission, the potential barrier that the electrons must overcome to escape the trap is lowered in the presence of a field, which enhances the probability of escape. This leads to increased conductivity (due to thermal excitation) in the presence of a field, a phenomenon known as Poole-Frenkel conduction. Additionally, the potential barrier width is smaller, meaning that, for a given electron with some thermal excitation, the nearest equienergetic state is closer, thus enhancing the likelihood of resonance tunneling out of a trap state. Electrons can escape from traps by either mechanism, so both of these factors (lower barrier height, shorter barrier length) combine to give a lower residence time of the trapped electrons, allowing for a higher current density. For Poole-Frenkel conduction, the conductivity is proportional to \( e^{p^{1/2}} \) (Dissado and Fothergill, 1988). Field-dependent mobility in polyethylene has been attributed to this lowering of the potential barrier of trapped electrons (Wintle, 1999). Meunier’s model also predicted lower residence times for trapped electrons under an applied field. Thus, as charge injection from electrodes and conductivity are field-enhanced, it follows that the current-density vs. applied potential for polyethylene is highly non-linear.

**Electrolyte-insulator interface**

The potential at an electrolyte-insulator interface cannot be analyzed with the same assumptions as a metal-vacuum interface. Lohmann and Mehl (Lohmann and Mehl, 1975) derived the expression for the potential at the interface between an electrolyte and a trap-free, organic crystal insulator. They assumed that three factors influence the potential drop over the electrode-electrolyte interface: space charge buildup at the surface of the insulator, the charge-neutral area in the electrolyte right next to the surface of the insulator, and the diffuse charge layer of the electrolyte (outside the Helmholtz layer). Their mathematical treatment was based on Poisson’s equation and Gauss’s law for both the electrolyte and the insulator, and it satisfied the requirement that the electric displacement at the interface be continuous.

Lohmann and Mehl concluded that the potential in the electrolyte and the potential of the carrier band in the organic crystal are both bent in such a way that the potentials are equal at the interface of the electrolyte and crystal, and a qualitative plot of energy vs. distance modeled after their work is shown in Figure 47 (Lohmann and Mehl, 1975). The bending of the carrier band potential in the organic crystal is significantly stronger than the change in redox potential in the electrolyte. The fact that the carrier band energy is lower in the vicinity of the interface provides support to an analog of field-assisted Schottky injection as the
height of the potential barrier between the electrolyte and the crystal would be lowered. This assertion is evident after looking at the plots of the energy profile for electron emission into a vacuum. If there is no "image charge" effect to lower the barrier height in Schottky injection, the energy profile would simply be the charge of an electron multiplied by the electric field, and there would be no field-lowering of the barrier height (the barrier would just be the work function of the metal). For a potential barrier to be lowered in the presence of a field, the energy of an electron in the insulator must be lower in the immediate vicinity of the injecting electrode. Coulombic forces in the presence of water are thought to be very weak (Lohmann and Mehl, 1975), so the potential change in the crystal near the electrolyte is necessary for field-enhanced injection.

Charge injection from electrolytes – a review of the experimental results

With respect to the experimental data collected from the various aqueous electrolytes presented in this work, many different redox systems are present in the tested solutions, including that of oxygen, iron, hydrogen, nitrate, chloride, and sulfur. Additionally, experiments show that iron and chloride (or nitrate) are necessary for high rates of charge injection when compared with 1 M NaCl electrolytes, while the presence of sulfate has very little effect. Hydrogen and oxygen are part of the aqueous solution and contributions from their redox reactions cannot be experimentally excluded to examine solely the effects of iron and chloride.

Ferric chloride in solution affects the current density vs. applied voltage curve of the polyethylene in two ways: one, it oxidizes the surface and creates carbonyl-containing functional groups, and two, ferric chloride enhances the charge injection rate. The former is known as a result of XPS analysis and fluorescence data, which show the presence of carbonyl groups on the surface. This is thought to be the source of the increased charge injection rates for pretreated polyethylene. The latter can be determined by comparing the current density for 1 M FeCl₃ + 1 M H₂SO₄ and 1 M NaCl in which the 1 M NaCl test is conducted with pretreated polyethylene, as shown in Figure 48. The measured current density at 2 kV is 34 nA/cm² for 1 M FeCl₃ + 1 M H₂SO₄ and is less than 6 nA/cm² for 1 M NaCl. Due to the pretreatment, both data points indicate that identical samples of polyethylene (exposed to 1 M FeCl₃ + 1 M H₂SO₄ for the same amount of time and voltage) respond differently to electron injection from different electrolytes. Polyethylene films with ferric chloride as the contacting electrolyte experience approximately 6 times the current density, indicating that the ferric chloride is not solely oxidizing the surface but also is participating in the charge transfer reaction.

The data in Figure 48 show current as a function of voltage for polyethylene samples that have been subjected to the same treatment (this statement is only explicitly true for the first data point; after the first data point, the 1 M FeCl₃ + 1 M H₂SO₄ data is still exposed to 1 M FeCl₃ + 1 M H₂SO₄ electrolyte, while the 1 M NaCl
data is not). The fact that both of these data sets are from samples that are expected to have identical bulk properties and surface states limits the parameters that are considered to be responsible for the different rates of charge injection. Specifically, any effect of surface states, trap states, or oxidation states as they relate to *electronic conduction in the polyethylene* should be the same for both data sets, because both data sets correspond to films that have been exposed to the same treatment. The experimental difference between these curves lies in the identity of the electrolyte. It follows that the source of this effect must be the interaction of the electrolyte with surface states, trap states, oxidation states, or bulk polyethylene near the interface of the electrolyte. Analysis of this phenomenon requires a mechanism that is due to effects in the electrolyte and not the insulator.

Examining charge injection rates at 2.1 kV for the samples represented in Figure 48, the two possible ways for the addition of ferric chloride to increase the charge injection rates are either by adding a charge transfer component or by changing some parameters of the exchange current density equation for one of the other redox systems. That is, either ferric chloride catalyzes a charge transfer reaction or is itself injecting charge. For ferric chloride to inject charge, it is necessary to look at some of the properties of the solutions with respect to the concentrations of different ions.

**Ferric chloride as a catalyst**

Combinations of iron and chloride are known to catalyze a variety of reactions. Chloride ions have been found to increase the exchange current of ferric and ferrous ions at electrodes (Hung and Nagy, 1987) in which chloride ions are thought to electrostatically adsorb to the electrode. Investigation of the oxidation of ferrous ions by oxygen was found to be extremely slow if only sulfate anions were present, but the reaction rate was found to be first-order with respect to chloride concentration (Colborn and Nicol, 1973). The decomposition of H$_2$O$_2$ in the presence of ferric chloride has been shown to occur at a faster rate than in the presence of ferric sulfate (Machulek et al., 2009). The addition of chloride to systems in which ferric ions were the oxidant was found to have a significant effect on the rate of oxidation of polyacrylamide (Dainton, 1960). Ferric chloride was the most active salt in catalyzing the esterification of fatty acids (Ieda et al., 2008) with the proposed mechanism involving chloride bridging between the carbonyl group in the acid and the ferric ion. Ferric chloride was also found to catalyze the photo-oxidation of alkanes (Shulpin and Kats, 1990), with the proposed mechanism consisting of electron transfer from the alkane to FeCl$_3$ followed by proton detachment from the alkane. The resulting carbon radical then reacts with oxygen in solution, quickly forming peroxyl, carbonyl, or alcohol groups. Wilputte-Steinert found that ferric chloride solutions oxidized isopropanol to acetone under UV irradiation (Wilputte-Steinert, 1978), and specifically noted that excess chloride ions are needed for sufficient regeneration of the ferric ions, but did not propose a mechanism in which chloride ions were involved in a reaction. Sugimoto et al. did
propose a mechanism of action of FeCl₃ with hydrogen peroxide through an FeCl₃O radical in the epoxidation of alkenes and oxidative cleavage of diols, but the mechanism only holds in the absence of additional ligands, so excess chloride or water molecules should deactivate the ferric ion (Sugimoto et al., 1987). This process was elucidated in an earlier work (Sugimoto and Sawyer, 1985), but that work does not provide a specific action for the chloride. The photogeneration of hydroxyl and chlorine radicals was found for solutions that contained ferric ions and chloride ions, however the reported results showed lower rates of radical generation with higher concentration of chloride ions (Lim et al., 2006). In short, very few mechanisms were proposed for the specific action of chloride ions in causing higher rates in either radical generation or exchange reactions, and for radical generation, UV light was necessary in all cited works for significant radical yields. Additionally, the concentrations of ferric chloride most commonly used in the literature were on the order of mM or lower.

The possible mechanism of oxidation and increased charge injection

The results presented in this work show different trends as the experimental conditions are varied, and a reasonable mechanism of action of the ferric chloride solutions should be consistent with the multitude of experimental observations. These observations can be converted into a set of requirements for the behavior of the mechanism. From this, any proposed mechanism of the effects of the ferric chloride must take into account the following experimental observations:

1. High rates of charge injection only happen when the ferric chloride electrolyte is injecting electrons into the polyethylene.
2. Both ferric and either chloride or nitrate ions must be present in solution (as shown in Figure 16).
3. The charge injection rate increases with increasing chloride/ferric ratio (as shown in Figure 18).
4. Gaseous oxygen in the ferric chloride pretreatment step is not needed to achieve an enhanced charge injection rate, as shown by pretreatment tests with deoxygenated 0.66M FeCl₃ + 2M KCl electrolyte in Figure 38.
5. The reaction by which the ferric chloride renders the polyethylene susceptible to charge injection from 1M NaCl electrolytes should be accelerated by an applied voltage but still occurs in the absence of a field (as evidenced by Figure 34).

The proposed mechanism also should show additional characteristics that are dictated by the equations believed to govern the processes that are occurring at the interface, specifically that the charge injection rate should depend on the concentration of the injecting component at the interface of the polyethylene. This last assertion is used to rule out ferric ions and atomic hydrogen as injecting species: the charge injection rate is relatively unaffected by orders of magnitude change in concentration. Both oxygen and chloride in water are present in high
concentration in the electrolytes that resulted in high charge injection rates when contacting polyethylene. To understand how oxygen and chloride may contribute, it is necessary to understand their redox properties.

The evidence of ferric chloride complexes

In the requirements for the mechanism listed above, the third requirement indicates a dependence on the relative concentrations of ferric ions and chloride ions. This experimental trend, combined with the research in the literature, point to a ferric chloride complex as an important component in the charge transfer reaction at the polyethylene-electrolyte interface. This assertion is discussed in the following section.

The most compelling evidence that indicates which components may be responsible for the high current density observed when using iron chloride solutions is the three tests in Figure 19, which shows that chloride and iron by themselves do not lead to high rates of charge injection. The data from Figure 19 in conjunction with Figure 18 indicate the necessity of having both iron and chloride in solution, as well as the chloride-iron ratio trends that increase charge injection. Specifically, increasing the concentration of iron from 0.5M to 1M in the presence of 1.5M chloride does not significantly change the current density, while a very low concentration of iron (0.16M in the 3.33M chloride) produces current densities that are similar to that of 1M ferric chloride. This trend of high charge injection rate for high chloride-iron ratios, paired with the knowledge that iron is readily complexed by chloride (discussed in the following section), leads to the conclusion that an iron chloride complex is involved in charge transfer with the polyethylene. This is supported by the fact that ferric sulfate solutions do not inject charge at a high rate into polyethylene samples that have been pretreated with 1M FeCl₃ + 1M H₂SO₄.

The complexing of FeCl₃ in solution

A significant amount of work has been published in the literature on investigations of the complexes of iron chloride solutions. Traditionally, this work is performed with Raman spectroscopy (Marston and Bush, 1972, Sharma et al., 1975, Kanno and Hiraishi, 1982), although other techniques can also be used, such as X-ray scattering and UV-vis spectroscopy. There is a lack of agreement in the literature with respect to which complexes dominate the ferric chloride solution, as well as the configuration of the complexes. Multiple authors have indicated that the FeCl₄⁻ complex is present in ferric chloride solutions (Connick and Coppel, 1959, Magini and Radnai, 1979), while other sources argue that trans-[FeCl₂(H₂O)₄]⁺ accounts for the significant features of X-ray diffraction. One source (Sharma et al., 1975) argues that the Raman data collected from frozen ferric chloride with different amounts of hydrochloric acid indicate the dominant presence of higher chloride-iron complexes - FeCl₄⁻, but it was also argued that FeCl₅²⁻ and FeCl₆³⁻.
contributed to the Raman spectrum. Liu et al. (Liu et al., 2006) predicted the presence of different complexes of iron and chloride, with calculations indicating that FeCl₄⁻ should dominate with high chloride-iron ratios. There is some disagreement in the literature as to whether FeCl₄⁻ exists in a tetrahedral or octahedral complex, although the low pH in high Cl/Fe solutions indicates a large degree of metal-ion hydrolysis, a process that only occurs when water solvates in the inner sphere. If FeCl₄⁻ were tetrahedral, there would be no inner sphere water molecules to be hydrolyzed. Marston and Bush (Marston and Bush, 1972) investigated the complexing of concentrated ferric and chloride containing compounds and found that the a Raman peak shifted from 318 cm⁻¹ to 335 cm⁻¹ as the Cl/Fe passed approximately 4, postulating that the peak at high Cl/Fe ratios was indicative of the formation FeCl₄⁻ and the decrease of hydrated FeCl₃ in solution.

The data presented in the work of Liu et al. as well as Lee et al. (Lee et al., 2003) shows calculations of the speciation of FeCl₃ solutions as a function of concentration of both FeCl₃ with additional chloride in the form of HCl and LiCl. While their calculations cannot be explicitly applied to the electrolytes in this work as the compositions and components differ, the ferric chloride complex speciation trends they report can be used to suggest the speciation in this work. While the formation constants of the ferric chloride complexes (and other possible components in the electrolyte) can be used to calculate the speciation of the electrolytes in this work, those calculations can be performed in future work.

The work of Liu et al. and Lee et al. both evaluate the relative concentrations of ferric chloride complexes of the form FeCl₃ⁿ⁻⁻. Lee et al. indicate the concentration of complexes for n=0 to n=4 as a function of added HCl, showing large concentrations of the n=0,1,2, with n=2 dominating at 1M additional HCl (all performed in 1M FeCl₃). The n=4 complex (FeCl₄⁻) shows the largest relative increase in concentration with additional HCl, starting at approximately 10⁻³ M with no HCl and ending at 10⁻² M at 3M HCl. Liu et al showed that with little additional chloride, the n=1 and n=2 complexes dominated, with the n=4 only dominating with chloride concentrations of 10-12M (Fe concentration of 0.033M).

Closer examination of the results shown by Lee et al. show an explanation for the experimental trends in this work. From Figure 18, increasing the chloride/iron ratio shows increased current density per ferric ion. Additionally, comparing the magnitudes of the current density for 1M FeCl₃ with the solution that is 0.16M Fe³⁺ + 3.33M Cl⁻ (with the assumption that the same component in both solutions is primarily responsible for charge injection) indicates that the dominant ferric chloride complex in the 1M FeCl₃ solution is not likely to be involved in the charge transfer reaction, otherwise the current density seen with the high chloride/ferric electrolyte would be significantly lower (as the ferric ion concentration is 0.16M instead of 1M). From the calculations by Lee et al., the only complex that increases significantly with additional chloride is the n=4 complex. Again, additional work on the subject could show the speciation of the different ferric chloride complexes in the different solutions prepared, with current densities correlated to the
concentrations of the specific components. In the absence of this information, the ferric complex deemed most likely to be responsible for the effect of the ferric chloride solution (based on the comparison of literature data to the experimental trends in this work) is the n=4 complex. The remainder of this work is based on a mechanism involving the n=4 complex (FeCl₄⁻).

**Electron injection**

For electrons to be injected into polyethylene, some component in the electrolyte must be oxidized, with the electron removed from the component in the electrolyte filling a vacant state in the polyethylene. There are many different possible components in the electrolyte that can be oxidized for this reaction, some of which have already been discounted by observing the invariability of the current density with the concentration and/or absence of the particular oxidizable component in the electrolyte. Other possible oxidizable components, namely, chloride and oxygen, are found in all solutions that exhibit high rates of charge injection. The next few sections examine these particular reactions in significantly greater detail.

Table 5. Oxidation reactions at the polyethylene-electrolyte interface.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction when complexed in ferric chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>( OH^- \rightarrow OH^- + e^- ) ( FeCl_4(H_2O)(OH)^{2-} \rightarrow FeCl_4(H_2O)(OH)^- + e^- )</td>
</tr>
<tr>
<td>Chloride</td>
<td>( Cl^- \rightarrow Cl^- + e^- ) ( FeCl_4^- \rightarrow FeCl_4 + e^- )</td>
</tr>
</tbody>
</table>

**Electron injection by Oxidized Aqueous Species – Oxygen as an Electron Donor**

For oxygen to be an electron donor, it must be oxidized. Oxygen in water can be oxidized through the following net reaction, which is comprised of multiple steps:

\[
2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{1}
\]

One mechanism (Kessler et al., 1994) for the beginning step of this reaction starts with the dissociation of water,

\[
H_2O \rightarrow H^+ + OH^- \tag{2}
\]

and proceeds with the partial oxidation of oxygen from the -2 to -1 oxidation state.
\[ \text{OH}^- \rightarrow \text{OH}^- + e^- \quad (3) \]

In the mechanism proposed for charge injection in this thesis, the hydroxide ion is complexed with the ferric ion as a product of the metal-ion hydrolysis, as shown in the following reaction:

\[ \text{Fe}(H_2O)_n^{3+} \rightarrow \text{Fe}(H_2O)_{n-1}(OH)^{2+} + H^+ \quad (4) \]

Metal ion-hydrolysis is known to occur in solutions containing ferric ions. The evidence for this is that the pH of a solution containing only 1M FeCl\(_3\) is very low (0.7), indicating [H\(^+\)] of approximately 0.2M. Thus, the source of the low pH must be through metal-ion hydrolysis and/or oxidation of oxygen in water producing hydrogen ions, because no acid was added to the solution. This means that, while the hydroxide concentration in the bulk of the electrolyte is very low, the hydroxide ion that was originally paired with the hydrogen ion as water must still be coordinating with the ferric ion. For a solution containing a high chloride/iron ratio, suggesting the presence of the FeCl\(_4^-\) complex with an octahedral symmetry, this reaction would proceed as follows:

\[ \text{FeCl}_4(H_2O)_2^- \rightarrow \text{FeCl}_4(H_2O)(OH)^2^- + H^+ \quad (5) \]

Although there is disagreement as to whether FeCl\(_4^-\) exists in solution as a tetrahedral or octahedral (with two water molecules in the inner sphere) complex, the pH measurements in this work indicate that metal-ion hydrolysis is happening to a smaller degree in high (>3) chloride to iron ratios, which gives credence to the tetrahedral symmetry. From the work of Lee et al., increased chloride to iron ratio leads to increased concentration of the FeCl\(_4^-\) ion, which would decrease the relative concentration of the other ferric chloride complexes. If tetrahedral symmetry exists, metal-ion hydrolysis would only happen with water molecules that are in the outer coordination shell, which would experience significantly lower Coulombic forces due to the increased distance from the positive iron ion. From Table 4, higher ratios of chloride to iron lead to lower hydrogen ion concentration, suggesting that either the tetrahedral conformation or that complexed chloride inhibits metal ion hydrolysis.

<table>
<thead>
<tr>
<th>[Fe]</th>
<th>[Cl]</th>
<th>Cl/Fe(^{3+})</th>
<th>pH</th>
<th>H(^+)/Fe(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.66</td>
<td>4</td>
<td>6</td>
<td>1.17</td>
<td>0.10</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>3</td>
<td>0.73</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Table 4. Ratios and pH of different ferric and chloride containing electrolytes.
If oxygen in hydroxide is the component that is oxidized for the charge injection reaction, the proposed mechanism for charge injection continues with radical-generating oxidation reaction following the metal ion hydrolysis:

$$FeCl_4(H_2O)(OH)^2_\text{–} \rightarrow FeCl_4(H_2O)(OH)^{–} + e^{–}$$  \hspace{1cm} (6)

**Electron injection by Oxidizable Aqueous Species – Chloride or Sulfate as an Electron Donor**

Similar to oxygen, chloride ions can be oxidized at an interface, in which

$$Cl^{–} \rightarrow Cl^{\cdot} + e^{–}$$  \hspace{1cm} (7)

In the presence of ferric or ferrous ions, a portion of chloride ions complex the iron ions in solution. From these complexes, an additional oxidation reaction that could result in electron injection into polyethylene is shown below. This reaction is analogous to the reaction that produces the hydroxyl radical but instead produces a chlorine radical

$$FeCl_4^{–} \rightarrow FeCl_4^{\cdot} + e^{–}$$  \hspace{1cm} (8)

Chlorine radicals rapidly combine with chloride ions, forming a negatively charged diatomic ion (Jacobi et al., 1997)

$$Cl^{\cdot} + Cl^{–} \rightarrow Cl_2^{–}$$  \hspace{1cm} (9)

Many additional reactions can occur between combinations of chlorine radical and hydroxyl radicals with hydroxide, water, or chloride, which have been thoroughly reviewed by Jacobi et al. and Nadtochenko and Kiwi (Nadtochenko and Kiwi, 1998).

The radical-generating processes resulting in either $OH^{\cdot}$ or $Cl^{\cdot}$ are known to occur with ferric chloride in water (Machulek et al., 2009), acetonitrile (Sugimoto and Sawyer, 1985), chloroform (Hoggard et al., 2003) and N,N-dimethylformanide (Dainton and Jones, 1967), although all proposed mechanisms for radical generation are UV driven or require the addition of peroxide. For the reaction in N,N-dimethylformanide, the chlorine radical is thought to originate from a $FeCl_4^{–}$ complex in solution. Quantum yields (reactions per absorbed photon) were reported in a few of the studies, but the generation of radicals in the absence of added peroxide or irradiation was not reported.

A radical also can be generated from complexed sulfate ions (Machulek et al., 2009):
The complexed ferric ions in solution can undergo photolysis when irradiated, a process in which the ferric ion is reduced and the complexing ligand is oxidized (Machulek et al., 2009, Nadtochenko and Kiwi, 1998, Hoggard et al., 2003), resulting in a ligand radical. The quantum yields (reactions per absorbed photon) for these processes are 0.47 for the production of chlorine radicals, 0.21 for the production of hydroxyl radicals, and significantly lower at 0.0016 for the production of the sulfate radical, as reported by Machulek et al. Additionally, ferric chloride complexes are significantly more absorptive than ferric hydroxide complexes in the UV range, which further contributes to higher rates of radical generation in the presence of chloride (Machulek et al., 2009).

A conclusion from this hypothesized mechanism is that an equivalent radical-generating reaction in the absence of chloride is slower, and the presence of complexed sulfate ions leads to very little radical generation. In the absence of chloride ions, metal-ion hydrolysis still occurs to a very significant degree, as indicated by the pH of the iron nitrate solutions, which was measured to be 0.06 for 1M ferric nitrate. This hydrolysis reaction is shown in the following reaction

\[ Fe(H_2O)_6^{3+} \rightarrow Fe(H_2O)_5(OH)^{2+} + H^+ \]  

(11)

with the subsequent radical generation reaction given as

\[ Fe(H_2O)_5(OH)^{2+} \rightarrow Fe(H_2O)_5(OH)^{3+} + e^- \]  

(12)

In iron sulfate solutions, metal-ion hydrolysis also occurs because the pH of 1M Fe_2(SO_4)_3 solutions (0.73) indicates an equivalent amount of metal-ion hydrolysis as the 1M FeCl_3 solutions. In order for the proposed mechanism to be consistent with the experimental results, solutions of ferric sulfate should be less effective at generating radicals than the ferric chloride solutions, an assertion that is discussed in a later section.

Each radical-generating process also liberates an electron, which can be injected into the polyethylene. In the presence of an applied field, the oxidation of an aqueous donor species at polyethylene’s surface should be faster due to lowering of the interface potential barrier due to Coulombic attraction between the injected carrier and its “image charge” (Bonham and Lyons, 1972). Specifically, for the reactions of ligands with the ferric ion, many electron transfer rates are measured with the ferric ion as the oxidizing agent and the different ligand being oxidized. For these radical-generating reactions to lead to charge injection into polyethylene, the state of the ferric ion must remain unchanged (an electron cannot be simultaneously injected into polyethylene and reduce a ferric ion).
Specific action of the chloride ions

Ligands have been found to change both the redox potential and exchange current density of ferric-ferrous systems. In a similar way, chloride ions complexing the ferric ion may serve to stabilize the radical or to lower the activation energy (Stasiw and Wilkins, 1969, Chen et al., 1982), thus increasing the rate of radical formation and consequently the rate of charge injection. The experimental results show that a high concentration of chloride is required (or at least a high ratio of Cl/Fe ions in solution), indicating that ferric ions with fewer complexing chloride ions do not result in high rates of charge injection.

The nature of the stabilization brought about by complexation by chloride ions may be similar to that of radical compounds in which bond delocalization is present. The delocalization of the radical electron through resonance is thought to lower the energy of the radical (Johnson, A, 1999), a phenomenon seen with alkane radicals. In the absence of chloride ions, ferric ions in ferric nitrate solutions are complex by water molecules, which may not stabilize the hydroxyl radical to the same extent that chloride ions stabilize a chlorine radical, thus reducing the rate of the charge injection reaction in chloride-free media. Sulfate ions complex ferric ions but have significantly lower rates of radical generation (in this instance, sulfate radicals), as reported by Machulek et al..

It follows that a stabilized product (the ligand radical) leads to a higher rate probability of oxidation of the aqueous component. Instead of electron transfer between the ferric ion and the complexing ligand, the electrons liberated by any of the oxidation reactions of aqueous components would then be injected into the polyethylene. The application of a field would decrease the energy of the injected electron, thereby facilitating the electron transfer reaction, as the difference between the electron energy in the ligand and the polyethylene is quite large, this field both creates a thermodynamic driving force as well as increases the probability of resonance tunneling, an injection mechanism that will be discussed in more depth in a later section.

Radical action at the polyethylene interface

Oxidation reactions of hydrocarbons have been extensively researched, and a number of mechanisms have been proposed (Dalinkevich et al., 1993). What is common among many of these mechanisms is that the initiation step involves the formation of a carbon radical through hydrogen abstraction. The C-H bond cleavage can be accomplished with UV light (Kaplan and Kelleher, 1971) or through reaction with a radical component (Wiberg and Eisenthal, 1964). The reaction in the presence of a chlorine radical (known as free radical halogenation) proceeds in the following steps:

\[ Cl^\cdot + R - CH_2 - R \rightarrow HCl + R - CH^\cdot - R \quad (13) \]
The alcohol can be subsequently oxidized to a ketone through the following reaction, where ferric ions behave as the oxidizing agent:

\[
R - CH\rightarrow R + H_2O \rightarrow R - CHOH - R + H^+ \quad (14)
\]

\[
H^+ + OH^- \rightarrow H_2O \quad (15)
\]

The X-ray photoelectron spectroscopy and fluorescence results presented in this work indicate that carbonyl, alcohol, and carboxylate groups were found with the surface characterization measurements on polyethylene exposed to 1M FeCl₃ + 1M H₂SO₄. An alternative mechanism to reaction (14) in ferric chloride would be one in which an additional chlorine radical reacts with the carbon radical, however the XPS results indicated that significantly less chlorine was found on the surface in comparison to oxygen, which suggests that either chlorine radicals do not bond to the surface of the polyethylene or are not generated in the electrolyte solution.

The complexes in other solutions

Ferric sulfate complexes were investigated by Magini in a separate work. X-ray diffraction data suggest that ferric ions are complexed by sulfate ions and water molecules, with the number of sulfate ions in the inner coordination shell of the ferric ion dependent on the concentration of sulfate ions (Magini, 1979). Both monosulfate and bisulfate ferric complexes were found by Kormanyos et al. (Kormanyos et al., 2008).

The presence of a ferric nitrate complex was investigated by Morris and Sturgess, and it was concluded that the complex present was a mononitrate complex in which the nitrate was found in the outer sphere, i.e., the ferric ion was solvated by six water molecules in addition to a weak interaction with a nitrate ion (Morris and Sturgess, 1969). This work was corroborated by the Raman studies of Kanno and Hiraishi that were referred to earlier, in which no characteristic peaks of ferric-nitrate interaction were found (Kanno and Hiraishi, 1982).

The work presented here seems to indicate that the high chloride-iron ratio complexes that are present at large chloride to iron ratios are integral to the charge transfer reaction. Additionally, the pH of the 1M FeCl₃ solution (pH~0.73) indicates a large degree of metal-ion hydrolysis, with approximately one hydrogen ion created for five ferric ions in solution, indicating that, in addition to chloride, hydroxide and water complex with the iron ions.
Charge injection that does not include the oxidation of a ferrous ion or sulfur atom requires the generation of a radical through reactions shown in a previous section. Combining the UV absorption of the different ferric complexes of chloride, sulfate, and nitrate with the quantum yields of chlorine radical (from a chloride ion, hydroxyl radical (from a hydroxide ion), and sulfate radical (from a sulfate ion), respectively, suggests a strong correlation between the radical generation of the different ferric complexes of chloride, nitrate, sulfate and the charge injection rates (shown in Figure 16).

The connection between radical generation rates and charge injection rates is that radical generation rates may be due to the stability of the radical; in the case of charge injection, the reduction of ferric ions is replaced by electron injection into polyethylene.

**Explanations for the radical formation of ferric salts**

In researching electrochemical processes at electrolyte/insulator interfaces, Mehl and Hale (Mehl and Hale, 1967) derived an expression for the maximum injection current density from an electrolyte at the surface of an insulator.

\[
i_0^* = vNC_D \exp\left\{-\frac{\lambda}{4RT} \left[1 + \frac{1}{\lambda} \times (\Delta + q(E_{FB} - E_{NHE}^0))^2\right]\right\}
\]

where \( v \) is a factor that includes the vibrational frequency of the donating complex, \( N \) is the number of empty states in the crystal, \( C_D \) is the concentration of donors at the surface, \( \lambda \) is the "reorganization" energy (to be discussed later), \( \Delta \) is the difference between the Fermi energy and the conduction band in the insulator, and \( E_{FB} - E_{NHE}^0 \) is the difference between the flat band potential of the insulator and the standard reduction potential of the injecting redox system. Additionally, it is mentioned (Lohmann and Mehl, 1975) that, if a part of the applied potential drops across the interface between the electrolyte and the insulator, the injection current density will be increased.

It is also reasonable to extend Mehl and Hale’s equation to cover a variety of different donors, in that the total current density at the surface is the sum of \( i_0^* \) for each injecting system. That is, each redox system may inject into polyethylene, although some systems are significantly more effective than others. From this, the addition of a redox system will introduce an electron donor to the interface between the polyethylene and the electrolyte but also may change the Fermi energy of the solution.

This derivation contains two components that may be of interest, including the reorganization energy and the energy difference between the conduction band of the insulator and the Fermi energy of the electrolyte (although in the instance of
traps in the insulator, the energy of the trap state would be used instead of the energy of the conduction band). While the formula presented by Lohmann and Mehl was derived given a trap-free crystal insulator, the existence of bulk traps in the crystal increases the slope of the potential vs. distance from the electrolyte-crystal interface. Although polyethylene is not an ideal dielectric (crystalline, no defect energy states), the general form of the derivation may be extended to fit polyethylene in a qualitative way. Specifically, for the data presented in this work, using this preceding equation for charge injection provides a framework to examine the role of different iron salts on charge injection into polyethylene. This is specifically applicable because the bulk of the polyethylene remains unchanged during oxidation (Banmongkol et al., 1998, Lewis, 2002).

The identity of \( C_D \) for the different solutions has already been shown in this work. As mentioned previously, the charge injection rate seems fairly insensitive to changes of ferric and ferrous concentrations, as determined by the open circuit potentials of platinum. For these two electrolytes (ferric chloride and ferric sulfate), the parameters that could be affected are \( v \), which has some dependence on the vibrational frequency, \( \lambda \), which comprises the energy shifts required to accommodate a new polarization both in the electrolyte and the crystal after electron transfer, or \( C_D \), the concentration of the donor.

If the effect of ferric chloride is catalytic in nature, then its role should be one in which some of the parameters of the equation proposed by Lohmann and Mehl (exchange current density at an electrolyte-crystal interface) are changed for the injecting redox system. The changeable parameters include \( v \), although the addition of a ferric chloride complex is unlikely to increase the vibrational frequency of a component undergoing electrochemical oxidation. Additionally, it is unlikely that additional complexing chloride ions would increase the vibrational frequency of a ferric chloride complex if the ferric chloride complex were itself the injecting component. A more likely effect would be to change a part of the ‘reorientation energy’ of a charge injecting component, or more simply, stabilize the oxidized (post electron transfer) component at the surface of the insulator. The identity of these components and the specific role iron may take are addressed in later sections.

**Marcus theory**

Explanations of the catalytic effect of ferric chloride on the oxidation reactions of the donor species can be examined through Marcus’ theory.

Marcus’ theory of charge transfer reaction rates (Marcus, 1956) starts with the Franck-Condon principle, which states that electron motion is significantly faster than that of atoms in molecules, and that in the time necessary to complete an electron transfer reaction the motion of the atoms is essentially negligible. From this, Marcus asserts that an extra term in the Gibbs free energy is needed, in particular, one that incorporates a change to a new equilibrium in the surroundings.
that interact with the products instead of the reactants. Additionally, an electron transfer reaction is most likely to occur when the conformation of a charge transfer atom or complex is in an energetic state that is very close to a conformation that is stable after the electron transfer. Solvated ions are consistently thought to have conformational energies that increase as the coordination spheres are displaced from their equilibrium positions, so the overlap of the energy-displacement curves for the reduced and oxidized forms of the component correlate with exchange current.

For example, both ferric and ferrous ions are solvated in water and undergo charge transfer with each other at a specific exchange current density. For each charge transfer reaction to occur, the ferrous ion must have the water molecules that solvate it located in positions that are also favorable for a solvated ferric ion; additionally, a nearby ferric ion must have its solvation sphere appropriately configured for a ferrous ion. The closer the solvation shells of the ferrous and ferric ions involved are to the equilibrium positions of the solvation shells post transfer, the more likely a charge transfer reaction is to occur.

For a reaction, Marcus states that the difference in energy between the products immediately after electron transfer and the equilibrium state of those products can be given by

\[ \Delta G = m^2 (\lambda_i + \lambda_o) \]

in which \( m \) is a thermodynamic quantity (Marcus, 1990), \( \lambda_i \) is a vibrational component of the inner coordination shell reaching new equilibrium positions, and \( \lambda_o \) is a polarization component of the outer coordination shell.

Looking only at the inner coordination sphere in isotopic electron exchange, \( \lambda_i \) is determined by the difference in equilibrium bond length for each charge transfer as well as the force constants associated with the bonds between the atoms undergoing charge transfer and the coordinating solute molecules (Marcus, 1956). To increase the injection current density through this mechanism, ferric chloride complexes would have to lower the reorganization energy of one of the redox systems in solution, specifically, that of the oxidized state of the system, to catalyze electron injection from the reduced state into the polyethylene.

For the proposed mechanism, in ferric chloride solutions, either complexing chloride or hydroxide ions are directly involved in charge injection into the polyethylene. Marcus’ theory of electron transfer cannot be directly applied to this scenario, because the chloride ions are not solvating but complexing. However, some of the foundation given in the theory may still be applicable. It may be reasonable to suggest that a number of chloride ions complexing a given ferric ion are in close proximity to the complexing hydroxide ion that must be oxidized in the electron transfer step. It may be that the large static isotropic polarizability of chloride ions relative to that of water molecules (25.5-31 in comparison to 9.28-
9.99) (Serr and Netz, 2006) allows for fast rearrangement of the mobile electron cloud around the chloride ions, quickly shifting to a lower energy electronic structure after electron transfer that is consistent with the Franck-Condon principle, requiring less displacement of the other atoms to arrive at the equilibrium position.

Role of carbonyl groups

Introduction of carbonyl groups by electrochemical means

Research by Briggs showed an XPS examination of polyethylene that had been subjected to various oxidizing treatments (Briggs et al., 2003). The XPS was used to determine the bonding state of the carbon atoms on the surface of the polyethylene, and by peak-fitting of the energy of the C1s electron they were able to differentiate between C-C bonds, C-O bonds, C=O, O-C=O bonds, and C-O-H bonds for each of the different treatments. Among their findings were results that indicated that electrochemical exposure (timed exposure at two different concentrations and two different temperatures) led to the formation of carbonyl and carboxylic acid functionalities on the surface of the polyethylene. The electrolytes they used were potassium dichromate (0.23M K2Cr2O7 + 15M H2SO4) and acid potassium permanganate (saturated solution of KMnO4 in 1:40 conc. H2SO4). They found that specifically for the potassium dichromate, a significant number (>10%) of carbon bonds had been oxidized to oxygen-containing functional groups when polyethylene was exposed for 30 minutes at 70°C.

Etches with chromic acid were also performed by a number of other researchers (Blais et al., 1974, Siperko, 1989, Rasmussen et al., 1976) along with the work performed by Briggs. The studies as a whole do point to an oxidation of polyethylene in the presence of chromic acid (or chromate, or dichromate), but the specifics of the surface oxidation results differ from one study to another. While some researchers found the presence of hydroxyl groups (Briggs 2003, Blais, 1974) and some did not (Rasmussen et al., 1977), each study reported carbonyl groups to be present.

Effect of carbonyl groups on conductivity and injection

Banmongkol et al. (Banmongkol et al, 1998) investigated the effect of carbonyl impurities on the conduction behavior and breakdown strength of oxidized polyethylene. The polyethylene used was subjected to oxidation by exposure to ozone created by gas discharge in oxygen. Using the IR absorption of carbonyl groups (1715 cm⁻¹), they were able to determine the depth profile of carbonyl concentration by looking at absorption as a function of thickness removed by grinding with sandpaper; as carbonyl groups were removed, IR absorbance decreased. From this they were able to conclude that the oxidation on the
polyethylene extended into the film and was not only present on the surface, with roughly 50% of the carbonyl groups found at least 2 μm into the film. While the IR absorbance was dependent on oxidation time, the depth profile of the oxidation groups was relatively unchanged with different oxidation times.

Additionally, they carried out experiments that investigated the dependence of current density on carbonyl absorption under an applied voltage, using evaporated gold electrodes. They found that higher carbonyl concentrations resulted in higher current densities in polyethylene: the most oxidized sample under a field of 2.5 MV/cm (much higher than the breakdown strength of 1.2 MV/cm attained in the present work) exhibited current densities that were three orders of magnitude higher than non-oxidized films. They rationalized their results with the fact that oxidation leads to an increase in surface states, and these surface states modify the potential seen by injecting electrodes. Polyethylene as a wide band-gap insulator has a large barrier to injection, and energy states created below the conduction band would facilitate electron injection, shown qualitatively in Figure 49.

Research corroborating these findings was performed by Mizutani et al., Suzuoki et al., Ieda et al., who investigated space charge profiles and electrode-polyethylene interfacial fields for oxidized and unoxidized polyethylene (Mizutani et al., 1980, Ieda et al., 1990, Suzuoki et al., 1991). They found that oxidation on the polyethylene surface causes an increase of current density, which they attributed to the introduction of surface energy states in the amorphous region of polyethylene that the electrons could move between. The experiments they performed also showed the electric field through the width of the polyethylene film, which indicated that for oxidized polyethylene, there is a larger negative charge located near the cathode. They also found that oxidation of a surface leads to greater injection (and net polyethylene charging) of the carrier at that interface, i.e. oxidation of the interface leads to greater injection of both positive and negative carriers, which will be discussed in greater depth in following sections. While Suzuoki et al. found that current increased with cast layers of an oxidized material on the surface of unoxidized polyethylene, a theory was not proposed by them as to why current density increased through the bulk even though the oxidized region was limited to a film ~1 μm thick on a 25 μm sample.

The findings of Banmongkol and Mizutani were further supported by the theoretical results of Huzayyin, Boggs and Ramprasad, who modeled the effect of a carbonyl impurity on the energy band structure of polyethylene (Huzayyin et al., 2008). They determined that carbonyl groups introduced two new states in the polyethylene, a shallow hopping state 0.4 eV below the conduction band, and a deep trap state 1.77 eV below the conduction band. The shallow state is thought to be the source of higher conductivity of oxidized polyethylene, as bulk conductivity is thought to be attributed to Poole-Frenkel hopping, a bulk analog of Schottky injection (thermionic excitation over a field-lowered potential barrier), and the presence of a shallow trapping state leads to a low potential barrier between the
electron in the trap state and the conduction band. When trap state densities are greater than $10^{18}$/cm$^3$, the trap energies levels interact with one another, lowering the energy barrier that the electrons have to overcome to escape the traps (Nath et al., 1990). Specifically for the case of platinum electrodes, the conduction band of polyethylene at the interface was calculated be 2.42 eV below the bulk energy level. The presence of carbonyl impurities is thought to decrease the energy level at the interface even further (Huzayyin et al., 2011), to 1 eV above the Fermi level of platinum (5.6 eV below vacuum).

The presence of carbonyl groups lowering the potential barrier for electron injection leading to increased injection is consistent with the findings of Bamji et al. that electrons were more easily injected than holes into polyethylene (Bamji et al., 1986). Electrons can be injected into polyethylene, but additional, more accessible energy states near the surface will make this process faster. For an injection-limited conductivity, more accessible surface states will increase conductivity and subsequent Joule-heating, leading to thermal degradation and subsequent electrical breakdown.

**Rationale for conductivity changes to polyethylene**

The effect of electron traps in the current-voltage curves of polyethylene has been previously discussed, but the microscopic effect of traps near the surface of an insulator requires further investigation. Traps will influence the mobility of electrons in a variety of ways and as well as the electron transfer characteristics at the polyethylene interface.

Electrons in a perfect crystalline insulator will move through a continuous energy band in a direction opposite the electric field. For polyethylene, the crystalline regions exhibit conduction bands that are aligned with the chains (Lewis, 2002). The mobility of the electrons in this situation depends on the time between collisions of the electron and the lattice. The presence of electron traps in an insulator removes a proportion of the electrons in the conduction band and confines them to localized energy states, with confinement times dependent on the energy level of the trap as well as the magnitude of the field (Anta et al., 2002). As a result, the effective mobility of the electrons in the presence of traps is significantly decreased.

Electrons in traps can escape through a variety of mechanisms. These mechanisms are thermionic emission over the potential barrier between the trap and the conduction band (Poole-Frenkel hopping), tunneling through the energy barrier to either the conduction band or another trap of equal energy (resonance tunneling), or thermal excitation followed by tunneling through a barrier.

The density of traps will have different effects on these different mechanisms. For thermionic emission, the electrons that leave the traps have
enough energy to exist classically in the conduction band. Once in the conduction band, they will exhibit a high mobility until they encounter another trap state and are trapped again. For this emission mechanism, the longer the distance between traps, the higher the mobility, as the electrons travel a further distance for each time they escape a trap. For both resonance tunneling and thermally-assisted tunneling, the waveform of a trapped electron decays through the classically forbidden region until it grows again at a nearby equienergetic state. For mechanisms involving tunneling, the probability of tunneling depends strongly on the tunneling distance, and a larger trap concentration will decrease the tunneling distance, increasing conductivity through this mechanism.

For trap states created through a surface treatment of the polyethylene, the trap density decreases with increasing distance into the interior of the polyethylene, with research by Banmongkol et al. indicating 50% of the traps were within 2 μm of the surface. As the traps do not extend through the bulk of the polyethylene, bulk properties of the polyethylene far enough away from the surface must remain unchanged after a surface treatment. Thus, the conductivity through the bulk of the polyethylene is unchanged, so bulk conductivity of polyethylene is not the factor that limits current density for 1M NaCl electrolytes, but rather charge injection for 1M NaCl electrolyte is low. However, one feature of charge injection into insulators is the development of space charge at the surface of the insulator, which creates a lower local field for charge injection. This space charge is thought to be one of the reasons why current decays as a function of time after an applied voltage.

In steady-state conduction, the current density must be constant through the depth of the insulator, or otherwise charge would build up at areas where there is an inequality of incoming and outgoing charge. Once charge is injected to a surface of the polyethylene, there is a larger charge density at the surface. That charge will move through the insulator towards the opposite interface by a combination of diffusion and conduction. At steady state, the charge through the insulator is non-uniform, which results in a depth-dependent field. In short, the electric field in areas of high charge density must be lower than areas of low charge density in order to keep the current density constant through the depth of the insulator, i.e., conservation of current density requires that $\partial i/\partial t = \text{div}\mathbf{i}$; conservation of charge density requires that $\partial q/\partial t = \text{div}\mathbf{q}$ and Poisson’s equation requires electric field = $\text{div}\mathbf{q}$.

The case of space-charge limited current is when so much charge has been injected at the surface of the insulator that the local field is zero between the injecting electrode and insulator. In this case, the maximum current that can flow through the insulator is dependent on the rate at which the space charge leaves the injecting surface. The charge density and electric field for an insulator undergoing space charge limited current has been solved explicitly, using Gauss’s law and setting the field at one interface to zero (zero field at the injecting interface is not the case with polyethylene, which requires an injecting field, a point which will be addressed later). The solution shows the electric field grows quickly from the value
of zero at the injecting interface with a slower rise through the bulk of the insulator, such that the average electric field is equal to the applied voltage divided by the thickness of the insulator. Explicitly, the electric field under these conditions is

\[ E = \left( \frac{2J}{\varepsilon_0\varepsilon_r\mu} \right)^{1/2} \tag{12} \]

in which \( x \) is the distance from the injecting surface, \( \mu \) is the electron mobility and \( J \) is the current density. Integrating over the length of the dielectric and rearranging, the familiar form of the Mott-Gurney law for conduction in solids is reached:

\[ J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8d^3} \tag{13} \]

in which \( d \) is the thickness of the insulator.

The existence of traps in an insulator removes a significant number of the free carriers in the insulator, which lowers the current density by the proportion of electrons in traps. Along with this treatment is the assumption that trapped carriers do not contribute to the current density.

If most of the conduction in the insulator is through electron hopping from one trap to another, then a much lower effective mobility of electrons can be used with the same equation for space charge limited current. Additionally, through the experiments performed by Banmongkol et al., which observed higher current density in the presence of polyethylene with carbonyl groups introduced, it follows that the presence of these traps distributed through the bulk of the polyethylene increase the conductivity of polyethylene, instead of reducing the number of free carriers.

In looking at how space charge would influence current-voltage curves, let us examine three different scenarios. For each of these scenarios, the simplifying assumption is that the electron mobility is not a function of the electric field. The cases to be examined are

1. The existence of traps creates a region in the insulator of finite width extending into the insulator of vastly higher electron mobility.
2. The number of traps decays exponentially into the insulator, and the trap states have a discrete probability of creating a free carrier by thermionic emission.
3. The number of traps decays exponentially into the insulator, and the main conduction mechanism is electron tunneling from trap to trap.

Finite width of high mobility region
This scenario is the easiest to envision. The insulator in this scenario can be thought of as two separate insulators with different properties in electrical contact. The boundary conditions we will use here are that current density is the same in both insulators (otherwise there would be charge buildup at the interface), the injecting electric field is zero at both insulators (space-charge limited current, so at the interface of the two insulators, the electric field is equal), and that these insulators have different mobilities, $\mu_h$ and $\mu_l$, for high and low.

It is quickly apparent from equation {12} that the electric field through the insulator section with a higher mobility is decreased compared to the uniform insulator with a lower mobility. Without solving this scenario explicitly, using the fact that the integral of the electric field over the total length of the insulators equals the applied potential, we see that a finite slab of higher mobility means a higher average field through the low mobility insulator. In the limit that the mobility of the high mobility insulator slab goes to infinity, the electric field over that section is zero, so the entire voltage drop occurs over the low mobility region. This is to be expected; that high enough mobility leads to properties of a conductor, which essentially creates space-charge limited current in a thinner film. If 10% of the insulator were perfectly conducting, there would be a 37% increase in current through this mechanism.

**Exponential decay of trap density, finite emission probability from traps**

In this scenario, we ascribe a higher mobility to the surface region of the polyethylene in which trap states have been introduced in the form of oxidation groups. For this analysis, the increased mobility is a function only of the number of traps. The trap density is given by $N_t(x) = N_0 e^{-cx}$ where $N_0$ is the trap density at the surface, and $c$ is a constant that determines the decay depth. For this situation, we say that each trap contributes to a higher mobility, so the mobility in this situation takes the form of

$$\mu(x) = \mu_1 e^{-cx} + \mu_2$$

where $\mu_2$ is the mobility of the unoxidized region and $\mu_1$ is a higher mobility due to the presence of traps in the surface region. Using this new mobility in the equation for the electric field in space-charge limited current, a different electric field profile is created. Compared to the electric field profile of the unoxidized film, the average electric field is lower. Knowing that the integral of the electric field over the depth of the insulator is the applied voltage drop, the electric field in the scenario with the exponentially decaying trap distribution must be multiplied by a constant to ensure that the total voltage drop across the polyethylene is the same as the applied voltage for both situations (with and without traps). The final electric field profile is shown in Figure 50.
As shown in Figure 50, a smaller electric field is required to produce the appropriate current density over the oxidized region, leading to a higher electric field through the unoxidized region. The higher electric field in the unoxidized region means a higher current density through the entire film. Additionally, this provides an explanation for the results of Suzuoki et al. as to why a finite region of increased oxidation in the polyethylene could lead to greater current through a polyethylene sample. It is important to note that by definition, the conductivity of the entire polyethylene sample has increased after oxidation of the surface, even though for most of the depth of the sample, there are no chemical changes to polyethylene; the increase in current comes through a larger potential drop over the majority of the film. The conductivity through the bulk of the film will increase a little bit through field-dependent mobility, but mobility effects are only one of the factors why the current increases with surface oxidation. Only taking into account the increased electric field (holding both conductivity and charge density unchanged) for polyethylene with an oxidized surface, this treatment would result in a 25\% increase of current.

**Exponentially decaying trap distribution, tunneling between traps**

Introducing tunneling conduction complicates the equation for mobility. The probability for an electron to tunnel through a barrier is a strong function of distance, in that

\[ P \propto \exp(-2\alpha r) \]  

\{15\}

where \( r \) is the average separation between two traps, and \( \alpha \) is a constant (Mott, 1987). If an electron successfully tunnels from one trap to another, it follows that the distance it will travel is also \( r \). It should be clear that \( r \) is proportional to \( 1/N_t(x)^{1/3} \). Combining these factors, the extra term in the mobility equation would take the following form:

\[ \mu = r\mu_1 N_t(x)\exp(-2\alpha r) + \mu_2 \]  

\{16\}

in which \( r = b/N_t(x)^{1/3} \). It should be evident that equation \{16\} has the expected form, in that the contribution to the mobility from the traps decreases quickly as the density of traps decreases. An additional factor that would make transport by tunneling an even stronger function of trap density is that for energy to be conserved, the two trap energies would have to be equal to within kT. The presence of an electric field necessarily lowers the energy of traps deeper into the insulator, so at high trap densities, isoenergetic trap levels are nearby and unoccupied.
The net effect of all of these scenarios of high mobility in a localized region of the insulator is that a field which decreases with distance is required in that region to provide the appropriate current density and, by extension, raise the average voltage drop over the unoxidized portion of the insulator. Also, for only electron injection, mobility at the interface where electrons are injected would have a stronger effect on current density as it is electron movement away from that interface that determines the limiting current. This effect may be seen in by comparing Figure 24 and 25 to Figure 8, in which for 1M KMnO₄ electrolytes, the current increase seen with oxidized films is greater when the oxidized surface is the surface in which electrons are being injected in the polyethylene.

However, the results presented in this work are not indicative of space-charge limited current. Space-charge limited current (SCLC) for a given film is governed by the properties of the film. What is seen in these results is that for films subjected to the same treatment, the current density is different depending on the contacting electrolyte, whereas SCLC is determined mainly by the ease with which electrons are moved away from the interface.

Injection-limited conduction in carbonyl-doped polyethylene was examined by Perlman and Kumar (Perlman and Kumar, 1992). They determined that although the field at the polyethylene-electrode interface where injection was occurring was non-zero, the space charge still decreased monotonically from the interface at which electrons were injected through the depth of the insulator. This depth-dependent charge density indicates that space charge does affect the current density, and that local increases in mobility will allow higher current densities in the film. However, a difference between injection limited conductivity and space-charge limited conductivity is that with injection limited conductivity, it is no longer entirely properties of the insulator that determine current density; rather that interfacial processes can play a large role. This assertion is supported by the action of pretreatment and subsequent effect on current density. It was already reported that oxidation products created by oxidation of polyethylene from a surface treatment do not extend through the bulk of the film, but rather the concentration decays over the course of a few microns (Banmonkgol et al., 1998). As shown previously, even if the affected region of the surface of polyethylene is modeled as a perfect conductor (infinite mobility), in the absence of increased injection, the expected increase of current density is less than what is seen in a comparison of pretreated vs. untreated polyethylene films. This result indicates that the presence of traps also leads to higher injection rates, which in turn lead to more space charge and a lower electric field at the interface.

Influence of traps on injection rate
As stated previously, Perlman and Kumar postulated a non-zero electric field at the surface of polyethylene under an applied potential. From the Maxwell-Wagner-Sillars equation, surface charge exists at an interface with unequal electrical properties, so there is no shortage of carriers to be injected, indicating that an interfacial charge-transfer process is limiting the current density.

The traditional models of charge injection have also been challenged: Schottky injection is thought to be too improbable (Lewis, 2002, Taleb et al., 2013), due to a combination of low chance of thermal excitation as well as the probability that electrons will lose energy to collisions or phonon reactions before the potential barrier is reached (and subsequently overcome). Additionally, the predictions of charge injection rate based off of either of the dominant mechanisms are strongly dependent on the work function of the injecting electrode, which in experiment does not follow the trends that are predicted by the model (Xiao et al., 2011, Taleb et al., 2013, Chen et al., 2001). Lewis has postulated the deviation from theory on oxidation products that are thought to exist between the deposited electrodes and the insulator (Lewis, 2002), on account of the oxide layer preventing injection through the normal mechanisms.

Traditional charge injection is usually thought to be through Schottky injection or Fowler-Nordheim injection, two theoretical approaches that are discussed here in more depth in another section. For polyethylene, at the electric fields in this work, it is very unlikely that electrons are tunneling through the potential barrier to the conduction band, as Fowler-Nordheim injection becomes significant at field strengths of $10^9$ V m$^{-1}$ (Dissado and Fothergill, 1988). Additionally, the Fermi level of electrons in solution (corrosion potential of platinum in the solutions ~ 0.69-0.42 vs. SCE) is approximately 5 eV lower than the conduction band of polyethylene, indicating a very small probability of thermal excitation from the solution to the conduction band. Lewis attributes charge injection from metallic contacts into polyethylene through a similar mechanism to bulk conduction, i.e. thermally-assisted resonance tunneling (Lewis, 1986), a mechanism also supported by Dissado and Fothergill as the main bulk conduction. In this mechanism, an electron in the injecting electrode (aqueous electrolyte in this work) with an energy within kT of an available energy state in the polyethylene can tunnel through the potential barrier to that available state.

While many articles refer to the presence of surface states (Lewis, 1986, 1990, 2002, Neagu and Dias, 2009, Banmongkol et al., 1998), there is very little explicit information as to how the energetics of a surface are changed in the presence of traps, unlike analyses of traps in the bulk of polyethylene. Part of the difficulty of investigating the role of surface energetics is that the traditional way of investigating trap energies is using log plots of current density vs. temperature in which the slope gives information about an energy
barrier. However, bulk conduction and charge injection barriers cannot be separated by this treatment. As such, it is a necessary assumption that bulk trap levels are very similar to the surface energy levels.

As injection to the conduction band of polyethylene is deemed unlikely by any mechanism, it is reasonable to extend the same argument to shallow states that are fractions of one electron volt below the conduction band. Patsch experimentally determined trap densities for unoxidized polyethylene, calculating shallow trap (within 0.3-0.6 eV of the conduction band) densities of $10^{18}$/cm$^3$, and deep trap (greater than 1.5 eV of the conduction band) densities of $10^{14}$/cm$^3$ (Patsch, 1990). If these deep traps are distributed evenly, this corresponds to a surface density (within 10 nm of the surface) of $10^8$/cm$^2$, while von Berlepsch predicted trap levels of $2.6*10^{11}$/cm$^2$ at the surface of polyethylene (von Berlepsch, 1988). This indicates a relatively low number of available states for injection. Additionally, once these states have been filled, the electrons must then escape from the traps via some conduction mechanism described earlier and move into the bulk in order for subsequent injection to occur. DFT calculations have shown that there are specific surface states (present only at the surface of crystalline polyethylene) with an available energy state 1-1.5 eV below the edge of the conduction band (Righi et al., 2001).

Deep traps are thought to originate from chemical impurities, while shallow traps originate from conformational defects in the bulk (Anta et al., 2002). Energetic effects of carbonyl groups in polyethylene chains have been examined computationally and are thought to introduce defect states with trap state between 1.63 and 1.77 eV below the conduction band of polyethylene, with other chemical impurities creating states as low as 2 eV below the conduction band (Huzayyin et al., 2008).

Support for the extension of Lewis’s idea that charge transfer occurs via tunneling to a vacant state is shown by the experimental results of Hays, in which the polyethylene was charged through contact electrification with mercury (Hays, 1973). Hays reported greater charging for polyethylene with a degree of surface oxidation. Banmongkol reported greater current density for polyethylene with a degree of surface oxidation, but did not discuss injection mechanisms. Neagu and Dias reported that charge injected into polyethylene is thought to be trapped right at the surface, and existence of additional traps at the surface and extending into the depth of the polyethylene would aid in the migration of that charge away from the surface, reducing the opposing field (Neagu and Dias, 2009).

A different mechanism of trap-aided injection has also been reported in which electron traps near the anode would trap charge, and lead to a greater localized field (Campbell and Crone, 2006). The extension of that field-enhancing mechanism to carbonyl groups in polyethylene would have to be a
‘hole’ trap, i.e. an ionizable neutral species in the polyethylene. The band gap of polyethylene in the presence of a carbonyl group was found through simulation to be 3.65 eV (instead of 8-9 eV) as reported by Huzayyin (Huzayyin et al., 2008). It may be possible that carbonyl groups are an ionizable source of electrons by which an electron is removed from the valence level of the carbonyl group and then escapes through a Poole-Frenkel lowered barrier to a nearby deep trap state (originating from a carbonyl group or some other chemical impurity). However, the ionization energy of carbonyl groups makes this mechanism an unlikely process.

Huzayyin et al (Huzayyin et al., 2011) calculated conduction band levels for crystalline polyethylene at a platinum interface. The simulation revealed a localized depression of the conduction band level, such that the injection of electrons from platinum (work function of 5.6 eV) to polyethylene involved an energy barrier of 3.15 eV for impurity free polyethylene, which was decreased to less than 1 eV if carbonyl groups were present at the interface. Huzayyin et al. concluded that the presence of chemical traps would have a large effect on the injection and subsequent conduction of polyethylene.

The concentration of surface states is thought to be non-uniform due to variation of alignment of lamellae as well as proximity of impurities and voids to the surface (Lewis, 1990), which would lead to non-uniform injection characteristics. Charge injection being a localized phenomenon is supported by the findings of Banmonkgol et al., who found localized temperature increases that were attributed to Joule heating (Banmonkgol et al., 1998).

**Experimental results with pretreatment**

Figure 29 shows the current density vs. applied potential of polyethylene contacted with an aqueous electrolyte of 1M NaCl and previously subjected to a 2 kV ramp pretreatment in aqueous electrolyte of 1M NaCl and 1M H$_2$SO$_4$ + 1M FeCl$_3$. Both XPS and fluorescence spectroscopy results of polyethylene immersed in an aqueous electrolyte of 1M H$_2$SO$_4$ + 1M FeCl$_3$ for one month showed evidence of carbonyl and other oxidation states on the surface of polyethylene. These states may have originated from reactions with radical ions whose formation was catalyzed by the FeCl$_4^-$ complex. We propose that these carbonyl groups are responsible for the increase in current density seen for pretreated polyethylene in contact with aqueous 1M NaCl electrolyte, through the mechanism discussed earlier, in which carbonyl groups allow lower injection fields and higher mobility in a finite region, allowing for a larger potential drop through the unaffected region of the polyethylene. If carbonyl groups are responsible for the high rate of current transport through polyethylene, it follows that production of carbonyl groups from a different process should also yield an increase in current density injected from aqueous 1M NaCl electrolyte.
To test whether different sources of carbonyl are equally capable of promoting charge injection into polyethylene, tests done with the 1M H₂SO₄ + 1M FeCl₃ electrolyte were compared to tests with K₂Cr₂O₇ electrolyte (same solution as used in the research by Briggs et al., 0.23M K₂Cr₂O₇ + 15M H₂SO₄). The tests with 0.23M K₂Cr₂O₇ + 15M H₂SO₄ showed the same dependence on voltage polarity as the tests with FeCl₃, in that when the solutions that produce oxidation groups on the surface of polyethylene are negative with respect to the 1M NaCl electrolyte (solutions that create oxidation groups are injecting electrons into the polyethylene), there is a much larger current than the opposite bias. In short, both carbonyl-creating solutions showed the same current-voltage behavior. To further test the similarities between the two electrolytes, pretreatment tests were performed with 7:12:150 K₂Cr₂O₇ as the oxidizing species of the electrolyte instead of 1M FeCl₃ + 1M H₂SO₄. The subsequent tests in aqueous 1M NaCl after exposure to the 0.23M K₂Cr₂O₇ + 15M H₂SO₄ electrolyte showed elevated current density as seen in Figure 36, with comparable current densities to those seen in tests with 1M NaCl electrolytes after pretreatment with 1M FeCl₃ + 1M H₂SO₄ in Figure 29. The results of pretreatment with both of these oxidizing electrolytes match up closely with each other, again consistent with the hypothesis that the introduced carbonyl groups in oxidized polyethylene are responsible for the increased current density.

**Mechanism of carbonyl introduction to the polyethylene**

Chromic acid etching of alkanes has been reported in the literature (Wiberg and Eisenthal, 1964) in which the attack of chromium VI is via an intermediate ester of chromium IV. The first step of this mechanism involves hydrogen radical abstraction by chromium V, meaning that the oxygen incorporated as a hydroxyl group in the carbon chain originated in the chromate compound. This alcohol is then further oxidized to a carbonyl and subsequent chain scission leads to shorter chain ketones and aldehydes (Blais et al., 1973).

However, a difference between the 1M FeCl₃ + 1M H₂SO₄ electrolyte and the 0.23M K₂Cr₂O₇ + 15M H₂SO₄ used in the electrochemical oxidations used by Briggs is that the ferric chloride compound does not contain any oxygen. The XPS results on a polyethylene sample indicated the presence of oxygen on the surface, both in carbonyl and carboxylate groups, but due to the absence of oxygen in FeCl₃ the mechanism of oxidation must be different than that reported by Wiberg and Eisenthal described previously (incorporated from the chromate ions). The source of this oxygen in polyethylene exposed to aqueous FeCl₃ therefore must be from another component in the electrolyte and the only other sources of oxygen atoms are dissolved O₂ gas, H₂O, OH⁻, and SO₄²⁻ (for cases in which sulfate has been added to the electrolyte). Looking at these components logically, some of them can be eliminated. One curve of Figure 16 shows the current voltage behavior of a polyethylene sample immersed in air-saturated, 1M FeCl₃ that is free of sulfate. The high current densities seen with this electrolyte indicate that sulfate ions are not necessary for high current densities. Using the proposed mechanism that FeCl₃ both
creates a surface state (carbonyl groups or other defects) on the polyethylene and subsequently injects electrons into that state, pretreatments consisting 1 M FeCl$_3$ in the absence of the various oxygen-containing components should yield lower current densities if the source of the oxygen is removed.

We can now examine the likelihood of each oxygen-containing component in the electrolytes contributing to the I-V measurement. The concentration of OH$^-$ of the ferric salt electrolytes, in which the pH ranges from -0.5 to 0.5, is less than $10^{-13}$ M, which is negligible. The remaining two possible sources of oxygen are O$_2$ gas and H$_2$O (when sulfate is excluded, current densities remain high, indicating sulfate is not directly involved). Removing O$_2$ gas as well as sulfate from the pretreatment conditions was accomplished using a deoxygenated solution of 0.66 M FeCl$_3$ + 2 M KCl. The data from this pretreatment step shown in Figure 38 is compared with the normal pretreatment tests in Figure 29. There is no significant difference between the two curves in 1 M NaCl, so it follows that the source of the oxygen in the oxidation products on the surface of polyethylene that lead to higher current densities is water molecules. Pretreatment with ferric/ferrous sulfate solutions does not lead to increased charge injection, indicating aqueous ferric chloride species are required for surface modification.

Additionally, neither sulfate ions nor oxygen gas is appreciably involved in charge injection into polyethylene. Current-voltage tests were performed on polyethylene films for a deoxygenated 0.66 M FeCl$_3$ + 2 M KCl electrolyte. The resultant plot (Figure 38) shows only a small difference between the current density of deoxygenated 0.66 M FeCl$_3$ + 2 M KCl electrolyte vs. oxygenated 1 M FeCl$_3$ + 1 M H$_2$SO$_4$ electrolyte (Figure 5). If dissolved O$_2$ gas were the primary source of the carbonyl groups that made polyethylene susceptible to charge injection, then deoxygenation of the electrolyte should have led to much lower current densities. Our results indicate that the source of oxygen in the carbonyl group is the water in the electrolyte.

**Nature of the oxidation reaction**

Comparing the results for two pretreatment protocols, the potential dependence on rate is clear. The first pretreatment involved a 2 kV ramp of the sample immersed in 1 M FeCl$_3$ + 1 M H$_2$SO$_4$. At 20 seconds per step, the entire pretreatment took 400 seconds, or 6 minutes and 40 seconds. The results of the 6 minute 40 second pretreatment can be compared to the results of the test that followed the pretreatment that consisted of a timed exposure to 1 M FeCl$_3$ + 1 M H$_2$SO$_4$ without the application of voltage, as seen in Figure 34. The subsequent tests in 1 M NaCl electrolyte for each pretreatment protocol indicated that the presence of an electric field during pretreatment led to higher charge injection rates, even if the duration of the pretreatment test in which voltage was applied was shorter than a pretreatment test without voltage. If the source of increased charge injection rates is the confirmed presence of oxidation groups on the surface of the polyethylene,
then the application of potential in the presence of ferric chloride leads to a higher rate of carbonyl formation. However, it is important to note that the potential has to be applied with the proper polarity – high rates of charge injection do not result when the 1M FeCl₃ + 1M H₂SO₄ electrolyte is polarized positively with respect to the polyethylene surface, and from the research performed by Ieda et al. (Ieda et al., 1990), if oxidation were present on the surface it would aid in the injection of holes.

There are two ways the application of potential could affect the rate or carbonyl formation. One of these ways is through changing the ionic distribution in the electrolyte between the platinum electrode and the surface of the polyethylene, bringing the active specie of the 1M FeCl₃ + 1M H₂SO₄ electrolyte closer to the polyethylene interface, thereby increasing its effective concentration. This is unlikely to be the dominant reason, as there is only a small voltage drop over the depth of the electrolyte (curve fitting of the EIS data indicates a total solution resistance of approximately 500Ω). The other effect of applied potential could be to influence the rate constant of the reaction that forms the oxidation groups. This effect is discussed in much greater depth in the section on radical generation at the polyethylene surface.

In summary, the introduction of oxidation groups to the surface of polyethylene provides an explanation for the increased current densities observed in the pretreatment tests. This explanation is based on two separate phenomena: a local increase of conductivity through trap-modulated hopping, and a decreased injection current at the interface of the polyethylene.
Characterization of the Surface of Polyethylene

Introduction to surface characterization of polyethylene

There are many experimental techniques that can provide different insight into the properties of surfaces, and different techniques will determine different information. The three techniques used in this work to characterize the surface of the polyethylene are (a) electrochemical impedance spectroscopy (EIS), (b) X-ray photoelectron spectroscopy (XPS), and (c) fluorescence microscopy. EIS entails applying small alternating potentials at various frequencies to the sample, while simultaneously measuring current, and sweeping through frequencies. XPS involves collecting photons that are emitted from a sample that is illuminated with X-rays. In fluorescence microscopy, we measure the fluorescence of molecules that have been attached to different functional groups on a surface.

Electrochemical Impedance Spectroscopy

EIS was performed on polyethylene films that had been exposed to three different treatments. The three treatments were exposure to either 2 kV or 2.5 kV in the presence of 1M FeCl₃ + 1M H₂SO₄ (similar to the pretreatment tests), and exposure to a ferric chloride voltage until breakdown. All tests were conducted in 1M NaCl and 1M FeCl₃ + 1M H₂SO₄, with the working electrode immersed in 1M FeCl₃ + 1M H₂SO₄ electrolyte.

Predicted spectrum of unoxidized polyethylene

The response of polyethylene to EIS can be modeled with the use of equivalent circuits. Looking at the electronic path between the two platinum electrodes, there is the electrolyte from one electrode to the polyethylene film, the polyethylene film, and then the electrolyte from the opposite side of the polyethylene film to the opposite electrode. Thinking of the polyethylene film as a material with both resistive and capacitative properties, we can model the electrical system with the schematic shown in Figure 51. In this schematic, Rs is a series resistance comprising the separate resistances of the Pt/electrolyte interfacial reactions and the solution resistance, and R_PE and C_PE are the resistance and capacitance of the polyethylene film, respectively. Using the equations for resistance of parallel and series components, the total impedance of this schematic is

\[ Z_{total} = 2R_s + \frac{R_{PE}(1 - i\omega R_{PE} C_{PE})}{1 + (\omega R_{PE} C_{PE})^2} \]  \hspace{1cm} (17)
Using the formula for capacitance

\[ C = \varepsilon_r \varepsilon_0 \frac{A}{d} \]  \hspace{1cm} \{18\}

and using the value 2.3 for the relative permittivity or polyethylene (Lanza and Herrmann, 1958), 1.77 cm\(^2\) for the area, and 25 \(\mu\)m as the thickness, the capacitance of the polyethylene film is calculated to be 140 pF. The resistivity of the film is very high, and if extracted from some of the data at the beginning of the voltage ramps, the current is on the order of 0.1 nA/cm\(^2\) at 100 V, so the resistance of the polyethylene film is approximately \(10^{12}\) \(\Omega\). With these numbers, the quantity \(R_{PE} C_{PE}\) is 140 s. Using these numbers with equation \{17\} and separating into real and imaginary parts, the impedance becomes

\[ Z_{real} = 2R_s + \frac{10^{12} \Omega}{1 + 19600(\omega \ast s)^2} \]  \hspace{1cm} \{19\}

\[ Z_{imag} = -i \frac{(140 \omega \ast s)10^{12} \Omega}{1 + 19600(\omega \ast s)^2} \]  \hspace{1cm} \{20\}

and a total impedance given by combining equations \{19\} and \{20\}:

\[ |Z| = \sqrt{Z_{imag}^2 + Z_{real}^2} \]  \hspace{1cm} \{21\}

and the phase angle calculated by

\[ \theta = \arctan \frac{Z_{imag}}{Z_{real}} \]  \hspace{1cm} \{22\}

Using these parameters, we can construct a plot of impedance vs. frequency, shown in Figure 52. In this plot, a value of 1000 \(\Omega\) was used for \(R_s\).

The calculated impedance and phase shows the impedance decrease monotonically as the resistance of the \(C_{PE}\) element becomes lower and lower. At high enough frequencies, the total impedance would asymptote to 2000 \(\Omega\), as \(R_s\) is the only component in both real and imaginary impedance equations that is not inversely proportional to frequency.

The calculated impedance and phase angle shown in Figure 52 can be compared to the measured EIS data shown in Figures 39-42. Comparing the calculations to the data, it is clear that for frequencies greater than 0.1 Hz, the model fits the experiment very well. Below 0.1 Hz, the measured values seem to fluctuate greatly, but some of this measurement discrepancy could be due to the necessary
measurement time at such a low frequency with a low driving voltage (10 mV). At such a low frequency, the impedance is very high, which results in very low current density, which may be close to the noise threshold of the potentiostat.

**Predicted EIS spectrum of oxidized polyethylene**

Oxidizing the surface of polyethylene can lead to changes in the electronic properties. With these changes, a separate equivalent circuit is introduced in which two films, each with a resistance and capacitance, are connected in series, shown in Figure 53. This circuit uses the same notation as the previous schematic shown in Figure 51, with the addition of \( R_{\text{OPE}} \) and \( C_{\text{OPE}} \) as the resistance and capacitance of the oxidized section and \( R_{\text{UPE}} \) and \( C_{\text{UPE}} \) as the resistance and capacitance of the unoxidized section of the polyethylene film. Additionally, \( R_{\text{PE}} \) and \( C_{\text{PE}} \) in the above schematic are not equivalent to the first schematic: as some of the polyethylene film has been oxidized, the resistance of the remaining unoxidized film is decreased according to the depth of the oxidation, and the capacitance is increased in accordance with the depth of oxidation.

Determining the parameters of \( R_{\text{OPE}} \) and \( C_{\text{OPE}} \) deserves some consideration. Banmongkol et al. showed large changes in DC current density with applied voltage as a result of surface treatments, indicating orders of magnitude change in resistance (Banmongkol, 1998), and the semicon layer of cables can have a permittivity as high as 10,000 (Heinrich, 2000). These numbers for permittivity and resistance are used to show how a large effect on a small layer of the polyethylene film will affect the predicted EIS spectrum of oxidized polyethylene film.

For the oxidized film, the altered schematic necessitates new equations for the impedance of the system. The capacitance of the oxidized section is given as

\[
C_{\text{OPE}} = \varepsilon_r \varepsilon_0 \frac{A}{d_{\text{OPE}}}
\]

and the capacitance of the unoxidized remainder is given as

\[
C_{\text{UPE}} = \varepsilon_r \varepsilon_0 \frac{A}{d - d_{\text{OPE}}}
\]

with \( d_{\text{OPE}} \) the thickness of the oxidized section. Likewise, the resistance of the oxidized section (with three orders of magnitude lower resistivity than unoxidized polyethylene)

\[
R_{\text{OPE}} = \frac{R_{\text{PE}} \ d_{\text{OPE}}}{1000 \ d}
\]

and the unoxidized section
These resistances are used in the total impedance of the circuit, given by

\[ Z_{total} = 2R_s + \frac{R_{OPE}(1 - i\omega R_{OPE}C_{OPE})}{1 + (\omega R_{OPE}C_{OPE})^2} + \frac{R_{UPE}(1 - i\omega R_{UPE}C_{UPE})}{1 + (\omega R_{UPE}C_{UPE})^2} \]  \{22\}

with a real component of

\[ Z_{real} = 2R_s + \frac{R_{OPE}}{1 + (\omega R_{OPE}C_{OPE})^2} + \frac{R_{UPE}}{1 + (\omega R_{UPE}C_{UPE})^2} \]  \{23\}

and an imaginary component of

\[ Z_{imag} = \frac{-i\omega R_{OPE}^2 C_{OPE}}{1 + (\omega R_{OPE}C_{OPE})^2} + \frac{-i\omega R_{UPE}^2 C_{UPE}}{1 + (\omega R_{UPE}C_{UPE})^2} \]  \{24\}

Using 10% of the thickness of the original polyethylene film as thickness of the oxidized layer (Bangmongkol et al., 1998 saw roughly 50% of the IR absorbance signal originated from deeper than 2 \( \mu \)m, 2.5 \( \mu \)m is 10% of the thickness of the film), \( \varepsilon_r \) of 10,000 for the oxidized region, and 10\(^8\) for \( R_{OPE} \), Figure 54, showing calculated impedance and phase angle of oxidized film, is generated.

Figure 54 looks remarkably similar to the plot of unoxidized polyethylene shown in Figure 39, in that the phase angle quickly approaches 90 degrees, and the impedance starts at a high value and decreases monotonically through the range of frequencies. To illustrate better the difference between the predicted EIS data, the fractional difference between the oxidized and unoxidized predicted results is shown in Figure 55. This plot illustrates some interesting features. First, as expected, the impedance of the unoxidized film is approximately 10% higher than the oxidized film at low frequencies (similar to D.C. conditions), which is attributable to the bulk resistance of the remaining unoxidized film. Secondly, at higher frequencies, the impedance is dominated by the imaginary term (when the phase angle is close to 90\(^\circ\)), and is still 10% higher. This is due to the fact that the quantity \( RC \) is invariant with respect to length as long as bulk resistivity and permittivity are unchanged. In the imaginary impedance term, there is an \( R^2C \) term, which causes the 10% increase to be constant in both low and high frequency regimes. At the highest frequencies, solution resistance becomes an important factor and is responsible for the phase difference between the two modeled circuits. As an error check, if the parameters of the oxidized region are replaced with bulk properties, the resulting impedance is identical to that of entirely unoxidized polyethylene.
The model of polyethylene with an oxidized surface used above predicts a new impedance based on properties of the modified section that are drastically altered from the unoxidized region. As the parameters used for the oxidized section vary less and less from the unoxidized section, the difference in impedance between the oxidized and unoxidized films will decrease accordingly, with the value of 10% shown above as the maximum change. For reasons discussed earlier, the maximum relative change in impedance is proportional to the depth of the oxidized region.

The current flow through polyethylene involves two processes – a charge transfer process at the interfaces between the electrolytes and the polyethylene, and a transport process of electrons through the polymer. The fact that oxidation reactions do not penetrate into the depth of the film, the transport of electrons through the bulk of the polyethylene should be unaffected. With this in mind, any resistance in an equivalent circuit of polyethylene attributed to the transport of electrons through the polyethylene is mostly unaffected. Coupling the transport resistance with the fact that 1M FeCl$_3$ + 1M H$_2$SO$_4$ injecting electrons results in currents approximately 25 times higher indicates that the bulk resistance is not the dominant resistance preventing the flow of charge. Looking at the increase in current density after pretreatment with 1M FeCl$_3$ + 1M H$_2$SO$_4$ for films contacted by 1M NaCl, it follows that the pretreatment lowers the resistance associated with charge injection.

For the EIS tests, the cyclic voltage used had a small amplitude (10 mV) compared with the voltages applied for the current-voltage tests (100-6000 V). With this in mind, the results of the EIS tests (exposure to 1M FeCl$_3$ + 1M H$_2$SO$_4$ does not significantly change the impedance) may be understood, given the small difference between the forward and reverse bias current densities of 1M FeCl$_3$ + 1M H$_2$SO$_4$ at low voltages, shown in Figure 5 (at 100 V, the reverse bias current density is 7% higher than 1M NaCl shown in Figure 6, within the standard deviation, while at 6 kV it is 580% higher). As discussed earlier, charge injection is strongly dependent on electric field, and with the fields used in the EIS tests, the influence on pretreatment seen at higher voltages are not apparent. EIS tests with a greater voltage amplitude may prove to be more instructive.

The EIS data of oxidized polyethylene are shown in Figure 40. As the maximum change possible between the results of Figures 39 and 40 depends on the depth of the oxidized region and the facility with which charge is injected into the oxidized region, it follows that the changes in impedance are likely to be small. Detecting changes of that magnitude on log-log plots is very difficult, so the relative difference in impedance of the EIS data is shown in Figure 56. Data below 0.1 Hz are omitted from Figure 56 due to the inherent scatter of the measured impedance as discussed earlier.

Figure 56 shows the percent decrease in impedance as a function of frequency for polyethylene that is immersed in 1M FeCl$_3$ and 1M NaCl and exposed to 2.5 kV. At frequencies between 1-1000 Hz, the change in impedance is fairly
constant, at about 1%. Above 1000 Hz, there is a much larger scatter in the data. Even with the consistent 1% variation in the middle frequencies, the difference between EIS spectra of the oxidized and unoxidized films is small enough that it is difficult to unequivocally attribute such a change to the electrochemical exposure. Again, a 2 kV voltage ramp (the pretreatment step) resulted in approximately four times the current density in 1M NaCl, as shown in Figure 29 (at much higher applied potentials than the potentiostat provides during EIS tests). Other possibilities to explain the discrepancy between EIS data and current-voltage data are that below certain fields, insulators are thought to have an ohmic response to an applied field. Note that the 10 mV potential applied by potentiostat is low enough that the dominant conduction may be Ohmic, and thus, the current that flows would mostly be due to intrinsic carriers in the polyethylene from bulk trap states.

Curve fitting of the EIS spectra to the equivalent circuit was performed with Gamry Echem Analyst software. The equivalent circuit used for the data fitting is shown in Figure 51. The results for the capacitance are shown in Table 5 below:

Table 5. Capacitance of the polyethylene film before and after the application of voltage.

<table>
<thead>
<tr>
<th>Test</th>
<th>C_{UPE} (pF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pre 2.5 kV</td>
<td>263</td>
</tr>
<tr>
<td></td>
<td>265</td>
</tr>
<tr>
<td>post 2.5 kV</td>
<td>271</td>
</tr>
<tr>
<td></td>
<td>264</td>
</tr>
<tr>
<td>pre 2 kV</td>
<td>251</td>
</tr>
<tr>
<td></td>
<td>254</td>
</tr>
<tr>
<td>post 2 kV</td>
<td>312</td>
</tr>
<tr>
<td></td>
<td>316</td>
</tr>
</tbody>
</table>

For these tests, two spectra were taken of each sample. First, what can be predicted from the circuit in Figure 51 is that the resistance of the polyethylene (the real part) is only going to significantly affect the impedance if it is comparable or less than the impedance due to the capacitance (the imaginary part) as both components are in parallel. The influence of the real part of the impedance would only be detectable at low frequencies whereas the imaginary component dominates at higher frequencies. This requires the model to determine parameters at low frequencies where a significant amount of scatter is present, causing order of magnitude variation in the resistance of the resistor in Figure 51. For this reason, the values for the resistor are omitted and the capacitance is reported. From Table 5 it is clear that that capacitance is unchanged before and after the application of 2.5 kV. For the test with 2 kV, the capacitance increases (lowering the imaginary component) by 24%.
What the EIS data do indicate is that the effect of oxidation brought about by electrochemical exposure does not mimic a thinning of the film; if the film were significantly thinned in a way that would influence charge injection rates, it would have also demonstrated a larger decrease of impedance through the range of frequencies tested.

**Surface chemical analysis using fluorescence microscopy**

The methodology of fluorescence spectroscopy is one that relies on a reaction between a fluorescing compound and a desired functional group. As this process is usually referred to as a ‘surface’ reaction, it is necessary to define what is meant by ‘surface’. The ability of a surface analytical technique to detect changes caused by a surface treatment is going to be limited by three factors:

1. The depth into the polyethylene at which the surface reaction occurs. For example, in Banmongkol’s work (Banmongkol et al., 1998), approximately 50% of the absorbing groups were found at depths greater than 2 microns from the treated surface.

2. The depth into the polyethylene at which the reaction binding the fluorescing component to the functional group can occur. In fluorescence spectroscopy, the normally non-fluorescing carbonyl groups are reacted with fluorescing compounds. If this reaction cannot proceed inside the polyethylene due to poor penetration of either the dye or the solvent (if the solvent is involved in the reaction), then the number of carbonyl groups created in the surface treatment will be underestimated by this technique, as not all the functional groups will have reacted with the fluorescing component.

3. The depth into the polyethylene that the specific spectroscopy is effective. Fluorescence spectroscopy depth is governed by the attenuation characteristics of the material surveyed, whereas the evanescent wave penetration of ATR-IR is limited to approximately one quarter of a wavelength, and the penetration of XPS is ~ 10 nm.

The confluence of these three factors and how they affect each measurement can influence the agreement between different analytical techniques.

**Fluorescence analysis of the polyethylene surface**

An effective analytical technique for surface chemical characterization should possess three qualities: it must be specific for the chemical group it is designed to detect (such that other chemical groups do not provide a positive signal), it must occur in high yield (surface groups introduced to the polyethylene are covalently bonded to the polymer backbone and thus cannot be separated and purified for better signal), and it must distinguish between surface and bulk groups.
Fluorescence assays are a technique that possess the attributes outlined above. Rasmussen (Rasmussen et al., 1977) functionalized the surface of polyethylene with oxygen-containing carbon groups through chromic acid treatment, and subsequently derivatized the introduced functional groups to fluorescing compounds. The subsequent fluorescence intensity between oxidized and unoxidized polyethylene indicated $2.5 \times 10^{15}$ carbonyl sites/cm$^2$, whereas unoxidized polyethylene had $2.2 \times 10^{12}$ carbonyl sites/cm$^2$. Of the oxygen containing groups introduced to the polyethylene, 60% were carboxyl groups and 40% were ketones/aldehydes. The characteristic absorbance of hydroxyl group was not detected with attenuated total reflectance infrared spectroscopy (ATR-IR) (Rasmussen et al., 1977), however Blais et al. reported hydroxyl groups introduced with chromic acid etching (Blais et al., 1973). It was also found in a different study that chromic acid treatment increased carbonyl concentration from 0.4% of surface carbons to 11% of carbon atoms (Homes-Farley and Whitesides, 1986).

In this work, polyethylene was exposed to 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte for one month before fluorescence analysis. The aim of the exposure was to create a large number of carbonyl groups on the surface of the polyethylene to give the maximum possible fluorescence signal.

Two fluorescence labeling schemes and results are presented in this work. Scheme 1 uses a reaction in which only carbonyl groups bind with the dye. Scheme 2 uses a reaction in which both carbonyl and carboxylate groups bind to the dye. For both schemes, the polyethylene was washed with DMSO to remove dye that was adsorbed onto the surface of the film and not reacted with a functional group.

**Fluorescence analysis of carbonyl groups**

The dye used in this scheme is known as sulforhodamine 101 acid chloride, referred to as Texas Red. The fluorescing compound is functionalized with a hydrazide group which reacts strongly with carbonyl groups, but no carboxylate groups. In the presence of EDC (1-ethyl-3-(3- dimethylaminopropyl)carbodiimide)), the functionalized dye can also react with carboxylate groups. After the reaction, it is important to wash the film with a solvent to remove dye molecules that are only weakly bonded to the surface.

**Spatial distribution of oxidation**

With the method of determining fluorescence intensity of the polyethylene, it is possible to construct 3-D plots indicating the intensity as a function of location. Due to the fact that polyethylene has discrete crystalline and amorphous regions, it may be possible to examine the relative reactivity/susceptibility of these regions to oxidation through the use of fluorescence intensities. If the amorphous and crystalline regions experience different reactivities, then the fluorescence intensity
plots should vary spatially according to the size of these regions. The spatial resolution of the fluorescence measurement is 25 points/cm, or 40 μm, which is on the order of the size of the crystalline regions in polyethylene. This comparison is performed in what follows for both reaction schemes used, so the spatial incidence of both carbonyl and carboxylate groups is investigated.

Figures 57 and 58 show the fluorescence intensity as a function of location. The scale of the measurements (the surveyed areas are 1.0 cm by 0.5 cm) would make the detection of oxidized regions on the same size scale as the spherulites quite difficult. In these figures, for just Texas Red (no EDC), there is a large variation in fluorescence intensity. One of oxidized polyethylene scans seems to increase almost monotonically in one direction, and the other scan has features that are about 100 microns in size. The same can be seen on scans of the unoxidized polyethylene. One scan has very low fluorescence, and the other has more fluorescence as well as non-uniform fluorescence. With EDC added, the two scans of oxidized polyethylene in Figure 59 show fairly uniform fluorescence, as do the unoxidized samples shown in Figure 60, albeit with lower intensity.

The spatial distribution of fluorescence intensity is somewhat surprising, given that the literature shows that amorphous regions are more reactive than the crystalline regions due to higher tensile stresses in the polymer chains (Popov et al., 1983) as well as higher diffusion rates of reactants (Hori et al., 1973), and should be more easily oxidized. One of the trends seen in the data is linearly increasing fluorescence intensities over the course of ~0.5 cm. The fact that the sizes of the fluorescence features are much larger than the sizes of the amorphous and crystalline regions indicates that it is not solely the crystallinity that determines susceptibility to oxidative attack.

**Fluorescence intensity of oxidized and unoxidized polyethylene films**

Both labeling schemes (with and without EDC) were used for oxidized and unoxidized regions of the same polyethylene film. For both oxidized and unoxidized tests, two different locations of the same sample were surveyed, and EDC tests were performed on separate areas of the same source material as the fluorescence tests without EDC. Without EDC, only aldehydes and ketones are labeled, with EDC, aldehydes, ketones, and carboxylate groups are labeled. The fluorescence intensity data from these tests are shown in Table 3.

From these data, a few observations can be made. First, for oxidized polyethylene, the fluorescence intensity is always higher by a factor of 1.5-3 than with unoxidized polyethylene. Secondly, there is a lot of variation in intensity between some of the sites surveyed. The variation of the intensities of the two oxidized sites is larger than difference between the intensity of the unoxidized sites and one of the oxidized sites. This variability is also demonstrated in Figures 57 and 58, in which there are large degrees of spatial non-uniformity – that the average
intensity of one of the sections surveyed is not indicative of the average intensity of
the entire exposed area. An additional manifestation of this issue is that the
fluorescence intensity of the unoxidized polyethylene + EDC is lower than
unoxidized polyethylene without EDC. EDC catalyzes reactions of the dye additional
functional groups on the surface, so the intensity of polyethylene that was reacted
with dye in the presence of EDC should be higher than without EDC.

With the concerns outlined above, it is difficult to obtain representative
numbers to accurately quantitatively compare the oxidation of the two samples.
However, the trend is still clear that exposure to the pretreating electrolyte
increases the number of carbonyl and carboxylate groups.

**XPS surface analysis of polyethylene surface**

XPS measurements, also referred to in the literature as ESCA (electron
spectroscopy for chemical analysis) has been performed on polyethylene by a
variety of authors (Terlingen et al., 1995, Medard et al., 2002, Bentjen et al., 1992,
Everhart and Reilley, 1981, Briggs et al., 2003), employing a variety of surface
treatments including exposure to corona discharge, plasma etching, and
electrochemical exposure (oxidizing electrolytes). Oxidation products could be
detected by two different measurement systems: presence of the O1s binding
energy, or higher energy shoulder on the C1s binding energy curve, indicating a
change in bonding environment for the carbon atoms (Everhart and Reilley, 1981).
The binding energy of carbon in the middle of a polyethylene chain is 285.0 eV, with
a width of 1.86 eV, as part of a carbonyl group the binding energy is 288.1 eV with a
width of 1.74 eV, and as part of a carboxylate group it is 289.4 eV with a width of
1.89 eV. Thus, with sufficient resolution of the XPS spectra, it is possible to employ
beam fitting to determine the specific contribution of each of the bonding
environments. Lower resolution can determine the atomic weight percent of
oxygen on the surface, but not the bonding environment.

Another trend in the literature is a saturation of oxidation level in the
polyethylene after treatment, as shown by the O1s scan. Some researchers report
saturation levels as low as 14% (Terlingen et al., 1995), others reported levels of
18% (Everhart and Reilley, 1981), and others at 21% (Medard et al., 2002). This
saturation is attributed to the removal of etched sections of polyethylene by carbon
bond scission.

Only some researchers used XPS to study the bonding environment (Briggs
et al., 2002); others used different techniques for determining the bonding state of
oxygen. Medard et al. used titration to determine carboxylate concentration,
Rasmussen et al. used ATR-IR to determine hydroxide concentration.

The XPS results presented in this work show the spectra from two different
parts of the same polyethylene film, one location that was exposed to 1M FeCl₃ + 1M
H₂SO₄ electrolyte for one month without the application of voltage, and another location that was not. These results are shown in the table below:

<table>
<thead>
<tr>
<th>XPS line</th>
<th>Peak ID</th>
<th>Chem Shift</th>
<th>BE</th>
<th>Assignment</th>
<th>Group%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Control</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁s</td>
<td>Pk01</td>
<td>0.0</td>
<td>285.0</td>
<td>C-C, C-H</td>
<td>97.3</td>
</tr>
<tr>
<td>C₁s</td>
<td>Pk02</td>
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<td>286.3</td>
<td>C-O</td>
<td>1.3</td>
</tr>
<tr>
<td>C₁s</td>
<td>Pk03</td>
<td>3.4</td>
<td>288.4</td>
<td>C-C-O, C=O, O-C=C*</td>
<td>1.4</td>
</tr>
<tr>
<td><strong>Control</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₁s</td>
<td>Pk01</td>
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<td>532.2</td>
<td>O=C</td>
<td>64.2</td>
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<tr>
<td>O₁s</td>
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<td>533.9</td>
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<td>35.8</td>
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This table summarizes the results from the XPS spectra. The labeled columns from left to right indicate the electron shell from which the photon originated, the individual peak that made up the spectrum of that photon, the shift in eV of that photon from the expected polyethylene binding energy, the binding energy in eV, the functional group it is ascribed to, and the relative amount of the group present in the sample. For the ‘assignment’ column, separating the different C-C-O, C=O, O-C=C groups was too difficult to do with the energy resolution of the available spectrometer.

What is immediately clear from this summary is that the amount of carbon atoms that are bound to an oxygen atom increases from 2.7% to 7.5% when the film is exposed to the oxidizing electrolyte. This increase of almost a factor of three in amount of oxidation groups is fairly symmetric between hydroxyl moieties (which would be included in the C-O peak) as well as carbonyl moieties.

Atomic spectra also indicated the percent composition of the two surveyed areas. These results are shown in Table 2.

What is seen in the Table 2 is that not only is the increased oxygen content in the etched sample, but there is also increased iron content. This finding is consistent with Briggs’ observation with polyethylene that was electrochemically etched with KMnO₄: there is a large oxygen content attributed to oxide deposits on the film surface. However, in this instance there is also data available from peak fitting the O₁s curve. This peak fitting indicated 79.4% of the oxygen on the surface.
was attributable to carbonyl bonds, and the rest bonded to iron. Briggs did identify in his work that peak fitting using the O1s spectrum is difficult, due to the large peak width relative to peak height and the chemical energy shifts expected. Likely some of the oxygen is bound up in oxide products, but from the common oxidation states of iron, no more than three oxygen atoms for every two iron atoms would be contained in deposited oxides. From these numbers, the oxygen bound to carbon atoms in various oxidation states is between 15-18% atomic weight, or a carbon-oxygen ratio of ~ 4-5. This is a little higher, but fairly close to what is reported in the literature for other processes of pretreatment.

**Role of morphology in the oxidation process**

Polyethylene is not a structurally homogenous material, but rather is composed of sections that are crystalline and amorphous. The difference between high density and low density polyethylene is the relative crystallinity: high density polyethylene is ~80% crystalline, low density is 40-50% crystalline, and crystallinity is directly related to density (Okada and Mandelkern, 1967). Research performed by Medard et al., (Medard et al., 2002) on high density polyethylene indicated that plasma treatment oxidized only the amorphous sections, which were found to have oxidation groups. This result may be due to the increased reactivity of carbon atoms next to methyl groups (Bentjen et al., 1992) compared to exposed chains. Side branches will interrupt the crystal packing, so carbon atoms near methyl groups are more likely to be in amorphous regions. It was also reported that there are bonds experiencing higher tension in amorphous regions (Popov et al., 1983). Additionally, as reactions that happen below the surface of the polyethylene require transport of reactants, it is reasonable to expect that the amorphous regions, being less dense, have higher diffusion rates for reactants (Hori et al., 1977).

In summary, evidence of oxidation groups on the polyethylene surface after exposure to ferric chloride electrolytes was observed with both XPS and fluorescence tests. The fluorescence tests showed spatially non-uniform fluorescence intensity, which may contribute the variation in current density between polyethylene samples.
Conclusions

The current density vs. voltage of polyethylene contacted by electrolytes was measured for applied voltages of 0.1 – 6 kV. Solutions that contained ferric ions and either chloride or nitrate ions lead to significantly higher current densities when 1M NaCl on the opposite side of the polyethylene was connected to the high voltage lead of the voltage supply. 1M KMnO₄ lead to high current densities when connected to the high voltage lead of the power supply and the 1M NaCl connected to ground. A solution that is 0.23M K₂Cr₂O₇ + 15M H₂SO₄ leads to the same current-voltage behavior as the solutions containing both ferric and chloride ions. Solutions with a high ratio of chloride to ferric ions lead to higher current densities.

Exposure of the polyethylene to some of the solutions (1M FeCl₃ + 1M H₂SO₄, 7 parts K₂Cr₂O₇, 12 parts H₂O, 150 parts H₂SO₄ and deoxygenated 0.66M FeCl₃ + 2M KCl) lead to higher current densities when subsequently tested with 1M NaCl, as compared with polyethylene contacted by 1M NaCl and no exposure. Exposure to a voltage ramp in the presence of 1M NaCl does not increase the current density vs. voltage on subsequent tests. The effect of these exposures was increased for longer exposure times, and larger voltage ramps.

Electrons can be injected into polyethylene either by thermionic emission over a potential barrier or a combination of thermal excitation and quantum tunneling through the barrier. Using metallic contacts, the combination of image charge effects and an applied electric field decreases the height of this barrier at higher applied electric fields. With electrolytic contacts, electron energy at the polyethylene-electrolyte interface is equal, such that an applied electric field also lowers the potential barrier to injection. Additionally, the conduction band of the polyethylene directly next to the electric contact can be much lower than bulk. In this model, an electron from an injecting component in the electrolyte would be either thermally excited over a lowered potential barrier, or thermally excited and tunnel through a shortened potential barrier, and injected into an empty state in the polyethylene.

Carbonyl groups provide additional surface energy states in polyethylene, providing vacant states into which electrons can be injected, and lowering the band gap from 8-9 eV to 3.65 eV. These carbonyl groups may persist past 2 μm into the polyethylene. Interaction of these carbonyl group energy states increases the conductivity of polyethylene, which allows more of the applied voltage to drop over the unoxidized region, which increases the conductivity in that region.

Analysis of polyethylene samples that had been exposed to 1M FeCl₃ + 1M H₂SO₄ for one month was performed by XPS and fluorescence microscopy. EIS
spectra were obtained before and after exposure of polyethylene to high voltage in the presence of 1M FeCl₃ + 1M H₂SO₄.

EIS spectra showed no significant change after the application of voltage to polyethylene contacted by 1M FeCl₃ + 1M H₂SO₄. For polyethylene exposed to 1M FeCl₃ + 1M H₂SO₄ for a month, oxidation products were detected by two surface analysis techniques: fluorescence spectroscopy and X-ray photoelectron spectroscopy.

A mechanism of action of the 1M FeCl₃ + 1M H₂SO₄ solutions was proposed in which FeCl₄⁻ complexes in solution catalyze the generation of radicals through the oxidation of an anion. It was also observed the 1M FeCl₃ + 1M H₂SO₄ had higher current densities than 1M NaCl even when the effect of the exposure was compensated for, indicating higher rates of charge injection into a similarly affected polyethylene surface.

Future work on this project would include the calculations of the speciation of the different electrolytes used in order to determine relative contributions of the different components in the electrolyte to charge injection behavior.

With a better understanding of the effects of different electrolytes on charge injection behavior in polyethylene (both in terms of introducing oxidation groups on the surface as well as participating in charge transfer reactions), more targeted diagnostics of power cable integrity could be developed based on electrolytic composition of the water in and around the ducts in which the cables are housed. This would allow more diagnostic resources to be used where they are most needed, and allow the remaining low-risk areas of our ageing electrical infrastructure continued use.
References

Marston AL, Bush SF, Appl. Spectr., Vol. 26, No. 6, pp. 579-584, 1972
Appendix 1: Current vs. time

Figures 4 and 61 show the current as a function of time for polyethylene contacted by the 1M FeCl₃ + 1M H₂SO₄ or 1M CuSO₄ electrolyte on one side and 1M NaCl on the opposite side, subjected to a potential ramp in which the electrode immersed in the 1M NaCl electrolyte was stepped 100 V with respect to the electrode immersed in the 1M FeCl₃ + 1M H₂SO₄ electrolyte every 20 s.

The current vs. time plots indicate that for each of these injecting electrodes, certain features are evident. Each step begins with a large current spike, which decays into a lower current. For the rest of the voltage step, three different behaviors may be observed. In Figure 4, at the lower potentials (V < 1.2 kV), the current decays almost monotonically, with a decay that becomes faster and faster with increasing voltage. At mid-level potentials (1.2 kV < V < 1.9 kV), the current still decays at each voltage step, but there are a number of small current spikes (followed by an immediate decay) at each voltage step, increasing in number at the higher potentials. At high potentials (V > 1.8 kV) for the 1M FeCl₃ + 1M H₂SO₄, the rate of current decay with time decreases, levels out, and eventually the current increases over the course of the voltage steps. In this region, the number of small current spikes at each step increases and the current vs. time graph appears to be very noisy.

Some of these features are also seen for a current vs. time plot for a sample in which a 1M CuSO₄ electrolyte is used instead of the 1M FeCl₃ + 1M H₂SO₄ electrolyte. The behavior at low potentials is the same as when 1M FeCl₃ + 1M H₂SO₄ is used, in that each step shows a current spike (followed by a fast decay) followed by a slow decay. At higher applied potentials for the CuSO₄ plot the current decays are faster, and small current spikes appear, just as with the 1M FeCl₃ + 1M H₂SO₄ plot. However, at high applied potentials, the current decays never stop or level out, and the number of current spikes at each voltage step is much fewer with 1M CuSO₄ than with 1M FeCl₃ + 1M H₂SO₄. It is also necessary to point out that the cell current with CuSO₄ is more than an order of magnitude smaller than with 1M FeCl₃ + 1M H₂SO₄.

The large-amplitude, short-duration current spikes and decays are thought to be due to charging and ion rearrangement in the electrolyte (and not charge conduction in the polyethylene). This was determined after the voltage source was set up so that each lead was immersed in separate beakers of electrolyte on a bench top. This setup was a very close approximation to an open circuit in that the only path for current to flow was across the table between the beakers. The power supply applied the same voltage steps used in the electrochemical tests with the polyethylene to the separated electrodes while the picoammeter recorded the current that flowed between the leads. The current vs. time plot for this experiment showed that for each voltage step there was a current spike followed by a fast decay to zero. This can be explained by the fact that the leads from the power supply injected or extracted charge from their surroundings until the potential between the
two electrodes was the potential set by the voltage source. The picoammeter recorded the injected charge as the current spike, but as the electrolytes reached the same potential as the electrode, then no charge flowed and the current was zero.

The small current spikes that appear in the current vs. time plots (Figures 4 and 61) in the middle voltages are thought to be partial discharges. Partial discharges were found in the literature to become more prevalent at higher voltages (which corresponded to higher currents), although the partial discharges were only recorded with one electrode material contacting the polyethylene (Watanabe, 1978). Without using different electrode materials, it is not clear from Watanabe’s work if higher currents lead to more partial discharges at a given voltage. For both of the current vs. time plots described (1M FeCl$_3$ + 1M H$_2$SO$_4$ or 1M CuSO$_4$, paired with NaCl), the current spikes appear at middle applied potentials (V > 1.2 kV) and increase in frequency at higher applied potentials. The frequency of partial discharges is also higher for the 1M FeCl$_3$ + 1M H$_2$SO$_4$ plot than the CuSO$_4$ plot.

At higher voltages with 1M FeCl$_3$ + 1M H$_2$SO$_4$, high currents are also present, and after the initial sharp decrease the current no longer decays with time at each voltage step. This behavior is consistent with thermal dissipation coupled with self-reinforcing injection mechanisms, in which electron injection leads to temperature increase, which leads to increased injection. Schottky injection is enhanced at elevated temperature, and the conduction process requires dissipation of energy as the electron interacts with the lattice in the presence of the field. At high enough currents, specific volumes of the polyethylene are not able to dissipate heat to the surroundings at an equivalent rate that is being produced through electron collisions. At this time, the sample heats up, which increases its conductivity, and further increases the amount of current that flows and energy produced. For 1M FeCl$_3$ + 1M H$_2$SO$_4$, this process slows the current decay at some voltage steps, stops the decay completely at higher voltage steps, and then the current increases during each voltage step. It is on top of this behavior that the partial discharges occur.

**Current decay**

For Figure 61 at all potentials and Figure 4 at potentials less than 1.9 kV, after an abrupt increase the current decays throughout the entire time following each voltage step. This decay has been seen in dielectrics and is referred to in the literature as absorption or transient currents (Wintle, 1974). Work by Das Gupta and Brockley (Das Gupta and Brockley, 1978) determined that the current followed an exponential decay, such that

$$I(t) = A(T)t^{-n}$$  \(\text{(25)}\)

in which \(n \approx 1\). If the temperature were constant throughout the voltage ramp, then \(A(T)\) would also be constant.
There are three different mechanisms that could result in current decay for an insulating film contacted by electrodes (Walden, 1972): dipole relaxation, ionic drift within the insulator, and space charge effects at the electrode interface. The effect of ionic drift can be essentially ruled out in our experiments due to the dependence of current density (and current decay) on the identity of the aqueous electrolyte contact. Dipole relaxation could lead to a monotonic current decay if the dipoles are non-uniformly distributed throughout the insulator.

A more likely cause of the current decay is through the development of space charges in the polyethylene. Polyethylene is a wide gap insulator (Lewis, 2002) and the available states that can accept an injected electron are highly localized (Anta et al., 2002), known as traps. While it is easier for electrons to be injected into polyethylene (Bamji et al., 1986), a donor state in the polyethylene would also be highly localized and due to an impurity as the carbon chains in polyethylene are extremely difficult to oxidize. The consequence of the localized nature of the traps is that the electrons, once injected into polyethylene, do not quickly move across the potential gradient, but rather are 'trapped' in the potential wells of the surface states. These trapped charges subsequently lower the apparent field across the polyethylene-electrode interface (Walden, 1972), leading to a decrease in the charge injection rate across that interface. As more charge is injected, more charge is trapped, leading to lower and lower currents. However, the trapped charge is able to move slowly away from the interface, allowing more charge to be injected, via various conduction mechanisms discussed earlier. The presence of the space charges in polyethylene has been experimentally measured in the literature (Suzuoki et al, 1991, Belgaroui et al., 2009), and space charge was measured in polyethylene at both the anode and cathode.

**Current at t=19s**

As is evident from the 1M FeCl₃ + 1M H₂SO₄ data in Figure 4, the current does not reach steady-state values at the end of a 20 second voltage step, when the current is measured. Thus, for different electrolytes leading to different rates of current decay at a particular voltage step, it is necessary to connect the current measured at 19 seconds to the charge injection ability of the various electrolytes used.

At t=0, when the voltage step is started, there are empty states at the polymer surface into which electrons could be injected. As electrons enter these empty surface states, they provide an electric field that will repel other electrons, which lowers the local field at the interface. This lower field at the surface decreases the injection rate of other electrons into the polyethylene. Electrons at the surface are subjected to two different gradients leading to electron current: a concentration gradient and a potential gradient. Steady-state current would be reached when current density at the interface is the same as the current density at any other depth into the polyethylene. At each subsequent voltage ramp directly
after application of the voltage, there are additional electrons (incorporated in ions in solution) brought to the polyethylene-electrolyte interface, which lead to a larger local field than was present before. This larger local field will make electron injection occur at a higher rate as some surface states will be more accessible through field-lowering of the energy barrier. Additionally, the larger electric field will cause electrons to move away from the surface at a faster rate.

While steady-state currents are not reached in the experiments presented in this work, it is still possible to arrive at qualitative conclusions about the relationship between current density at t=19 seconds and the magnitude of the steady-state current density. Comparing two different electrolytes injecting charge into identical polyethylene films, at t=0 the current density through that interface should directly reflect each electrolytes ability (based on energy level, concentration, catalysis, etc.) to inject charge. However, immediately after any difference in charge injection rates between the two electrolytes, the polyethylene surfaces of these two cases are no longer the same – the surface in which greater charge had been injected would have a lower local field due to increased space charge at the interface. From this opposing field, the higher the initial injection rate (due to electrolyte ability), the higher the rate of decrease of injection rate. The question, therefore, is whether or not space-charge lowering of the local field can cause a lower current density.

Figure 62 shows the current vs. time for 1M FeCl$_3$ + 1M H$_2$SO$_4$, and 1M CuSO$_4$, in which the 1M CuSO$_4$ current has been multiplied by a constant (in the case a value of 22 was chosen) so that the currents for both electrolytes were comparable (if we assume that the current decays according to equation (26), then multiplying one curve by a constant will not change its decay behavior). For this comparison, 1M CuSO$_4$ was chosen as it has the same low current density as 1M NaCl, and can be compared to the high current density with 1M FeCl$_3$ + 1M H$_2$SO$_4$. Additionally, the CuSO$_4$ plot was smoothed for comparison. For this Figure, the times compared are 200 to 400 seconds, corresponding to voltage steps between 1 kV to 1.9 kV. These times were chosen so that the currents were high, but not so high that partial discharges and thermal runaway would play a large role.

What is clear from the data in Figure 62, especially in the first voltage step corresponding to 1 kV, is that the current vs. time plots do not have the same exponential decay constant as proposed by Das Gupta and Brockley, but rather an additional absorption mechanism is operative and is only apparent when current densities are low. At the beginning of the magnified 1M CuSO$_4$ 1 kV step, the current is much higher than the 1M FeCl$_3$ + 1M H$_2$SO$_4$ step, but for the latter part of the voltage step the current decrease is fairly similar. This last point may be made more clearly by using a log-log plot of the 1 kV voltage step showing the data for 1M FeCl$_3$ + 1M H$_2$SO$_4$ and 1M CuSO$_4$, shown in Figure 4 (with the beginning of the voltage step reset to t=0). Firstly, it is necessary to change the current decay equation (25) to account for steady-state current, leading to equation (26):
\[ I(t) = A(T)t^{-n} + I_{ss} \]  \hspace{1cm} \{26\}

where \( I_{ss} \) is the steady-state current reached at infinite time. Comparing the top two plots shown in Figure 62, it is clear from the magnified 1M CuSO\(_4\) curve that the current decays at much faster rate at the beginning of the step, and towards the end of the step the currents decay at roughly the same rate as the 1M FeCl\(_3\) + 1M H\(_2\)SO\(_4\) test. From this, we can propose an additional decay term in equation \{27\}:

\[ I(t) = A t^{-n} + B t^{-m} + I_{ss} \]  \hspace{1cm} \{27\}

in which \( n < m \). If \( B \) is independent of current density, then it follows that current decay due to the \( B \) term would be more prevalent in the magnified 1M CuSO\(_4\) curve in Figure 63, and the same magnitude of decay due to the \( B \) term would be insignificant on the 1M FeCl\(_3\) + 1M H\(_2\)SO\(_4\) curve. The absorption process from the \( B \) term in this example would be a phenomenon that is due to applied voltage and not charge injection, as the effect is only visible when the charge injection rates are low. An absorption process that fits this description is dielectric relaxation: current decay due to reorganization of the dielectric (Wintle, 1974).

The important point is that the rate of current decay for 1M FeCl\(_3\) + 1M H\(_2\)SO\(_4\) test is lower than that of 1M CuSO\(_4\) throughout the voltage test. If this behavior is extrapolated, it indicates that steady-state current for 1M FeCl\(_3\) + 1M H\(_2\)SO\(_4\) is greater than 1M CuSO\(_4\).
Figures
Figure 1. Cross section of an insulating cable. At the center is the central conductor, in this case braided aluminum. The semi-con layer is the thin black layer around the central conductor. The thick orange layer is the insulation. The next layer is the insulation shield, followed by concentric neutral copper wires, which are imbedded in the outer jacket.
Figure 2. Schematic of the test apparatus. The 25 µm thick polyethylene film is sandwiched between two glass L-shaped tubes with an inner diameter of 15 mm. An 18 mm inner diameter rubber o-ring is used to keep a water-tight seal.
Figure 3. L-shaped glass tubes clamped around a 25 μm thick LDPE sample. 1M FeCl$_3$ + 1M H$_2$SO$_4$ is in one side and 1M NaCl is in the other. The picoammeter is located between the resistor and the ground connection of the power supply.
Figure 4. Current vs. time for polyethylene contacted by 1M \( \text{FeCl}_3 \) + 1M \( \text{H}_2\text{SO}_4 \) on one side and 1M \( \text{NaCl} \) on the other. The 1M \( \text{NaCl} \) side started at 100 V relative to the grounded 1M \( \text{FeCl}_3 \) + 1M \( \text{H}_2\text{SO}_4 \) electrolyte and was raised 100 V every 20 s.
Figure 5. Current density at 19 s vs. voltage for polyethylene contacted by 1M FeCl₃ + 1M H₂SO₄ on one side and 1M NaCl on the other. Each curve is represented by the average of four tests with the error bars denoting standard deviation. The “reverse” curve indicates the polarity of the cell when the 1M NaCl is subjected to the increasing voltage and the 1M FeCl₃ + 1M H₂SO₄ is held at ground. The “forward” curve is the opposite polarity.
**Figure 6.** Current density at 19 s vs. voltage for polyethylene contacted by 1M NaCl on both sides. The curve is represented by the average of four tests with the error bars denoting standard deviation.
**Figure 7.** Current density at 19 s vs. voltage for polyethylene contacted by 1M CuSO$_4$ on one side and 1M NaCl on the other. Each curve is represented by the average of four tests with the error bars denoting standard deviation. The “reverse” curve indicates the polarity of the cell when the 1M NaCl is subjected to the increasing voltage and the 1M CuSO$_4$ is held at ground. The “forward” curve is the opposite polarity.
Figure 8. Current density at 19 s vs. voltage for polyethylene contacted by 1M KMnO₄ on one side and 1M NaCl on the other. In this Figure, the forward curve is given by the average of five tests, while the reverse curve is the average of four tests, with the error bars denoting standard deviation. The “reverse” curve indicates the polarity of the cell when the 1M NaCl is subjected to the increasing voltage and the 1M KMnO₄ is held at ground. The “forward” curve is the opposite polarity.
Figure 9. Current density at 19 s vs. voltage for polyethylene contacted by 1M FeCl$_3$ + 1M H$_2$SO$_4$ and 1M KMnO$_4$ (curve "FeCl3/KMnO4", two tests) compared with 1M FeCl$_3$ + 1M H$_2$SO$_4$ (curve "FeCl3", four tests), both in reverse bias with 1M NaCl as the opposite electrolyte. The data represent the average and the error bars are the standard deviation for each curve.
**Figure 10.** Current density at 19 s vs. voltage for polyethylene contacted by 1M FeCl$_3$ + 0.1M H$_2$SO$_4$ on one side and 1M NaCl on the other. The data show the average of four tests in reverse bias with the standard deviation shown on the error bars.
Figure 11. Current density at 19 s vs. voltage for polyethylene contacted by different concentrations of FeCl₃ in 1M H₂SO₄ on one side, 1M NaCl on the other. The concentrations of FeCl₃ are indicated in the legend. Each curve is the average of at least four tests, with the error bars indicating the standard deviation.
Figure 12. Current density at 19 s vs. voltage for polyethylene contacted by 1M FeCl$_3$ + 1M H$_2$SO$_4$ on one side and 1M NaCl on the other. In this Figure, two thicknesses of LDPE are used: 25 µm (curve “1 mil”) and 76 µm (curve “3 mil”). Each curve is the average of four tests and the error bars are the standard deviation.
Figure 13. Same data as Figure 12, but with electric field as the x-axis.
Figure 14. Current density at 19 s vs. voltage for polyethylene contacted by Galinstan on both sides. The curve is represented by the average of four tests with the error bars denoting standard deviation.
Figure 15. Current density at 19 s vs. voltage for polyethylene contacted by 1M HCl + 3M NaCl on one side and 1M NaCl on the other, in reverse bias. The curve is represented by the average of four tests with the error bars denoting standard deviation.
Figure 16. Current density at 19 s vs. voltage for polyethylene contacted by different ferric salts at with equal concentrations of ferric ions on one side, 1M NaCl on the other. The curve “Fe2(SO4)3” is 0.5M Fe2(SO4)3, “ferric nitrate” is 1M Fe(NO3)3, and “FeCl3 no acid” is 1M FeCl3. Each curve is the average of four tests, with the error bars indicating the standard deviation.
Figure 17. Current density at 19 s vs. voltage for polyethylene contacted by different iron sulfate salts at with equal concentrations of iron ions on one side, 1M NaCl on the other. The curve “FeSO4 + Fe2(SO4)3” is 0.5M FeSO4 + 0.25M Fe2(SO4)3 “Fe2(SO4)3” is 0.5M Fe2(SO4)3, ”FeSO4” is 1M FeSO4. Each curve is the average of four tests, with the error bars indicating the standard deviation.
Figure 18. Current density at 19 s vs. voltage for polyethylene contacted by different concentrations of ferric sulfate, ferric chloride, and sodium chloride, with the concentrations of ferric and chloride ions in each solution represented in the legend. Each curve is the average of four tests, with the error bars indicating the standard deviation.
Figure 19. Selected data from Figures 4, 15, and 17 showing current density at 19 s vs. voltage for polyethylene contacted by ferric ions (with no chloride), chloride ions (with no ferric) and both ferric and chloride ions, with electrolyte composition represented in the legend. Each curve is the average of four tests, with the error bars indicating the standard deviation.
Figure 20. Current density at 19 s vs. voltage for polyethylene contacted by KMnO₄ solutions both with and without NaOH added and 1M NaCl on the other, in forward bias. The curve “forward” is 1M KMnO₄, and the curve “forward 5.29” is 1M KMnO₄ + solid NaOH, such that the corrosion potential of platinum in solution is lowered from 0.957 V to 0.549 V vs. SCE. The curves are represented by the average of four (“forward 5.29”) or five (“forward”) tests with the error bars denoting standard deviation.
**Figure 21.** Current density at 19 s vs. voltage for polyethylene contacted by KMnO$_4$ solutions both with and without NaOH added and 1M NaCl on the other, in reverse bias. The curve “reverse” is 1M KMnO$_4$, and the curve “reverse 5.29” is 1M KMnO$_4$ + solid NaOH, such that the corrosion potential of platinum in solution is lowered from 0.957 V to 0.547 V vs. SCE. The curves are represented by the average of four tests with the error bars denoting standard deviation.
Figure 22. Current density at 19 s vs. voltage for polyethylene contacted by 1M FeCl₃ + 1M H₂SO₄ on one side and 1M NaCl on the other, in forward bias. The polyethylene samples in this test were previously exposed to a pretreatment consisting of a 2 kV voltage ramp in the presence of 1M FeCl₃ + 1M H₂SO₄ in reverse bias. The polyethylene was subjected to a forward bias voltage ramp in the presence of 1M FeCl₃ + 1M H₂SO₄ after the pretreatment step. The curve is the average of four tests with the standard deviation represented by the error bars.
Figure 23. Current density at 19 s vs. voltage for polyethylene contacted by 1M FeCl₃ + 1M H₂SO₄ on one side and 1M NaCl on the other, in reverse bias. The polyethylene samples in this test were previously exposed to a pretreatment consisting of a 2 kV voltage ramp in the presence of 1M FeCl₃ + 1M H₂SO₄ in reverse bias. The polyethylene was subjected to a reverse bias voltage ramp in the presence of 1M FeCl₃ + 1M H₂SO₄ after the pretreatment step. The curve is the average of four tests with the standard deviation represented by the error bars.
Figure 24. Current density at 19 s vs. voltage for polyethylene contacted by 1M KMnO$_4$ on one side and 1M NaCl on the other, in forward bias. The polyethylene samples in this test were previously exposed to a pretreatment consisting of a 2 kV voltage ramp in the presence of 1M FeCl$_3$ + 1M H$_2$SO$_4$ in reverse bias. The polyethylene was subjected to a forward bias voltage ramp in the presence of 1M KMnO$_4$ after the pretreatment step. The curve is the average of four tests with the standard deviation represented by the error bars.
Figure 25. Current density at 19 s vs. voltage for polyethylene contacted by 1M KMnO$_4$ on one side and 1M NaCl on the other, in reverse bias. The polyethylene samples in this test were previously exposed to a pretreatment consisting of a 2 kV voltage ramp in the presence of 1M FeCl$_3$ + 1M H$_2$SO$_4$ in reverse bias. The polyethylene was subjected to a reverse bias voltage ramp in the presence of 1M KMnO$_4$ after the pretreatment step. The curve is the average of four tests with the standard deviation represented by the error bars.
Figure 26. Current density at 19 s vs. voltage for polyethylene contacted by 1M CuSO₄ on one side and 1M NaCl on the other, in forward bias. The polyethylene samples in this test were previously exposed to a pretreatment consisting of a 2 kV voltage ramp in the presence of 1M FeCl₃ + 1M H₂SO₄ in reverse bias. The polyethylene was subjected to a forward bias voltage ramp in the presence of 1M CuSO₄ after the pretreatment step. The curve is the average of three tests with the standard deviation represented by the error bars.
Figure 27. Current density at 19 s vs. voltage for polyethylene contacted by 1M CuSO₄ on one side and 1M NaCl on the other, in reverse bias. The polyethylene samples in this test were previously exposed to a pretreatment consisting of a 2 kV voltage ramp in the presence of 1M FeCl₃ + 1M H₂SO₄ in reverse bias. The polyethylene was subjected to a reverse bias voltage ramp in the presence of 1M CuSO₄ after the pretreatment step. The curve is the average of three tests with the standard deviation represented is by the error bars.
Figure 28. Current density at 19 s vs. voltage for polyethylene contacted by 1M NaCl on both sides. The polyethylene samples in this test were previously exposed to a pretreatment consisting of a 2 kV voltage ramp in the presence of 1M FeCl$_3$ + 1M H$_2$SO$_4$ in reverse bias. The polyethylene was subjected to a voltage ramp of the opposite polarity with 1M NaCl on both sides after the pretreatment step. The curve is the average of four tests with the standard deviation represented is by the error bars.
Figure 29. Current density at 19 s vs. voltage for polyethylene contacted by 1M NaCl on both sides. The polyethylene samples in this test were previously exposed to a pretreatment consisting of a 2 kV voltage ramp in the presence of 1M FeCl$_3$ + 1M H$_2$SO$_4$ in reverse bias. The polyethylene was subjected to a voltage ramp of the same polarity with 1M NaCl on both sides after the pretreatment step. The curve is the average of three tests with the standard deviation represented by the error bars.
Figure 30. The data point “after pretreatment” correspond to the current density at 3 kV for polyethylene subjected to a voltage ramp in the presence of different electrolytes after a 2 kV ramp in the presence of 1M FeCl₃ + 1M H₂SO₄ in reverse bias. In this graph, “FeCl₃” corresponds to 1M FeCl₃ + 1M H₂SO₄, “KMnO₄” corresponds to 1M KMnO₄, “NaCl” corresponds to 1M NaCl, and “CuSO₄” corresponds to 1M CuSO₄. After each electrolyte on the x-axis, “f” means the test after the pretreatment was done in forward bias, and “r” means reverse bias. All data points are the average of four tests except for “CuSO₄” points which are the average of three test. The standard deviation is indicated by the error bars. The curve “no pretreatment” is the data for polyethylene not subjected to a pretreatment test with 1M FeCl₃ + 1M H₂SO₄.
Figure 31. The curve “no treatment” for all three data points is the current density at the 3 kV voltage step of a standard test for a polyethylene sample contacted by 1M NaCl on both sides. The “after exposure” data points are the current density at the 3 kV voltage step of a voltage ramp for polyethylene samples that are subjected to different pretreatment protocols. The data point “feCl3/NaCl F” is the pretreatment step from Figure 28, the data point “feCl3/NaCl R” is the pretreatment step from Figure 29, and the data point “NaCl/NaCl” is when 1M NaCl is used for the 2 kV pretreatment instead of 1M FeCl3 + 1M H2SO4. Each point is the average of four tests with the standard deviation indicated by the error bars.
Figure 32. Current density at 19 s vs. voltage for 1M NaCl on both sides of polyethylene. The two curves result from two different pretreatment protocols that preceded the 1M NaCl test. Each pretreatment involves a voltage ramp in the presence of 1M FeCl$_3$ + 1M H$_2$SO$_4$. For the “.5 kV pretreat” curve, the voltage ramp ended at 0.5 kV. The “2 kV pretreat” is the data from Figure 29. Each data point is the average of four tests with the error bars indicating the standard deviation.
Figure 33. Current density at 19 s vs. voltage for polyethylene contacted by 1M NaCl on both sides. The polyethylene samples in this test were previously exposed to 1M FeCl$_3$ + 1M H$_2$SO$_4$ for either 10 minutes or 1 minute with no voltage applied. The polyethylene was then subjected to a voltage ramp of the same polarity with 1M NaCl on both sides after the pretreatment step. The curves are the average of four tests with the standard deviation represented is by the error bars.
Figure 34. Current density at 19 s of the 3 kV step of a voltage ramp for polyethylene contacted by 1M NaCl on both sides. Both data points are from different pretreatment protocols, with “10 min” indicating a 10 minute exposure to 1M FeCl$_3$ + 1M H$_2$SO$_4$ with no applied voltage, and “2 kV ramp” exposure to a 2 kV ramp in the presence of 1M FeCl$_3$ + 1M H$_2$SO$_4$. Both points are the average of four tests with the standard deviation represented by the error bars.
Figure 35. Current density at 19 s vs. voltage for polyethylene contacted by a solution of 0.23M K$_2$Cr$_2$O$_7$ + 15M H$_2$SO$_4$ on one side and 1M NaCl on the other. Each curve is represented by the average of four tests with the error bars denoting standard deviation. The ‘reverse’ curve indicates the polarity of the cell when the 1M NaCl is subjected to the increasing voltage and the K$_2$Cr$_2$O$_7$ solution is held at ground. The ‘forward’ curve is the opposite polarity.
Figure 36. Current density at 19 s vs. voltage for polyethylene contacted by 1M NaCl on both sides. The polyethylene samples in this test were previously exposed to a pretreatment consisting of a 2 kV voltage ramp in the presence of 0.23M K$_2$Cr$_2$O$_7$ + 15M H$_2$SO$_4$ in reverse bias. The polyethylene was subjected to a voltage ramp of the same polarity with 1M NaCl on both sides after the pretreatment step. The curve is the average of three tests with the standard deviation represented is by the error bars.
Figure 37. Current density at 19 s vs. voltage for polyethylene contacted by 1M FeCl$_3$ + 1M H$_2$SO$_4$ on one side and 1M NaCl on the other, in reverse bias. The 1M FeCl$_3$ + 1M H$_2$SO$_4$ electrolyte is deoxygenated. The curve is represented by the average of four tests with the error bars denoting standard deviation.
Figure 38. Current density at 19 s vs. voltage for polyethylene contacted by 1M NaCl on both sides following one of two different pretreatments. The pretreatment for the curve “2 kV pretreatment” is 2 kV ramp with 1M FeCl₃ + 1M H₂SO₄ in reverse bias. The pretreatment for the curve “20 minutes deoxygenated pretreatment” is 20 minute exposure to deoxygenated 0.66M FeCl₃ + 2M KCl without an applied voltage. Each curve is the average of four tests with the error bars indicating the standard deviation.
**Figure 39.** EIS spectra of polyethylene contacted by $1\text{M FeCl}_3 + 1\text{M H}_2\text{SO}_4$ on one side and $1\text{M NaCl}$ on the other side. This spectrum was obtained before the application of voltage.
**Figure 40.** EIS spectrum of polyethylene shown in Figure 39 contacted by 1M FeCl$_3$ + 1M H$_2$SO$_4$ on one side and 1M NaCl on the other side. This spectrum was obtained after the application of any 2.5 kV.
**Figure 41.** EIS spectrum of polyethylene contacted by 1M FeCl$_3$ + 1M H$_2$SO$_4$ on one side and 1M NaCl on the other side. This spectrum was obtained before the application of any voltage.
Figure 42. EIS spectrum of polyethylene contacted by 1M FeCl$_3$ + 1M H$_2$SO$_4$ on one side and 1M NaCl on the other side, same sample as Figure 41. This spectrum was obtained after the application of 2 kV.
Figure 43. XPS results showing counts vs. binding energy for unetched polyethylene, indicating the relative elemental concentrations at the surface.
Figure 44. XPS results showing counts vs. binding energy for etched (exposed to 1M FeCl₃ + 1M H₂SO₄ for one month) polyethylene, indicating the relative elemental concentrations at the surface.
Figure 45. Electron energy as a function of distance from a metal with a work function of 4.5 eV. The curve “Image charge” is the contribution of the image charge effect to the electron energy, the curve “Electric field” is the contribution of the applied electric field to the electron energy, and the curve “Total potential” is the sum of the two previous curves. These curves are described by equations (4), (5), and the equation of electron energy in a constant electric field.
Figure 46. The energy of electrons in an insulator is shown by the ‘Total energy profile’ curve. The ‘Total energy profile’ curve is the addition of the ‘Energy from traps’ and the ‘Energy from applied electric field’ curve. These curves are described by equation \{4\} and the equation of electron energy in a constant electric field.
Figure 47. Qualitative plot of energy vs. distance for an electron on both sides of an electrolyte-organic crystal interface (from Lohmann and Mehl, 1975).
Figure 48. The curves from Figures 5 and 29 are shown, with the curve “FeCl3” corresponding to Figure 5 and curve “Pretreated with FeCl3, tested with NaCl” corresponding to Figure 29.
**Figure 49.** Diagram of electron energy as a function of distance into the insulator. Electron energy in the conduction band is calculated from equation (5). Defect states indicate localized energy states that exist below the level of the conduction band. In this plot, the defect states are shown close to the conduction band in order to show the detail of the image charge and electric field effects in the conduction band. The defect states can be much lower in energy than shown above.
Figure 50. Electric field as a function of distance for an insulator under space charge limited conditions. The curves are represented by equations {12} and {14}. 
Figure 51. Equivalent circuit of the Pt-electrolyte-polyethylene-electrolyte-Pt system. $R_s$ comprises solution and electrolyte-wire resistances, $R_{pe}$ and $C_{pe}$ are resistance and capacitance of polyethylene films.
Figure 52. Predicted impedance and phase angle as a function of frequency according to the equivalent circuit in Figure 51.
Figure 53. Equivalent circuit for polyethylene that has been exposed to an etchant. This figure uses the same notation as Figure 50, with the addition of $R_{OPE}$ and $C_{OPE}$ as the resistance and capacitance of the oxidized section and $R_{UPE}$ and $C_{UPE}$ as the resistance and capacitance of the unoxidized section of the polyethylene film.
Figure 54. Predicted impedance and phase angle as a function of frequency according to the equivalent circuit in Figure 53.
Figure 55. Predicted change in impedance if 10% of the film is conducting, according to the schematic in Figures 51 and 53.
Figure 56. Decrease in impedance as a function of frequency by comparing the data in Figures 39 and 40.
Figure 57. Texas Red fluorescence intensity as a function of location for two separate areas of oxidized polyethylene.
Figure 58. Texas Red fluorescence intensity as a function of location for two separate areas of unoxidized polyethylene.
Figure 59. Texas Red with EDC fluorescence intensity as a function of location for two separate areas of oxidized polyethylene film.
Figure 60. Texas Red with EDC fluorescence intensity as a function of location for two separate areas of unoxidized polyethylene film.
Figure 61. Current vs. time of polyethylene contacted by 1M CuSO$_4$ and 1M NaCl in reverse bias. Applied voltage started at 100 V and was increased 100 V every 20 s.
Figure 62. Current vs. time plots for 1M FeCl$_3$ + 1M H$_2$SO$_4$, 1M CuSO$_4$, and the same curve of 1M CuSO$_4$ multiplied by a factor of 22. Each curve is generated with an initial applied voltage of 100 V and increased 100 V every 20 s. Both tests were done in reverse bias.
Figure 63. Log-log plot of current vs. time for both multiplied 1M CuSO$_4$ (Figure 60) and 1M FeCl$_3$ + 1M H$_2$SO$_4$ (Figure 4). This specific section corresponds to the voltage step at 1 kV.