Prevention of marine biofouling is vital to the survivability and performance of ships, buoys, and wave energy devices. Coatings that contain metal biocides are currently used to prevent marine biofouling. These coatings have a limited lifetime and are under environmental scrutiny. As a result, it is necessary to research and develop alternative antifouling methods. One promising alternative is the electrochemical generation of oxidized chemical species.

Graphite-polyurethane thin film electrodes were prepared with < 20 µm synthetic graphite powder mixed with a polyurethane coating. Up to 89% sheet resistance uniformity was achieved. Open seawater tank experiments, conducted at Hatfield Marine Science Center, with 55 wt% graphite-urethane electrodes on fiberglass substrates were found to inhibit fouling when a constant potential of 1.5 V, 1.2 V, 1.1 V, or -1.5 V versus Ag/AgCl in seawater was applied. Electrodes held at extreme potentials (-1.5 V and 1.5
V) suffered damage after two weeks of use while the others showed no damage. A 22” long thin film electrode held at 1.1 V was unable to prevent fouling 10” from the electric power contact point, indicating that the local surface potential dropped below a threshold necessary to prevent fouling. It was also found that steel and aluminum substrates were unsuitable as a small scratch in the film electrode exposes the metal to rapid oxidation.

Because electrode voltage is vital to its own survivability and antifouling efficacy, voltage profiling experiments were conducted in 3.5 wt % solution of NaCl with 67 ppm Br\(^-\) from NaBr. A MATLAB program was created to fit model parameters to the experimental results and yielded R\(^2\) values better than 0.99. Mass transport effects on total current and voltage profile were insignificant for 43 wt % test panels. Both 43 and 55 wt % test panels yielded similar voltage profiles but differed in total current magnitudes.
Study of Graphite-Polyurethane Composite Thin Film Electrodes for Their Use In Electrochemical Antifouling Systems

by
Matthew A. Delaney

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Matthew A. Delaney, Author
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Study of Graphite-Polyurethane Composite Thin Film Electrodes for Their Use In Electrochemical Antifouling Systems

Chapter 1

INTRODUCTION

1.1: Marine Biofouling

All surfaces exposed to the marine environment are susceptible to biofouling, that is, the gradual growth and accumulation of biomass. Biofouling can occur on the hulls of ships, buoys, and wave energy converters if unprotected. Increased water drag, vessel weight, hull corrosion and crevice formation are some of its detrimental effects [1]. This in turn adversely affects the overall performance and lifetime of these ocean-faring structures. For these reasons, it is vital to prevent biofouling.

1.2: Preventing Marine Biofouling

Traditional methods to protect surfaces from biofouling use paints laced with metal biocides. Copper biocides are the most common after tin biocides were banned globally in 2001 due to increasing evidence and concerns regarding their impact on surrounding ecosystems [1]. Though less harmful than tin, copper also poses some environmental risks and is likely to face regulatory scrutiny in the near future. Another problem with biocide paints in general is that the coating eventually becomes vulnerable after biocide depletion, requiring the reapplication of a fresh coat approximately every three years [1]. Consequently, researchers are studying new methods to improve the lifetime and antifouling efficacy while also minimizing their environmental impact. One
such promising alternative antifouling system is the electrochemical prevention of marine biofouling.

1.3: Electrochemical Prevention of Marine Biofouling

Electrochemical marine antifouling systems offer some advantages over biocide coatings. Accumulation of biocides was not observed in preliminary studies conducted on electrochemical antifouling systems [2]-[4]. The lifetime of electrochemical antifouling systems may exceed those of biocide coatings because they do not eventually deplete their biocide.

Proof of concepts for different electrochemical antifouling systems have been published by researchers in Japan [2],[3],[5]. All systems share the following components:

- Protected surface electrode.
- Counter electrode to complete electric circuit.
- Reference electrode (if potentiostatic control is desired).
- Voltage and current monitor device (possibly a potentiostat).

Electrochemical antifouling systems control electric power dissipation either by holding the voltage constant (potentiostatic) or holding the current constant (galvanostatic). A diagram of a complete electrochemical antifouling circuit is presented in Figure 1.
A majority of the research into electrochemical antifouling technology goes into the type of material used as the surface electrode and its performance. Rigid graphite polyurethane plates, graphite-polyurethane coatings, and titanium alloys are all documented as being suitable electrodes [2],[6]. However, little research is presently available that investigates how to apply electrochemical systems to large structures like ship hulls and wave energy converters. The following issues must be investigated and resolved prior to applying electrochemical antifouling technology onto large structures:

- Survivability of the counter electrode material.
- Antifouling performance of large area electrode (i.e. variations in surface potential and current density).
- Relationship between voltage and current densities of various electrode materials and their effectiveness in preventing biofouling.

**Figure 1.** Graphite-polyurethane antifouling experiment setup conducted by Matsunaga et. al. [2].
1.4: Goals and Objectives

The primary goal of this thesis is to investigate issues currently unaddressed in literature for the graphite-polyurethane thin film electrode antifouling system. Further benefits of this system include the possibility of protecting any surface simply by applying a graphite-polyurethane coat in a similar manner that conventional coatings are applied today [2]. This allows for a smooth transition into electrochemical antifouling systems from conventional antifouling coatings. Successful electrochemical systems are contingent on resolving the remaining issues, and the objectives for this thesis attempt to resolve these concerns:

- Develop a testing protocol to evaluate the antifouling efficacy of various coatings at Hatfield Marine Science Center.
- Investigate different counter electrode materials.
- Investigate the relationship between electrode potential to current density.
- Obtain surface voltage profiles for graphite-polyurethane thin film electrodes.
- Develop a model for voltage profiles.

It would be ideal to find an electrode which may serve as both the cathode and anode and apply a voltage duty cycle to offer protection to both electrode surfaces. It may even be possible to use the same electrode film in different areas as the cathode and anode, and this is why obtaining a voltage profile model is important designing large-scale electrochemical antifouling systems.
2.1: Marine Biofouling Mechanism and Effects

Marine biofouling involves the colonization of marine organisms on a submerged marine surface. Its occurrence is noted around marinas and docks across the globe and is the bane of many man-made ocean-faring structures. Examples of marine biofouling on different substrates are shown in Figure 2.

![Image of marine biofouling occurring on PVC pipe, fiberglass tank wall, and cinder block.](image.png)

**Figure 2.** Marine biofouling occurring on PVC pipe, fiberglass tank wall, and cinder block.

Substrate biofouling occurs sequentially, starting with the adsorption of inorganic and organic molecules followed by the colonization of organisms. The surface energy, chemistry, and physical roughness of the substrate all influence the colonizing organism
distributions; however, the biofouling trend remains generic [7],[8]. The sequential biofouling steps are:

1. Adsorption of inorganic and organic ions onto the surface [9]
2. Attachment of marine bacteria and their formation of an Extracellular Polymeric Substance (EPS), commonly referred to as a biofilm [1]
3. Colonization by macro organisms, such as barnacles, mussels, and colonies of algae [1]

Even though this order of fouling is typically observed, there are reported cases where macro fouling (step 3) occurs in the absence of micro fouling (step 2) [9]. Micro and macro fouling harm the substrate through different mechanisms.

Micro fouling harms the substrate mainly due to adverse effects of the EPS [1]. It increases hydrodynamic drag of the surface [10], hinders heat transfer [6], and acts as a diffusion barrier between the substrate and ocean [11]. The mass transfer resistance of the EPS may lower oxygen concentration on the surface of the metal which facilitates its corrosion [11][1]. When a metal oxidizes, it must transfer its electron to an oxidizing agent. In areas of low oxygen concentration, the electrons conduct through the substrate to an area of high oxygen concentration to facilitate the reduction of oxygen into hydroxyl ions. This sets up an electrochemical cell where the substrate covered by the EPS acts as an anode and rapidly corrodes. Acidic metabolites and consumption of oxygen by bacteria in the EPS accelerate the corrosion process [12]. Although not necessary, the EPS promotes macro fouling that further harms the substrate.
Mussels secrete adhesive proteins that form a plaque which secures them permanently to the substrate [13]. Similarly, barnacles adhere to a substrate with cement comprising 10 different proteins [14]. At this stage, the barnacles can be mechanically cleaned; however, some remnant of the cement persists. For this reason, power plants prefer continuous injection of chlorine to prevent biofouling on cooling pipes as opposed to intermittent chlorine injection. Others have observed evidence that barnacles form crevices on steel substrates [11]. Biofouling also affects the mechanical properties of polymer substrates (polycarbonate, low and high density polyethylene, and polypropylene), resulting in increased surface roughness and surface energy [7].

Marine biofouling also affects the overall performance of ocean craft. For large commercial vessels, drag due to biofouling can result in a 40% fuel consumption increase [1]. Researchers studied the impact of macro fouling on buoys located in Lysekil Project Test Park [15]. They determined that a 2-ton point absorber—a buoy connected by a mooring to a power takeoff system directly underneath it—was unaffected by the additional 137 kg biofouling mass. Biomass remained relatively constant because blue mussels, the dominant fouling organism, would grow on top of other mussels to a point where it became too heavy for the connecting mussel to support and detach from the buoy [15]. Beyond the minimal effects on point absorber forces, marine biofouling poses significant risk to survivability and device operation resulting in mechanical and chemical damage to their surfaces. Therefore, it is important to prevent marine biofouling on vulnerable surfaces.
2.2: History of Antifouling Technology

Marine antifouling methods date back to the early 1600s where either copper or lead strips were placed on the wooden hulls of ships to prevent biofouling by releasing metal ions [16]. In 1625, William Beale patented the first copper-based antifouling coating [1]. Historically, antifouling technology has remained reliant on biocide release coatings to protect vulnerable surfaces. In 2006, Chambers et. al. published a review article on the “Modern Approaches to Marine Antifouling Coatings.” The article discusses the different antifouling strategies utilized in coatings. The two main antifouling coating technologies are (1) foul release and (2) biocide release.

2.2.1: Foul Release Coatings

Foul release coatings are engineered so that the top layer of the coating and any biomass attached to it sloughs off the surface. The most common type of foul release coatings are self polishing copolymers [1]. All foul release coatings rely on moving fluids parallel to their substrate in order to provide sufficient shear force to dislodge the top layer. Generally, a water speed between 10-20 knots is necessary to dislodge fouling organisms [1]. Stationary vessels with foul release coatings are left vulnerable to biofouling. In order to compensate for this shortcoming, most foul release coatings incorporate a biocide.

2.2.2: Biocide Releasing Coatings

Biocide release coatings are formed by incorporating biocides into a paint matrix. The biocide, traditionally metals or metal oxides, gradually leaches out and protects the surface from fouling. Copper biocide coatings were the first to appear. Tin biocide
coatings appeared in 1976 [1]. Though copper biocide paints offer good antifouling performance, tin biocide paints provided to be more effective. Unfortunately, tin coatings cause damage to surrounding ecosystems and so were banned by the United States Environmental Protection Agency (EPA) in 1987 [17]. Tin was banned globally in 2001 [1]. Afterwards, copper biocide paints once again emerged; however, their impact on the environment is currently being scrutinized, and it will probably meet the same fate as tin biocide coatings.

2.3: Need for Alternative Antifouling Methods

There are two main disadvantages to using metal biocide paints that are driving the research and development of alternative antifouling technologies. Depending on water temperature and the populations of different fouling organisms in surrounding waters, copper biocide paints have a limited lifetime of roughly three years due to biocide depletion [1]. Afterwards, the costly endeavor of dry docking and repainting the surface occurs. Bioaccumulation and its impact on the surrounding ecosystem is another disadvantage. Studies have been conducted on the lifecycle of tin, copper, and other biocides as well as their effects on the environment [18].

Bioaccumulation of copper is worst in docks, where numerous vessels release copper into the surrounding waters [17]. A case study in the San Diego Bay determined that copper levels peaked at 21 ppb, exceeding the EPA limit of 3 ppb; the authors concluded that this is likely due to the large number of boats docked in the marina [17]. Copper ions tend to aggregate and sink to the ocean floor [18]. This poses a risk of releasing a large quantity of copper when dredging or otherwise disturbing the sediment
surface. Copper concentrations around 0.2 ppb adversely begin to adversely affect cyanobacteria growth rates [18]. Larvae of invertebrates, such as mussels and barnacles, reproductive harm copper levels exceed 12 ppb whereas fish can generally tolerate copper levels less than 120 ppb [18]. Consequently, the bioaccumulation of copper observed in the San Diego Bay poses harm to mussels and barnacles in the nearby ecosystem. From this we may conclude that it is possible to observe copper levels toxic to marine organisms near large groupings of stationary ocean-faring vessels.

2.4: Alternative Antifouling Technologies

The driving forces behind investigating and developing alternatives to conventional antifouling systems are to improve antifouling efficacy and lifetime while also minimizing environmental impact. Alternative antifouling technologies fall under these three classifications:

- Environmentally friendly biocide release coatings
- Surface chemistry modification
- Electrochemical antifouling systems

Environmental-friendly biocide coatings utilize chemical biocides that do not accumulate in the surrounding waters. Surface chemistry modifications work by tuning the surface energy and adjusting the molecular functional groups on the surface to prevent attachment of organisms. Both alternative biocide and surface chemistry modification are passive, meaning that no other measures are necessary for them to inhibit fouling. Conversely, electrochemical methods are active, meaning that electric power must be dissipated continuously in order to prevent biofouling.
The alternative biocide, iron benzoate, is rendered biologically inert to adjacent marine life [19]. It protects the surface from fouling by lowering the pH near the substrate while also reducing hull corrosion. Medetomidine, a sedative commonly used in veterinary medicine, has been shown to be effective at preventing macro fouling. It protects the surface by lowering the activity of invertebrate larva [20]. A toxicology study of medetomidine on juvenile turbot showed that the sedative had no lasting harm on marine organisms [20]. Further studies showed no significant bioaccumulation of medetomidine in various marine organisms [21].

These next two alternatives are inspired by natural biocides secreted by marine organisms. Tannins are organic compounds which act as a sedative to marine invertebrates, such as mussels and barnacles [22]. It’s a chemical precursor to bromoageliferin, a nature biocide secreted by sponges and operates similarly to medetomidine to prevent fouling [22]. Pyridyl alkaloids are compounds that paralyze mussels and barnacles and are secreted by one of their predators [23]. Research has shown that pyridyl alkaloids are effective in preventing the settlement of mussels and barnacles onto a protected substrate. Though preliminary results of these alternative biocides are effective at preventing macro fouling, literature doesn’t report their effect on micro fouling organisms.

Others are investigating ways to alter and change the surface chemistry in order to prevent marine biofouling. Altering the surface energy to around 20-30 mN/m has been shown to reduce biofouling observed on polymer substrates [7]. Adding nickel phosphorus functional groups on Teflon has been reported to decrease bacteria
attachment between 82-97% versus control plates [8]. Numerous articles document the use of immobilized enzymes for marine biofouling prevention [9]. Enzymes are diverse in their method and selectivity in biofouling prevention. Some enzymes break down the EPS while others break up the adhesive molecules secreted by invertebrates. In general, most surface chemistry methods prevent micro fouling while most alternative biocides prevent macro fouling.

Another way to prevent marine biofouling is to use electrochemistry. Before diving into the specifics on the various electrochemical antifouling systems, it is best to review the theory of electrochemical phenomena. It is important to keep in mind that electrode material, electrolyte, and voltage are vital electrochemical parameters.

2.5: Electrochemistry Overview

Electrochemistry is a branch of chemistry that studies the electrical effects coupled with oxidation and reduction chemical reactions in electrical cells. A few examples of electrochemical cells are cell phone batteries, copper electroplating tanks, and electrochemical antifouling systems [24]. The subsections of electrochemistry are the study of (1) charge transfer thermodynamics, (2) charge transfer reaction kinetics at the electrode-electrolyte interface, and (3) the movement of chemical species in the electrolyte. Knowledge of electrochemistry makes it possible to predict and model important parameters in electrochemical cells, such as current density versus applied voltage and provide clues about chemical pathways.
2.5.1: Electrochemical Thermodynamics

When dealing with electrochemical cells, it is often convenient to represent the overall chemical reaction as a combination of half-cell potentials. Half-cell potentials state the negative change in free energy per unit charge (as volts) when a chemical species is reduced from its oxidized form at standard conditions. The standard conditions are that the activity of all electrochemically active species are at unity (i.e. the equilibrium constant, $Q$, is 1), the temperature is maintained at 298 K, and the partial pressure is 1 atmosphere for all gaseous species involved [24]. An example of a half-reaction is the hydrogen reduction reaction into hydrogen gas, which is given by:

$$2H^+ + 2e^- \rightarrow H_2(g) \quad E^0 = 0 \text{ V} \quad (2.1)$$

The standard half-cell potential of hydrogen is set to zero and serves as a reference for the electrochemical half-reaction tabulated set, and is referred to as the Standard Hydrogen Electrode (SHE). Half-cells may be combined in order to describe the overall cell standard potential by subtracting the half-cell with the larger potential by the half-cell with the smaller standard potential so long as both half-cells share the same reference potential state.

$$2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2(\text{g}) \quad E^0 = 0 \text{ V}$$
$$+ 2 \times \text{Ag(s)} + \text{Cl}^- (\text{aq}) \rightarrow \text{AgCl(s)} + e^- \quad E^0 = 0.222 \text{ V} \quad (2.2)$$

The resulting potential of the total reaction is the sum of the standard potentials of each reaction, which is 0.222 V. When doubling a half-cell reaction to balance the overall equation, the standard potential remains unchanged. This is because the standard potential is represented as per unit charge, so even though the free energy of the half-cell
doubled, so did the number of electrons and the standard potential therefore remains unchanged [25].

Electrochemical potentials are really just a permutation of the change in Gibbs’ free energy, and the two are related by the simple equation [26]:

\[ \Delta G_{T,P} = -zFE^0 \]  

(2.3)

where \( z \) is the number of electrons involved in the reaction stoichiometry, \( F \) is Faraday’s constant, and \( E^0 \) is the cell voltage. Because the free energy of the system likes to minimize, the spontaneity of chemical reactions may be determined from half-cell potentials. If the half-cell potential is positive, the chemical species prefers to be reduced and vice versa. As the chlorine to chloride half-cell potential is +1.36 V, chlorine spontaneously reduces to form chloride.

When electrochemical systems are not at standard conditions, a correcting term must be included to calculate the overall cell potential, and this is included in the Nernst equation as given below [27]:

\[ E = E^0 - \frac{RT}{ZF} \ln Q = E^0 - \frac{RT}{ZF} \ln \left( \prod \frac{a_{product}^y}{a_{reactant}^y} \right) \]  

(2.4)

The Nernst equation may be applied to both half-cell reaction and overall cell potentials. The activity of all species is difficult to obtain or calculate. For dilute solutions, the activities of species becomes close to their actual concentration [24]. For preliminary analysis and shortcut methods, the concentration may be used in place of activity for solutions of ionic strength similar to sea water; however, one must be aware that error as ionic strength increases. The mean activity coefficients may be estimated by Debye-
Hückel theory; however, the mean activity coefficients of sodium chloride at different ionic strengths have been experimentally determined [24].

2.5.2: Electrode-Electrolyte Interface Theory

Whenever two dissimilar materials come into contact, the chemical potential at the interface must be equal [24]. In semiconductor junctions, this results in a built-in potential by setting the Fermi level of each dissimilar material equal [28]. The Fermi level is a representation of the chemical potential of the material, and it defines the charge carrier density [28]. An analogous process occurs when an electrolyte comes into contact with a solid interface. Whether the solid surface is conductive or insulating, adsorption of ions on the surface occurs, which is the physical representation of minimizing the chemical potential at the interface [24]. Some ions absorb onto the surface and become stationary in a hydrodynamic sense while others remain close to the electrode. The type, charge, and number of ions absorbed onto the surface are influenced by a wide range of material and solution properties [29]. The electrode surface becomes charged due to ion absorption and so the ions of opposite charge accumulate nearby the surface and set up a dielectric field. This charge separation at the interface is known as the electric double layer [29]. The electric double layer is where charge transfer reactions occur, and it’s considered to be the focus of electrochemistry as it is the potential barrier for charge transfer reactions at the interface [29].

The thickness of the electric double layer is on the order of nanometers, and the voltage drop is in the magnitude of a volt [24]. This allows electric fields in the double layer to be some of the highest observed in nature, achieving field strengths in the
gigavolt/meter range. For comparison, the electric field observed in lightning is on the order of megavolt per meter, or 1,000 times less potent than the double layer strength [30]. The degree of the double layer charge is characterized by the zeta potential, which is defined as the potential where the immobilized ions on the interface touch mobile ions near the interface [24]. Models of the double layer have been proposed by both Helmholtz and Gouy to model the spatial charge distribution at the interface and predict capacitive properties of the electrode interface [24].

Electrochemical reactions involve charge transfer chemical reactions, and this takes place at the electric double layer of the electrode-electrolyte interface. A thermodynamic driving force must be present to facilitate the reaction. This driving force may be supplied by the chemical species themselves, where the cell produces energy, or by feeding electrical energy into the system. In either case, the electrodes are said to become polarized when an electrochemical reaction occurs. This may cause a shift in the chemical potential of the electrode, which in turn changes its Fermi level which changes the charge carrier distribution which in turn affects the electric double layer.

In a two-electrode cell with current flow, the electrode potentials cannot be determined relative to SHE because each electrode is polarized. The only measurable voltage reading is the overall cell potential, which is simply a difference in potential between the two electrodes with no indication of their potentials relative to SHE. This is problematic because most analytical and control techniques in electrochemistry require measurement and control of the electrode potential where the reaction of interest occurs, and this electrode is referred to as the working electrode. In order to resolve this issue, a
third electrode which carries no current is added to the cell; it is known as the reference electrode. Because no current flows through the reference electrode, its potential is stable and the potential of the working electrode may be compared to it in order to maintain its potential relative to SHE.

A good reference electrode must be resistant to polarizing and maintain a stable potential all the while not interfering with the electrochemical cell’s operation itself [26]. Most reference electrodes are half-cells separated by the electrochemical cell by a glass frit. If the composition of the electrolytes between the cell and reference electrode are severe, it causes a junction potential to form at the glass frit and offset working electrode potential readings [26]. Therefore, it is important to choose a reference electrode that is compatible with the cell chemistry in order to minimize junction potential. For aqueous systems with chloride ions present, silver/silver chloride electrodes surrounded by potassium chloride solution are very resilient reference electrodes. Table 1 lists the reference electrodes applicable for aqueous saline solutions.

**Table 1.** List of selected reference electrodes and their potentials. All standard potentials are from same source [26].

<table>
<thead>
<tr>
<th>Reference Electrode</th>
<th>E, V</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/AgCl in sat. KCl/NaCl</td>
<td>0.197 V</td>
<td>Ag/AgCl</td>
</tr>
<tr>
<td>Ag/AgCl in 3 M KCl/NaCl</td>
<td>0.209 V</td>
<td>Ag/AgCl 3M</td>
</tr>
<tr>
<td>Standard Calomel Electrode</td>
<td>0.241 V</td>
<td>SCE</td>
</tr>
<tr>
<td>Standard Hydrogen Electrode</td>
<td>0 V</td>
<td>SHE</td>
</tr>
</tbody>
</table>
A theory of electrochemical kinetics was originally developed between John A. V. Butler and Max Volmer. The model starts by considering the number of electrochemically active ions that collide with the electrode surface per time, similar to a collision frequency utilized in heterogeneous gas-solid phase reactions. Then, it’s postulated that only a certain number of species that collide with the surface have enough kinetic energy to overcome the potential barrier that arises from the double layer; the distribution of chemically reactive species with enough thermal energy to overcome the barrier is modeled by the Boltzmann distribution. Also, both the oxidation and reduction reactions must be considered simultaneously. Combining all these considerations yields the Butler-Volmer equation [24]:

\[
i = A i_0 \left[ \frac{C_r}{C_{r,\infty}} \exp \frac{\beta F(E - E_0)}{RT} - \frac{C_o}{C_{o,\infty}} \exp \frac{\alpha F(E - E_0)}{RT} \right]
\] (2.5)

Where C represents the concentration of the reduced or oxidized (sub r or sub O, respectively) species near the electrode interface and in the bulk (sub infinite); E is the cell voltage; \(E_0\) is the zero-current voltage of the cell; \(i_0\) is the exchange current in current/electrode area; A is the electrode area; and \(\alpha\) and \(\beta\) are the charge transfer coefficients which together sum to one. The overpotential is the voltage difference between E and \(E_0\). The exchange current is the current magnitude of both the reduction and oxidation currents when they are equal but opposite (i.e. overpotential and net current are both zero). The ratio of species concentration near the surface compared to the bulk represents mass transport issues that may arise when the electrochemical reaction rate exceeds or is similar to the mass transport rate. Understanding the transport of electrochemically active species is important in deriving a relation to describe the ratio.
It turns out that equation (2.5) does a good job at matching experimental results; and it may be simplified for different overpotential ranges, depending on the operating potential of the cell.

2.5.3: Electrolyte Theory and Transport

In order for electrochemical cells to operate, the electrolyte must be capable of conducting current. This is accomplished by the movement of dissolved ions in solution. The movement of ions in solution is driven by two mechanisms, and they are diffusion by concentration gradient and drift in an electric field. As the species reacts, the concentration at the surface depletes and forms a concentration gradient which induces movement of charge by diffusion. The governing equation for diffusion is given by:

\[ N_a = -D_{a-b} \nabla C_a \]  

(2.6)

Where \( D_{a-b} \) is the diffusivity of species \( a \) in solvent “b” [24],[26],[29]. When the electric potential in a cell is sufficient to overcome the potential drop at the electrode-electrolyte interface at both the anode and cathode, an electric field exists in the electrolyte and charged ions begin to drift. The governing equation for drift is given as:

\[ N_a = -C_a \frac{\Lambda_a}{zF} \nabla V \]  

(2.7)

Where \( \Lambda_a \) is the molar conductivity, \( z \) is the charge number of the species “a,” and \( \nabla V \) is the voltage gradient of the electrolyte [29],[31]. All ions in solution, even the ones which are not electrochemically active are influenced by the electric field and charge separation occurs in the electrolyte, where cations are attracted to the negatively charged electrode (cathode) and anions are attracted to the positively charged electrode (anode). Current transport by diffusion occurs when an electrochemically active species reacts on an
electrode, either donating or accepting an electron [24][29]. If no electrochemically species are present, or the potential is too low to initiate the reaction, the current stops flowing and spatial charge separation along the path of the electric field in the electrolyte occurs [29].

2.5.4: Electrochemistry Summary

When considering all aspects of the electrochemical cell, it is important note that the electrolytes, electrodes, and mass transport are all coupled and impact electrical cell performance. When the ion concentrations change, the chemical potential of the electrolyte changes and therefore influences the ionic double layer at the electrode – electrolyte interface. The same applies for changes in the electrode, such as alloying or doping if it’s a semiconductor. Changing the concentration of ions which are not electrochemically active can also impact the transport rates of electrochemically active species by shielding the influence of the electric field in solution. Figure 3 shows an electrochemical cell in action with all the previously discussed mechanisms highlighted.
Figure 3. Overview of electrochemical cell. The spatial potential drop of the cell is marked in dashed orange. The ion concentration profiles are also drawn.

In this setup, the potential of the working electrode is being controlled by a Potentiostat, which utilizes a reference electrode. It is ideal to place the reference electrode as close to the working electrode as possible to prevent potential shifts due to IR drops in the solution. In some circumstances where either the conductivity of the electrolyte is very high or the overall cell potential is low, the IR drop of the solution becomes negligible. The concentration profiles for both the anion and cation are given for when the ion transport is diffusion dominated. Other instances may occur when the electric field in solution is strong enough that concentration profiles may appear opposite, and this occurs when the electrochemical reaction rate is extremely slow compared to ion transport due to charge drift. Some electrochemical analytical techniques prefer to operate in mass
transport mode of operation without influence from electric field drift. In order to ensure this condition, an abundance of chemical ions which are not electrochemically active are added to solution in order to form another dielectric field in the circuit to cancel out the electric field induced between the electrodes, and these are known as supporting electrolytes [29].

2.6: Electrochemical Antifouling Technology Overview

Not much literature currently exists on electrochemical methods to prevent marine biofouling. Most of the work comes out of the Dr. Matsunaga’s research group, located at Tokyo University of Agriculture and Technology. However, other studies have been conducted on electrochemical disinfection systems for wastewater treatment and food equipment sterilization. These antifouling technologies are reviewed to supplement the lack of electrochemical marine biofouling literature.

2.6.1: Electrochemical Antifouling Technology for Marine Applications

Researchers in Japan have demonstrated that carbon-polyurethane electrodes cycled between being held at 1.2 V versus SCE for an hour and -0.6 V versus SCE for 10 minutes are capable of preventing marine biofouling for up to a year [2]. An iron rod served as the counter electrode in order to complete the electric circuit, and its condition throughout the experiment wasn’t reported. For this work, the authors claim that no change in pH or generation of chlorine was observed. The lethality of the electrochemical system on marine bacteria V. alginolyticus was plotted versus electrode potential as shown in Figure 4.
Figure 4. Effect of applied potential on survival of *V. alginolyticus* cells attached to graphite-polyurethane paint electrode 30 min in sterilized seawater [2]. [Reprinted with permission from Copyright Clearance Center on behalf of John Wiley and Sons]

The proposed mode of sterilization is the direct electron transfer between the electrode and bacteria cell wall as no change in pH was observed and cyclic voltammetry of the cell yielded no oxidation peaks [2].

Titanium nitride films deposited by arc sputtering deposition have also been shown effective at preventing marine biofouling. The titanium nitride film was cycled between being held at 1.0 V vs. Ag/AgCl for 60 minutes and -0.6 V vs. Ag/AgCl for 10 minutes [3]. The titanium nitride electrode’s operating potential is roughly 241 mV less than the graphite-urethane paint when accounting for the different reference electrodes utilized in each experiment. It was reported that no oxidation peaks were observed between the potential window of 1.0 and -0.6 V vs. Ag/AgCl, and the suspected antifouling mechanism is through direct electron transfer between fouling organisms and the electrode surface. Although, other research on titanium nitride microelectrodes
observed oxidation of the titanium nitride film itself within this potential window in acidic, neutral, and alkaline conditions [32].

Titanium plates held at constant current density between 50-100 mA/m² near the cooling water intake at Matsuura Thermal Power Stations in Nagasaki, Japan were successful in preventing marine biofouling throughout the course of the two year experiment [6]. The plates were cycled between 0.9 V and -0.9 V vs. Ag/AgCl and the authors state that disinfection mechanism is direct electron transport between the organism and electrode. It was also reported that free available chlorine was not generated in bench scale experiments until 7.0 V vs. Ag/AgCl [6].

2.6.2: Electrochemical Water Treatment Technology

Ruthenium dioxide and iridium dioxide electrodes were used as anodes in the electrochemical disinfection of drinking water. The electrodes generated free available chlorine to serve as the disinfectant [31]. The overpotential activation range between 1.4 V at 5 ppm chloride to 1.25 V at 250 ppm, with both potentials versus SHE and pH =7.0. At this potential at the RuO₂ electrode, the chloride oxidation reaction must compete with the water oxidation and hydroxide oxidation reactions, and a current efficiency of 150 A-m⁻² was observed to yield the best current efficiency for chloride oxidation. Part of the efficiency losses may arise from stripping due to oxygen gas evolution as well as reactions with nitrites in solution [31][33].

The electrochemical generation of hydrogen peroxide was studied by researchers in France as a method to disinfect drinking water [34]. The electrolyte was tap water without any additional chemical species, and the anode was RuO₂ while the cathode was
vitreous graphite. Because of low cell conductivity, voltages around 25 V were necessary to maintain cell current at the 2 A with a current efficiency of 21% [34]. A summary of the different electrochemical antifouling and disinfection methods is given in Table 2.
<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Voltage</th>
<th>Proposed Mechanism</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Marine Applications</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite/carbon black urethane paint</td>
<td>Sea Water</td>
<td>1.2 V for 1 hr / -0.6 V for 10 min</td>
<td>Direct electron transfer between electrode and bacteria</td>
<td>[2]</td>
</tr>
<tr>
<td>Sputtered film of titanium nitride</td>
<td>Sea Water</td>
<td>1.0 V for 1 hr / -0.6 V for 10 min</td>
<td>Direct electron transfer between electrode and bacteria</td>
<td>[3]</td>
</tr>
<tr>
<td>Titanium plate</td>
<td>Sea Water</td>
<td>0.9 V / -0.9 V (50-100 mA/m²)</td>
<td>Direct electron transfer between electrode and bacteria</td>
<td>[6]</td>
</tr>
<tr>
<td><strong>Water Treatment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanium coated with iridium dioxide / ruthenium dioxide</td>
<td>pH ~=7 with [Cl⁻] ranging from 10 – 125 ppm</td>
<td>Controlled by current density, E not reported</td>
<td>Electrochemical generation of chlorine dioxide</td>
<td>[33]</td>
</tr>
<tr>
<td>Titanium coated with ruthenium dioxide</td>
<td>Tap water with no additives</td>
<td>Not specified, but probably exceeding 1.77 v. (SHE)</td>
<td>Electrochemical generation of hydrogen peroxide</td>
<td>[34]</td>
</tr>
<tr>
<td>Titanium coated with iridium dioxide / ruthenium dioxide</td>
<td>125 ppm NaCl, 240 ppm NaSO₄ with varying pH from 3.02 – 10.0</td>
<td>Up to 500 A/m² (20 V cell voltage)</td>
<td>Generation of free available chlorine</td>
<td>[31]</td>
</tr>
<tr>
<td>Graphite electrode</td>
<td>0.1 M phosphate buffer solution (pH 7)</td>
<td>0.74 V versus SCE</td>
<td>Direct electron transfer between electrode and bacteria / yeast</td>
<td>[5]</td>
</tr>
</tbody>
</table>

Most marine antifouling methods utilize low voltage and currents whereas the opposite is true for water treatment. This probably arises for the need to disinfect the bulk water for such systems, and a tremendous amount of charge must pass through the
cell to generate an adequate amount of disinfectant in solution. Marine biofouling methods are only concerned about surface preservation, so their voltages and current are much lower.

2.7: Conductive Composites Theory

Conductive composites are composed of conductive filler particles entrapped in a binder. Some common types of conductive composites are silver-epoxy and conductive carbon paint, carbon fiber epoxy, and the graphite-polyurethane electrodes that are the focus in this thesis. Therefore, it is important to gain a better understanding of composite electrodes. Conductivity of a composite is influenced by the bulk resistivity of the filler material and the percent loading [35]. The relation between % loading of filler and composite resistance is nonlinear and follows percolation theory. Percolation theory is a general mathematical model used to describe a randomly connected network of particles and their related properties, such as resistivity [36]. Figure 5 shows the relation between % loading and composite resistivity.
At low filler volume fraction, each particle is effectively isolated from one another and the composite resistance is very high. As the filler concentration slowly increases, it reaches a point where some filler particles are connected and the resistance begins to decrease as more filler particles are introduced. At a higher filler loading, the particles are networked together and the composite resistance is substantially lower. Increasing the filler particle density further after this point has a negligible impact on the resistance. Generally, the maximum composite conductivity is only around 1% of the conductivity of the bulk filler material [35].

2.8: Thin Film Electrode Considerations

Thin film electrodes obtain some of their properties from the filler’s bulk properties while others are determined by percolation theory and filler fraction loading.
into the composite. The resistance of the composite is governed by both filler fraction loading and filler bulk resistivity. On the other hand, some electrochemical properties remain the same as that of the bulk material while others depend on filler fraction loading.

2.8.1: Electric Properties of Thin Film Electrodes

Conductive composites at best can only achieve conductivities 2 orders of magnitude less than that of the pure conductive filler [35]. When composites are deposited as a thin film electrode, the overall resistance can become large. For conductive thin films, it is often convenient to describe the bulk resistivity in terms of sheet resistance. Sheet resistance has units of Ω per “square” and is defined by the relation [37]:

\[ R = R_{sh} \square = \frac{\rho}{t \square} = \frac{\rho L}{t W} \]  

(2.8)

Where \( R \), \( R_{sh} \), \( \square \), \( \rho \), \( t \), \( L \), and \( W \) are total resistance, sheet resistance, square, bulk resistivity, film thickness, length, and width, respectively. Using sheet resistance allows us to forget about film thickness when calculating the total resistance between two locations on a thin film electrode. The only necessary parameter then becomes the number of squares which can be placed between the two points, or the ratio of length to width.

2.8.2: Electrochemical Properties of Thin Film Electrodes

The apparent exchange current density and diffusion flux observed in a composite electrode are influenced by filler loading, because these two properties are related to the
spacing density of microelectrodes on the surface. If the spacing density is small, the effective exchange current density decreases and the conductive filler act as micro electrodes spaced far apart. This changes the diffusion profile from linear to spherical. Research into the characterization and utilization of micro electrode and their arrays is well established [26],[29]. On the other hand, the charge transfer coefficient and overpotential properties are determined by the filler’s surface properties. For graphite-polyurethane thin film electrodes, this is graphite.

2.8.3: Electrochemical Properties of Graphite

Graphite has been the focus on many studies in electrochemistry, and its electrochemical activity has been widely investigated [38]-[41]. Graphite electrodes are chemically described as carbon atoms with 3 coordinate bonding to other carbon atoms on a sheet with sheet stacked onto sheet. The reference frame for the order of these graphite sheets brings up the different forms of carbon electrodes, such as the boron-doped diamond electrode, glassy electrode, and sintered graphite rod electrodes to name a few.

Electrochemical methods for detecting halogens in river water have been investigated [42]. Their method for detecting chloride and bromide is to first electrochemically oxidize them in 0.1 molar nitric acid and measure the reduction peak. Various types of carbon electrodes were tested, and they are: edge plane, glassy carbon, basel electrode, and boron-doped diamond. Their analysis showed that chloride has an oxidation and reduction peak within the -0.6 V to 1.2 V versus SCE window [42]. Also, the oxidation of bromide was studied and found to contain oxidation and reduction peaks
within the voltage -0.6 V to 1.2 V versus SCE voltage window [43]. Both chloride and bromide studies occurred in acidic conditions, so these results cannot be directly translated to sea water conditions. The basal site of graphite is not as electrochemically active with halogens, such as bromide or chloride, than compared to edge plane sites [38],[39],[42].

2.9: First Principles Voltage Profile Model

Voltage variations in resistive electrodes are known as terminal effects. Most of the literature on terminal effects concern either high current load on battery electrodes or copper electroplating onto resistive semiconductor substrates [44]-[47], and they show good agreement between experimental results and models based on first principles. Current must flow through the thin film electrode to reach a surface and initiate the electrochemical reaction. As a result, the local electrode overpotential magnitude decreases the further away it is from the current source. These voltage losses may cause the potential on the surface to drop below the threshold necessary to prevent biofouling. Therefore, it is important to be able to predict the voltage profile on graphite-polyurethane thin film electrodes in order to insure biofouling protection.

2.10: Antifouling Testing Methods

Long-term studies have been used to gauge the effectiveness of various electrochemical antifouling systems [2],[3],[4]. These field tests take at least a few months and rely on percent fouling coverage via visual inspection and weight accumulation as metrics for antifouling efficacy. On the other hand, other studies have found that biofouling accumulation may be observed after just two weeks of submersion
in marine waters [1],[11],[48]. This relatively short colonization time allows for the somewhat quick screening of antifouling technologies which show promise including electrochemical antifouling methods.
Chapter 3

MATERIALS AND METHODS

3.1: Preparation of Thin Film Graphite Electrodes

All proceeding sections in this chapter utilize the electrodes described here. Filler composition of all graphite-polyurethane paints is specified by dry weight percent of graphite.

3.1.1: Materials

Table 3 lists all materials used in the fabrication of graphite-urethane thin film electrodes. Substrate material, which differed between experiments, is also shown.

Table 3. List of materials used to construct thin film graphite-urethane electrodes and their source.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Item Description</th>
<th>Supplier</th>
<th>Used in:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductive Paint</td>
<td>Synthetic graphite powder (&lt;20 micron)</td>
<td>Sigma Aldrich</td>
<td>All experiments</td>
</tr>
<tr>
<td></td>
<td>MinWAX® Fast-Drying Polyurethane Clear Gloss Finish</td>
<td>Home Depot</td>
<td></td>
</tr>
<tr>
<td>Substrates</td>
<td>Electrically insulating fiberglass</td>
<td>McMaster Carr</td>
<td>Open seawater tank experiments</td>
</tr>
<tr>
<td></td>
<td>75 mm x 25 mm x 1mm glass slide</td>
<td>OSU Chem Store</td>
<td>Resistivity characterization</td>
</tr>
<tr>
<td></td>
<td>Graphite bars: 6 “ x ½” x ¼” (item # 1763T22)</td>
<td>McMaster Carr</td>
<td>Electrochemical characterization</td>
</tr>
<tr>
<td></td>
<td>Cast Acrylic rectangular bars (item # 7729A23)</td>
<td>McMaster Carr</td>
<td>Resistivity characterization and voltage profiling experiments</td>
</tr>
<tr>
<td>Wire-electrode connection</td>
<td>Conductive silver epoxy</td>
<td>MG Chemicals</td>
<td>All</td>
</tr>
</tbody>
</table>
Electrically insulating fiberglass was selected as the substrate for open seawater tank experiments because of its ruggedness. The graphite bars were chosen as a substrate for the electrochemical characterization studies because it is very conductive. This kept the surface potential of the thin film electrode uniform. Metal substrates were originally considered for the electrochemical characterization studies; however, a small scratch in the paint resulted in rapid metal corrosion. Glass and acrylic substrates were selected for resistivity characterization because they are smooth and produce the most uniform films. Only acrylic substrates were used in the voltage profile experiments because glass slides were too small to yield meaningful profile data and uniform panel resistivity is important.

3.1.2: Preparing Graphite-Polyurethane Paint for Deposition

The graphite and polyurethane compositions were weighed independently before mixing together. Mixing either occurred with flat metal spatula by hand or through the use of a vortexer. Typically, uniform paint consistency was achieved after 5 minutes of mixing. Afterwards, the paint was immediately deposited onto the substrate. Graphite urethane paint cannot be stored for too long due to graphite settlement.

3.1.3: Preparation of Open Seawater Tank Experiment Electrodes

All thin film electrodes used in the open seawater tank experiments have fiberglass substrates and are composed of 55 dry wt % graphite. The graphite-polyurethane layer of the smaller electrodes was painted on with a brush. A straight edge was used on the longer electrodes to apply a uniform film on its surface. The wire-electrode connection point changed through the seawater tank experiments as it was a
common fail point. Table 4 describes the types of connections employed on which experiment.

**Table 4.** Type of wire-electrode connections used on open seawater tank experiment electrodes.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Graphite-polyurethane deposition technique</th>
<th>Wire-electrode connection type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Graphite-polyurethane painted electrode on urethane substrate</td>
<td>Tin marine wire connected to Al foil current spreader and coated with urethane paint</td>
</tr>
<tr>
<td>2</td>
<td>Graphite-polyurethane painted electrode on urethane substrate</td>
<td>Tin marine-grade wire connected to paint and sealed with mastic and regular electric tape (submerged)</td>
</tr>
<tr>
<td>4 and 5</td>
<td>Graphite-polyurethane thin film electrode applied by straight edge smoothing</td>
<td>Tin marine-grade wire connected to paint and sealed with mastic and regular electric tape (not submerged)</td>
</tr>
</tbody>
</table>

3.1.4: Preparation of Graphite-Polyurethane Films for Electric Conductivity Analysis

All thin film electrodes for electrical resistivity characterization were made with a straightedge to improve film uniformity. A 0.06 mm thick adhesive-back plastic film, supplied from McMaster-Carr (item # 1227T16), was placed onto the acrylic substrate prior to paint deposition. Transfer Length Method (TLM) resistivity measurement features were cut out from the film, leaving those parts of the substrate exposed. The paint was then applied and a straight edge used to form a uniform film. Once the film dried, silver epoxy contacts for TLM resistivity measurements were added as shown in Figure 6.
Electrician tape was used to protect the film surface from shorting and subsequently skewing TLM resistivity data.

3.1.5: Preparation of Electrochemical Analysis Electrodes

A specified area was coated with graphite-polyurethane paint while the rest of the rod was coated with pure polyurethane to prevent unwanted secondary reactions. Conductive silver epoxy was used to connect the wire to the graphite bar. These parts were also wrapped in electrician tape to further prevent electrochemical reactions from occurring on the graphite rod’s surface. Figure 7 shows a 55 wt % graphite-polyurethane electrode with an area of 1.65 cm$^2$. 

Figure 7. Graphite-polyurethane electrode used in electrochemical characterization experiments.
3.1.6: Preparation of Voltage Profiling Electrodes

Voltage profiling electrodes were prepared on 4” x 22” acrylic substrates. Half millimeter diameter holes were drilled on the centerline and spaced two inches apart. Pentel Hi-polymer Super pencil graphite (0.5 mm) was sized and placed into each hole so they were level with the topside and slightly exposed on the backside. These served as voltage probes and were secured by applying silver epoxy on the backside. A 0.06 mm thick adhesive-back plastic film was placed on the topside. Two lines running parallel along the length of the acrylic substrate were cut 1” away from each end and the inner film was removed. The graphite-polyurethane paint was applied to the center and smoothed with a straightedge. Wires were connected to the voltage probes on the backside and insulated with West System’s 105 Epoxy resin mixed with 205 hardener as shown in Figure 8.

Figure 8. Image of voltage profile electrodes. Voltage probes are wired on the panel bottom and are insulated with epoxy.
3.2: Open Seawater Tank Experiments

This section outlines the methods and materials used to conduct open seawater tank experiments at Hatfield Marine Science Center (HMSC) in Newport, Oregon. Open seawater tank experiments were performed at Hatfield Marine Science Center. The purpose of these experiments was to assess both novel and conventional antifouling coatings for their antifouling performance.

3.2.1 Equipment and Materials

A total of five open seawater tank experiments were conducted. All experiments were conducted in an 8’ diameter x 4’ deep open seawater tank that was continuously fed filtered seawater from Yaquina Bay. Figure 9 shows the seawater tank with experiment 3 in progress.

Figure 9. Image of open seawater tank from HMSC with test panels deployed.
The electrodes were secured onto a PVC frame by Nylon screws. Conventional copper biocide paints, obtained from Pettit Paint Company, were also deployed in open seawater tanks to compare their effectiveness to electrochemical antifouling systems.

A field-portable potentiostat system was developed in-house over the course of these experiments. The first prototype, crafted onto a breadboard, was used on the first two experiments. It was then implemented as a PCB by Advanced Circuits. Each potentiostat was controlled with a TekBot Atmel Mega 128 microcontroller board (version 1.2) from Oregon State University and is capable of performing cyclic voltammetry and potentiostatic analysis [49]. A comparison between the cyclic voltammogram by a Gamry Reference 3,000 potentiostat and the field potentiostat yielded no significant differences as shown in Figure 10.

![Cyclic voltammogram comparison between Gamry potentiostat and in-field potentiostat. Platinum wires served as both working and counter electrodes. FeCl₃ in NaCl supporting electrolyte.](image)

**Figure 10.** Cyclic voltammogram comparison between Gamry potentiostat and in-field potentiostat. Platinum wires served as both working and counter electrodes. FeCl₃ in NaCl supporting electrolyte.
The data from the in-house, low-cost potentiostat is slightly noisier but otherwise closely matches the one obtained from the Gamry potentiostat. Please refer to Appendix A for more information regarding the Potentiostat system and program code.

All seawater tank experiments utilized a silver-silver chloride wire submerged in seawater as the reference electrode. It was made from twelve gauge 99.99 % pure silver wire obtained from Olufson’s Jewelers of Corvallis, OR. It was oxidized in 1 M HCl as specified in the Handbook of Electrochemistry [26]. Using the Nernst Equation (2.4), the predicted half-cell potential of Ag/AgCl in 0.612 M NaCl is:

\[ E = 0.222 \, V - 25.68 \, mV \ln[0.612] = 0.235 \, V \quad (3.1) \]

The Ag/AgCl in seawater reference electrode potential was validated by comparing peak shifts in cyclic voltammograms of 5 mM potassium ferrocyanide with 100 mM potassium nitrate as supporting electrolyte. Table 5 summarizes the reference electrode potential results.

<table>
<thead>
<tr>
<th>Table 5. Ag/AgCl wire in seawater reference electrode potential measurements.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
</tr>
<tr>
<td>March 23, 2010 w/ 3.5 wt % NaCl soln.</td>
</tr>
<tr>
<td>September 20, 2010 w/ Filtered seawater from test site</td>
</tr>
</tbody>
</table>

The measured potential shift observed in the filtered seawater agrees with results in literature [50], and the difference between the two measurements is probably due to
electrolyte used in half-cell. In either case, the voltage is offset by 0.1 V and doesn’t harm the performance of open seawater tests.

Experiments were monitored by visual inspection and daily digital images. In addition, experiments 4 and 5 included a Logitech HD webcam attached to a Dell netbook to upload images online every 10 minutes. A Pelican case protected electrical components from the elements as shown in Figure 11.

![Figure 11. Pelican case housing with potentiostat (lower right PCB), TekBot controller (upper right PCB), and Dell netbook.](image)

3.2.2: Seawater Tank Experiments

A total of 5 open seawater tank experiments were conducted, and they are summarized in Table 6. All experiments utilized graphite-polyurethane thin film electrode controls in addition to the polarized electrode.
### Table 6. Summary of all seawater tank experiments performed.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Duration</th>
<th>Electrode</th>
<th>Potential, v. Ag/AgCl in seawater</th>
<th>Goal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6/23/2010 to 7/21/2010</td>
<td>Graphite-polyurethane painted electrode on fiberglass substrate</td>
<td>1.5 V</td>
<td>Compare effectiveness of electrochemical to copper biocide</td>
</tr>
<tr>
<td>2</td>
<td>8/20/2010 to 9/10/2010</td>
<td>Graphite-polyurethane painted electrode on fiberglass substrate</td>
<td>-1.0 V</td>
<td>Determine whether graphite-urethane paint cathodic protection was possible</td>
</tr>
<tr>
<td>3</td>
<td>10/15/2010 to 11/19/2010</td>
<td>Sanded carbon fiber epoxy electrode</td>
<td>-1.0 V</td>
<td>Determine whether carbon fiber epoxy plate electrode is suitable cathode</td>
</tr>
<tr>
<td>4</td>
<td>2/11/2011 to 4/1/2011</td>
<td>Graphite-polyurethane thin film electrode applied by straight edge smoothing</td>
<td>1.2 V</td>
<td>Find evidence to support voltage profile on electrode surface</td>
</tr>
<tr>
<td>5</td>
<td>4/1/2011 to 5/24/2011</td>
<td>Same as # 4</td>
<td>1.1 V</td>
<td>Same as # 4</td>
</tr>
</tbody>
</table>

3.3: Graphite-Polyurethane Thin Film Electrical Characterization

This section outlines the techniques used to characterize the electrical properties of the graphite-polyurethane paints. The resistance of the conductive films is important parameter in the model to predict the voltage profile of the electrified panels undergoing electrochemical antifouling. The two methods used to determine sheet resistance are (1)
Transfer Length Method (TLM) and (2) Four Point Probe (4PP). All techniques use the graphite-polyurethane thin film electrodes as described in section 3.1.4.

3.3.1: Transfer Length Method (TLM)

TLM operates by applying highly conductive contacts of given width at different locations along a strip of the conductive carbon test sample as shown in Figure 12.

![Figure 12. Diagram for Transfer Length Method resistivity measurements. Blue areas represent highly conductive contacts on top of the gray carbon paint film.](image)

The resistance between each contact is measured and a plot of observed resistance versus contact separation distance yields a straight line, whose slope and intercept contain the electrical properties of the film. The governing equation to find sheet resistance is given as [37]:

\[ R = \frac{\rho}{Wt} L + 2R_c = \frac{R_{sh}}{W} L + 2R_c \]  

Where \( R \) is the resistance between silver epoxy contacts, \( \rho \) is the resistivity of the film, \( t \) is the film thickness, \( L \) is the distance between the ends of each contact, \( W \) is the film width, and \( R_c \) is the contact resistance. This method is simple and effective; however, the measurement destroys the sample. Table 7 details the TLM experiments conducted.
Table 7. Summary of TLM experiments conducted.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Graphite wt %</th>
<th>Film Thickness</th>
<th># of trials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>60</td>
<td>~ 80 um</td>
<td>3</td>
</tr>
<tr>
<td>Glass</td>
<td>55</td>
<td>~ 80 um</td>
<td>3</td>
</tr>
<tr>
<td>Glass</td>
<td>49</td>
<td>~ 80 um</td>
<td>3</td>
</tr>
<tr>
<td>Acrylic</td>
<td>49</td>
<td>~ 30 um</td>
<td>2</td>
</tr>
<tr>
<td>Acrylic</td>
<td>43</td>
<td>~20 um</td>
<td>3</td>
</tr>
</tbody>
</table>

3.3.2: Four Point Probe (4PP)

Four point probe measurements operate by injecting current into a conductive film with two outer probes and recording the observed potential between the two inner probes. The diagram of a 4PP measurement system is given in Figure 13.

![Diagram of four point probe](image)

**Figure 13.** Diagram of four point probe. The two outer contacts conduct current while the two inner contacts measure voltage difference. Knowing the supplied current and observed voltage allows one to determine resistivity.
The governing equation for the four point probe is given as [37]:

\[
R_{sh} = \frac{\pi}{\ln 2} \frac{V}{I}
\]  

(3.3)

The derivation of this equation assumes that the film thickness is much smaller than contact spacing and there are no edge effects. The four point probe used to conduct the measurements was formed using a 1 x 4 spring-loaded contact supplied by digikey.com (part # ED90476-ND). The contacts are uniformly spaced 0.100” apart and are 0.042” diameter. The contacts are soldered onto a development board, obtained from Radio Shack, as shown in Figure 14.

![Figure 14. Four point probe used to measure paint electrode resistivity.](image)

The constant current source supplying the four point probe is provided by the following circuit shown in Figure 15. The 5V regulator (part # 7805) and resistors were purchased from Radio Shack.
Figure 15. Wire diagram for 4 point probe. The 5V regulator maintains 5 V between the middle and left contact. The current depends on \( R_i \). Measuring the voltage across the 10 ohm resistor measures the current.

The current is monitored by placing a 10 ohm resistor in series and monitoring the potential with a multimeter and is governed by the equation:

$$ I = \frac{5 \text{ Volts}}{R_i} $$

For resistive films, such as graphite, lower current is preferred. As a result, the current for the four point probe is maintained around 380 \( \mu \text{A} \). Another multimeter is used to measure the potential across the 10 ohm resistor to calculate the current flowing through the system. The benefit of this measurement system is that it is non-destructive to the electrode sample.
3.4: Electrochemical Characterization of Graphite-polyurethane Electrodes

This section outlines the methods used to study the electrochemical properties of the graphite-polyurethane electrodes. The purpose is to gain insight about the electrochemical reactions occurring at different electrode potentials. All experiments were carried out using the Gamry 3000 Reference Potentiostat. Test electrodes were prepared as described in section 3.1.5, and the chemicals used to make the various electrolytes for these experiments are listed in Table 8.

Table 8. Chemicals used to prepare electrolytes for electrochemical studies of graphite-polyurethane thin film electrodes.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Chloride, 99.8 %</td>
<td>J.T. Baker and VWR</td>
</tr>
<tr>
<td>Sodium tetrafluoroborate, 97 %</td>
<td>Riedel-de Haen</td>
</tr>
<tr>
<td>Sodium Bromide, 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Yaquina Bay seawater, filtered</td>
<td>Hatfield Marine Science Center</td>
</tr>
</tbody>
</table>

All experiments were carried out in a 250 mL round bottom flask with an accompanying magnetic stir rod and a salt bridge to an Erlenmeyer flask containing a graphite bar counter electrode. A Gamry Ag/AgCl in saturated KCl reference electrode was used for all cyclic voltammetry and potentiostatic experiments.

3.4.1: Potentiostatic Analysis

A 49 wt % graphite-polyurethane thin film electrode underwent potentiostatic analysis. The purpose of these experiments were to determine steady state current
densities at varying potentials while minimizing mass transport limitations by including vigorous stirring. The potentiostatic analysis procedure is as follows:

1. Set the graphite test electrode’s potential to a specified value.
2. Three minutes into the experiment, start up the stir bar to decrease mass transport effects.
3. Six minutes into the experiment, turn off the stir bar.
4. At 10 minutes, shut off power to the cell.
5. Repeat for different electrode potentials.
6. Plot electrode current density when stir bar is active for each electrode cell potential.
7. Fit data to simplified Butler-Volmer expression.

The potentials used in the analysis were 1.0, 1.05, 1.1, 1.15, and 1.2 V v. Ag/AgCl. Figure 16 shows a potentiostatic profile run. The current and electrode potential are recorded when the stir bar is active.
Figure 16. Potentiostatic scan profile. Current increases by over two fold when the stir bar is active.

Assuming no mass transport limitations and that operating potentials are 50 mV higher than the overpotential, the Butler-Volmer expression may be simplified to only include the oxidation reaction term:

\[ i = A i_0 \exp \frac{\beta F(E - E_0)}{RT} = A i_{0,exp} \exp \frac{\beta F E}{RT} \]  

(3.5)

Where \( i_{0,exp} \) absorbs the overpotential exponential term. A plot of log of current density versus electrode potential allows one to find the charger transfer coefficient from the slope and apparent exchange current density from the intercept.

3.4.2: Cyclic Voltammery Analysis

The purpose of these cyclic voltammetry experiments was to detect electrochemically active species. It operates by sweeping the voltage potential for a
specified voltage window and at a specified voltage sweep rate and recording the current.

Plotting current versus voltage allows one to identify oxidation and reduction peaks.

Table 9 specifies the operating parameters for all cyclic voltammetry experiments.

Table 9. Summary of cyclic voltammetry experimental parameters. All experiments utilized a 55 wt % graphite-polyurethane electrode. Scan rate for all cyclic voltammogram experiments is set at 100 mV/sec. Filtered seawater was obtained from Hatfield Marine Science Center.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Electrolyte</th>
<th>Voltage Window</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Filtered Seawater</td>
<td>-0.5 to 1.7 V</td>
</tr>
<tr>
<td>2</td>
<td>Filtered Seawater</td>
<td>-0.4 to 1.5 V</td>
</tr>
<tr>
<td>3</td>
<td>0.6 M NaBF₄</td>
<td>-0.4 to 1.5 V</td>
</tr>
<tr>
<td>4</td>
<td>0.6 M NaBF₄ and 612 mM NaCl</td>
<td>-0.4 to 1.5 V</td>
</tr>
<tr>
<td>5</td>
<td>612 mM NaCl</td>
<td>-0.4 to 1.5 V</td>
</tr>
<tr>
<td>6</td>
<td>612 mM with 67 ppm Br⁻</td>
<td>-0.4 to 1.5 V</td>
</tr>
<tr>
<td>7</td>
<td>612 mM NaCl</td>
<td>-0.4 to 1.2 V</td>
</tr>
<tr>
<td>8</td>
<td>612 mM with 67 ppm Br⁻</td>
<td>-0.4 to 1.2 V</td>
</tr>
</tbody>
</table>

3.5: Voltage Profile Experiments

This subsection describes the experimental setup in order to measure localized voltages on the surface of uniformly-coated graphite-polyurethane thin film electrodes. The purpose of this is to predict the protection distance provided by electrochemical disinfection.
3.5.1: Materials and Equipment for Voltage Profile Experiment

The test cell consists of a retrofitted Nalgene Pipette Washer from OSU surplus store. A 1” diameter graphite rod, obtained from the Graphitestore.com (item # MT001008) served as a counter electrode. A vertical mixing bar was fabricated out of polypropylene rod and fins in order to stir the solution. A Caframo Stirring Motor rotated the stirring rod at a speed of 172 RPM, and a Gamry Ag/AgCl reference electrode was utilized along with the Gamry Reference 3000 Potentiostat operating in potentiostatic scan mode. Figure 17 shows a diagram of the experimental setup used in voltage profile experiments.

![Figure 17. Voltage profile experimental setup.](image-url)
All tests used 0.612 M NaCl with 67 ppm Br\(^-\) supplied by NaBr. The potential difference between voltage probes was measured by an HP 34401-A multimeter and recorded in a lab notebook.

3.5.2: Voltage Profile Model Development

The voltage profile model for the test plates is derived from first principles and is governed by the following assumptions:

- 1-D mass transport normal to electrode surface.
- 1-D current flow in the graphite-polyurethane thin film electrode.
- A single, dominant electrochemical species exists (no multiple reactions).
- Uniform sheet resistance.
- Negligible voltage drop due to electrolyte resistance.

When deriving the mathematical model to predict surface voltage versus distance from electrode source, it is best to imagine it as a charge balance. Charge enters a differential length element uniformly along the film width. Charge can either leave by participating in the electrochemical reaction or by traveling to an adjacent differential length element.

The charge balance equation becomes:

\[
\frac{dI(x)}{dx} = -j_{\text{rxn}} * W
\]  

(3.6)

where \(I(x)\), \(j_{\text{rxn}}\), and \(W\) represent current at length \(x\), electrochemical current density, and electrode width, respectively. The electrochemical current density is a function of both surface voltage and reduced compound concentration and is given as:
where $c$ and $c_0$ represent the concentration of the reduced compound at the electrode surface and bulk, respectively. Solving for the ratio between surface and bulk concentration requires setting the charge flux due to the electrochemical reaction equal to the charge flux in solution due to mass transport as done in the equation below:

$$I_0 \exp \left( \frac{\beta FE}{RT} \right) \frac{c}{c_0} = k_m (c_0 - c) * z * F$$  \hspace{1cm} (3.8)$$

where $k_m$ is the convective mass transfer coefficient. Solving for $c/c_0$ and plugging back into the electrochemical current density equation (3.7) yields:

$$j_{rxn} = \frac{I_0 \exp \left( \frac{\beta FE}{RT} \right)}{k_m * z * F \left( \frac{1}{c_0} \right) + 1}$$  \hspace{1cm} (3.9)$$

The current density equation (3.9) is then substituted into the charge balance equation (3.6) to yield:

$$\frac{dI(x)}{dx} = \frac{I_0 \exp \left( \frac{\beta FE}{RT} \right)}{k_m * z * F \left( \frac{1}{c_0} \right) + 1}$$  \hspace{1cm} (3.10)$$

A differential element of Ohm’s law for thin film electrodes is given as:

$$\frac{dV}{dx} = -I(x) \frac{R_{sh}}{W}$$  \hspace{1cm} (3.11)$$

Differentiating Ohm’s law with respect to $x$ and substituting in the current balance relation yields the final expression which models the surface voltage of the electrode.
Inspecting equation (3.12) reveals that current density and sheet resistance are strongly coupled. Therefore, the sheet resistance must be measured through other methods in order to obtain the other model parameters. Boundary conditions for the voltage profile experiment are:

\[
\frac{dV}{dx} = 0 \quad \text{at } x = L \text{ (end of electrode)}
\]

\[
V = V_{set} \quad \text{at } x = 0 \text{ (begining of electrode)}
\]  

(3.13)

3.5.3: In-line voltage profile

Measuring the voltage difference across adjacent voltage probes allows one to calculate the sheet resistance based on the following relation:

\[
R_{sh} = \frac{V_{a-a+1} W}{I \Delta x}
\]

(3.14)

where \( V_{a-a+1} \), I, W, and \( \Delta x \) are voltage between adjacent probes, current, width of plate, and distance between voltage probes, respectively. The average sheet resistance for each electrode was used in the data analysis.

3.5.4: Experimental Procedure

All voltage profile experiment operated under potentiostatic scan. The current was allowed to stabilize prior to collecting data. Experiments were done at 1.2, 1.15, and
1.10 V with two trials on each electrode. The potential was mapped on five test panels, and their composition provided in Table 10.

**Table 10. Voltage profile electrode composition.**

<table>
<thead>
<tr>
<th>Panel</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-3-21-1</td>
<td>43 %</td>
</tr>
<tr>
<td>D-3-21-2</td>
<td>43 %</td>
</tr>
<tr>
<td>D-3-9-1</td>
<td>43 %</td>
</tr>
<tr>
<td>D-3-21-3</td>
<td>55 %</td>
</tr>
<tr>
<td>D-3-21-4</td>
<td>55 %</td>
</tr>
</tbody>
</table>

3.5.5: Voltage Profile Data Analysis

MATLAB code was written to determine the physical electrode properties to yield the best fit to experimental results. The code is provided in Appendix B. The algorithm to determine the best equation parameters is as follows:

1. Start with parameter guesses and numerically solve 2nd order nonlinear differential equation.
2. Compare model with experimental data and determine R².
3. Choose a parameter to adjust and resolve model¹ and recalculate R².
4. If R² improves, keep new data and adjust a different parameter¹.
5. Repeat steps 3 and 4 until the R² value has met its optimal point.

The nonlinear second order equation is solved numerically using the three-stage IIIa formula via the built-in bvp4 function in MATLAB. The model parameters are adjusted to optimize the R² value by using the Nelder-Mead algorithm [51] built into MATLAB.

¹ The logic in determining which parameter to adjust and by how much is part of the Nelder-Mead algorithm.
The Nelder-Mead solver is non-derivative and works by constructing an n+1 simplex, where n is the number of open parameters [52]. In the case of n=3, the simplex is a Tetrahedral shape in 3D. Optimization is found by comparing the whole simplex with an adjacent one, which is calculated by evaluating one additional point as the other three points were calculated for the starting simplex. If the new simplex is better, it will switch over to that one. If all neighboring simplexes do not yield better results, the simplex size is reduced and the algorithm continues.
Chapter 4

RESULTS AND DISCUSSION

4.1: Filtered Seawater Tank Experiments

All experiments showed biofouling after two weeks of deployment. This observation agrees well with results published in literature [1],[11],[48].

4.1.1: Experiment 1

The purpose of this experiment was to demonstrate that electrochemical antifouling is as effective as conventional copper biocide coatings. It occurred between June 23rd, 2010 and July 21st, 2010. The working electrode was held at a potential of 1.5 V versus Ag/AgCl in seawater with a mild steel counter electrode. A carbon-urethane film electrode was also present to serve as a control. Three conventional paints from Pettit marine paint company were also included on the test plate array. Figure 18 shows the test plate array at one and two weeks into the experiment.
Figure 18. Seawater tank experiment 1 on 1st (left) and 2nd (right) week after deployment. From top to bottom, the test plates are: graphite-polyurethane film electrode held at 1.5 V vs. Ag/AgCl in seawater, control carbon paint electrode, Pettit Trinidad Antifouling, Ultima SSA Antifouling, and Antifouling yacht copper paints. All copper biocide coatings offer protection to the adjacent PVC frame as highlighted in the photograph.

Experimental results show that the electrochemical antifouling system performs comparable to copper biocide coatings. The PVC frame and graphite-polyurethane control plate were fouled. One difference between the electrified test plate and the copper biocide paints is in adjacent antifouling efficacy. All three biocide paints, which operate by the continuous leaching out of the coating, also keep part of the PVC frame protected by algae formation.

Both images in Figure 18 show a white precipitate forming on the mild steel counter electrode. The precipitate on the counter electrode was later determined to be magnesium hydroxide via ICP-AES, and this conclusion is supported by literature [53]. The precipitate is likely caused by localized increase in pH at the counter electrode, resulting from the reduction of hydronium to hydrogen gas [53],[54]. Aside from the magnesium hydroxide precipitate, the counter electrode remained free of algae fouling and showed minimal corrosion damage. The electrochemical antifouling mechanism
failed at week 3 due to the degradation of the graphite paint electrode wire contact point. The aluminum foil substrate suffered catastrophic degradation and broke the circuit, indicating that some metal are not suitable substrates as they rapidly corrode.

4.1.2: Experiment 2

The purpose of this experiment was to investigate the feasibility of using the graphite paint as both the reference and counter electrode. It took place between August 20th, 2010 and September 10th, 2010. The working electrode voltage was maintained at 1.5 V vs. Ag/AgCl in sea water. Antifouling performance of both graphite paint electrodes lasted for 3 weeks until the system failed. Inspection of the test plates after the experiment revealed that the counter electrode was blistering as shown in Figure 19.

![Test plate array after second seawater tank experiment.](image)

Figure 19. Test plate array after second seawater tank experiment. The coatings are Pettit (1) Trinidad antifouling, (2) Ultima SSA antifouling paints, (3) graphite urethane paint control, (4) counter electrode, and (5) working electrode.

Blistering on the counter electrode was worse near the contact point and is the likely cause of electrochemical antifouling failure. Some white precipitate formed near the connection point on the counter electrode, but the buildup was nowhere near the amount
observed on the mild steel counter electrode from the previous experiment. The working electrode shows some signs of degradation near the electrode contact point, suggesting that 1.5 V causes electrode damage.

4.1.3: Experiment 3

The purpose of this experiment was to investigate whether a carbon fiber epoxy panel would be a suitable cathode material. It took place between October 15th, 2010 and November 19th, 2010. The working electrode was held at -1.0 V versus Ag/AgCl in seawater with a graphite rod counter electrode. The carbon fiber panel electrode is shown in Figure 20 two weeks into the experiment.

![Figure 20. Reinforced carbon fiber epoxy panel cathode (right) two weeks into experiment. Other visible test panels are (left) Pettit Ultima SSA Antifouling and (middle) graphite-polyurethane control.](image)
Accumulation of magnesium hydroxide was observed; however, no signs of algae colonization appeared. Working electrode seemed not to be permanently damaged after scrapping some magnesium chloride off its surface. This indicates that the polyurethane binder is the likely source of failure as opposed to graphite itself.

4.1.4: Experiment 4 and 5

The purpose of the final two tank experiments was to find evidence of an antifouling minimum protection distance. All previous experiments have shown that graphite-polyurethane coatings become fouled in the absence of applied potential as observed on the control electrodes. Therefore, it seems reasonable that biofouling would occur on the surface of a polarized electrode some distance away from the voltage source. These two experiments utilized the same working electrode, which was a 4” x 20” 55 wt % graphite-polyurethane thin film electrode. A 24” long mild steel rod served as the counter electrode. The biofouling progress was also monitored with a webcam connected to a laptop computer.

The forth experiment occurred from February 11, 2011 through April 1st, 2011. The potential was set to 1.2 V on the forth experiment, and the entire surface remained free of biofouling until the end of the experiment as shown in Figure 21.
Figure 21. Image of test electrodes after completion of experiment 4 on April 1st, 2011. The control plate (left) is completely fouled while the graphite-polyurethane thin film electrode that was held at 1.2 V vs. Ag/AgCl in seawater by the potentiostat shows no evidence of biofouling along its length. Some biofouling has spilled over from the PVC frame onto the edges of the film.

The experiment lasted a total of 49 days, and the surface of the thin film electrode held at 1.2 V vs. Ag/AgCl in seawater remained relatively free of biofouling. Some biofouling on the edges was observed and attributed to algae adjacent to the plate. Everything else was completely covered in algae. The potential was lowered from 1.2 to 1.1 V vs. Ag/AgCl in seawater for the fifth and final experiment. It occurred between April 1st, 2011 and May 24th, 2011. Figure 22 shows the test panel at the completion of the experiment.
Figure 22. Test plates after 5th seawater tank experiment after completion of experiment on May 24th, 2011. The control graphite-polyurethane electrode is completely covered in biofouling whereas the electrode held at 1.1 V v. Ag/AgCl in seawater is free of biofouling up to a depth of 6 inches.

Unlike the previous experiment, biofouling occurred 6 inches past the water-air interface and on the test plate end opposite of the electrode-wire contact. Earlier research on graphite-polyurethane thin film electrodes have shown that antifouling efficacy depends on applied potential on its surface as documented in Figure 4.
If antifouling efficacy is dependent on surface potential, the experiment five results suggest that a potential profile forms on the electrode surface. At a certain distance, the potential drops to the point where it is no capable of preventing biofouling. Referring to equation (3.12), the factors which influence voltage profile are the electrical and electrochemical properties of the graphite-polyurethane thin film electrode. In order to predict the voltage profile, these properties must be studied.

The voltage window where the fouling was observed on the electrode surface also corresponds to equilibrium hypochlorite and hyprobromite concentrations near the toxicity limits for biofouling organisms. Seawater contains 2.16 wt % chloride ions and 67 ppm bromide anions. For the half-reactions of both chlorine and bromine, it is possible to plot the equilibrium constant, Q, versus cell potential as shown in Figure 23. For chlorine and bromine, the standard half-cell potentials are 1.36 V and 1.07 V, respectively. Plugging these values into the Nernst equation, one may plot the equilibrium activity of chlorine and bromine redox species versus electrochemical potential.
Figure 23. Equilibrium concentration of chlorine and bromine in sea water versus cell potential. Numbers based on a sea water temperature of 10 degrees Celsius, 3.5 wt % salinity, and 67 ppm Br\textsuperscript{-} concentration.

It is evident from Figure 23 that the equilibrium concentration of both bromine and chlorine only start to become significant in the voltage range past 1.0 V versus SCE, where the equilibrium ppm approaches levels that are toxic to marine organisms (~0.5 – 1.5 ppm) [55].

4.2: Electrical Properties of Graphite-Polyurethane Thin Film Electrodes

This subsection describes the material characterization results of the graphite urethane thin film electrodes. Characterizing the electrical properties is important to predicting the voltage profile. The results from open seawater tank experiment five suggest that a voltage profile on the surface can predict vulnerability to biofouling.
4.2.1: Transfer Length Method Results

Various TLM structures were conducted on both glass and acrylic substrates. The results are tabulated in Table 11.

Table 11. Tabulated results from TLM resistivity measurements. The average sheet resistance was determined by averaging the individual TLM measurements. When there was an outlier, the average was taken over the two closer values, indicated by the superscript on the average sheet resistance value.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Wt %</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>60</td>
<td>113</td>
<td>80</td>
<td>77</td>
<td>78.2(^{2,3})</td>
</tr>
<tr>
<td>Glass</td>
<td>55</td>
<td>57</td>
<td>70</td>
<td>72</td>
<td>71(^{2,3})</td>
</tr>
<tr>
<td>Glass</td>
<td>49</td>
<td>147</td>
<td>114</td>
<td>N/A</td>
<td>147(^1)</td>
</tr>
<tr>
<td>Acrylic</td>
<td>49</td>
<td>285</td>
<td>287</td>
<td>136</td>
<td>286(^{1,2})</td>
</tr>
<tr>
<td>Acrylic</td>
<td>43</td>
<td>998</td>
<td>1020</td>
<td>N/A</td>
<td>1,009</td>
</tr>
</tbody>
</table>

The general trend between increase in graphite filler loading and decrease in sheet resistance is observed. Lowest sheet resistance was observed for 55 wt % rather than 60 wt %. The difference between the two is small, and may be attributed to error in the samples. The electrode film thickness was lower on acrylic substrates than on glass. This is why the resistance measurements for 49 wt % on glass and acrylic differ so much. Assuming that the bulk resistivity is the same for all samples, the sheet resistance may for glass substrates may be normalized by multiplying them by a factor of two. Upon doing so and plotting the sheet resistance versus filler weight composition in Figure 24 shows a relation that looks very similar to what one would expect for percolation theory.
**Figure 24.** Normalized sheet resistance versus graphite filler loading. The trend appears to follow percolation theory.

The sheet resistance drops sharply between 43 and 49 wt % samples. Changes in sheet resistance after 49 wt % are not as steep, suggesting that the graphite filler network is nearing saturation. Increasing the film thickness will yield lower film resistance, but this also has limitations that must also be considered.

4.2.2: Four Point Probe Results for Graphite-Polyurethane Thin Film Electrode

The purpose of 4PP characterization was to verify the accuracy of TLM resistivity measurements. TLM and 4PP measurements were performed on different 49 % graphite-polyurethane thin films on acrylic substrate as shown in Figure 25.
Figure 25. Comparison of sheet resistance measurements for 49 wt% graphite-polyurethane paint. Resistivity determined by TLM and 4PP. It seems that paint strips were very uneven on the center plate, where its resistance is 100 ohm less than the two upper bands.

TLM resistance measurements are obtained by plotting the resistance between the silver epoxy contacts, and all yield very high $R^2$ values, suggesting that each section of the film share the same sheet resistance. On the other hand, 4PP resistance measurements ranged from 165 to 204 $\Omega/\square$ with a uniformity of 89 %. This is probably due to the fact that the localized resistivity of the graphite urethane paint is uneven on the scale size used in the four point probe measurements. However, 4PP measurements conducted on the 20 mm wide TLM features were off by at most 7.5 %. This suggests that the deposition

$$R_{sh} = 285 \text{ ohm/sqr (} R^2 = 0.992)$$
$$R_{sh,8} = 265 \text{ ohm/sqr (} 7.5\% \text{ error})$$

$$R_{sh} = 287 \text{ ohm/sqr (} R^2 = 0.923)$$
$$R_{sh,7} = 298 \text{ ohm/sqr (} 3.8\% \text{ error})$$

$$R_{sh} = 136 \text{ ohm/sqr (} R^2 = 0.948)$$
$$R_{sh,6} = 145 \text{ ohm/sqr (} 6.5\% \text{ error})$$

$$R_{sh,1} = 192 \text{ ohm } R_{sh,2} = 165 \text{ ohm}$$
$$R_{sh,3} = 185 \text{ ohm } R_{sh,4} = 228 \text{ ohm}$$
$$R_{sh,5} = 204 \text{ ohm}$$

\[ U = \left(1 - \frac{\text{Standard deviation}}{\text{average}}\right) \times 100\% \]

\[ U = \left(1 - \frac{\sigma}{\mu}\right) \times 100\% \]

\[ U = \left(1 - \frac{\text{Standard deviation}}{\text{average}}\right) \times 100\% \]
uniformity may be too difficult to maintain for 4” wide electrodes. Consequently, the voltage profile electrodes were constructed as 2” wide strips to help improve uniformity.

4.3: Electrochemical Properties of Graphite-Polyurethane Thin Film Electrodes

The electrochemical properties of graphite-polyurethane thin film electrodes are necessary in order to estimate its voltage profile per equation (3.12). It is important to estimate the relationship between current density and surface potential and also attempt to identify electrochemically active species in seawater.

4.3.1: Potentiostatic Results

The purpose of the potentiostatic experiments was to obtain a relationship between surface voltage and current density. These experiments were conducted with a 49 wt % graphite-polyurethane thin film electrode in filtered seawater. Figure 26 shows a plot of the natural log of current density versus electrode voltage obtained from numerous potentiostatic trials. A linear fit may then be applied to obtain electrochemical reaction parameters for the simplified Butler-Volmer equation (3.5) rearranged into:

\[
\ln \frac{i}{A} = \ln I_{0,exp} + \frac{\beta F E}{RT}
\]  

(4.1)

where the slope is proportional to the charge transfer coefficient and the intercept is related to the current pre-exponential factor.
Figure 26. Ln(I0) versus Vworking versus Ag/AgCl in Sat. KCl. All transfer coefficients seem to be around 9.84, but the exchange current varies over run, approaching negative 8.9.

All plots were obtained from the same electrode in the same electrolyte solution of filtered seawater at different times. D-2-105-0 represents the first potentiostatic scan and run L was the last. The nonlinearity potentiostatic profiles suggest that two or more electrochemical reactions are occurring in the voltage window. It seems that another reaction begins to dominate at around 1.1 V v. Ag/AgCl, or 1.2 V v. SHE. There are a few electrochemical possibilities for the reactions occurring near this potential, and they are investigated via cyclic voltammetry section.
The overall current of the electrode increases over time, suggesting that the electrode is being conditioned. As the conditioning continues, the nonlinearity relationship between natural log of current and voltage is better approximated linearly. Although this is not ideal, it provides simpler reaction kinetics for the overall voltage profile equation (3.12), which is preferred. After experiment L, the electrolyte was replenished and three additional potentiostatic experiments were conducted and plotted on Figure 27.

![Figure 27. Potentiostatic analysis after fresh electrolyte flush. The transfer coefficient jumped from around 9 to 14.](image)
The log of current for 1.2 V is about the same where it left off from the previous runs.

However, log of current between 1.0 and 1.05 is much lower, favoring a linear fit assumption. The exchange current also continues to increase. A best fit linear approximation is done for each potentiostatic profile and the results are tabulated in Table 12.

**Table 12.** Potentiostatic data along with calculated charge transfer coefficient and exchange current density. The electrolyte was replaced between run L and M.

<table>
<thead>
<tr>
<th>Potentiostatic run letter</th>
<th>Slope, ( V )</th>
<th>Intercept</th>
<th>( R^2 )</th>
<th>( \beta )</th>
<th>Exchange Current Density, ( \mu A/cm^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.78</td>
<td>-7.67</td>
<td>0.927</td>
<td>0.199</td>
<td>2.14E-08</td>
</tr>
<tr>
<td>B</td>
<td>9.17</td>
<td>-8.79</td>
<td>0.909</td>
<td>0.234</td>
<td>1.62E-09</td>
</tr>
<tr>
<td>D</td>
<td>10.81</td>
<td>-10.25</td>
<td>0.928</td>
<td>0.276</td>
<td>5.62E-11</td>
</tr>
<tr>
<td>E</td>
<td>10.77</td>
<td>-10.11</td>
<td>0.927</td>
<td>0.275</td>
<td>7.76E-11</td>
</tr>
<tr>
<td>I</td>
<td>9.38</td>
<td>-8.48</td>
<td>0.932</td>
<td>0.239</td>
<td>3.31E-09</td>
</tr>
<tr>
<td>J</td>
<td>9.84</td>
<td>-8.92</td>
<td>0.946</td>
<td>0.251</td>
<td>1.20E-09</td>
</tr>
<tr>
<td>K</td>
<td>9.96</td>
<td>-9.01</td>
<td>0.938</td>
<td>0.254</td>
<td>9.77E-10</td>
</tr>
<tr>
<td>L</td>
<td>9.50</td>
<td>-8.49</td>
<td>0.952</td>
<td>0.242</td>
<td>3.24E-09</td>
</tr>
<tr>
<td>M</td>
<td>13.87</td>
<td>-13.99</td>
<td>0.973</td>
<td>0.354</td>
<td>1.02E-14</td>
</tr>
<tr>
<td>N</td>
<td>14.07</td>
<td>-13.95</td>
<td>0.965</td>
<td>0.359</td>
<td>1.12E-14</td>
</tr>
<tr>
<td>O</td>
<td>13.93</td>
<td>-13.59</td>
<td>0.982</td>
<td>0.355</td>
<td>2.57E-14</td>
</tr>
</tbody>
</table>

The slope remains relatively stable around 9.5 V, indicating a charge transfer coefficient of 0.242. However, the intercept gradually increases in value. The charge transfer coefficient remains constant but the current density increases. This suggests that the
composite electrode is changing such that more graphite surface area is exposed. Although, when the cell is flushed with fresh electrolyte, the slope and current density change. However, for their data set the slope remains relatively constant while the current density increases.

Potentiostatic scan results indicate that there may be more than one electrochemical occurring in the voltage window and the electrode needs time to condition. For these reasons, electrode used for the cyclic voltammetry studies was conditioned for three days. The electrodes used for voltage profiling analysis were conditioned for 1 day. Voltage profile experiments were performed at voltages less than 1.15 V vs. Ag/AgCl to reduce nonlinearity.

4.3.2: Cyclic Voltammetry Results

The purpose of cyclic voltammetry analysis was to obtain a preliminary understanding of the electrochemical reactions occurring in the voltage 0.8 to 1.2 V vs. Ag/AgCl voltage window. A 55 wt% graphite-polyurethane thin film electrode on graphite substrate served as working electrode and conditioned at 1.2 V vs. Ag/AgCl for 3 days. The first cyclic voltammetry was done in filtered seawater, and it is shown in Figure 28.
Figure 28. Cyclic voltammogram of 55 wt % graphite urethane paint after 76 (dashed/green line) and 82 (solid/blue line) hours conditioning at 1.2 V vs. Ag/AgCl, respectively.

This cyclic voltammogram clearly shows electrochemical activity in the given voltage window, contrary to reports in literature [2]. An oxidation peak begins to form around 0.9 V but gets mixed up with another peak, suggesting two electrochemical reactions are occurring. In order to determine the chemical species associated with the oxidation, addition cyclic voltammetry in various electrolytes were conducted. Figure 29 shows the cyclic voltammogram 0.612 M NaBF$_4$ overlaid with 0.612 M NaBF$_4$ and 0.612 M NaCl.
Figure 29. Cyclic voltammogram overlay of 55 wt% graphite urethane paint in 0.612 M NaBF₄ electrolyte (solid blue line) and 0.612 M NaBF₄ with 0.612 M NaCl (dash/green line). The current limit was reached in the NaBF with NaCl solution before it reached 1.5 V.

The oxidation peak on the NaBF₄ voltammogram does not begin to emerge until after 1.3 V, and this is most likely due to oxidation of water into oxygen. A reduction peak occurs around 0.96 V after sodium chloride is added to solution, suggesting the reduction of oxidized chlorine species. Possible chloride redox half-reactions for acidic standard conditions are [25]:

\[
\text{HClO} + \text{H}^+ + 2 \, \text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad E^0 = 1.5 \, \text{V} \quad (4.2)
\]

\[
\text{Cl}_2 + 2 \, \text{e}^- \rightarrow 2 \, \text{Cl}^- \quad E^0 = 1.358 \, \text{V} \quad (4.3)
\]
The redox potential of chloride to chlorine is 1.158 V v. Ag/AgCl in saturated KCl, which rests between oxidation and reduction peak, making it a possible reaction pathway. The redox potential of chloride to hypochloric acid is dependent on the pH of solution. Using the Nernst Equation (2.4) to adjust for pH of NaBF₄ solution (pH 4) yields a redox potential of:

\[
E = 1.5 \ V - \frac{RT}{zF} \ln Q = 1.5 \ V - 295 \ \text{mV} \times 4 = 1.376 \ \text{V}
\]

(4.4)

The redox potential of hypochloric acid at pH 4 occurs at 1.176 V v. Ag/AgCl, which also rests between the observed oxidation and reduction peaks observed in Figure 29. The electrochemically active species may be either of these. Electrode degradation reactions are not likely the cause as those peaks wouldn’t be limited to mass transport and would exhibit a sharper peak [29].

Researchers studying various graphite electrodes for detection of halides under acidic conditions attribute the reduction peak at 0.9 V to bromine reduction, while chlorine reduction occurs at lower potentials [42],[43]. As the concentration of bromide in seawater is 67 ppm, cyclic voltammetry under both 0.612 NaCl and 0.612 NaCl with 67 ppm Br⁻ from NaBr solutions as shown in Figure 30 and Figure 31.
Figure 30. Cyclic voltammogram of 0.612 M NaCl (dashed green line) and 0.612 M NaCl with 67 ppm NaBr (solid blue line).

The reduction peak for both voltammograms in Figure 30 are located at about 0.9 V as opposed to the 0.96 V observed in acidic solution. This suggests that the reduced species is not chlorine as its standard potential is unaffected by pH. Aside from peak intensity, the cyclic voltammograms are similar. However, when the cyclic voltammogram window is reduced from 1.5 V to 1.2 V, as shown in Figure 27, some differences are observed.
Figure 31. Cyclic voltammogram of 0.612 M NaCl soln (dashed green line) and 0.612 M NaCl with 67 ppm NaBr (solid blue line). Potential window decreased from 1.5 V to 1.2 V versus Ag/AgCl in Sat. KCl.

Lack of reduction peak at 0.9 V in the sodium chloride voltammogram suggests that only oxidized bromine species are being produced in this potential window. The analysis of cyclic voltammetry data from various solutions and potential ranges show that bromide oxidation product hypobromite is important in the potential window for electrochemical antifouling systems. The results suggest that 0.612 M sodium chloride spiked with 67 ppm bromide from sodium bromide is an acceptable substitute for filtered sea water when conducting voltage profile experiments as their oxidation and reduction peaks match up. Using a synthetic solution is preferred as it allows more control in the voltage profile parameters.
4.4: Thin Film Electrode Surface Potential Profile

This section attempts to bridge both the electrical and electrochemical properties of the graphite-polyurethane thin film electrode in order to model the measured voltage profiles on several graphite-polyurethane thin film electrodes. Previous experiments have shown that antifouling efficacy depends on surface voltage, and surface voltage decreases along the path way from the voltage source. Voltage profile experiments occurred in 0.612 M NaCl with 67 ppm Br\textsuperscript{-} solutions, and all voltage profile electrodes were conditioned for a day at 1.2 V v. Ag/AgCl in saturated KCl.

4.4.1: Plate Resistivity

Test electrode average resistivity was measured by use of the built-in voltage probes as described in the materials and methods section; the results are shown in Figure 32.

**Figure 32.** Local average sheet resistance of test electrodes. The average sheet resistance for each test electrode was obtained from this data and input into the MATLAB model.
The test plate with the worst resistance uniformity is D-3-21-4, which is a 55 wt % graphite urethane coating. All others have acceptable tolerances of +/- 10 % of the overall average sheet resistance. The average sheet resistance, provided in Table 13, was used in calculating the model parameters under MATLAB.

Table 13. Average sheet resistance and composition of test panels used in potential profiling experiments.

<table>
<thead>
<tr>
<th>Plate ID</th>
<th>% composition</th>
<th>$R_{sh}$, avg in ohm/sqr</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-3-21-1</td>
<td>43</td>
<td>1,217</td>
</tr>
<tr>
<td>D-3-21-2</td>
<td>43</td>
<td>697</td>
</tr>
<tr>
<td>D-3-21-3</td>
<td>55</td>
<td>126</td>
</tr>
<tr>
<td>D-3-21-4</td>
<td>55</td>
<td>173</td>
</tr>
<tr>
<td>D-3-9-1</td>
<td>43</td>
<td>730</td>
</tr>
</tbody>
</table>

The results from average sheet resistance show how much variability in resistance is possible. This was observed in earlier graphite urethane thin film electrodes analyzed in Figure 25 where the sheet resistance varied from 136 to 285 ohm/square. Fortunately, individual test electrode resistance uniformity is acceptable for the following voltage profile experiments.

4.4.2: Voltage Profile Experimental Data versus Model Predictions

Preliminary results showed that electrode voltage profiles differed over time even after conditioning for 1 day. However, so long as the electrolyte wasn’t replaced, voltage profiles stabilized after a few hours. This behavior was also observed in the potentiostatic scans, indicating that voltage profile modeling may not be useful as a
design tool in for large-scale antifouling systems. All voltage profiles were obtained in the same electrolyte. The voltage profile results are shown in Figures 33 through Figure 37. The predicted current profile (shown as dashed lines) is also presented.

**Figure 33.** D-3-21-1 test plate experimental voltage profile (points) plotted together with model (solid line) and current (dashed line on secondary axis).
Figure 34. D-3-21-2 test plate experimental voltage profile (points) plotted together with model (solid line) and current (dashed line on secondary axis).

Figure 35. D-3-9-1 test plate experimental voltage profile (points) plotted together with model (solid line) and current (dashed line on secondary axis).
Figure 36. D-3-21-3 test plate experimental voltage profile (points) plotted together with model (solid line) and current (dashed line on secondary axis).

Figure 37. D-3-21-4 test plate experimental voltage profile (points) plotted together with model (solid line) and current (dashed line on secondary axis). Voltage probe #3 is bad; therefore, its experimental point is missing.
All but one test panel fits the experimental model with $R^2$ value exceeding 0.99. The worst match agreement was observed with electrode D-3-21-3 as shown in Figure 36. D-3-21-3 also has the worst resistance uniformity, as shown in Figure 32, and these two results are probably linked. The electrochemical parameters obtained for the two 50 wt % electrodes (D-3-21-1 and 2) are very similar as shown in Table 14.

<table>
<thead>
<tr>
<th>Plate #</th>
<th>$R_{sh}$, Ω/□</th>
<th>$K_M$, cm/s</th>
<th>$K_V$, V$^{-1}$</th>
<th>β</th>
<th>$I_{0\exp}$, A/cm$^2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-3-21-1</td>
<td>1,217</td>
<td>22</td>
<td>12.5</td>
<td>0.32</td>
<td>2.1e-12</td>
<td>0.995</td>
</tr>
<tr>
<td>D-3-21-2</td>
<td>697</td>
<td>23</td>
<td>11.8</td>
<td>0.30</td>
<td>2.2e-12</td>
<td>0.999</td>
</tr>
<tr>
<td>D-3-21-3</td>
<td>126</td>
<td>6.7</td>
<td>13.1</td>
<td>0.33</td>
<td>1.5e-12</td>
<td>0.968</td>
</tr>
<tr>
<td>D-3-21-4</td>
<td>173</td>
<td>23</td>
<td>10.3</td>
<td>0.26</td>
<td>2.9e-11</td>
<td>0.995</td>
</tr>
<tr>
<td>D-3-9-1</td>
<td>730</td>
<td>76</td>
<td>14.4</td>
<td>0.37</td>
<td>8.4e-13</td>
<td>0.998</td>
</tr>
</tbody>
</table>

The electrochemical parameters obtained for the two 43 wt % electrodes (D-3-21-1 and 2) are similar and that suggests graphite-polyurethane thin film electrode composition is also similar. The difference in sheet resistance is thus concluded to be a result of varying film thickness. The parameters for the other 43 wt % electrode differ from the other two, and this was attributed to electrode wear as it had been conditioned additionally during the preliminary experimental setup and design. Electrochemical parameters for 55 wt % electrodes did not match likely as consequence to the uneven uniformity of D-3-21-3. No agreement was observed for mass transfer coefficients, and
this suggests that mass transport is not a factor at 172 RPM stirring. Other experiments confirmed that mass transport has minimal impact to the overall current draw and voltage profile for 43 % and 55 wt % electrodes in the absence of stirring.

The charge transfer coefficients are relatively close and comparable to results obtained in earlier potentiostatic scans in filtered sea water. This further validates that 0.612 M NaCl with 67 ppm Br⁻ is a suitable alternative for filtered seawater when investigating electrochemical properties between 0.8 and 1.2 V v. Ag/AgCl. The predicted total current determined by model is compared to experimental data in Table 15.

<table>
<thead>
<tr>
<th>Plate #</th>
<th>Voltage, V</th>
<th>I_{exp}, µA</th>
<th>I_{model}, µA</th>
<th>I % error</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-3-21-1</td>
<td>1.142</td>
<td>85</td>
<td>104.6</td>
<td>23.06%</td>
</tr>
<tr>
<td></td>
<td>1.107</td>
<td>65</td>
<td>83.29</td>
<td>28.14%</td>
</tr>
<tr>
<td></td>
<td>1.067</td>
<td>48</td>
<td>64.39</td>
<td>34.15%</td>
</tr>
<tr>
<td>D-3-21-2</td>
<td>1.170</td>
<td>112</td>
<td>112.7</td>
<td>0.63%</td>
</tr>
<tr>
<td></td>
<td>1.128</td>
<td>87</td>
<td>86.40</td>
<td>-0.69%</td>
</tr>
<tr>
<td></td>
<td>1.084</td>
<td>62</td>
<td>64.75</td>
<td>4.44%</td>
</tr>
<tr>
<td>D-3-21-3</td>
<td>1.153</td>
<td>411.5</td>
<td>383.1</td>
<td>-6.90%</td>
</tr>
<tr>
<td></td>
<td>1.116</td>
<td>300</td>
<td>291</td>
<td>-3.06%</td>
</tr>
<tr>
<td></td>
<td>1.076</td>
<td>217</td>
<td>211.7</td>
<td>-2.44%</td>
</tr>
<tr>
<td>D-3-21-4</td>
<td>1.173</td>
<td>465</td>
<td>362.2</td>
<td>-22.11%</td>
</tr>
<tr>
<td></td>
<td>1.130</td>
<td>334</td>
<td>282.6</td>
<td>-15.39%</td>
</tr>
<tr>
<td></td>
<td>1.086</td>
<td>240</td>
<td>216.8</td>
<td>-9.55%</td>
</tr>
<tr>
<td>D-3-9-1</td>
<td>1.023</td>
<td>76</td>
<td>95.00</td>
<td>25.00%</td>
</tr>
<tr>
<td></td>
<td>1.001</td>
<td>63</td>
<td>80.06</td>
<td>27.08%</td>
</tr>
<tr>
<td></td>
<td>0.975</td>
<td>53.5</td>
<td>65.34</td>
<td>22.13%</td>
</tr>
</tbody>
</table>
The only inputs for the theoretical model were the voltage at given points on the test plate and the sheet resistance of the film. Using only this data, the predicted current matches the actual total current recorded by the potentiostat. Total plate current prediction for test plates D-3-21-2 and D-3-21-3 did not exceed 5%, which is phenomenal. Electrode current prediction error may be due in part to the difference in local sheet resistance near the current source on the test plate, corresponding to x=0 cm on Figure 32.

In sum, the voltage model closely matches experimental data. Electrode properties differ for the most part between electrodes, indicating the difficulty in obtaining uniform films. Sheet resistance uniformity is important to ensure good model fit to data, and mass transport has minimal effect on current and voltage profile. Voltage profiles differ slightly between 43 and 55 wt % electrodes; however, current profiles are much larger in 55 wt % electrodes.
5.1: Conclusions

A Graphite-polyurethane thin film composite electrode was developed and characterized for electrochemical antifouling systems. Open seawater tank experiments revealed that it is as effective as conventional biocide coatings. They also showed that metal substrates are vulnerable to electrochemical corrosion. Consequently, substrates must be corrosion resistant. If the substrate is an insulator, the thin film’s electrical resistivity leads to significant voltage drops on the surface. Experimental evidence and literature support the claim that antifouling efficacy depends on voltage.

Graphite-polyurethane thin films of roughly 90% uniformity were prepared by gliding a straight edge over a plastic film to evenly distribute coating. The film resistivity relationship to conductive filler loading trend obeys Percolation theory, and the maximum graphite loading possible is 60%. TLM analysis showed that the overall average resistivity is very uniform as opposed to the local 4PP measurements.

Electrochemical analysis indicates that multiple reactions occur in the antifouling voltage window. The electrochemical kinetics changed over the electrode’s life, which is evidence of electrode conditioning. Considering that charge transfer coefficient remained relatively constant, the change probably lies in the composite slowly hydrolyzing and exposing more graphite particle surface area. Electrodes stabilize if electrolyte is not refreshed. The cyclic voltammograms evidence suggests that both chloride and bromide
are important chemical species in the electrochemical oxidation. Their most probable oxidized forms are hypochlorite and hypobromite. Further analysis must be done to fully understand the reaction mechanism and interactions.

Experimental voltage profile data matches model predictions for each individual test electrode. It was not possible to match up parameters to a group of test panels because of variations in the composite electrode properties as well as lifetime differences for each panel. This suggests that the model works and is sound, but the production quality and reproducibility of the voltage profile electrodes must be improved. Further research on creating large electrode surfaces and developing a model that accounts for electrochemical and resistive irregularities is necessary.

5.2: Recommendations for Future Work

Future work must continue the effort to get thin film electrode antifouling technology to a point where it is a feasible alternative to copper biocide paints. With that in mind, future work should focus on:

- Develop a multi-contact thin film electrode system to demonstrate bipolar operation, eliminating the need for a counter electrode.
- Extending the voltage profile model to account for multiple anodic and cathodic reactions and their interactions.
- Search for more robust thin film electrodes with high electrical conductivity.
- Explore eco-friendly biocide integration into electrode which activate under non-polarized conditions.
Literature and experiments have shown that counter electrodes comprised of steel and iron suffer rapid degradation. It would be great to eliminate the counter electrode altogether and use the same thin film surface as both the anode and cathode by connecting multiple power probes on its surface. This assumes that the sheet resistance is high enough so that the electrochemical current pathway is favored. A voltage cycle pattern could vary the total cathode and anode area to optimize surface voltages of each. An advanced voltage profile which accounts for both anodic and cathodic reactions as well as the electrode sheet resistance is necessary to predict and model this type of system.

Searching for new thin film electrode materials is also vital. An ideal thin film electrode would have a fairly uniform resistance profile and stable electrochemical properties. It is also necessary to conduct future work to determine protection time after electrode polarization goes offline. If the surface becomes fouled almost immediately after loss of power, it then becomes important to include a biocide to compensate for power outages. A biocide that only leaches out of the film during loss of polarization would be ideal. After the completion of these tasks, thin film electrode antifouling systems will be ready for large-scale deployment.
Bibliography


Appendix A.

POTENTIOSTAT DESIGN

Design of the potentiostat is based on the one described in the article “An Inexpensive Field-Portable Programmable Potentiostat.” The potentiostat we developed has a few design differences. For example, this one utilizes ground as the counter electrode whereas their working electrode is ground. Our design allows multiple potentiostats to operate under the same circuit and electrical cell for higher throughput of electrochemical experiments. Figure A.1 shows the circuit layout of the potentiostat.

Figure A.1. Potentiostat design schematic.
The working electrode voltage is controlled by input from a 12 bit Digital-to-Analog Converter (DAC) and follows the following formula:

\[ V_{\text{W.E}} = 2 \times V_{\text{DAC}} - 2.5 \text{ V} \]  \hspace{1cm} (A.1)

The current reading is sent as a voltage single to the 10 bit Analog-to-Digital Converter (ADC) and the equation relating current to voltage signal is:

\[ I = \frac{(V_{\text{ADC}} - 2.5 \text{ V})}{R_i} \]  \hspace{1cm} (A.2)

Where \( R_i \) is the variable resistor noted in Figure A.1 and may be changed to accommodate different current ranges. The circuit design was imported to PCB software to mass produce the design; Figure A.2 shows the PCB diagram.

Figure A.2. PCB diagram of Potentiostat. Blue-green lines represent silkscreen marks; teal and red represent copper bottom and top layer, respectively.
The mega 128 microcontroller on a TekBot Mega 128.2 platform was used to control the potentiostat and interface it to the computer for cyclic voltammetry. The potentiostat program was compiled in AVR Dude as part of the Win-AVR package (May 25\textsuperscript{th}, 2007 release). A Tekbot universal programmer was used to code the microcontroller. Special thanks to Matt Shuman for his help in understanding microcontrollers and coding.

The Tekbot microcontroller is capable of connecting to a PC via serial port. MATLAB code was developed to carry out and plot cyclic voltammogram data. Table A. 1 contains all the MATLAB code. It is important to note that one needs to determine which COM port connects to the potentiostat. This can be done by using Hyperterminal and monitoring which COM port appears after connecting the potentiostat to the computer. This COM number must be substituted into the MATLAB code so that they can communicate. Cyclic voltammograms are performed by running “Voltametric_Ver_5.m” and following the prompts for voltage window and scan rate.

\textbf{Table A. 1. MATLAB functions and m-file used to conduct cyclic voltamograms.}

<table>
<thead>
<tr>
<th>Function</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>\texttt{ReadADC.m}</td>
<td>Instructs potentiostat to read and send current data</td>
</tr>
<tr>
<td>\texttt{function} [voltage] = ReadADC(channel)</td>
<td></td>
</tr>
<tr>
<td>s1 = serial('COM6', 'BaudRate', 19200);</td>
<td></td>
</tr>
<tr>
<td>fopen(s1);</td>
<td></td>
</tr>
<tr>
<td>fwrite(s1, ['a',channel,10]);</td>
<td></td>
</tr>
<tr>
<td>data = fread(s1, 18);</td>
<td></td>
</tr>
<tr>
<td>result=zeros(9,1);</td>
<td></td>
</tr>
<tr>
<td>for i=0:1:8</td>
<td></td>
</tr>
<tr>
<td>result(i+1,1) = (data(1+2*i)<em>256 + data(2+2</em>i));</td>
<td></td>
</tr>
<tr>
<td>end</td>
<td></td>
</tr>
<tr>
<td>fclose(s1);</td>
<td></td>
</tr>
<tr>
<td>voltage=mean(result)*5/1023;</td>
<td></td>
</tr>
<tr>
<td>end</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Function</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>\texttt{SetDAC.m}</td>
<td>Instructs potentiostat to set voltage</td>
</tr>
</tbody>
</table>
function [data] = SetDAC(DAC_Voltage)

s1 = serial('COM6', 'BaudRate', 19200);
fopen(s1);
tic

DAC_Value = DAC_Voltage/2.77*4095;
fwrite(s1, ['d',DAC_Value/256,mod(DAC_Value,256),0,10]);
toc

fclose(s1);
end

Voltammetric_Ver_5.m
% Cyclic Voltammetry MatLab program Version 5
% Changes to this version include support for different potentiostat
% circuits.  The data requisition protocols have been streamlined to
% prevent hang-ups and timeouts.  Repeating cycles option has been
% included.
% This version is meant to be used in tandem with the
% PotentiostatMD_Ver_4
% code installed on the potentiostat microcontroller.
clear all;

Vmax=0;
Vmin=0;
scanrate=0;
toggle=4;
cycle=0;
while ((toggle==4))
toggle=input('old potentiostat (1) or new potentiostat (2): ');
  if((toggle>=3))||((toggle<=-1))
    display('invalid input');
  end
end
while ((cycle<=0)||((cycle>=21))
cycle=input('Please specify the number of cycles: ');
  if ((cycle<=0)||((cycle>=21))
    display('Error: please try again.');
  end
end
while ((scanrate<=0))
scanrate=input('Please specify Scan Rate in mV/sec: ');
  if ((scanrate<=0))
    display('Scanrate should be nonzero and positive.');
  end
end
while ((Vmin>=Vmax))
  Vmax=input('Please specify max voltage, V: ');
  Vmin=input('Please specify min voltage, V: ');
  if((Vmin>Vmax)
    display('Vmax cannot be greater than Vmin!');
  end
end

Stepmax=(Vmax+2.5)/(2.77*2)*4095;  % DAC setting for Vmax
Stepmin=(Vmin+2.5)/(2.77*2)*4095;  % DAC setting for Vmin
Scan=round((scanrate/40000)/(2*2.77)*4095);  % count per 100ms cycle
s1=serial('Com6','BaudRate',19200);
set(s1,'InputBufferSize',16384);
fopen(s1);
fwrite(s1, ['.V',Stepmax/256,mod(Stepmax, 256),Stepmin/256,mod(Stepmin, 256),round(Scan),toggle,10]);

display('Please be patient; the potentiostat is working.');
headup=input('is the potentiostat cycle complete?');
pause(2);
i=0;
j=0;
stopp=0; % added an extra p because stop is already a built-in matlab function :
while (stopp==0);
datastream(i+1,1+2*j)=fread(s1,1);
datastream(i+1,2+2*j)=fread(s1,1);
i=i+1;
if ((datastream(i,1+2*j)==255)) && ((datastream(i,2+2*j)==0))
    if ((datastream(i-1,1+2*j)==255)) && ((datastream(i-1,2+2*j)==0))
        j=j+1;
        i=0;
    end
end
if ((j == cycle))
    stop=1;
end
end
fclose(s1);

for m=0:1:cycle-1
    Numbers(:,m+1)=datastream(:,1+m*2).*256.+datastream(:,2+m*2);
    % combines msb and lsb into one column.
end

for j=0:1:cycle-1
    for i=0:1:(size(Numbers,1)-2)/8-1
        Table(1+i,1+j*2)=Numbers(1+i*8,j+1)*2.77/4095*2-2.5; % V working electrode
        Table(1+i,2+j*2)=46.909-18.95*mean(Numbers(i*8+2:i*8+7,j+1))*5/1023; % V ADC
    end
end

% y = -18.95x + 46.909
% R² = 0.9999

for j=0:1:cycle-1
    for i=0:1:size(Table,1)-1
        Plotdata(1+i,1+2*j)=Table(i+1,1+j*2);
        Plotdata(1+i,2+2*j)=Table(i+1,2+j*2);
end
end

% \( y = -9.4749x + 23.455 \)
% \( R^2 = 0.9999 \)

plot(Plotdata(:,cycle*2-1),Plotdata(:,cycle*2),'r');
xlabel('V working electrode WRT reference, V');
ylabel('Current, mA');
Appendix B.

MATLAB CODE TO DETERMINE PARAMETERS FOR VOLTAGE PROFILES

The built-in function fminsolve initiates the Nelder-Mead non-derivative minimizing algorithm. It is used to minimize the sum of square error output of residualgen44_100.m function, which compares the theoretical model to experimental results. The charge transfer coefficient, convective mass transport coefficient, and exchange current density parameters are adjusted to minimize the error. Table B. 1 contains the MATLAB code used to find voltage profile model parameters.

**Table B. 1.** MATLAB files used to optimize voltage model parameters to yield best fit to experimental data.

```matlab
residualgen44_100.m
function [output]=residualgen44_100(x)

% This function spits out sample correlation between the theoretical model and the experimental data tabulated below and also Sum of Square of the Error (SSE). It is meant to be used in the built-in Matlab fminsolve function to determine the physical parameters that make the model fit experimental results the best.

% these global variables are called up by the other functions below
global km kv Iex Cblk Rsh L V0 z F mesh

km = x(1);    % mass transfer coefficient in cm/sec
kv = x(2);    % Voltage exponential constant in V^-1
Iex = x(3);   % Exchange current in Amps/cm^2
Cblk = 0.000623; % bulk concentration of chloride in Mole/cm^3
Rsh = 1217;   % sheet resistance in ohm/sqr
L = 50.8;     % Length of electrified plate, cm
V0 = 1.157;   % Voltage at x=0 in volts
z = 1;        % ion charge number
F = 96485.3399; % units of C/mol
mesh = 401;   % Initial number of how many discrete voltage sections

% this is the experimental data set
```
experimentalx = [1 2 4 6 8 10 12 14 16 18];
expl = [1.133955 1.03295 0.97433 0.929475 0.89569 0.868155 0.8443 0.8259 0.811435 0.80094];
exp2 = [1.095775667 1.012093333 0.960103333 0.9185 0.886266667 0.85959 0.835966667 0.817806667 0.803443333 0.79332];
exp3 = [1.055736667 0.985896667 0.943483333 0.902393333 0.872866667 0.853443333 0.826333333 0.809566667 0.79268 0.786];

sse = 0;
sstot = 0;
ssecurrent = 0;
V0 = expl(1); % sets up boundary condition for this set of data
solinit = bvpinit(linspace(0,L,mesh),[1 0]);
sol = bvp4c(@odesys,@odebc,solinit,bvpset('Nmax',2000)); % solves the 2nd order nonlinear ODE

% the following code specifies the array location in the solution matrix to
% compare with experimental data as sometimes the bvp4c increases the
% size to achieve the appropriate error tollarances

for i=1:size(sol.x,2)
    if sol.x(1,i) <= 5.08
        experimentalx(2) = i;
    elseif sol.x(1,i) <= 10.16
        experimentalx(3) = i;
    elseif sol.x(1,i) <= 15.24
        experimentalx(4) = i;
    elseif sol.x(1,i) <= 20.32
        experimentalx(5) = i;
    elseif sol.x(1,i) <= 25.4
        experimentalx(6) = i;
    elseif sol.x(1,i) <= 30.48
        experimentalx(7) = i;
    elseif sol.x(1,i) <= 35.56
        experimentalx(8) = i;
    elseif sol.x(1,i) <= 40.64
        experimentalx(9) = i;
    elseif sol.x(1,i) <= 45.72
        experimentalx(10) = i;
end

% the following calculates the average voltage of the plate
vavg = mean(expl);
%localcurrent = exp(sol.y(1,:).*kv).*Iex*2.54*2;
%totalcurrent = trapz(sol.x(1,:),localcurrent);
%ssecurrent = ssecurrent + (totalcurrent - 85*10^-6)^2/(85*10^-6);
%---------------------------------------------------------------

% this compares the 10 experimental data sets to the model's prediction and % adds to the sum of square error term (sse)
%---------------------------------------------------------------
for i=1:1:10
    sse = sse+(exp1(i)-sol.y(1,experimentalx(i)))^2; % Sum of Square Error
    ssstot = ssstot+(exp1(i)-vavg)^2; % total sum of squares (proportional to sample variance)
end
%---------------------------------------------------------------
% this repeats the step for the other set of data; it's all similar to % above so look at above comments to make sense of it
V0 = exp2(1); % sets up boundary condition for this set of data
solinit = bvpinit(linspace(0,L,mesh),[1 0]);
sol = bvp4c(@odesys,@odebc,solinit,bvpset('Nmax',2000)); % solves the 2nd order nonlinear ODE
% the following code specifies the array location in the solution matrix to % compare with experimental data as sometimes the bvp4c increases the % mesh size to achieve the appropriate error tollarances
%---------------------------------------------------------------
for i=1:1:size(sol.x,2)
    if sol.x(1,i) <= 5.08
        experimentalx(2) = i;
    elseif sol.x(1,i) <= 10.16
        experimentalx(3) = i;
    elseif sol.x(1,i) <= 15.24
        experimentalx(4) = i;
    elseif sol.x(1,i) <= 20.32
        experimentalx(5) = i;
    elseif sol.x(1,i) <= 25.4
        experimentalx(6) = i;
    elseif sol.x(1,i) <= 30.48
        experimentalx(7) = i;
    elseif sol.x(1,i) <= 35.56
        experimentalx(8) = i;
    elseif sol.x(1,i) <= 40.64
        experimentalx(9) = i;
    elseif sol.x(1,i) <= 45.72
        experimentalx(10) = i;
end
end

% the following calculates the average voltage of the plate
vavg = mean(exp2);
%localcurrent = exp(sol.y(1,:).*kv).*Iex*2.54*2;
%totalcurrent = trapz(sol.x(1,:),localcurrent);
%ssecurrent = ssecurrent + (totalcurrent - 65*10^-6)^2/(65*10^-6);
%
% this compares the 10 experimental data sets to the model's prediction and
% adds to the sum of square error term (sse)
%
for i=1:1:10
    sse = sse+(exp2(i)-sol.y(1,experimentalx(i)))^2; % Sum of Square Error
    sstot = sstot+(exp2(i)-vavg)^2; % total sum of squares
        % Total sum of squares (proportional to sample variance)
end

V0 = exp3(1); % sets up boundary condition for this set of data
solinit = bvpinit(linspace(0,L,mesh),[1 0]);
sol = bvp4c(@odesys,@odebc,solinit,bvpset('Nmax',2000)); % solves the
2nd order nonlinear ODE

% the following code specifies the array location in the solution
matrix to
% compare with experimental data as sometimes the bvp4c increases the
% mesh size to achieve the appropriate error tollarances
%
for i=1:1:size(sol.x,2)
    if sol.x(1,i) <= 5.08
        experimentalx(2) = i;
    elseif sol.x(1,i) <= 10.16
        experimentalx(3) = i;
    elseif sol.x(1,i) <= 15.24
        experimentalx(4) = i;
    elseif sol.x(1,i) <= 20.32
        experimentalx(5) = i;
    elseif sol.x(1,i) <= 25.4
        experimentalx(6) = i;
    elseif sol.x(1,i) <= 30.48
        experimentalx(7) = i;
    else
        experimentalx(8) = i;
    end
end
elseif sol.x(1,i) <= 35.56
    experimentalx(8) = i;
elseif sol.x(1,i) <= 40.64
    experimentalx(9) = i;
elseif sol.x(1,i) <= 45.72
    experimentalx(10) = i;
end
end

% the following calculates the average voltage of the plate
vavg = mean(exp3);
%localcurrent = exp(sol.y(1,:).*kv).*Iex*2.54*2;
%totalcurrent = trapz(sol.x(1,:),localcurrent);
%ssecurrent = ssecurrent + (totalcurrent - 49*10^-6)^2/(49*10^-6);
%

% this compares the 10 experimental data sets to the model's prediction
% and
% adds to the sum of square error term (sse)
%
for i=1:1:10
    sse = sse+(exp3(i)-sol.y(1,experimentalx(i)))^2; % Sum of Square Error
    sstot = sstot+(exp3(i)-vavg)^2; % total sum of squares (proportional to sample variance)
end
%

R2 = 1-sse/sstot
output=sse/stot

odesys.m – this function describes the voltage profile equation
function [ dvdx ] = odesys(x,V)

    global km kv Iex Cblk Rsh z F

dvdx(1)=V(2);
dvdx(2)=Rsh*Iex*exp(kv*V(1))/(1+Iex*exp(kv*V(1))/(km*F*z*Cblk));

dvdx=dvdx(:);
end

odebc.m – this function describes the boundary conditions for the voltage profile experiments
function res = odebc(ya,yb)
global V0
res = [ ya(1)-V0
       yb(2)];
end