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TOWARD UNDERSTANDING COMMERCIAL ADDITIVES FOR ZINCATE

ELECTROGALVANIZING

by

MARGARET SARAH SCOTT

A THESIS

Presented to the Graduate Faculty of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

in

METALLURGICAL ENGINEERING

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## PUBLICATION THESIS OPTION

This thesis consists of the following two articles, formatted in the style used by the Missouri University of Science and Technology:

Paper I, found on pages 21-36, has been published as Scott, M. & Moats, M. (2020). Optimizing Additive Ratios in Alkaline Zincate Electrodeposition. In *PbZn 2020: 9th International Symposium on Lead and Zinc Processing* (pp. 123-131). Springer, Cham.

Paper II, found on pages 37-65, is intended for submission to the *Journal of Applied Electrochemistry*.

## ABSTRACT

Cyanide zinc electrogalvanizing has been used for many years to produce high quality and uniform zinc coatings. Due to toxicity concerns, a significant amount of research has occurred to remove the use of cyanide while still producing a similar deposit. One of the resulting plating chemistries is the alkaline zincate bath.

Alkaline zincate plating has the advantages of low startup cost, low toxicity, and low corrosion rate. Despite these advantages, alkaline bath conditions do not produce acceptable zinc deposits without the use of plating additives, which can promote lustrous, smooth deposits. This research aims to: (1) generate fundamental electrochemical data in the presence of commercial additives (a carrier, a brightener, and a leveler), (2) correlate the fundamental data with deposit appearance and structure, and (3) optimize the concentration of carrier, booster, leveler at the current industrial operating parameters to result in a bright and smooth zinc deposit over the largest current density (CD) range.

## ACKNOWLEDGMENTS

I wish to give thanks to the many individuals who have helped me accomplish this much. First, I would like to thank my family and friends for their uplifting spirits whilst I worked on my research, and writing. Special thanks go to students past and present in my research group: Joseph Bauer, Florian Verbuggen, Mike Campbell, and Kevin Foster for their help in conducting my various research while I was on and off campus. I also am thankful to the staff of the Materials Research Center, for their assistance in running characterization of my various materials. Most of all I wish to thank Dr. Moats and Kevin Foster for their help in writing my thesis, editing, and their seemingly endless patience. Without the help of any of these wonderful individuals, I would not be where I am today.

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## 1. INTRODUCTION

Steel, the most common metal alloy, is used for many purposes, but is highly susceptible to rust. Corrosion results in significantly shorter life spans for parts. This leads to many steel pieces being protected from the environment by coating with paints and/or other metals. A very common coating technology is galvanizing. In galvanizing, steel is coated with an adherent zinc or zinc alloy deposit. Zinc acts as a sacrificial protective layer for steel as it more readily corrodes than iron.

Hot-dip galvanizing, both batch and continuous, have been the main methods of galvanizing steel parts since the 1800s. This is especially true for the automotive industry, as it is low cost, and provides a thick and shiny zinc coating on the steel piece. In the early 1900s, several industries moved away from hot-dip galvanizing for electrogalvanizing, in favor of a thinner and more controlled coating [1].

However, many impurities, if present during any stage in the zinc plating process can result in dull, rough, or non-adherent deposits. More noble metals such as tin are also available, however over time the passivated outer layer remains the same despite allowing the iron to corrode wherever it is open to the surrounding atmosphere [2].

Early electrogalvanizing baths contained cyanide as a means to complex zinc in solution. Cyanide baths produce uniform shiny coatings with high throwing power and were very tolerant to impurities and plating conditions. Unfortunately, cyanide is toxic. With more stringent regulations, the presence of cyanide in plating wastes vastly increased the cost of bath disposal [3].

The toxicity of the cyanide baths prompted research into low cyanide containing baths as well as cyanide free baths. Two resulting baths, acid zinc and alkaline zincate, were free of the cyanide, but were not able to achieve the throwing power or deposit brightness of the cyanide containing baths [4].

Considerable attention has been directed to the development of zinc electroplating baths which will produce zinc deposits of higher quality. Research has been devoted to improving zinc electroplating baths with regards to several plating properties such as: brightness, absence of pitting, providing a uniform coating thickness over a wide range of current densities, corrosion resistance, the capability of utilizing high zinc concentrations for increased efficiency, and providing of a zinc alloy coating which is relatively uniform in composition.

Thus, a review of the various methods available to galvanize zinc is useful for those working and studying in the field. The methods discussed will include hot dip galvanizing; regular, mid, low, and micro cyanide zinc electrogalvanizing; acid chloride and acid sulfate zinc electrogalvanizing, as well as alkaline zincate electrogalvanizing.

### **1.1. RESEARCH OBJECTIVE**

The ultimate objective for this research is to identify the optimum bath conditions to allow for production of quality electrogalvanized conduit in an alkaline zincate system. The effect of each additive and combination of additives has on electrochemical polarization, structure and appearance of electrodeposited zinc was investigated to optimize the electrolyte.

To achieve these goals, two studies were performed. The first study sought to optimize the bath chemistry, using both industrial and synthetically prepared solutions, by running various Hull cell tests for each electrolyte and its additive combinations, and analyzing the deposit structure by visual observation, scanning electron microscopy, and x-ray diffractometry.

The second study sought to use synthetic electrolyte containing different combinations of additives, individually and in combination, to determine the effects of each additive on electrodeposition. This was accomplished via electrochemical and Hull cell experiments along with characterization using visual observations and x-ray diffractometry.

## **1.2. PAPERS**

The two papers included in this thesis have been formatted for acceptance in a conference proceeding and archival journal. Paper I – has been published as Scott, M. & Moats, M. (2020). Optimizing Additive Ratios in Alkaline Zincate Electrodeposition. In *PbZn 2020: 9th International Symposium on Lead and Zinc Processing* (pp. 123-131). Springer, Cham. Paper II, found on pages 37-65, is intended for submission to *Journal of Applied Electrochemistry*.

Prior to presenting the two papers, an overview of galvanizing and specifically electrogalvanizing is given to familiarize the reader with the field of interest.



## 2. LITERATURE REVIEW

### 2.1. HOT DIP GALVANIZING

Hot-dip galvanizing is the most common form of galvanizing due to ease of use and cost of operation. There are two methods of hot-dip galvanizing: continuous and batch. Continuous hot dip galvanizing is when semi-finished products, prior to further processing, continuously pass through a zinc bath. Batch, or discontinuous hot dip galvanizing, is when a steel part is dipped into a molten zinc bath [1]. Batch hot dip galvanizing produces a thicker deposit ( $>20\mu\text{m}$ ), whereas continuous results in thinner coatings ( $\sim 10\mu\text{m}$ ) [1].

Due to the oxidative tendencies of iron and steel, there is always an oxide layer present on its surface. In order to allow the Zn coating to properly adhere, this oxide film must be removed by cleaning the surface prior to dipping. This may be accomplished in a multitude of ways: scrubbing, electrolytic cleaning, scaling, and pickling. Scrubbing with abrasive material is used if insoluble materials such as metallic soaps are present, as they cannot be removed by solution. Scaling, when a part is heated to a bluing/scaling temperature, is used if lubricating materials have bonded to the surface of the piece to be galvanized. Electrolytic cleaning can be used for a rapid cleaning. It contains an alkaline cleaner that can be utilized at current densities up to  $1000\text{ A/m}^2$  for 3 seconds [1]. Following degreasing, the steel substrates are pickled in a heated bath of sulfuric or hydrochloric acid. The pickling solutions are commonly 6-10% sulfuric acid at  $60\text{-}80^\circ\text{C}$ , or 8-10% hydrochloric acid at  $30\text{-}40^\circ\text{C}$  [3].

After cleaning, the steel is covered in flux, ammonium chloride and zinc chloride, to remove any metal salt or oxides remaining on the metal surface. If aluminum is present in the zinc bath, dry molten flux is added to the piece which forms a layer on the molten zinc surface that the piece penetrates through before galvanizing. However, if aluminum is not present in the bath, then the piece is fluxed in an aqueous solution and then dried prior to dipping [5].

The hot dipped galvanizing process, unlike electrodeposition, creates a two-layer zinc deposit. The molten zinc reacts with the steel substrate and produces an inner layer of a Zn-Fe alloy. Then zinc solidifies on the alloy layer generating a second layer of protective Zn. The thickness of coatings made by hot dip galvanizing is difficult to accurately control. The thickness of the alloy layer is related to the time of immersion as well as the temperature of the zinc bath. The Zn protective coating thickness is dependent on the extent to which the molten zinc drains from the piece as it is removed from the bath [5,6].

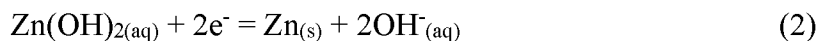
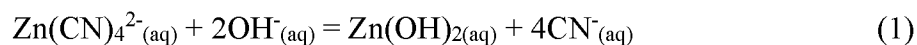
## **2.2. ELECTROGALVANIZING**

As mentioned previously there are two methods of galvanizing, hot-dip and electrogalvanizing. The latter is comprised of producing a zinc coating on a steel substrate by electrodeposition or plating. Electrogalvanizing is favored over hot-dip galvanizing when parts to be plated are irregular in shape or need a thinner coating, as the application of current allows for tighter control of coating thickness. Table 2.1 addresses the main rationalizations in choosing hot-dipping or electrogalvanizing.

Table 2.1. Advantages and disadvantages of hot-dip galvanizing and electrogalvanizing [7].

Category	Hot-dip galvanizing	Electrogalvanizing
Cost	Low maintenance cost	High chemical cost or High maintenance cost
Coating	>55 $\mu\text{m}$	<50 $\mu\text{m}$
Thickness	Controlled by immersion time, and temperature	Determined by plating time, current density, temperature
Toxicity	Low	Some are high due to cyanide

**2.2.1. Cyanide Zinc.** The earliest examples of electrogalvanizing baths that produced bright deposits used cyanide to complex the zinc in solution. The use of cyanide, despite its toxicity, results in natural leveling of the deposit produced during the reduction of zinc as seen in Reactions 1 and 2. This creates smooth zinc deposits, regardless of the zinc concentration with lower power consumption than previously used hot-dip methods.



The use of cyanide however became more regulated resulting in the development of lower cyanide containing baths. Cyanide baths are now categorized by the cyanide concentration: regular, mid, low, and micro. Concentrations of these baths are provided in

Table 2.2. Regular cyanide baths were used historically; micro or cyanide free baths are used currently in production.

Table 2.2. Composition of cyanide zinc baths (g/L) [7].

Parameters	Micro	Low	Mid	Regular
Zn(CN) <sub>2</sub>	3-5	10	30	60
NaCN	1	8	20	40
NaOH	75	65	75	80
Na <sub>2</sub> CO <sub>3</sub>	-	15	15	15
Na <sub>x</sub> S <sub>y</sub>	-	-	2	2
Brightener	1-5	1-4	1-4	1-4
Temperature (°C)	20-40	20-40	20-40	20-40
Current Density (A/m <sup>2</sup> )	200-500	200-500	200-500	200-500

The advantages of the cyanide bath lie in its good throwing and covering powers, ease of control, non-corrosiveness, and versatility of application. As the cyanide zinc electrolyte is non-corrosive, corrosion resistant materials are not required for line/cell construction, which lowers initial costs [8].

The main concerns regarding a cyanide containing zinc bath are toxicity, low bath conductivity, low current efficiency, and hydrogen embrittlement. Despite the cyanide bath previously being the cheapest zinc finishing bath, the cost of power is much higher than that of an acid chloride bath due to the cyanide baths having both lower current efficiency, in certain instances <50%, as well as a lower bath conductivity [8].

**2.2.2. Acid Zinc.** To overcome the toxicity issues of cyanide baths, acid baths have been formulated. Primarily, acid zinc baths are based on ammonium chloride, potassium chloride, and zinc sulfate. The ammonium chloride baths can run at higher current densities than the baths consisting of potassium chloride. The ammonium chloride baths are also capable of a wider high current density plating range at low Zn levels, and high temperatures [9]. Several common acid zinc baths are shown in Tables 2.3 and 2.4.

There are advantages and disadvantages to choosing acid zinc baths. Advantages include reduced hydrogen embrittlement, high current efficiencies even at high current densities, and higher electrical conductivity. Disadvantages are the corrosivity of the electrolyte, porous deposits, and lower throwing/covering power [7]. Due to the low pH of the acid bath, the solution corrodes soluble anodes significantly faster than in the cyanide or alkaline non-cyanide baths. To prevent the corrosion of the tank itself, the tank must contain a rubber or plastic lining, resulting in a higher maintenance cost [8].

Throwing power and covering power in acid chloride baths are significantly less than cyanide baths. Lower covering power and the ability to plate into simple recesses results in differences in thickness between the recesses and peaks of the Zn coating with acid chloride baths [10].

Many brighteners and levelers have been examined and are commercially used to fix the plating issue. These include gelatin, glycerin, caffeine, thiourea, glucose, dextrin, molasses, sodium bisulfate, and licorice. Even so, it is very difficult to produce bright zinc deposits from acid plating baths [8].

Table 2.3. Composition of acid chloride zinc plating baths [7].

Parameters	NH <sub>4</sub> Cl	KCl, low ammonium	NaCl, low ammonium
Zn (g/L)	15-30	15-30	15-30
NH <sub>4</sub> Cl (g/L)	120-180	30-45	30-45
KCl (g/L)	-	120-150	-
NaCl (g/L)	-	-	120
H <sub>3</sub> BO <sub>3</sub> (g/L)	-	-	-
Carrier Brightener (volume %)	4	4	4
Primary Brightener (%)	0.25	0.25	0.25
pH	5-6	5-6	5-6
Temperature (°C)	15-55	15-55	15-55
Current Density (A/m <sup>2</sup> )	30-100	30-100	30-100

Table 2.4. Composition of acid sulfate zinc plating baths [9].

Parameters	Compositions (g/L)
ZnSO <sub>4</sub> *7H <sub>2</sub> O	220
Na <sub>2</sub> SO <sub>4</sub>	30
NaCl	15
Dextrine	3
Glycerine	2.5
Thiourea	2.5
pH	2.5-3.0
Temperature (°C)	25-30
Current Density (A/m <sup>2</sup> )	200-700

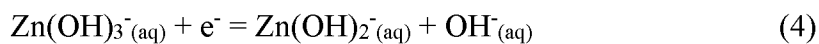
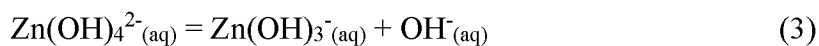
**2.2.3. Alkaline Zincate.** In contrast to the other zinc plating systems, alkaline zincate systems have: (1) lower capital and maintenance costs than acid baths due to less corrosion, (2) the lowest toxicity, and (3) an intermediate throwing power as shown in Table 2.5.

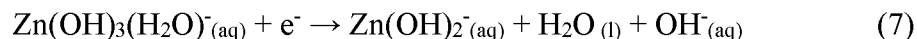
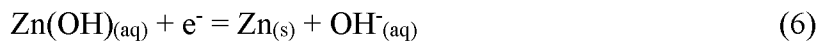
There are several issues with the alkaline non-cyanide plating process [8,9]. It tends to produce brittle deposits that are dark or yellow. The process exhibits lower efficiencies than cyanide, no inherent leveling ability, a limited operating window for current density, and low cleaning ability. Additives are highly important in the alkaline zincate system as without them only dendrites or powders would form.

Table 2.5. Throwing power of various electrolyte baths as measured in a Haring-Blum cell shown as a percentage of metal deposited in relation to electrode spacing [9].

Cell	%
High cyanide zinc	19
Low cyanide zinc	15
Alkaline zincate	12
Acid Zinc	6

In highly alkaline solutions, the proposed zinc reduction reactions are shown in Reactions 3-6 with Reaction (4) being the rate limiting step [7].





As  $\text{Zn}^{2+}$  prefers to be a tetra or hexa-coordinate species,  $\text{Zn(OH)}_3^{-}$  is more likely to exist as  $\text{Zn(OH)}_3(\text{H}_2\text{O})^{-}$  [11] resulting in Reaction (7) in place of (4). Reaction (4) is faster than the transport of Zn atoms into the growing zinc lattice. This results in the production of dendritic and non-adherent deposits. Despite the dendritic deposits, the throwing power remains higher than the acid zinc process.

**2.2.3.1. Surface pretreatment.** A very important step for alkaline zincate electrogalvanizing is substrate pre-treatment. If the substrate is not properly cleaned, then the zinc will not be able to adhere to the steel resulting in a poor deposit. As the deposition process is delicate to irregularities on the substrate surface many, different cleaning methods have been developed to ensure the cleanliness of the surface. The most common cleaning methods are alkaline cleaners. They consist of NaOH,  $\text{Na}_2\text{CO}_3$ , sodium silicate, phosphate, and organics or surfactants. The alkalis are added to neutralize soils, which are acidic. NaOH is typically used for particle separation. Silicates help to break apart water to allow soils to disperse [12]. Sodium carbonate is added to buffer the solution, by providing alkalinity, but does not directly affect the cleaning. Phosphates, EDTA, or chelating agents are added to complex Ca or Mg from the process water, due to their harmful reaction with the cleaning agents [12]. Surfactants, commonly anionic or nonionic, may be introduced to reduce the surface tension of the surface and oil, due to the oil forming an emulsion and remaining in the water. Antifoam agents may be added to the bath to help prevent surface contamination from moving to the pickling tank [12].



Electrolytic cleaning can further improve the removal of contamination. This is accomplished by passing current through the solution, causing large amounts of hydrogen and oxygen formation, during the cathodic and anodic cycles, respectively. The contaminants are removed from the surface as the gas bubbles collect hydrophobic contaminants like oils and waxes [13].

The electrolytic cleaning is done frequently in two stages - anodic and cathodic. The anodic stage of cleaning is advantageous as it creates an oxidizing condition preventing the co-deposition of metallic impurities from the bath. It also helps to remove any metallic oxides or metals that may already be present on the metal substrate. Another benefit to anodic cleaning is that hydrogen is not produced during the cleaning process [14].

Cathodic electrocleaning is advantageous as the bubbles formed cause a scrubbing motion allowing for more surface contamination to be removed. The volume of bubbles per amp of current applied is more in cathodic electrocleaning than anodic because of the monovalent state of hydrogen as opposed to the divalent nature of oxygen. The surface is also negatively charged, leading to the repulsion of organics. The cleaning materials are designed to be non-corrosive, as pitting is harmful to the plating process [14].

**2.2.3.2. Pickling.** After the metal substrate is cleaned, the piece is rinsed with water and then moved to a pickling bath to remove any remaining oxides. Sulfuric or hydrochloric acid may be used for pickling to remove the oxide films. Often sulfuric acid is used as it is low cost. Inhibitors may be added to the bath to prevent the acid from deteriorating the steel underneath the oxide. To speed up the process, electrolytic pickling

may be done. However, due to the cost of electricity, it is more expensive than increasing the concentration of the acid and temperature of the pickling tank [6].

**2.2.3.3. Plating bath.** Following the pickling tank, the pieces are rinsed and moved into the plating tank. Direct current is applied, and zinc is plated onto the surface of the steel part. Compositions of common alkaline non-cyanide zinc baths for low (LC) and high (HC) concentrations of Zn are listed in Table 2.6.

Table 2.6. Composition of alkaline non-cyanide zinc baths (g/L) [7].

Parameters	LC	HC
Zn	6-9	13.5-22.5
NaOH	75-105	120-150
Proprietary Additives	1-3%	1-3%

Alkaline zinc plating baths are primarily comprised of zinc ions and an excess of sodium hydroxide. With high pH baths, the zinc forms rough and spongy deposits if no additives (carriers, brighteners, or levelers) are present in solution. However, if the concentrations of additives are too high then the zinc deposit can blister [15]. To control the additive concentration in the bath, careful addition is needed. If excess additive is present, the bath can be filtered, and/or potassium permanganate can be added to the bath to “kill” excess or spent organic.

Temperature must also be carefully monitored and controlled. If the operating temperature falls below 20 °C, either thin milky deposits or no deposits will be produced. If the temperature exceeds 40 °C, then the current density range that produces a bright

surface narrows due to increased brightener consumption and dullness to occur at low current density areas [8].

Due to high NaOH concentrations in the plating tank, carbonates can form in solution. Carbonates form because of elevated levels of CO<sub>2</sub> entering the system and reacting with the NaOH to form Na<sub>2</sub>CO<sub>3</sub>. Carbonates are also able to form when there is an increase in solution agitation or solution temperature. Increased carbonate concentrates decrease solution conductivity. Two methods can be used to remove carbonates from solution. The first is to allow the carbonates to precipitate by cooling the solution to 5-10 °C, and then filtering the solution. Another method is to precipitate the carbonates by the addition of calcium hydroxide [3].

**2.2.3.4. Additives.** In the absence of additives, level zinc deposits can only be produced from alkaline zincate baths if a uniform current distribution is present on the steel substrate and the thickness of the coating is equal to or exceeding the depth of any grooves [16].

The additives gather at the higher current density areas/areas of greatest flux and adsorb to the surface. As the additives adsorb, the surface is blocked, resulting in current redistribution from the high areas to the low current density areas. The redistribution promotes growth in the recesses and forms a level deposit, however, only when proper concentrations of the aforementioned additives are used [6].

The concentration range for the additives to have the desired effect is minimal, mg/L for many. Despite the visible change in appearance of the Zn coating when additive concentrations change, the growth mechanism and the morphology of electrodeposited metal is relatively unknown for many additive systems, due to the volatility of the

alkaline non-cyanide system. In alkaline non-cyanide zinc plating, there are three main types of additives to promote level and bright deposits: levelers, brighteners, and carriers [17,18].

The effect of a leveler is to produce deposits with reduced height of surface irregularities such as recesses and protrusions. There are two methods of leveling - geometric and true leveling. Geometric leveling of deposits implies the uniform distribution of the current density over the cathode surface. True leveling of certain additives requires higher current densities in recessed areas of the cathode and lower current densities on protrusions caused by the presence of the additive [19]. Levelers are typically molecules that have an amine functionality [18,17,20] or aromatic rings, such as polyvinyl alcohol (PVA). The working principle of leveling is the result of varying adsorption kinetics for different diffusion layer thicknesses on a surface. The electrodeposition reaction cannot occur on places where the organic molecule adsorbs on the surface. If the adsorption kinetics of the additive molecule depends on the length of the diffusional path, the rate of adsorption and hence inhibition is higher on protruding areas of the surface [21]. Conversely, less inhibition occurs in recessed areas and the rate of uneven vertical growth is suppressed. The degree of inhibition of the cathodic process can be measured electrochemically as the decrease of the cathodic potential for a specific current density [16, 22].

Brighteners (boosters) result in a shiny surface by affecting the surface roughness. The roughness is changed by altering the grain size as a result of pinning specific grain orientations [21]. The desired brightness, a mirror-like finish, has small grains (e.g.  $< 0.4 \mu\text{m}$ ) [23,24]. Dominant grain orientation might be the result of selective adsorption on

growth sites. However, the existing theories of inhibition and growth are contradictory, so research continues to provide experimental data. Commonly tested brightener molecules have a sulphonic acid group, thiol and disulphide bonds [17,18], and tend to be aromatic aldehydes [7].

Carrier additive molecules are usually polyalkylene glycols and simply improve the efficiency of brighteners and levelers. Several common carriers are polyvinyl alcohol (PVA), polyaliphatic amines, aliphatic polyamines, and heterocyclic amines [7].

Due to the similar nature of the additives within the heterocyclic amine grouping, PVA, and gelatin were evaluated in place of the booster and leveler used in the current industrial process as more research of their effect on zinc deposits was conducted.

**2.2.3.5. Polyvinyl alcohol.** [25] Polyvinyl alcohol (PVA), a carrier commonly used in alkaline zincate solution, has been proven useful, possibly due to the C-O bond being polar. [26] The polarity of the bond increases the possibility of the PVA being largely present in the cathode film. This film forms a weak barrier, which in turn hinders zinc deposition. It is also possible that PVA replaces the H<sub>2</sub>O present in the zinc oxide complex. Addition of PVA enables grain refinement of the deposits but at the same time, produces a leaf like polymeric surface film [27]. Due to the formation of compact deposits, as against the mossy or spongy deposits, the cathode efficiency increases slightly.

**2.2.3.6. Gelatin.** Gelatin, a leveling agent, is often used in zinc electrodeposition. The gelatin adsorbs onto the zinc substrate and migrates by random walk theory onto higher charge areas. The gelatin then polarizes, thus preventing the zinc from adsorbing, and promoting random growth [28].

**2.2.3.7. Vanillin.** When o-vanillin is used in zinc electrolyte, the o-vanillin causes a larger overpotential for both zinc deposition and hydrogen evolution, in comparison to when no additive is introduced. This effect is increased during an early stage of electrodeposition in which the interlayer adhesion is affected. This was proven by the determination of current efficiencies for the zinc deposition. Several experiments show that o-vanillin is readily absorbed onto an iron surface, thus increasing the overpotential for hydrogen evolution and zinc deposition. This speculation was confirmed by EQCM experiments and linear sweep voltammetry. They confirmed the corrosion properties are greater for the zinc layer electrodeposited during anodic dissolution experiments with o-vanillin present as the additive [29].

O-vanillin affects the overpotential region in addition to an earlier stage of electrodeposition in the underpotential deposition region. Similar to benzoic acid, o-vanillin acts as a leveling agent as it is adsorbed on the peak of the dendrites that were formed during crystal growth. If vanillin is introduced while in the presence of other additives, for example polyethylene glycol, an additive which strongly adsorbs on the surface, may further improve the deposit quality of the zinc layers, as it helps to limit the transport of Zn ions [29].

It is believed that when mixed with polyethylene glycol, o-vanillin should provide better performances in zinc plating compared to a polyethylene glycol benzoic acid, an additive commonly used in industrial zinc plating baths. This may be a result of the o-vanillin having a better performance than benzoic acid does under similar circumstances. A stable mono-layer adsorption of o-vanillin is evidence for the suppression of hydrogen evolution as well as Zn reduction at the surface of the electrode [29].

**2.2.4. Nitric Strike.** Following the plating tank, the pieces are rinsed and then passed through a nitric acid bath to prime the surface for chromate coating. The pieces run through a 0.3-1 %v/v nitric acid bath, for several minutes to remove surface contaminants remaining from the plating bath [13]. If the surface is overcleaned etching may occur, resulting in a dull or matte appearance [30].

**2.2.5. Chromate Bath.** To increase the longevity of the zinc coating, the coated part is often run through a trivalent chrome bath. Currently two types of chromate coatings are used for zinc coatings. Type 1, a thin clear coating provides decent corrosion protection for electroplated zinc coatings at relatively low cost. The durability is increased with a clear organic coating applied following the chrome coating [13]. Type 2, a heavily colored coating is thicker than the previous type. Mainly used in hot-dip galvanizing, it offers more corrosion protection due to its increased thickness. Regardless of coating type the coating is rinsed and promptly dried to protect the gel-like quality of the surface [30]. However, if the alloy underneath is non-homogeneous then the chromate coating will not be satisfactory, and the piece will be stripped and re-plated.

## **2.3. QUALITY ASSURANCE**

**2.3.1. Hull Cell.** A common quality control method to determine the effectiveness of the additives in a zinc plating bath is Hull cell testing. Commonly made of lucite or other insulating material, this trapezoidal box houses an anode on one side and a cathode against the angled side. A 37° angle results in an array of current densities across the cathode [7]. Several materials can be used as the cathode material, the two most prevalent

are bronze and zinc coated steel cathodes. If a steel cathode is desired, then the zinc coated cathode can be stripped using a strongly acidic solution.

The Hull cell tests can be run at 1-5A for 3-5 minutes. If desired, the test can be run longer to simulate the process the Hull cell test is mimicking; however, most defects and impurities are present by 5 minutes, so a longer time is unnecessary. The amperage can be adjusted to better reflect the current density of the simulated bath [7].

The analysis of the cathodes following testing can be used to evaluate several of the bath components such as: throwing power, presence of organic or metallic contamination, covering power, effectiveness of bath treatment to prevent impurities, concentration of additives in the plating tank, or the range of brightness. Despite the vast range of applications, Hull cell testing should not be used in place of titrations to check the concentrations of the electrolyte components [8].

**2.3.2. Titrations.** Controlling the Zn concentration in the electrolyte is the most important factor regarding proper plating. If the concentration rises past an acceptable amount, the plating in the low current density areas suffers. If the concentration is too great, the bright deposits at the low current density areas begin to turn to a dull grey. This may be mistaken for a lack of brightener, which would result in a larger than acceptable amount of brightener to be added to the bath. This in turn may cause the coating to blister, as the brightener polarizes causing hydrogen to evolve in place of zinc.

A secondary concern is that the caustic concentration may fall or rise to an unacceptable value. The caustic concentration must be monitored, as it affects the bath conductivity and promotes the dissolution of Zn into the bath. If the NaOH concentration



rises too great, the rate of Zn buildup increases, as well as the Zn brightener consumption, and the tendency of the bath to attack and stain the plated work during transfer [8].

#### **2.4. SUMMARY**

Electroplating has been found to be favorable in comparison to hot-dip galvanizing for forming thin, even, bright zinc deposits on steel substrates. However, if using a cyanide free process, additives must be added to produce level deposits. Alkaline zincate is used in place of acid zinc for its lower cost and greater ability for plating in low CD regions causing a more even coating.

Two studies were conducted to investigate one such industrial alkaline zincate plating bath and the deposits formed from the additive system implemented. The first study investigates the optimum concentration of additives in the plating bath, and the resulting zinc structure and appearance at the current operating parameters. The second study investigates the correlation between electrochemical polarization with deposit appearance and structure as a function of additive concentration.

**PAPER****I. OPTIMIZING ADDITIVE RATIOS IN ALKALINE ZINCATE  
ELECTRODEPOSITION**

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**ABSTRACT**

Alkaline non-cyanide zinc electrogalvanizing is utilized in some plating applications. This study was conducted to evaluate the effects of a commercial carrier, booster, and leveler in a strong zinc (37.5 g/L) and alkaline (210 g/L) plating solution. The results were compared with an optimization of industrial solution containing 38.2g/L Zn, 210g/L NaOH, and a 5:1:2 ratio of carrier, booster, and leveler. Hull cell plating was used to assess the roles of each additive on the appearance of the zinc deposits produced from synthetic solutions. Bright white deposits were generated with several different combinations of additives at current densities of 170-420 A/m<sup>2</sup>. The zinc structures were characterized using x-ray diffraction and scanning electron microscopy to understand the microstructure which produced the bright deposits in order to determine the optimal conditions leading to mirror-like deposits.

## 1. INTRODUCTION

Steel is the world's most widely used metal. Unfortunately, steel is highly susceptible to rust; leading to many steel pieces to be coated to prevent corrosion. Galvanizing with zinc is a common method to cover the steel substrate and provide a sacrificial protective layer. Galvanization can be achieved through hot dipping or electroplating. Hot-dip galvanizing has been and continues to be the primary coating method. In a few applications, electrogalvanizing is the preferred method of applying zinc to steel.

In the early 1900s, several industries moved away from hot-dip galvanizing for electrogalvanizing, in favor of a thinner and more controlled coating [1]. Over time, zinc electrogalvanizing baths used cyanide as a means to complex the zinc in solution and form a stable zinc coating bath. Zinc cyanide plating baths produce excellent coatings with significant throwing power and can tolerate impurities. In more modern times, the presence of cyanide as resulted in significant disposal costs for spent plating baths [2]. The toxicity of the cyanide baths prompted research into low cyanide containing baths as well as cyanide free baths. The resulting cyanide-free baths (acid zinc and alkaline zincate) can produce acceptable coatings but are not able to achieve the throwing power or brightness of the cyanide containing baths [3].

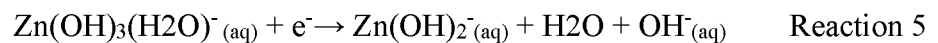
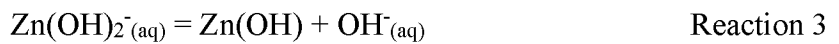
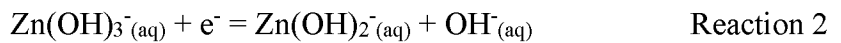
Alkaline zincate solutions offer the potential of lower operating costs due to reduced corrosion of steel supports and structures and lower waste disposal costs than acid baths [4]. Zincate baths also exhibits better throwing power than acid baths [5]. The major drawback with zincate baths is inferior plating appearance and properties leading

to the need for smaller variations in zinc concentration, temperature, and current density during operation than the other zinc plating baths [4]. The compositions of two typically alkaline non-cyanide zinc baths are presented in Table 1.

Table 1. Composition of alkaline non-cyanide zinc baths [6].

<b>Component</b>	<b>Low Zinc</b>	<b>High Zinc</b>
<b>Zn (g/L)</b>	6-9	13.5-22.5
<b>NaOH (g/L)</b>	75-105	120-150
<b>Proprietary Additives</b>	1-3%	1-3%

In highly alkaline solutions, the proposed zinc reduction reactions are presented in Reactions 1-4 with Reaction 2 being the rate limiting step. As  $Zn^{2+}$  prefers to be a tetra or hexa-coordinate species,  $Zn(OH)_3^-$  is more likely to exist as  $Zn(OH)_3(H_2O)^-$  [7] resulting in Reaction 5 instead of Reaction 2. The rate of Reaction (5) is faster than the transport of Zn atoms into the growing zinc lattice. This results in a depletion of zinc ion at the deposit surface which in turn produces dendritic and non-adherent deposits [8]. To overcome this tendency, additives are introduced to facilitate the production of a coherent, compact, and smooth coating [5, 6, 9].



In alkaline zincate baths, three different types of additives can be used – carrier, booster, and leveler. The carrier polarizes the zinc surface which increases the energy available to speed up the transport of Zn atoms into the growing Zn lattice. The booster produces smaller and more faceted grains which leads to a brighter surface. Finally, the leveler inhibits deposition at high points on a rough deposit and promotes deposition at the low points. Common carriers are polyvinyl alcohol (PVA) [10,11], polyaliphatic amines, aliphatic polyamines, and heterocyclic amines. Brighteners (booster) tend to be aromatic aldehydes [12]. Vanillin is a common leveler [13]. The correct combination of the plating additives is critical to producing smooth, bright deposits [10,13].

A common method to evaluate a plating bath's ability to produce a bright and shiny appearance is Hull cell testing [9]. The Hull cell is trapezoidal in shape with the cathode angled away from the anode. The changing distance between the anode and cathode produces a uniform current density. This allows the Hull cell to produce an electrodeposit over a range of current densities in one experiment. The resulting plate can be examined to determine if the desired appearance is produced within the current density range exhibited in the plating operation [9].

## **2. EXPERIMENTAL**

### **2.1. HULL CELL TESTING**

A standard 267 mL Lucite Hull cell from Kocour was utilized. The anode was a low-carbon steel mesh with dimensions of 8.6 cm x 0.6 cm. The cathode was a zinc coated stainless steel plate with the zinc removed prior to plating. The zinc coating was

removed by immersing the plate in a 50% v/v HCl solution for ~15 seconds until no gassing was detected. The de-zincing plate was rinsed with de-ionized (D.I.) water prior to placing in the Hull cell.

Synthetic plating solutions were prepared using a commercially available zinc “pre-mix” solution (Technilloy ZN NI 7222). The “pre-mix” solution contained 162-170 g/L Zn and 500 g/L NaOH as determined by titration. The “pre-mix” was diluted using reagent grade NaOH and/or D.I. water to achieve zinc concentrations ranging from 30 to 40 g/L Zn at a NaOH concentration of 210 g/L. Additives were introduced into the electrolyte 20 minutes prior to each experiment. Three commercially available additives were investigated - a carrier (Eldiem Carrier), a booster (Eldiem Booster) and a leveler (Bright Enhancer 2x). They were examined individually and in combination.

Industrial solution samples were taken directly from an operational plating bath. The samples had concentrations of 36-40g/L Zn and 210-225g/L NaOH. The bath was believed to contain a 5:1:2 ratio of carrier, booster, and leveler at concentrations of 25mL/L carrier, 5mL/L booster, 10mL/L leveler based on addition rates of these additives. Hull cell tests were performed with additional amounts of the additives to determine the effect of each on the zinc surface quality. Tests were run at operating temperatures of 40-44°C. Due to the presence of additives already in plating solution, the extra additions were made one minute prior to plating.

2.0 amps of direct current was supplied from a 20V Extech, Model #382275 power supply for 5 minutes to plate zinc in the Hull cell. No external agitation was used. The plating was performed at elevated temperature. The solution was preheated to 44 °C and then transfer to the Hull cell. The plating test was started immediately without

heating. The temperature decreased by approximately 1 °C during the 5-minute experiment.

Following the experiment, the zinc plated cathode was removed from the Hull cell and rinsed with D.I. water. To simulate the actual plating line, the coated part was dipped in a 0.25% v/v nitric solution for one minute and then rinsed again with D.I. water. Finally, the coated plate was dried with a hot air to avoid water spots.

## **2.2. PHYSICAL CHARACTERIZATION**

Following the Hull cell test, the plate was visually inspected. The appearance was graded using the following terms burnt (blackish in color), matte (gray and non-reflective), white, shiny (gray, reflective, sparkly) or no plating. These appearances were assigned to various areas of the deposit which were correlated to current density using the 2 amps scale on a standard Hull cell ruler. The zinc coated plates were sheared to create samples with known current density ranges for further examination.

X-ray Diffraction (XRD) was performed using a Philips Analytical X'Pert Pro Multipurpose Diffractometer to identify the preferred crystal orientation for samples plated at 170-260 A/m<sup>2</sup>. The measurements were taken using Cu K-alpha radiation with an angle range in 2-theta of 50-90° and scanning rate of 3 degrees per minute.

Zinc coatings plated at 170 A/m<sup>2</sup> were characterized by scanning electron microscopy (SEM) to observe the deposit morphology. An Aspex Pica 1020 scanning electron microscope was used with 20kV bias and 34 μA emission current.

### 3. RESULTS AND DISCUSSION

While other researchers [14-19] have examined the effects of additives on the alkaline zincate plating, this project focused on a unique bath chemistry as the zinc concentration (30-40 g/L) and sodium hydroxide concentration (210-220 g/L) is significantly higher than standard baths in both zinc and NaOH.

To understand the role of each additive, synthetic solutions with constant initial zinc and NaOH concentrations of 37.5 g/L and 210 g/L respectively, were studied with various additive additions. The resulting zinc coatings produced in the Hull cell were characterized visually, with XRD and microscopically with SEM.

#### 3.1. HULL CELL

The results of the visual characterization are presented in Table 2. The addition of individual additives or combinations of additives did not produce any areas with the desired mirror finish. Generally at high current densities, the coating had a burnt appearance. At lower current density, the coating generally had a matte appearance.

The surfaces that were closest to the desired appearance were categorized as white. These surfaces were bright but not completely reflective. As expected, plating without additives did not produce any white areas. Several plating conditions yielded white surfaces at the current densities of interest (e.g. 170-430 A/m<sup>2</sup> or 16-40 A/ft<sup>2</sup>). The conditions that produced the widest range of a white appearance centered on the target current density range were:

1. [Zn] = 37.5 g/L, Carrier = 0.75 mL/L, Booster = 0.33 mL/L



2. [Zn] = 37.5 g/L, Carrier = 1.5 mL/L, Leveler = 1.3 mL/L
3. [Zn] = 37.5 g/L, Carrier = 0.75 mL/L, Booster = 0.33 mL/L, Leveler = 0.65 mL/L

The appearance data indicate that in several instances increasing additive concentrations eliminated the white appearance produced at lower concentrations.

Hull cell testing was performed with industrial samples to examine the effect of increasing the concentrations of the additives. To minimize operation variability, all samples and experiments were taken during one day. All hull cell experiments using industrial solutions produced shiny deposits at the current densities of interest (170-430A/m<sup>2</sup>) as shown in Table 3. The shiny deposit appearance was believed to be caused by higher additive concentrations present in the industrial solution as compared to the synthetic solutions used in this study.

The experimental conditions that increased the current density range that produced a shiny deposit were (additive concentrations listed were added to the existing additives already present in the industrial solution):

1. [Zn] = 38.2 g/L, Extra Carrier = 0.13 mL/L, Extra Booster = 0.043 mL/L, Extra Leveler = 0.043 mL/L
2. [Zn] = 38.2 g/L, Extra Carrier = 0.21 mL/L, Extra Booster = 0.085 mL/L, Extra Leveler = 0.085 mL/L

The first electrolyte was proven to be more effective at lower current densities, whereas the second was more effective at higher current densities. This may be due to the lower and higher concentrations of carrier, respectively.

Table 2. Hull cell results from various synthetic solutions. Visual appearance was assigned as b = burnt, m = matte, w = white, s = shiny and n = no plating. The Hull cell ruler with current densities in A/ft<sup>2</sup> is provided. 1 A/ft<sup>2</sup> = 10.76 A/m<sup>2</sup>. Dashed lines indicate industrially relevant current density range.

[Zn] g/L	Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	Hull Cell Appearance									
				80	60	40	30	20	12	4	1		
37.5	0	0	0	b						m			n
37.5	0	0	0	b						m			n
37.5	0.75	0	0	b			w						m
37.5	1.5	0	0	b			m						b
37.5	0	0.33	0	b						m			
37.5	0	0.65	0	b			w						m
37.5	0	0	0.33	b						w			
37.5	0	0	1.3	b						m			
37.5	0.75	0.33	0				w						m
37.5	1.5	0.65	0	b	w					m			
37.5	0.75	0	0.65	b			w						m
37.5	1.5	0	1.3	b			w						m
37.5	0	0.65	1.3	b			s					w	
37.5	0.75	0.33	0.65	b			w						m
37.5	1.5	0.65	1.3	b						m			
30	1.5	0.65	1.3	b			w						m
40	1.5	0.65	1.3	b						m			

Table 3. Hull cell results from various industrial solutions. Concentrations of additives listed were quantities added extra to the concentrations already in the industrial solution. Visual appearance was assigned as b = burnt, m = matte, w = white, s = shiny and n = no plating. The Hull cell ruler with current densities in A/ft<sup>2</sup> is provided. 1 A/ft<sup>2</sup> = 10.76 A/m<sup>2</sup>. Dashed lines indicate industrially relevant current density range.

[Zn] (g/L)	Extra Carrier (mL/L)	Extra Booster (mL/L)	Extra Leveler (mL/L)	Hull Cell Appearance									
				80	60	40	30	20	12	4	1		
38.2	0.00	0.00	0.00	b			s				m		w
38.2	0.12	0.043	0.043	b			s					m	w
38.2	0.21	0.085	0.085	b			s					m	w
38.2	0.43	0.085	0.17	b			s					m	w
38.9	0.00	0.13	0.13	b			s					m	w
38.9	0.17	0.13	0.085	b			s					m	w

### 3.2. XRD AND SEM

To understand the visual observations, XRD and SEM were performed on the samples produced from synthetic solutions. Sample XRD data from 170 A/m<sup>2</sup>-260 A/m<sup>2</sup> and SEM images from 260 A/m<sup>2</sup> are provided in Table 4 and Figure 1, respectively. The XRD data was interpreted using the zinc deposit structure nomenclature used by Mackinnon et al. [20].

The XRD data reveals that without additives a basal zinc structure is produced at 170 A/m<sup>2</sup>. This is confirmed in Figure 1a where the expected hexagonal plates are observed. The addition of 0.65 mL/L of booster did not change the structure as shown in the XRD and SEM image (Figure 1c), however a 0.33 mL/L booster addition did change the structure. Upon the addition of carrier, the structure and morphology changed to yield primarily triangular growth and a nodular/bumpy surface (Figure 1b). The addition of 0.65 mL/L of leveler did not change the structure, but 1.3 mL/L did to triangular, but the surface morphology revealed a variable appearance which might be caused by the strong secondary vertical growth seen in the XRD data (Figure 1d).

Carrier and booster addition produced a structure similar (Figure 1e) to what only carrier addition produced with the nodules being smaller. This is expected result of the grain refining properties of the booster. When leveler and carrier were added a smooth triangular structure formed (Figure 1f) with a few large nodules. Booster and leveler addition created a mixed basal/triangular structure with caused a rough faceted surface (Figure 1g). Upon the addition of all three additives, the structure was more level causing a brighter deposit (Figure 1h). The structure and surface morphology did not change over the range of 30-40 g/L zinc.

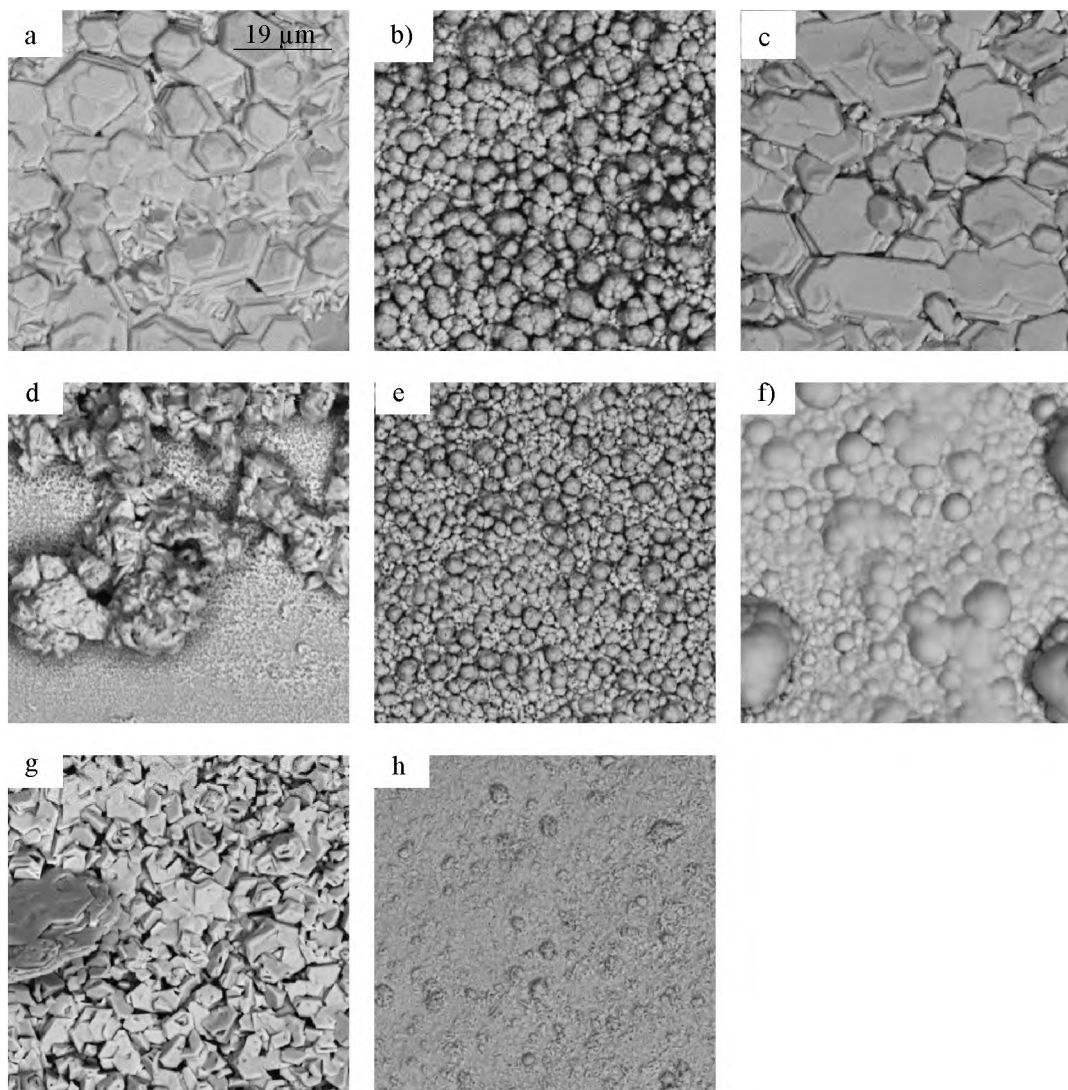


Figure 1. SEM images of zinc coating surfaces produced in a 267 mL Hull cell with 2 amps of direct current. Images correspond to a current density of  $170 \text{ A/m}^2$ . Synthetic solution conditions: 37.5 g/L Zn, 210 g/L NaOH and – a) No additives, b) 1.5 mL/L carrier, c) 0.65 mL/L booster, d) 1.3 mL/L leveler, e) 1.5 mL/L carrier + 0.65 mL/L booster f) 1.5 mL/L carrier + 1.3 mL/L leveler g) 0.65 mL/L booster + 1.3 mL/L leveler, h) 0.75 mL/L carrier + 0.33 mL/L booster + 0.65 mL/L leveler.

To determine if the results from the synthetic trials would correlate to the zinc growth found in industrial solutions XRD data was gathered on samples plated in the industrial electrolyte, as shown in Table 5. The industrial solution resulted in greater

amounts of basal growth and lower amounts of vertical growth than seen in synthetic electrolyte.

Table 4. Summary of XRD data of zinc coatings produced at 170-260 A/m<sup>2</sup> in a Hull cell using synthetic solutions. Intensities were normalized so the maximum crystallographic plane intensity was set equal to 100.

[Zn] (g/L)	Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	Basal (0 0 2)	Triangular (1 0 3)	Intermediate (1 0 1)	Intermediate (1 0 2)	Vertical (1 0 0)	Vertical (1 1 0)
37.5	0	0	0	100.0	0.3	0.5	0.1	0.5	0.1
37.5	0	0	0	100.0	41.2	49.5	16.2	15.3	23.5
37.5	0.75	0	0	4.6	7.8	100.0	9.2	45.9	8.0
37.5	1.5	0	0	10.7	14.5	100.0	18.3	32.8	14.3
37.5	0	0.33	0	8.9	19.1	100.0	24.8	24.6	12.1
37.5	0	0.65	0	100.0	10.4	48.7	10.0	53.4	6.3
37.5	0	0	0.65	100.0	20.1	62.3	14.2	54.7	11.6
37.5	0	0	1.3	9.8	15.7	100.0	14.1	70.1	10.0
37.5	0.75	0.33	0	13.1	37.5	100.0	29.5	34.9	32.5
37.5	1.5	0.65	0	4.0	9.0	100.0	10.1	35.2	6.3
37.5	0.75	0	0.65	3.5	8.3	100.0	10.6	41.0	7.9
37.5	1.5	0	1.3	6.6	12.4	100.0	13.1	46.1	11.2
37.5	0	0.65	1.3	91.3	51.3	100.0	18.7	15.4	31.5
37.5	0.75	0.33	0.65	4.8	7.9	100.0	11.2	35.2	7.1
37.5	1.5	0.65	1.3	18.8	10.6	96.4	6.7	100.0	8.8
30	1.5	0.65	1.3	1.2	2.4	100.0	3.8	75.8	1.8
40	1.5	0.65	1.3	1.8	3.4	100.0	4.7	74.5	2.5

Table 5. Summary of XRD data of zinc coatings produced at 170-260 A/m<sup>2</sup> in a Hull cell using industrial solutions. Intensities were normalized so the maximum crystallographic plane intensity was set equal to 100.

[Zn] g/L	Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	Basal (0 0 2) (1 0 3)		Triangular (1 0 1)	Intermediate (1 0 2)	Vertical (1 0 0) (1 1 0)	
38.2	0.00	0.00	0.00	16.6	25.8	100.0	10.8	71.9	17.3
38.2	0.13	0.043	0.043	20.4	15.2	100.0	11.6	41.4	8.9
38.2	0.21	0.085	0.085	23.3	16.3	100.0	12.0	44.7	12.1
38.2	0.43	0.085	0.17	11.1	30.5	100.0	8.5	82.5	18.2
39.2	0.00	0.13	0.13	24.3	9.5	100.0	11.3	43.3	16.7
39.2	0.17	0.13	0.085	21.4	9.4	100.0	11.6	46.0	18.4

The bright white finish general was produced when the XRD pattern indicates a primary triangular growth with minimal basal growth. Additionally, the vertical growth plane was detected at ~50% of the intensity of the triangular plane.

After consultation with our industrial partner, it was decided that the lack of a mirror finish was perhaps caused by the additives not being in the correct concentration range. Based on industrial experience, it was decided to pursue a combination of all three additives in later trials with commercial bath samples. The results using industrial solution with additives already present indicated that shiny deposits can be produced with these additives.

#### 4. SUMMARY

This study provides zinc coating data for a unique zincate plating bath with high zinc and caustic concentrations. The effects and interactions of commercial additives

(carrier, booster and leveler) were examined using a Hull cell. Coatings were characterized using visual appearance, XRD and SEM.

Bright white deposits were produced at current densities of 170-420 A/m<sup>2</sup> using synthetic solutions. The conditions that produced bright white deposits generally formed a zinc structure with predominate (101) planes, minimal (002) planes and (100) planes with an intensity ~50% of the (101) planes.

Surface morphologies correlated with the expected structures indicated from the XRD data. The addition of carrier changed the morphology from hexagonal platelets to compact grains with a knobby surface. Adding booster with carrier appears to refine this structure. Finally adding all three additives can produce a fairly smooth compact structure.

Despite studying various combinations of additives, no mirror-like deposits were observed when using synthetic solutions as seen in industrial practice. This is believed to be caused by additive concentrations in the incorrect range. Even so, the white deposits formed in the same current density regions as the mirror-like deposits in industrial practice, allowing for electrolyte comparisons.

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## **II. EFFECTS OF ADDITIVES ON MORPHOLOGY AND NUCLEATION OVERPOTENTIAL IN ALKALINE ZINCATE ELECTRODEPOSITION**

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### **ABSTRACT**

Alkaline zincate electrodeposition relies heavily on the use of additives to promote level, smooth deposits. This research was conducted to examine the effects of three commercial additives: a carrier, a booster, and a leveler, on the energy required for nucleation as well as the strength of their inhibition. Synthetic electrolyte with concentrations of 37.5 g/L Zn and 210 g/L NaOH were used. Additives were investigated individually and in combination. Results from cyclic voltammetry (CV) showed that the carrier had the most pronounced effect on nucleation overpotential and deposit structure. A correlation was made between crystal structure and CV results.

### **1. INTRODUCTION**

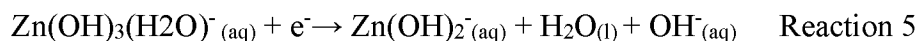
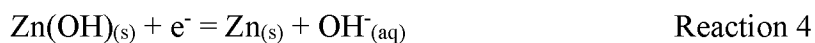
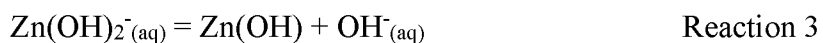
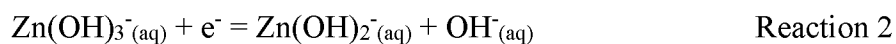
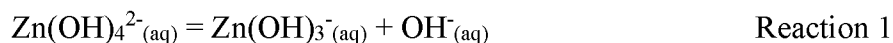
Alkaline zincate baths require the use of inhibitors to prevent powder formation, in favor of a uniform reflective coating [1]. The inhibitors, as organics, are difficult to

accurately measure once added to the plating bath. Due to the unknown life span of the additives and narrow window of operating conditions, this poses a risk to the appearance of the overall coating. To maintain an adequate concentration of additives, Hull cell tests can and are performed. Unfortunately, the Hull cell provides only visual and qualitative results.

Cyclic voltammetry experiments using a rotating disk electrode (RDE) could provide useful fundamental electrochemical data to better understand the additives in the plating system. Cyclic voltammetry has been used in other zinc electrodeposition systems for control and scientific investigation (2-5). Overpotentials (OPs) have been gathered for solutions containing additives and compared to clean solutions to determine additive polarization and effectiveness. OPs were also gathered continuously to locate maximum current efficiencies with the current additive systems [3]. CVs have been deemed adequate for maintaining a constant concentration of two or more polarization agents in solution [4,5] by measuring the nucleation and plating overpotentials, which can be directly correlated to the concentration of additives in solution. The nucleation overpotential can be correlated to the concentration of the grain refining agent, and the plating overpotential can be correlated to leveling agent. [4]

In alkaline zincate solutions, the four step dissolution of zincate to base metal occurs as follows in Reactions 1-4; Reaction 2 being the rate limiting step. Due to  $Zn^{2+}$  preferring to reside in solution as a tetra or hexa-coordinate species,  $Zn(OH)_3^-$  is more likely to form the species  $Zn(OH)_3(H_2O)^-$  [7], resulting in Reaction 5 replacing Reaction 2. Due to greater rate of Reaction (5) than the atomic transport of Zn to the growing zinc lattice a depletion of ionic zinc at the deposit surface results. In turn, this produces

dendritic and non-adherent deposits [8]. The growth of these deposits may be inhibited by the facilitation of certain additives. Instead forming a compact and cohesive coating. [5, 6, 9].



Three types of additives are commonly used to form coherent deposits in alkaline solution: carrier, booster, and leveler. Carrier is believed to polarize the zinc surface, thus increasing the available energy to expedite the transport of Zn atoms to the growing Zn lattice. Booster aids in brightening the surface by producing smaller faceted Zn grains. Finally, leveler inhibits deposition, on a rough deposit, at the high points while promoting deposition at the low points. Several common carriers are polyaliphatic, aliphatic, or heterocyclic amines and polyvinyl alcohol (PVA) [10,11]. Brighteners (booster) are commonly formed of aromatic aldehydes [12]. Levelers are made of similar components to boosters; a common leveler being vanillin [13]. The optimal combination of these plating additives is crucial in the production of smooth, bright deposits [10,13]. These combinations are the result of electrochemical testing [15-20].

To evaluate the ability of a specific plating bath to produce a bright, shiny deposit the Hull Cell method is commonly utilized [9]. This cell, trapezoidal in nature, forms Zn deposits across a range of current densities in one experiment by having a varying distance between the anode, and the cathode. The resulting plate can be examined to

determine if the desired appearance is able to be plated for that specific electrolyte composition within the operating current density range [9].

## 2. EXPERIMENTAL

### 2.1. CYCLIC VOLTAMMETRY

A Gamry 3000 potentiostat was used to determine the effect of each additive on the nucleation overpotential for zinc electrodeposition. A rotating disk electrode (RDE) was used at 960 rpm to minimize mass transport limitations on current. Cyclic voltammetry tests were conducted in a three-electrode glass cell using a RDE with a 5 mm diameter stainless steel (SS) cathode disk as the working electrode, a 316L stainless steel counter electrode, and a Mercury/Mercury Sulfate (MSE) reference electrode. Each test was conducted in 250 mL of synthetic electrolyte. All experiments were conducted at 25°C. The potential was scanned between -1.6 V and -2.3 V vs. MSE at a rate of 10 mV/s with a step size of 1 mV. Additives of various concentrations were added 40 minutes prior to each test to allow for activation.

Cyclic voltammograms were used to determine overpotentials. Figure 1 illustrates this by showing the plating, nucleation, and cross-over potentials for a representative CV.

Four overpotentials were taken from the current densities of interest 0, 86, 172, and 258 A/m<sup>2</sup> as they are of interest to industry. The overpotential taken at 0 A/m<sup>2</sup> is the nucleation overpotential ( $\eta_0$ ). The plating overpotentials were taken at 86, 172, and 258 A/m<sup>2</sup> respectively. These values are shown graphically in Figure 1.

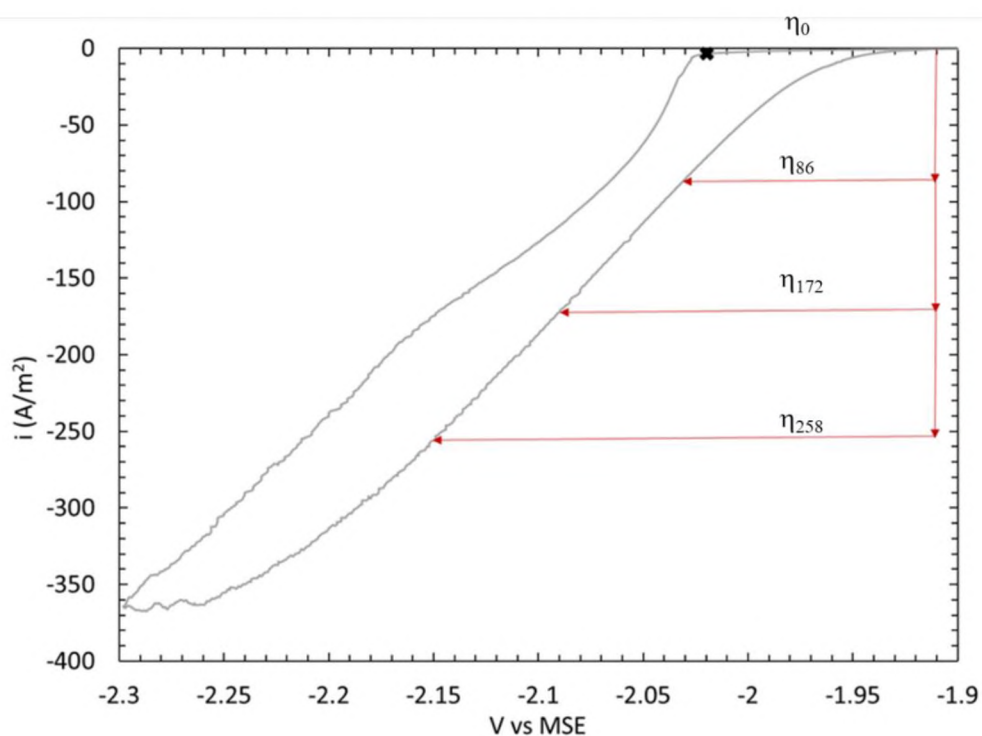


Figure 1. Representative cyclic voltammogram for zinc electrodeposition from an alkaline zincate electrolyte. The arrows represent the plating overpotentials ( $\eta$ ) at 86, 172 and 258  $A/m^2$ . The cross marks indicate the potential used to calculate the nucleation overpotential.

## 2.2. HULL CELL TESTING

Plating tests were conducted using a Kocour 267 mL Lucite Hull cell. The anode was an 8.6 cm x 0.6 cm low-carbon steel plate similar to the industrial anode grating. The cathode was a galvanized stainless steel plate with the zinc stripped prior to plating. To strip the Zn, the cathode was immersed in a 50% v/v HCl solution for ~15 seconds until no further gas was detected. The stripped plate was then rinsed with de-ionized (D.I.) water and placed in the Hull cell.

Electrolyte was prepared using a commercial zinc “pre-mix” solution (Technilloy ZN NI 7222). The “pre-mix” solution was determined by titration to have higher [Zn],

162-170 g/L Zn and higher [NaOH], 500 g/L NaOH, than was necessary. The “pre-mix” was then diluted to 37.5g/L Zn and 210g/L NaOH by use of reagent grade NaOH and/or deionized (D.I.) H<sub>2</sub>O. Additives, 40 minutes prior to plating, were introduced to the electrolyte. Three commercial additives were investigated - carrier (Eldiem Carrier), booster (Eldiem Booster) and leveler (Bright Enhancer 2x).

The electrodeposition was performed at ambient temperature for 5 minutes using 2.0 amps of direct current (DC) provided by a 20V Extech, Model #382275 power supply. Unlike the industrial plating process, no external agitation was used.

Following plating, the cathode was promptly removed and rinsed with D.I. water. To simulate the bright dip process conducted in the industrial plating line, the zinc coating was dipped in a 0.25% v/v nitric solution for 30 seconds before rinsing with D.I. water. The coating was then dried using hot air to avoid the formation water spots.

### **2.3. PHYSICAL CHARACTERIZATION**

Following each Hull cell test, the zinc coating was visually inspected. The coating appearance was qualitatively categorized using the following terms: burnt (powdery and/or black in color), matte (non-reflective and light gray), shiny (light gray and reflective), white (dull white color), or no plating (substrate visible). These appearances were denoted to various deposit sections, correlating to the current density range following the 2 amps scale on a standard Hull cell ruler. After visual inspection, samples were gathered from each cathode by shearing along known current density ranges for further analysis.

To identify the preferred crystal orientation for Zn deposits formed at 170-260 A/m<sup>2</sup>, x-ray diffraction (XRD) analysis was performed using a Philips Panalytical X'Pert Pro Multipurpose Diffractometer. Measurements were conducted using a 2-theta angle range of 50-90°, using Cu K-alpha radiation at a scanning rate of 3 degrees per minute.

### 3. RESULTS AND DISCUSSION

While prior research [15-20] has examined additive effects on alkaline zincate plating, this project was prompted by the unique bath chemistry. The zinc concentration (30-40 g/L) and sodium hydroxide concentration (210-220g/L) are significantly higher than standard baths reported in literature [1].

To understand the effects of the commercial additives, synthetic electrolytes were generated with various additive ratios with constant [Zn] and [NaOH] of 37.5 g/L and 210 g/L, respectively. The resulting coatings generated were characterized visually and using XRD.

#### 3.1. CYCLIC VOLTAMMETRY

To determine if the additives affected zinc nucleation overpotential or plating overpotential, the various solutions were examined using cyclic voltammetry. The CV results were examined starting with individual additives and then combinations.

**3.1.1. Carrier.** Cyclic voltammograms or CV plots for zinc deposition in the presence of three concentrations of carrier are presented in Figure 2. The nucleation



overpotential ( $\eta_0$ ) and plating overpotentials at three current densities ( $\eta_{86}$ ,  $\eta_{172}$ ,  $\eta_{258}$ ) were obtained from the CV data and are summarized in Table 1.

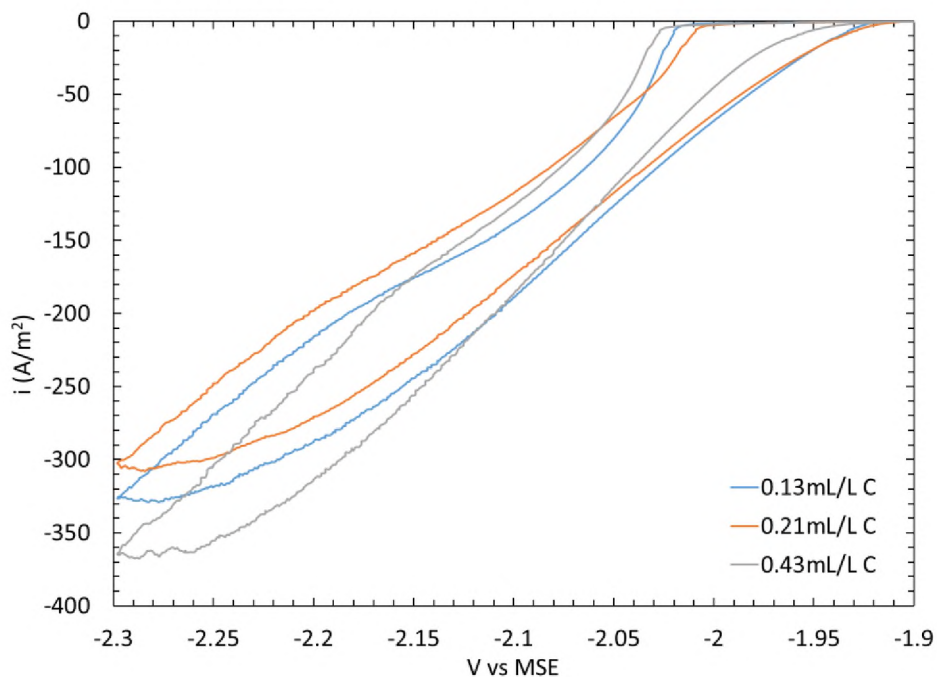


Figure 2. CV for synthetic solution with various concentrations of carrier (C).

Table 1. Overpotentials taken at 0, 86, 172, and 258 A/m<sup>2</sup> for various carrier concentrations.

[Zn] (g/L)	Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	$\eta_0$ (V)	$\eta_{86}$ (V)	$\eta_{172}$ (V)	$\eta_{258}$ (V)
37.5	0.13	0.00	0.00	-0.094	-0.095	-0.163	-0.240
37.5	0.21	0.00	0.00	-0.099	-0.117	-0.195	-0.279
37.5	0.43	0.00	0.00	-0.112	-0.120	-0.180	-0.242

With only carrier present, the nucleation overpotential ( $\eta_0$ ) became more negative with increasing carrier concentration indicating the carrier increased the energy needed to

nucleate zinc on the stainless steel substrate. The plating overpotentials at  $86 \text{ A/m}^2$  also increased as carrier concentration increased. Plating overpotentials at higher current densities ( $\eta_{172}$ ,  $\eta_{258}$ ) were greater than the nucleation overpotential and were the largest at  $0.21 \text{ mL/L}$  concentration.

**3.1.2. Booster.** Cyclic voltammograms or CV plots for zinc deposition in the presence of two concentrations of booster are presented in Figure 3.

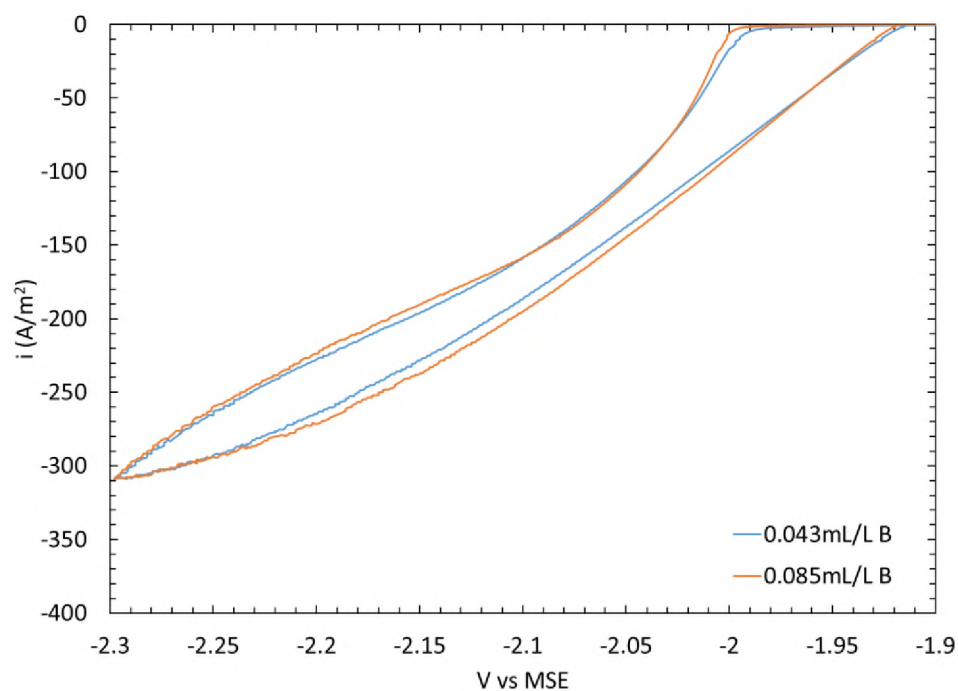


Figure 3. CV for synthetic solution with various concentrations of booster (B).

The nucleation overpotential ( $\eta_0$ ) and plating overpotentials at three current densities ( $\eta_{86}$ ,  $\eta_{172}$ ,  $\eta_{258}$ ) were obtained from the CV data and are summarized in Table 2.

Table 2. Overpotentials taken at 0, 86, 172, and 258 A/m<sup>2</sup> for various booster concentrations.

[Zn] (g/L)	Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	$\eta_0$ (V)	$\eta_{86}$ (V)	$\eta_{172}$ (V)	$\eta_{258}$ (V)
37.5	0.00	0.043	0.00	-0.074	-0.088	-0.173	-0.277
37.5	0.00	0.085	0.00	-0.075	-0.080	-0.160	-0.263

Increasing booster concentration did not alter the nucleation overpotential or  $\eta_{86}$  value. Plating overpotentials at higher current densities ( $\eta_{172}$  and  $\eta_{258}$ ) decreased as booster concentration increased.

**3.1.3. Leveler.** CV plots for zinc deposition in the presence of three concentrations of leveler are presented in Figure 4.

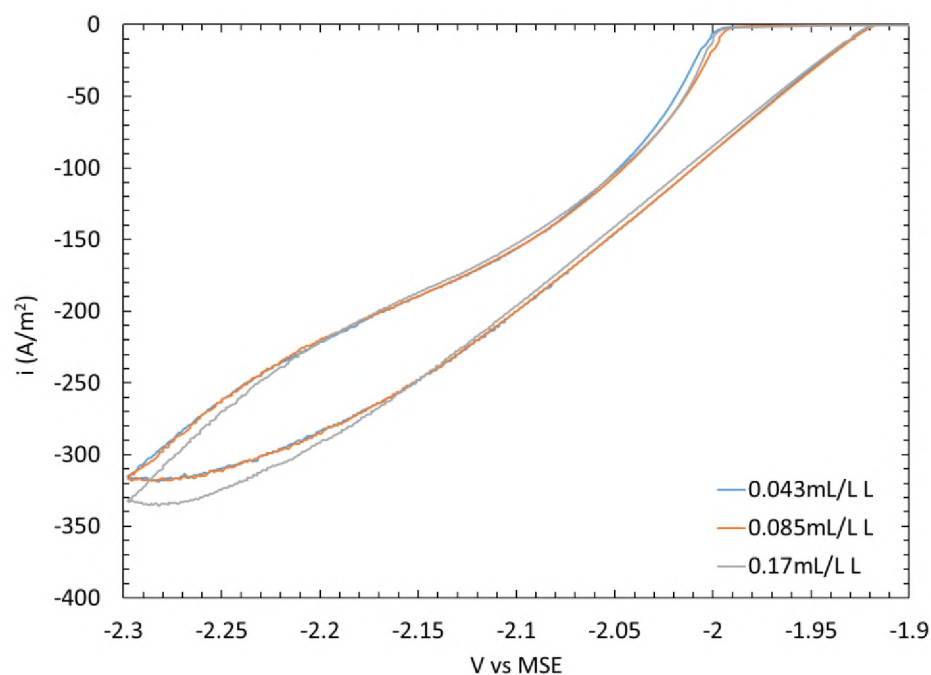


Figure 4. CV for synthetic solution with various concentrations of leveler (L).

There was no detectable difference in overpotentials with changes in leveler concentrations (Table 3), indicating it is not active during deposition at these amounts.

Table 3. Overpotentials taken at 0, 86, 172, and 258 A/m<sup>2</sup> for various leveler concentrations.

[Zn] (g/L)	Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	$\eta_0$ (V)	$\eta_{86}$ (V)	$\eta_{172}$ (V)	$\eta_{258}$ (V)
37.5	0.00	0.00	0.043	-0.073	-0.080	-0.156	-0.244
37.5	0.00	0.00	0.085	-0.070	-0.083	-0.159	-0.248
37.5	0.00	0.00	0.17	-0.074	-0.084	-0.161	-0.244

**3.1.4. Carrier and Booster.** CV plots for zinc deposition in the presence of carrier and booster are presented in Figure 5.

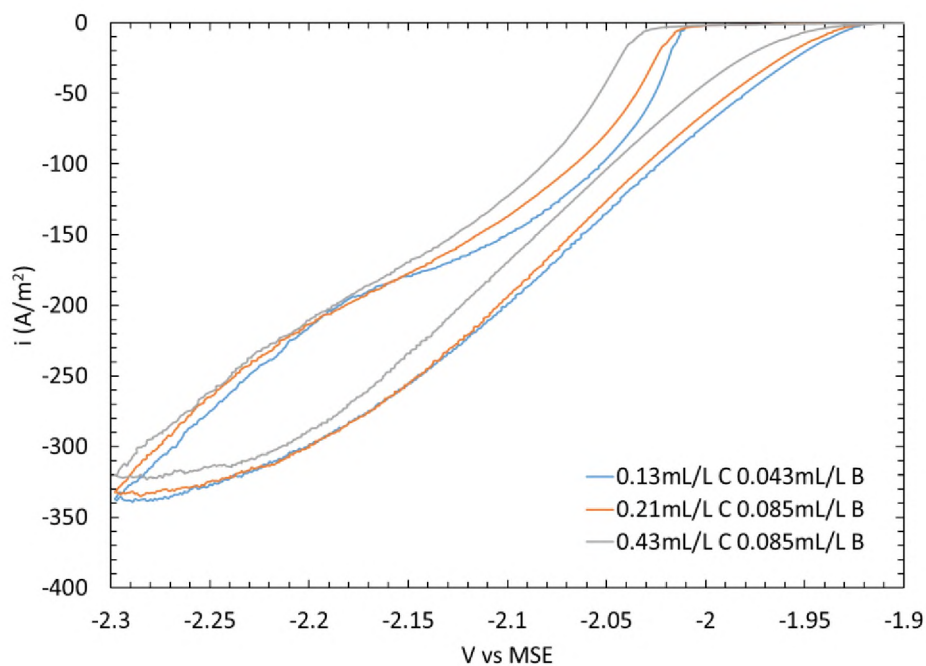


Figure 5. CV for synthetic solution with various concentrations of carrier and booster.

As described in Table 4, nucleation overpotentials and  $\eta_{86}$  increased with carrier and booster concentration.  $\eta_{172}$  and  $\eta_{258}$  were greatest for 0.21 mL/L carrier and 0.085 mL/L booster. The overpotential values were very similar ( $\pm 8$  mV) to those measured with carrier only. Thus, it did not appear that the carrier and booster interacted electrochemically and the overpotentials were dominated by the carrier.

Table 4. Overpotentials taken at 0, 86, 172, and 258 A/m<sup>2</sup> for various carrier and booster concentrations.

[Zn] (g/L)	Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	$\eta_0$ (V)	$\eta_{86}$ (V)	$\eta_{172}$ (V)	$\eta_{258}$ (V)
37.5	0.13	0.043	0.00	-0.092	-0.095	-0.163	-0.236
37.5	0.21	0.085	0.00	-0.094	-0.123	-0.200	-0.282
37.5	0.43	0.085	0.00	-0.107	-0.118	-0.183	-0.250

**3.1.5. Carrier and Leveler.** CV plots for zinc deposition in the presence of carrier and leveler are presented in Figure 6. The nucleation overpotential ( $\eta_0$ ) and plating overpotentials are summarized in Table 5.

Nucleation overpotentials and  $\eta_{86}$  increased with carrier and leveler concentrations.  $\eta_{172}$  and  $\eta_{258}$  were greatest for 0.21 mL/L carrier and 0.085 mL/L leveler. The overpotential values were very similar ( $\pm 6$  mV) to those measured with carrier only except for  $\eta_{258}$  at the highest concentrations. The leveler appears to polarize the reaction by 14 mV at this condition. It appears that the overpotentials were dominated by the carrier.

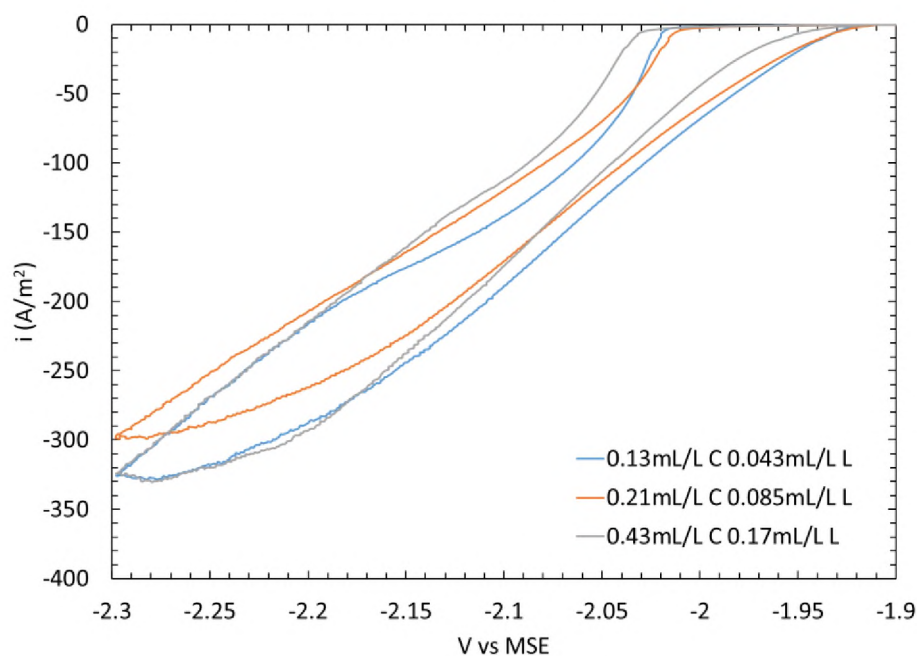


Figure 6. CV for synthetic solution with various concentrations of carrier and leveler.

Table 5. Overpotentials taken at 0, 86, 172, and 258 A/m<sup>2</sup> for various carrier and leveler concentrations.

[Zn] (g/L)	Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	$\eta_0$ (V)	$\eta_{86}$ (V)	$\eta_{172}$ (V)	$\eta_{258}$ (V)
37.5	0.13	0.00	0.043	-0.094	-0.100	-0.169	-0.246
37.5	0.21	0.00	0.085	-0.093	-0.117	-0.192	-0.285
37.5	0.43	0.00	0.17	-0.112	-0.123	-0.188	-0.256

**3.1.6. Booster and Leveler.** CV plots for zinc deposition in the presence of booster and leveler are presented in Figure 7. The nucleation overpotential ( $\eta_0$ ) and plating overpotentials are summarized in Table 6.

The overpotential values in the booster and leveler experiments were very similar (+/- 7 mV) to those measured with booster only. Thus, it did not appear that the booster

and leveler interact electrochemically. The overpotentials appeared to be determined by the booster concentration and not the leveler concentration.

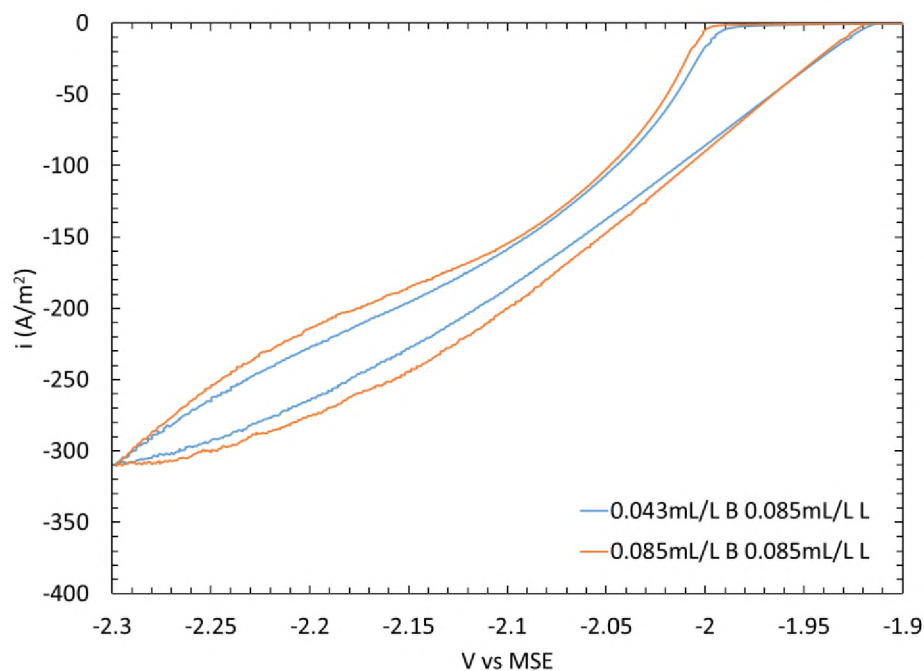


Figure 7. CV for synthetic solution with various concentrations of booster and leveler.

Table 6. Overpotentials taken at 0, 86, 172, and 258 A/m<sup>2</sup> for various booster and leveler concentrations.

[Zn] (g/L)	Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	$\eta_0$ (V)	$\eta_{86}$ (V)	$\eta_{172}$ (V)	$\eta_{258}$ (V)
37.5	0.00	0.043	0.085	-0.071	-0.092	-0.177	-0.276
37.5	0.00	0.085	0.085	-0.076	-0.080	-0.157	-0.256

**3.1.7. Carrier, Booster and Leveler.** CV plots for zinc deposition in the presence of booster and leveler are presented in Figure 8.

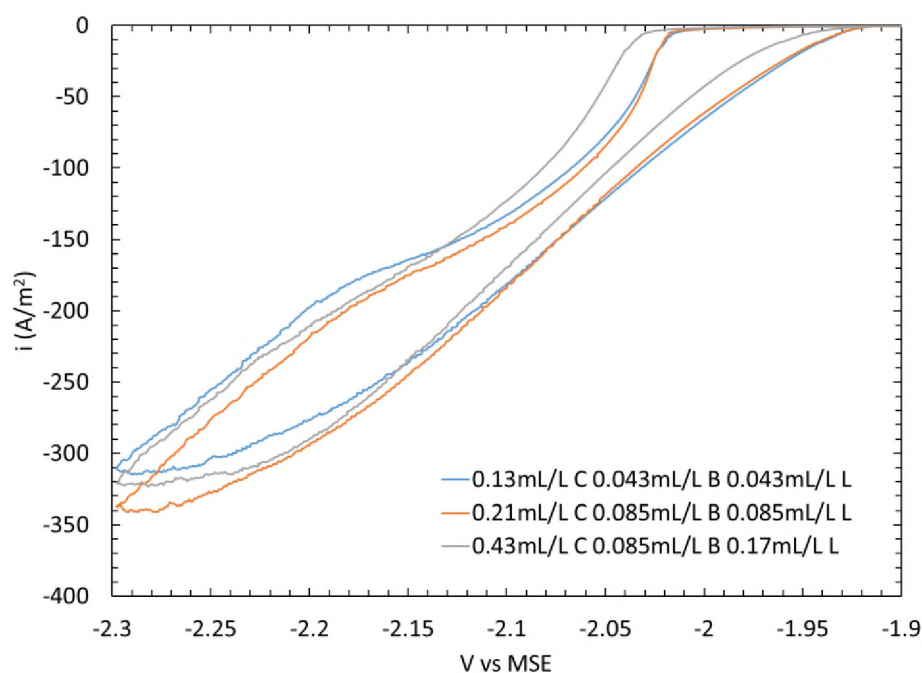


Figure 8. CV plots for synthetic solution with various concentrations of carrier, booster, and leveler.

The nucleation overpotential ( $\eta_0$ ) and plating overpotentials are summarized in Table 7. Comparing the overpotentials with all three additives to those measured with only carrier added indicates that the carrier concentration controlled the nucleation overpotential. Plating overpotentials ( $\eta_{86}$ ,  $\eta_{172}$ ,  $\eta_{258}$ ) for the combination of all three additives were like the carrier only overpotentials when the carrier concentration was 0.21 mL/L. At the highest carrier concentration, 0.43 mL/L carrier, the plating overpotentials were like those with carrier + leveler. At a concentration of 0.13 mL/L carrier, the addition of 0.043 mL/L booster increases the plating overpotentials as compared to carrier + leveler.



Table 7. Overpotentials taken at 0, 86, 172, and 258 A/m<sup>2</sup> for various carrier, booster, and leveler concentrations.

[Zn] (g/L)	Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	$\eta_0$ (V)	$\eta_{86}$ (V)	$\eta_{172}$ (V)	$\eta_{258}$ (V)
37.5	0.13	0.043	0.043	-0.098	-0.104	-0.177	-0.260
37.5	0.21	0.085	0.085	-0.100	-0.121	-0.198	-0.288
37.5	0.43	0.085	0.17	-0.114	-0.125	-0.191	-0.257

These data indicated that carrier is the dominant additive in defining the nucleation and plating overpotentials. If the carrier concentration is high, then the addition of a leveler increases the overpotential while at low carrier concentration the booster and leveler are needed to inhibit zinc reduction.

### 3.2. XRD

The effect of additive concentration on deposit structure was examined using XRD analysis of the zinc deposits resulting from the Hull cell experiments. The XRD results were examined to determine which crystallographic planes were the highest intensity. The preferred crystallographic planes have been correlated to different types of zinc deposits [21]. The correlation between deposit type (basal, triangular, intermediate, and vertical) and preferred crystallographic planes are shown in each table when the XRD data is discussed. Like the CV data, the XRD data will be presented by examining the effect of individual additives and then combinations.

**3.2.1. Carrier.** The XRD data for Hull cell deposits produced with only carrier added to the electrolyte are summarized in Table 8. With increasing carrier concentration, a shift from a primarily basal deposit (002 dominant) to a triangular deposit was

observed. This suggests that increasing carrier concentration inhibits basal growth in favor of triangular.

Table 8. XRD results for 170-260 A/m<sup>2</sup> (16-24 A/ft<sup>2</sup>) section of Hull cell deposits with only the carrier additive present. Intensities were normalized so the maximum crystallographic plane intensity was set equal to 100 for each sample.

Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	Basal (0 0 2) (1 0 3)		Triangular (1 0 1)	Intermediate (1 0 2)	Vertical (1 0 0) (1 1 0)	
0.13	0.00	0.00	100.0	2.0	12.8	1.3	1.1	1.2
0.21	0.00	0.00	100.0	9.3	72.2	10.9	24.1	6.1
0.43	0.00	0.00	6.5	1.7	100.0	1.9	3.0	1.5

**3.2.2. Booster.** The XRD data for Hull cell deposits produced with only booster added to the electrolyte are summarized in Table 9. Changing the booster concentration did not alter the preferred growth orientation of the zinc deposit.

Table 9. XRD results for various booster compositions. Results correlate to the 170-260A/m<sup>2</sup> region of the above Hull cells. Intensities were normalized so the maximum crystallographic plane intensity was set equal to 100.

Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	Basal (0 0 2) (1 0 3)		Triangular (1 0 1)	Intermediate (1 0 2)	Vertical (1 0 0) (1 1 0)	
0.00	0.043	0.00	100.0	0.2	0.6	0.1	0.4	0.1
0.00	0.085	0.00	100.0	1.1	6.5	1.2	17.5	0.9

**3.2.3. Leveler.** The XRD data for Hull cell deposits produced with only leveler added to the electrolyte are summarized in Table 10. Leveler concentrations were found

to produce no discernable changes in deposit structure. This is similar to the results of booster alone.

Table 10. XRD results for various leveler compositions. Results correlate to the 170-260A/m<sup>2</sup> region of the above Hull cells. Intensities were normalized so the maximum crystallographic plane intensity was set equal to 100.

Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	Basal (0 0 2)	Triangular (1 0 3)	Intermediate (1 0 1)	Vertical (1 0 2)	Vertical (1 0 0)	Vertical (1 1 0)
0.0	0.00	0.043	100.0	0.8	3.2	0.1	0.6	0.6
0.0	0.00	0.085	100.0	2.8	17.4	3.6	7.8	1.7
0.00	0.00	0.17	100.0	2.5	13.7	1.0	0.9	1.5

**3.2.4. Carrier and Booster.** The XRD data for Hull cell deposits produced with carrier and booster in the electrolyte are shown in Table 11. The preferred growth plane appears to be controlled by the carrier concentration as the XRD results are like those with carrier only in the electrolyte.

Table 11. XRD results for various carrier and booster compositions. Results correlate to the 170-260A/m<sup>2</sup> region of the above Hull cells. Intensities were normalized so the maximum crystallographic plane intensity was set equal to 100.

Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	Basal (0 0 2)	Triangular (1 0 3)	Intermediate (1 0 1)	Vertical (1 0 2)	Vertical (1 0 0)	Vertical (1 1 0)
0.13	0.043	0.00	100.0	0.0	6.9	1.4	6.4	0.0
0.43	0.085	0.00	37.3	10.8	100.0	14.8	24.8	9.9

**3.2.5. Carrier and Leveler.** The XRD data for Hull cell deposits produced with carrier and leveler additions to the electrolyte are provided in Table 12. Combining the leveler with the carrier appears to depress the likelihood of one strong preferred crystallographic growth. At 0.13 mL/L carrier, the addition of 0.043 mL/L leveler promoted more triangular and vertical growth while at 0.43 mL/L carrier, the addition of 0.085 mL/L leveler encouraged more (002) planes. This indicated the leveler interacted with the carrier and produced different orientations than only the carrier.

Table 12. XRD results for various carrier and leveler compositions. Results correlate to the 170-260A/m<sup>2</sup> region of the above Hull cells. Intensities were normalized so the maximum crystallographic plane intensity was set equal to 100.

Carrier (mL/L)	Booster (mL/L)	Leveler (mL/L)	Basal (0 0 2)	Triangular (1 0 3)	Intermediate (1 0 1)	Vertical (1 0 2)	Vertical (1 0 0)	Vertical (1 1 0)
0.13	0.00	0.043	94.6	15.8	100.0	18.2	30.9	12.1
0.21	0.00	0.085	100.0	3.9	32.4	4.8	16.6	2.2
0.43	0.00	0.17	100.0	2.8	10.5	0.5	31.4	1.3

**3.2.6. Booster and Leveler.** The XRD data for Hull cell deposits produced with booster and leveler added to the electrolyte are tabulated in Table 13. Addition of 0.043 mL/L booster to 0.085 mL/L of leveler produced no discernable change in deposit structure. The booster and leveler do not appear to interact significantly as the XRD data are similar to those for the booster only deposits with almost the entirety of the primary growth consisting of the (002) crystalline planes.

Table 13. XRD results for various booster and leveler compositions. Results correlate to the 170-260A/m<sup>2</sup> region of the above Hull cells. Intensities were normalized so the maximum crystallographic plane intensity was set equal to 100.

Carrier	Booster	Leveler	Basal		Triangular	Intermediate	Vertical	
(mL/L)	(mL/L)	(mL/L)	(0 0 2)	(1 0 3)	(1 0 1)	(1 0 2)	(1 0 0)	(1 1 0)
0.00	0.043	0.085	100.0	0.5	3.1	0.5	26.7	0.5
0.00	0.085	0.085	100.0	4.8	27.3	6.1	8.0	2.7

**3.2.7. Carrier, Booster and Leveler.** The XRD data for Hull cell deposits produced with carrier, booster and leveler in the electrolyte are summarized in Table 14. The presence of all three additives appeared to facilitate more random deposits with stronger intensities of secondary growth planes.

Table 14. XRD results for various carrier, booster, and leveler compositions. Results correlate to the 170-260A/m<sup>2</sup> region of the above Hull cells. Intensities were normalized so the maximum crystallographic plane intensity was set equal to 100.

Carrier	Booster	Leveler	Basal		Triangular	Intermediate	Vertical	
(mL/L)	(mL/L)	(mL/L)	(0 0 2)	(1 0 3)	(1 0 1)	(1 0 2)	(1 0 0)	(1 1 0)
0.13	0.043	0.043	52.0	14.8	100.0	18.3	19.9	8.4
0.21	0.085	0.085	100.0	2.2	13.6	2.7	23.3	2.0
0.43	0.085	0.17	67.0	12.4	100.0	16.3	21.0	7.9

**3.2.8. CV and XRD Comparison.** The voltammetry and x-ray diffraction data were examined to determine if correlations between the measurements could be made. The Hull cell deposit growths were grouped into four categories based on the peak intensities of the (002) and (101) planes. These groupings are summarized in Table 15.

Table 15. Hull cell deposit category by normalized XRD plane intensity.

Deposit Category	(002) Normalized Intensity	(101) Normalized Intensity
1	100	<50
2	100	50-99
3	50-99	100
4	<50	100

Using these deposit category designations (1-4), the relationship between plating overpotential at 172 A/m<sup>2</sup> ( $\eta_{172}$ ) and nucleation overpotential ( $\eta_0$ ) were examined for each group. This analysis is illustrated in Figure 9.

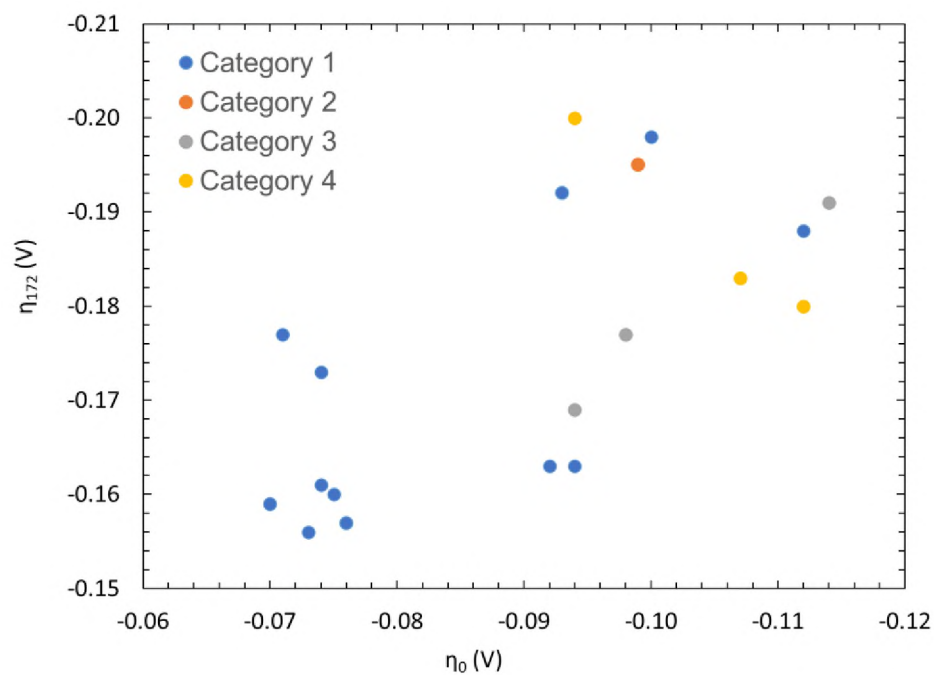


Figure 9. Comparison of 172 A/m<sup>2</sup> overpotential with nucleation overpotential by deposit morphology.

While there is not a strong correlation between overpotentials and preferred growth orientation, the data seems to indicate that low overpotentials and low plating potentials appear to favor category 1 (strong basal) deposits. As the nucleation overpotential and plating overpotential increase, other deposit categories are encountered.

### 3.3. HULL CELL TESTING

To determine the effect of additive concentration on deposit appearance, Hull cell tests were conducted and visually inspected. Favorable deposits are shiny for the widest current density range, including the preferred industrial range of 170-260 A/m<sup>2</sup>. White deposits would be deemed acceptable if no shiny deposits form, matte less so. Burned deposits or no plating are unacceptable in industrial practice.

**3.3.1. Carrier.** The visual appearance of the Hull cell experiments conducted with carrier in the electrolyte are summarized in Table 16. The most favorable deposit occurred at 0.13mL/L carrier with a white deposit observed up to 323 A/m<sup>2</sup> (30 A/ft<sup>2</sup>). The deposit appearance decreased as carrier concentration increased, however the minimum current density at which burned deposits form increased.

Table 16. Hull cell results for solutions with carrier additive only. Visual appearance was assigned as b = burnt, m = matte, w = white, s = shiny and n = no plating. The Hull cell ruler with current densities in A/ft<sup>2</sup> is provided. 1 A/ft<sup>2</sup> = 10.76 A/m<sup>2</sup>.

Carrier (ml/L)	Booster (mL/L)	Leveler (mL/L)	Hull Cell Appearance							
			80	60	40	30	20	12	4	1
0.13	0.00	0.00	b				w			
0.21	0.00	0.00	b				m			n
0.43	0.00	0.00	b	m			w			

**3.3.2. Booster.** The visual appearance of the Hull cell experiments conducted with booster in the electrolyte is illustrated in Table 17. As booster concentration increased, the amount of burned deposit decreased. However, the deposit appearance in the desired current density range decreased from white to matte.

Table 17. Hull cell results for two booster concentrations. Visual appearance was assigned as b = burnt, m = matte, w = white, s = shiny and n = no plating. The Hull cell ruler with current densities in A/ft<sup>2</sup> is provided. 1 A/ft<sup>2</sup> = 10.76 A/m<sup>2</sup>.

Carrier (ml/L)	Booster (mL/L)	Leveler (mL/L)	Hull Cell Appearance						
			80	60	40	30	20	12	4
0.00	0.043	0.00	b		m		w		
0.00	0.085	0.00	b	m				n	

**3.3.3. Leveler.** The visual appearance of the Hull cell experiments conducted with leveler in the electrolyte is provided in Table 18. The most favorable deposit occurs at 0.043mL/L leveler concentration. Increased leveler concentration was found to decrease the appearance at low current densities.

Table 18. Hull cell results for various leveler compositions. Visual appearance was assigned as b = burnt, m = matte, w = white, s = shiny and n = no plating. The Hull cell ruler with current densities in A/ft<sup>2</sup> is provided. 1 A/ft<sup>2</sup> = 10.76 A/m<sup>2</sup>.

Carrier (ml/L)	Booster (mL/L)	Leveler (mL/L)	Hull Cell Appearance						
			80	60	40	30	20	12	4
0.00	0.00	0.043	b			w			
0.00	0.00	0.085	b			m			n
0.00	0.00	0.17	b		m	w			



**3.3.4. Carrier and Booster.** The visual appearance of the Hull cell experiments conducted with carrier and booster in the electrolyte is shown in Table 19. The most favorable deposit occurred at concentrations of 0.43mL/L carrier and 0.085mL/L booster but was only a matte finish. Increased additive concentration was found to increase the current density range for the matte appearance and also increased the current density needed to produce a burnt deposit. No white or shiny deposits were observed for any of the solutions.

Table 19. Hull cell results for various carrier and booster compositions. Visual appearance was assigned as b = burnt, m = matte, w = white, s = shiny and n = no plating. The Hull cell ruler with current densities in A/ft<sup>2</sup> is provided. 1 A/ft<sup>2</sup> = 10.76 A/m<sup>2</sup>.

Carrier (ml/L)	Booster (mL/L)	Leveler (mL/L)	Hull Cell Appearance						
			80	60	40	30	20	12	4
0.13	0.043	0.00	b			m		n	
0.21	0.085	0.00	b		m				n
0.43	0.085	0.00	b		m				n

**3.3.5. Carrier and Leveler.** The visual appearance of the Hull cell experiments conducted with carrier and leveler in the electrolyte is summarized in Table 20. The best deposit occurs at concentrations of 0.43mL/L carrier and 0.17mL/L leveler within this series. Increasing additive concentration was found to increase appearance at low current densities from no plating or matte appearance to a white deposit. A burnt appearance region was always present at consistently lower current density than observed for other additive combinations.

Table 20. Hull cell results for various carrier and leveler compositions. Visual appearance was assigned as b = burnt, m = matte, w = white, s = shiny and n = no plating. The Hull cell ruler with current densities in A/ft<sup>2</sup> is provided. 1 A/ft<sup>2</sup> = 10.76 A/m<sup>2</sup>.

Carrier (ml/L)	Booster (mL/L)	Leveler (mL/L)	Hull Cell Appearance						
			80	60	40	30	20	12	4
0.13	0.00	0.043	b			m		n	
0.21	0.00	0.085	b			m		n	
0.43	0.00	0.17	b			w			

**3.3.6. Booster and Leveler.** The visual appearance of the Hull cell experiments conducted with booster and leveler in the electrolyte is illustrated in Table 21. The amount of burned deposit increased with an increased booster concentration. No white deposits were observed.

Table 21. Hull cell results for various booster and leveler compositions. Visual appearance was assigned as b = burnt, m = matte, w = white, s = shiny and n = no plating. The Hull cell ruler with current densities in A/ft<sup>2</sup> is provided. 1 A/ft<sup>2</sup> = 10.76 A/m<sup>2</sup>.

Carrier (ml/L)	Booster (mL/L)	Leveler (mL/L)	Hull Cell Appearance						
			80	60	40	30	20	12	4
0.00	0.043	0.085	b			m		n	
0.00	0.085	0.085	b			m		n	

**3.3.7. Carrier, Booster and Leveler.** The visual appearance of the Hull cell experiments conducted with carrier, booster, and leveler in the electrolyte is provided in Table 22. The most favorable deposit was from the test containing 0.43 mL/L carrier, 0.085mL/L booster, and 0.17mL/L leveler. Increased additive concentration increased overall appearance, despite no white or shiny appearance occurring.

Of the four solutions producing a white deposit, only three produced white deposits in the entire desired current density range: 0.13 mL/L carrier, 0.043 mL/L leveler, and 0.43mL/L carrier with 0.17mL/L leveler. This indicates that the introduction of booster worsens the appearance of the zinc deposit at the temperature of these experiments. As the increased carrier and leveler concentrations worsened overall appearance, the best solutions were those of low concentration. The best solution that prevented burning of a deposit and lack of deposition was 0.43mL/L carrier, 0.085mL/L booster, and 0.17mL/L leveler, but it only produced a matte finish.

Table 22. Hull cell results for various carrier, booster, and leveler compositions. Visual appearance was assigned as b = burnt, m = matte, w = white, s = shiny and n = no plating. The Hull cell ruler with current densities in A/ft<sup>2</sup> is provided. 1 A/ft<sup>2</sup> = 10.76 A/m<sup>2</sup>.

Carrier (ml/L)	Booster (mL/L)	Leveler (mL/L)	Hull Cell Appearance							
			80	60	40	30	20	12	4	1
0.13	0.043	0.043	b							n
0.21	0.085	0.085	b	m		b				
0.43	0.085	0.17	b	m					n	

This observation does not match industrial observations as a triple additive mixture typically produces excellent deposit appearance. The poor appearance of the studied deposit is likely the result of not using the correct additive concentrations.

No correlation was found between the overpotentials measured by cyclic voltammetry or the preferred growth orientation determined by XRD and the visual appearance of the Hull cell test. This was an unexpected result.

#### 4. SUMMARY

This study was conducted to investigate the effects that additives have on the appearance, crystal structure and electrochemical overpotentials of electroplated zinc from a zincate electrolyte with industrial additives present. Of the additive types, carrier had the greatest effect on nucleation overpotential, morphology, and appearance. Carrier was found to create the greatest change in nucleation overpotential, change primary growth type and promote triangular growth. Booster was found to have minimal impact on overpotential, did not significantly affect the crystal structure, and never produced a good appearance in the desired current density range. Leveler was found to have no significant effect on nucleation overpotentials or morphology under the conditions studied but can improve deposit appearance at low concentrations.

These results suggest that carrier is the most important additive to consider when altering an electroplating bath. Small concentrations of leveler could be employed to improve deposit appearance without interfering with carrier. It is not clear that the booster is working as intended.

Future work should study the interactions between carrier, booster, and leveler, as well as examine the appearance of deposits under different additive concentrations while operating at temperatures that better reflect industrial electroplating conditions.

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## SECTION

### 3. CONCLUSIONS AND RECOMMENDATIONS

#### 3.1. CONCLUSIONS

To conclude, three industrial additives: carrier, booster, and leveler were investigated to examine their effects on physical appearance of deposits, crystal structure and electrochemical overpotential. In the first study conducted at an industrially relevant temperature, correlations were made between the best appearance (white) in Hull cell testing and conditions that produced triangular (101) growth and smooth deposit observed by SEM. In the second study, experiments were conducted at ambient temperature and produced less encouraging results. Correlations were made between crystal structure and electrochemical overpotential, but the same correlation between crystal structure and appearance was not observed. This highlights the importance of temperature in producing visually good-looking zinc deposits from zincate baths. Overall, the carrier concentration was found to have the strongest impact on appearance, crystal structure and deposition overpotentials.

#### 3.2. RECOMMENDATIONS

Recommendations for future work are to investigate methods to increasing the window of operation for the plating bath; a new additive system or increase in operating current density would prove useful. A study of the molecular structure of each additive may be warranted to confirm how they inhibit grain growth. Additionally, a kinetic study

to quantify how much the growth is inhibited for each additive may prove useful. Both in tandem would be used for a design of experiments (DOE) study to determine the optimal concentrations of each additive.



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