ELECTROCHEMICAL DEPOSITION OF ALUMINUM-BASED COATINGS FROM AQUEOUS SYSTEMS

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ABSTRACT

The electroplating of aluminum has represented a challenge for the coatings industry for decades. The reactivity of aluminum metal leads to a very negative reduction potential. This leads to abundant gas evolution instead of aluminum reduction in water. Current aluminum deposition technology overcomes this limitation by excluding oxygen and water from the process with rigorously dry solvent and airtight plating tanks. These adaptations yield metallic aluminum depositions with significant impurities affecting its properties. In addition, this approach requires a great capital investment and cost of process maintenance.

An alternative approach to Al electrodeposition has been developed based on the the use of organic ligands to stabilize the Al^{3+} ion in water-based solutions. By using a ligation approach, we can create aluminum species that remain stable in water while lowering the reduction potential of the aluminum complex by 0.5V. This improvement in reduction potential gives the possibility for the deposition of aluminum without significant competition from hydrogen evolution. With this platform we can deposit highly adherent aluminum-based layers on metal surfaces. The aluminum/aluminum oxide layers appear as thin, coherent and highly adherent coatings. This aluminum/alumina layer can then be chemically treated to achieve desirable surface properties which were previously inaccessible. For example, the coating can be made hydrophobic, highly adherent to different polymer coatings or even dyed using common anodizing dyes.

INTRODUCTION

Electroplating is a mature technology for the application of coatings to conductive surfaces. [1] The process requires the submersion of parts to be coated into an electrolyte solution, commonly water, containing metal ions and supporting electrolyte (Figure 1). A voltage is applied between the part to be coated (the cathode) and another metal/carbon electrode (the anode). As current is passed through the solution, metal ions are reduced at the surface of the cathode and become bound to the surface as a growing metallic layer. The anode process is then chosen to dissolve metallic ions, in a reverse process, to replenish lost ions in solution to deposition process. Alternatively the anode process may be chosen to promote oxygen evolution to provide electrons to support the deposition process without loss of anode material. [2]

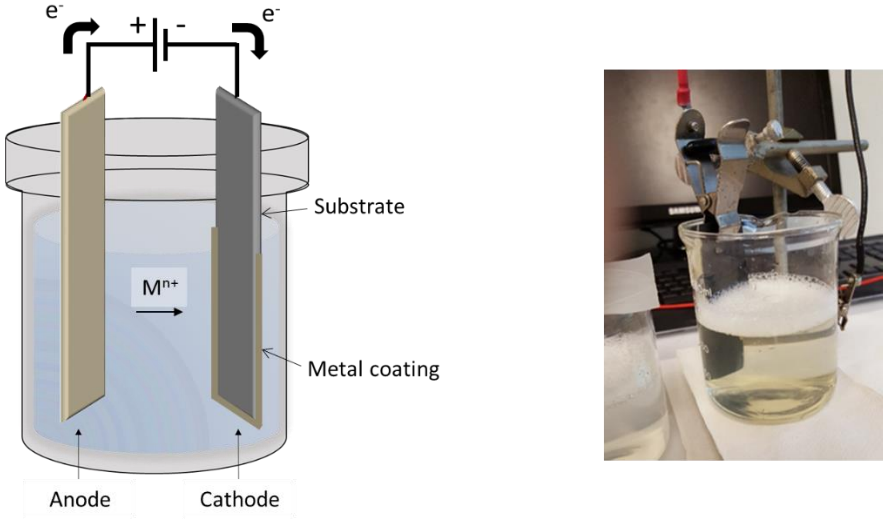


Figure 1. Electrochemical cell: schematic and photograph of the true set up.

In practice, the electrodeposition is a more complex process than simple metal reduction due to additional side processes, engineering constraints and the electrolyte complexity. Additional materials may be added as chemical additives, adhesion promoters and wetting agents, further complicating the mixture. Furthermore, different metals are more readily reduced to their metallic form than reactive metals such as aluminum. This situation necessitates an extremely high reduction voltage to obtain any appreciable amount of Al in the deposit. The voltage required to reduce solution borne metal ions is determined by the reduction potential of the metal and is tabulated according to the electrochemical series. [3] The harder to reduce the metal, the more negative the reduction potential and the more susceptible the metal is to oxidation. The most reactive metals are therefore the most difficult to electroplate and additional precautions must be taken. Indeed, water/hydrogen appears on the electrochemical series and any metal appearing with a more negative reduction potential than this reaction cannot be electrodeposited due to the overwhelming concentration of water (55 M) competing for electrons. Therefore, hydrogen evolution mainly occurs at the cathode.

In the case of aluminum, the metal ions themselves also tend to be highly reactive with water forming aluminum hydroxide species in solution immediately. These problems are generally overcome by electroplating reactive metals in the absence of oxidative species in sealed tanks using rigorously dry solvents. [4] This approach has yielded aluminum with poor performance and at great process expense. [5] It is clear, that for widespread adoption of aluminum coatings, these limitations must be removed, and the expense of the coating reduced.

We have focused on the development of an alternative strategy for aluminum electrodeposition by way of ligation. This strategy allows aluminum coatings to be used for commodity applications and in a wider range of industries. In order to make this a reality, we have developed a new ligation strategy for aluminum using electrochemically stable organic ligands which bind to the aluminum center even in the presence of water. Our aluminum salt is stable in water but is dissociated under plating conditions to allow an aluminum rich coating to be produced. The formed coating is not a pure aluminum metal, due to the oxidizing nature of the aqueous medium, but instead a metal bound, thin and compact aluminum oxide network. This aluminum oxide surface is then able to serve as an excellent surface for chemical modification steps to tune the surface properties of the coating.

An obvious application for such a coating is as a polymer adhesion promotion layer. Aluminum oxide is well known as an excellent surface for paint adhesion due to the hydroxyl bond rich surface it presents. Currently, surface preparation for paint adhesion is achieved either through a chemical dip process as an iron or zinc phosphate, [7] or through a labor-intensive physical abrasion method such as grit-blasting. Phosphating presents both environmental and health hazards in its use and alternatives are sought. Our aluminum oxide coating forms a metal bound layer that is able allowing the chemically bond directly to top-coats, giving a high level of chemical adhesion.

The aluminum oxide may also be thought of as an anodized like surface for any conductive surface and as such may be treated similarly to anodized aluminum. For example, anodized aluminum is well known for its dyeability, presenting attractive intrinsic color for consumer goods. [8] Using the same dye chemistry and preparation, our aluminum oxide surface can also be dyed to open the possibility of applying the same attractive surface finish to steel and steel alloys. This comes with the obvious benefit that a part may preserve the bulk properties of the steel, such as strength, but with the attractive finish of anodized aluminum.

TECHNICAL DISCUSSION

We first synthesized uniquely ligated aluminum salts in 2013 based on an electron-withdrawing organic ligand system which formed an air stable aluminum salt. [9] This initial salt was electrochemically characterized by cyclic voltammetry in dry acetonitrile (Figure 2A), but it was quickly found that upon exposure to water (Figure 2B), the salt remained stable in solution and still exhibited a robust reduction signal.

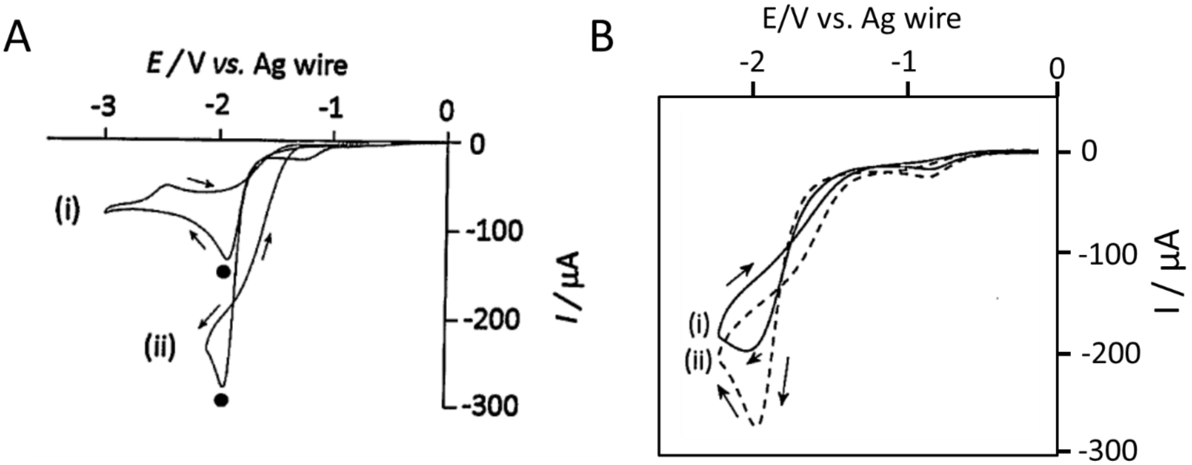


Figure 2. Cyclic voltammetry in dry acetonitrile at a 3mm glassy carbon working electrode at 50 mVs^{-1} vs Ag wire (A) (i) 10mM and 20 mM $Al(LS)_n$ + 0.1M NBu_4PF_6 in MeCN under N_2. (B) 20mM $Al(LS)_n$ + 0.1M NBu_4PF_6 in MeCN (I) open atmosphere, (ii) 1 wt% water added.

Further testing showed that even under a purely aqueous solvent system in air, the reduction could be observed and showed an almost 0.5V shift in reduction potentials when compared with a standard aluminum chloride salt (Figure 3B). In an aqueous environment it would be expected that any aluminum salt would break down to an aluminum hydroxide species in solution and would have a similar reduction profile regardless of the initial ligation (Figure 3A). However, the salt that we had synthesized showed significantly different behavior, suggesting that ligation is preserved in solution and deposition of aluminum from aqueous solution may be possible.

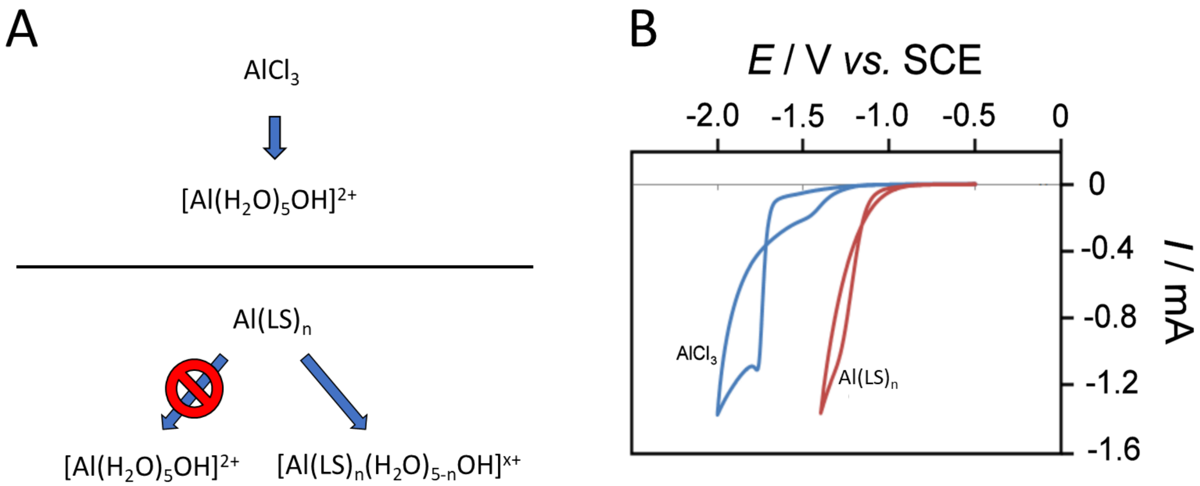


Figure 3. Different behavior of our aluminum salt $Al(LS)_n$ vs $AlCl_3$ in water (A) anticipated break down of $AlCl_3$ in water vs $Al(LS)_n$ (B) Cyclic voltammetry on 3mm glassy carbon working electrode at $10mVs^{-1}$ in aqueous solution at 1M Al salt concentration vs. SCE and with a platinum anode.

The deposition process was investigated in real time by electrochemical quartz crystal microbalance (EQCM). EQCM essentially measures the weight of an adhered deposit in real time under applied voltage (Figure 4). This means that the deposition process could be monitored with increasing reduction voltage and then investigated by X-ray photoelectron spectroscopy (XPS) of the resultant surface.

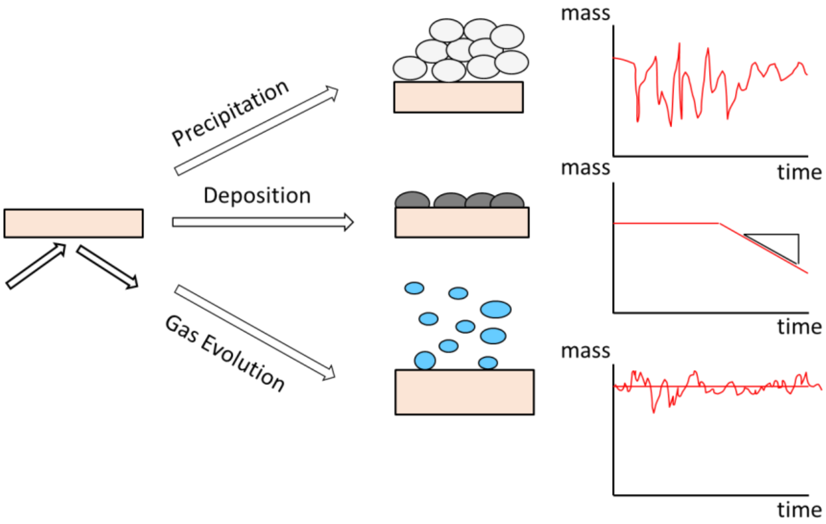


Figure 4. Theory of EQCM. Frequency changes of quartz crystal determines mass changes on the gold surface. Precipitation and gas evolution give unstable readings. Electrodeposition gives a generally linear mass change with time under galvanostatic deposition conditions.

Initial EQCM data showed that there was indeed a voltage dependent mass change of the surface with a deposition process starting at about -1.1V vs. Ag/AgCl. Importantly, the mass change was retained on multiple scans between lower and higher voltage showing the coating building over time (Figure 5). The onset of the reduction signal did not correspond to the onset of mass change for the system. This initial current is attributed to some proton reduction which does not show an associated mass change. Around -1.1V a small shoulder process is visible that does correspond to a mass change and is attributed to aluminum deposition. This process is visible on each of the 3 cyclic voltammetry scans as the voltage becomes high enough to facilitate the process.

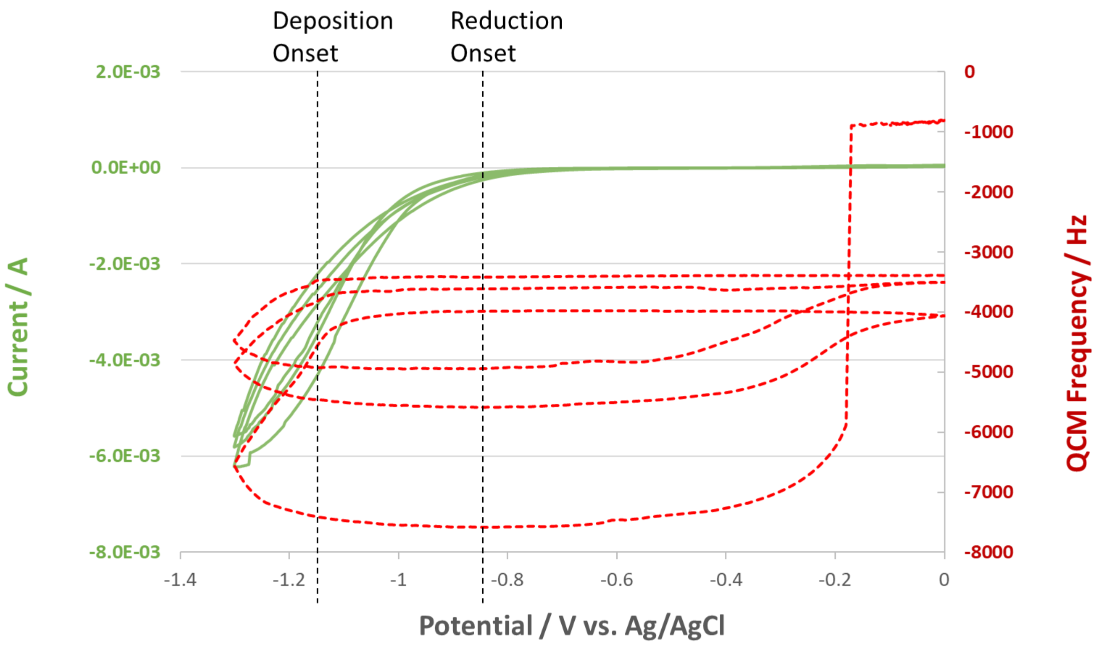


Figure 5. Cyclic voltammetry at $10mVs^{-1}$ of $Al(LS)_n$ in water with concurrent EQCM frequency measurement showing mass changes with scanned voltage.

To further investigate the growth profile, a potentiostatic measurement was made in 10-minute increments at an increasing reduction voltage (Figure 6). In this case, the same -1.1V was the lowest value required to see a linear mass change with time. Higher applied voltages led to increases in deposition rate as expected.

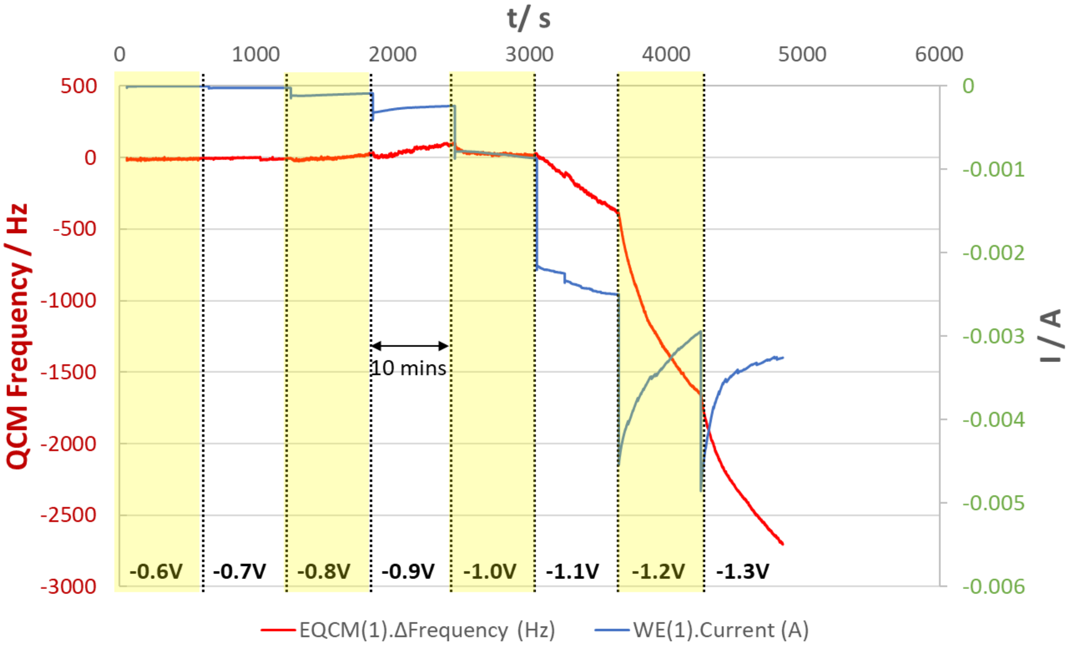
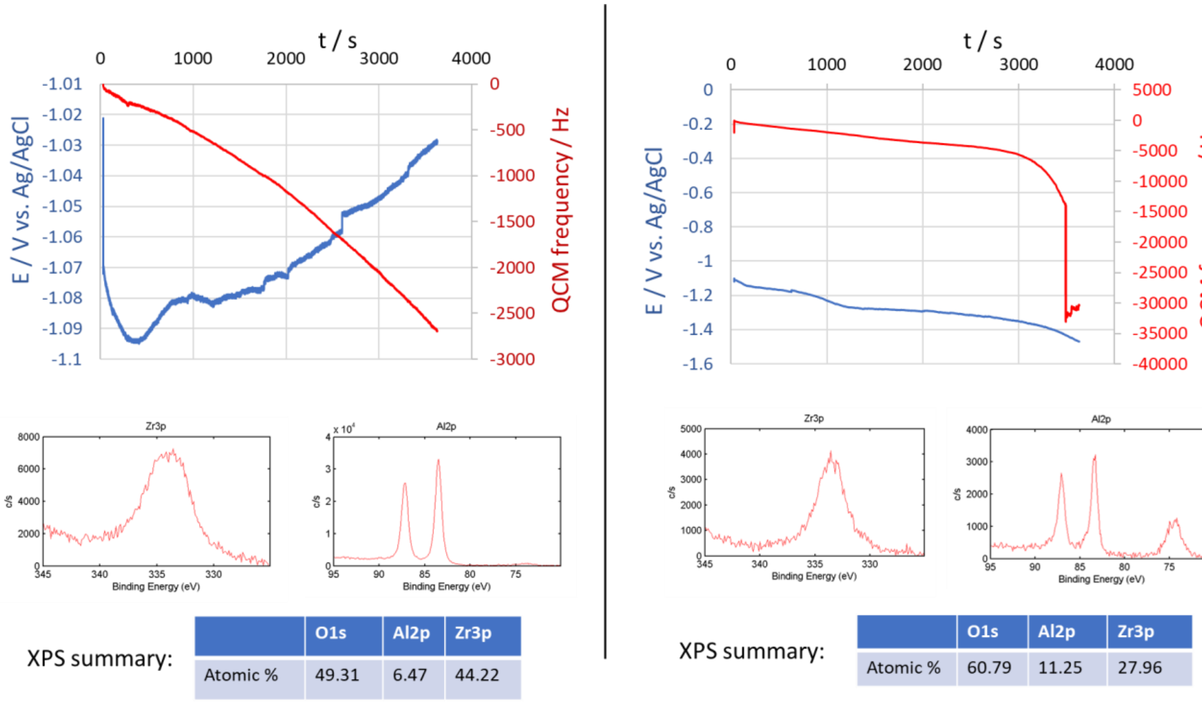


Figure 6. Potentiostatic EQCM testing at increasing reducing voltages.

During this study it was found beneficial to add a co-metal to facilitate the adhesion of the aluminum oxide coating to the surface. For this purpose, a zirconium salt was synthesized using a similar approach and added to the aluminum plating solution at a low mole fraction. To simulate a true electroplating process and generate surfaces that may be assessed for composition, a galvanostatic approach was also used. At low applied currents, a linear deposition rate was found and corresponded to voltages found in potentiostatic testing.

As currents above 10mA/cm^2 were applied, gas evolution was found to dominate, leading to unstable mass measurements that could not be easily quantified. At low applied currents zirconium was found dominant constituent of the coating despite much lower initial concentration in solution. The resultant coatings of each test were characterized by X-ray photoelectron spectroscopy (XPS) to determine composition of the surface. At higher currents the ratio of aluminum to zirconium was found to change in favor aluminum (Figure 7). This finding explains the improved adhesion of the aluminum oxide via deposition of an initial thin zirconium layer that is succeeded by a thicker aluminum oxide matrix. It should be noted, however, that with a solution containing only zirconium salt, no layer growth occurred at any applied currents and so a synergistic impact of the dual metal system is clearly highly important.



XPS summary:

	O1s	Al2p	Zr3p
Atomic %	49.31	6.47	44.22

XPS summary:

	O1s	Al2p	Zr3p
Atomic %	60.79	11.25	27.96

Figure 7. Galvanostatic EQCM summary for Al(LS) / Zr(LS) solution at 7mA/cm^2 (left) and 10mA/cm^2 (right) with XPS compositional data for the resultant surfaces.

Mechanistically it is likely that the high adhesion of the coating is determined by an initial metal deposition leading to strong metallic bonding. This metallic layer, being reactive to the aqueous environment, is then vulnerable to oxidation without the influence of the ligand structure and becomes a thin, surface bound, hydroxide. Further growth then proceeds via a pH driven precipitation to increase the layer thickness to its maximum value up to 4µm maximum. The influence of zirconium co-metal improving adhesion is then attributable to a catalytic mechanism in which the presence of the ligated aluminum salt further lowers the reduction potential for the zirconium reduction process. An initial zirconium oxide layer is first formed, onto which an aluminum rich matrix can be adhered. Upon drying, the coating densifies into a plate like growth structure of aluminum oxide.

Scale-Up

With a fundamental understanding of the Al electrodeposition, progress has been made towards the deployment of the scale up process for aluminum oxide coating on steel and aluminum parts using a developmental plating line. The scale-up development was first moved to a 4L container using a 2-electrode system in which the anode process was tested to favor water splitting so careful control over metal content and their ratio could be achieved. For this purpose, a dimensionally stable, custom designed mixed metal oxide anode was used.

Development testing showed promising results, with an aluminum oxide coating being deposited and confirmed by optical microscopy and compositional analysis. Achieving uniformity over the entire electrode surface was a challenge. Edges of the coupon samples, having higher intrinsic current density, were powdery and non-adherent, while at the same time, the center of the coupons was not fully coated. To better control the process and layer growth, a pulsed plating technique was applied with finer control of solution conditions such as flow, temperature and pH. For this reason, development was moved to a 5-gallon test plating line.

The 5-gallon test plating line was designed to mimic all relevant processes for coating development with separate tanks for cleaning, electrocleaning, activation and multiple rinse steps. The 5-gallon plating process tank was designed to simulate the control and design features of a full-scale plating process with an overflow chamber, solution recirculation agitation and a heating/cooling coil (Figure 8).

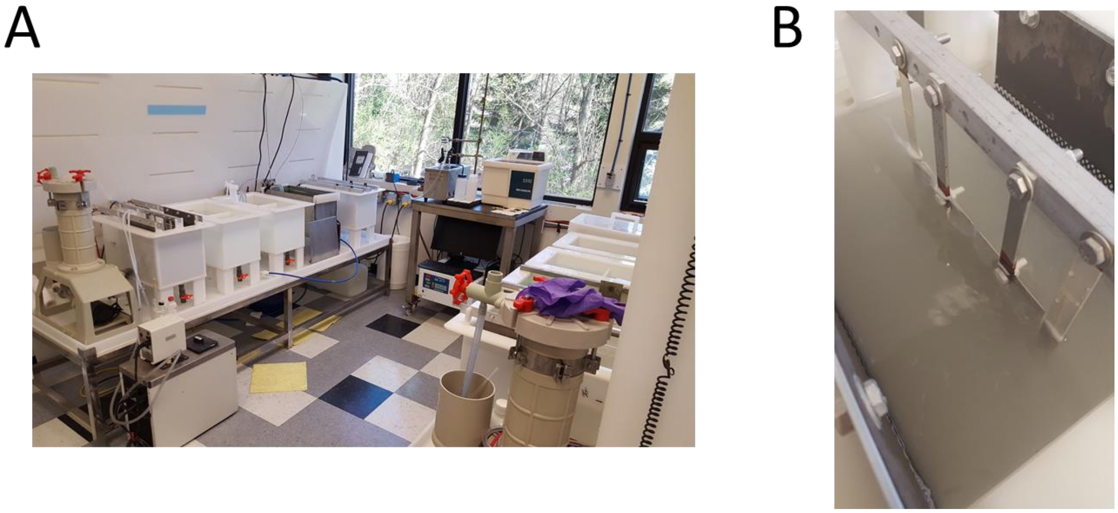


Figure 8. (A) 5-gallon developmental plating line (B) 5-gallon plating tank.

In the 5-gallon developmental plating line the pulse scheme was optimized to facilitate the uniform growth of the aluminum oxide across the entire steel-coupon surface. By varying the pulse period and current, the progression the aluminum oxide growth could be finely controlled by balancing metal reduction and hydroxide precipitation processes.

Under the application of DC currents, the layer close to the electrode surface became rapidly depleted in metal content. Meanwhile, the pH of this layer tended toward higher values as protons are concurrently reduced. The increasing pH caused additional metal salts to begin to precipitate into the solution, leading to a thick, non-adherent powdery deposit that offered no beneficial properties. Although coating thickness relies on this precipitation mechanism, an uncontrolled precipitation that is too fast was found to be undesired.

With a pulsed current deposition, the pH change and surface concentration of the deposition ions may be periodically replenished by using low current, or “off” steps. By varying the pulse period, current and progression, conditions can be varied to grow a more structured layer. Initially, longer periods at low current density are used to grow a metal-metal bound seed layer across the entire surface, as observed in the EQCM testing. Once this seed layer is developed, ramped currents are used in increasing steps but with pulse times in the 0.1s range to control the surface pH and slowly grow a dense, adherent precipitation layer onto the seed layer (Figure 9).

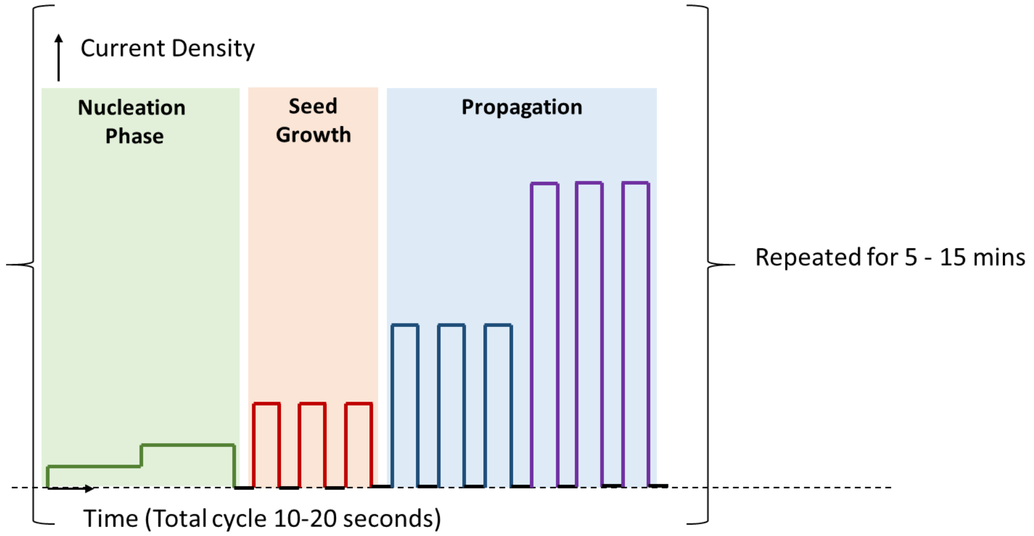


Figure 9. Example of pulsed plating technique for aluminum oxide coating process.

By changing both solution properties and process parameters different morphologies were accessible for the aluminum oxide coatings, each with beneficial characteristics (Figure 10).

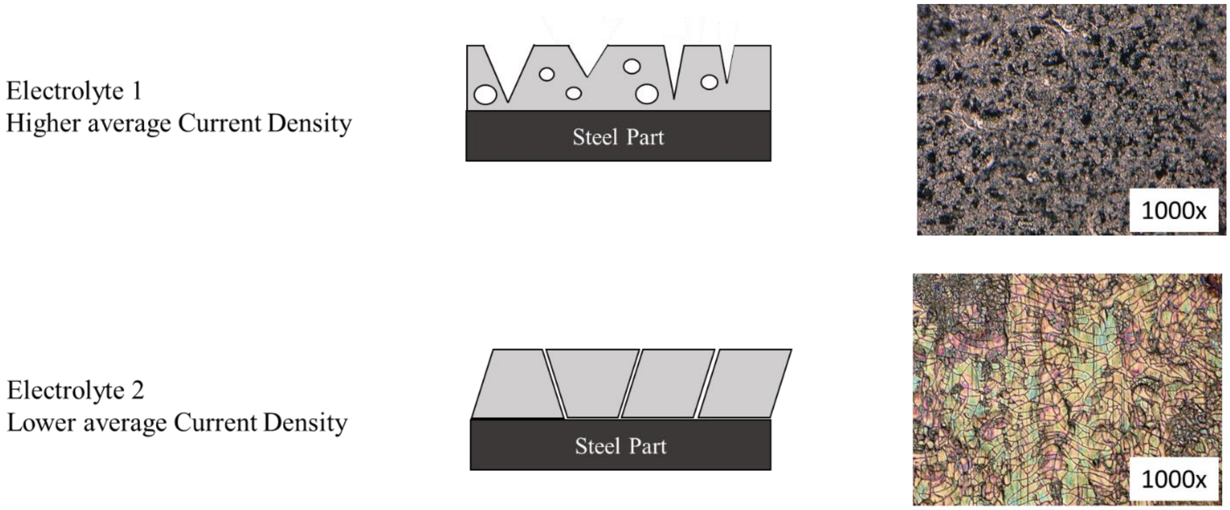


Figure 10. Surface morphology changes for two different conditions of aluminum oxide deposition process.

For example, by using electrolyte 1 with a stepped growth mechanism a porous coating appeared, with a white matte finish. Due to the intrinsic porosity, this coating was highly susceptible to the uptake of functional molecules into the layer. This unique property was used for the uptake of dye molecules to create intrinsically colored steel surfaces (Figure 11).

Figure 11. Examples of dyed steel surfaces with anodizing dyes. Left image shows the original panel and the right image shows the subsequently dyed panel in green, red and black.

The dyes and process used are analogous to that used to color anodized aluminum, in fact creating an ‘anodized’ steel surface.

Using electrolyte 2, and lower current pulse steps, a more coherent, plate like layer can be created with a controllable degree of microcracking. This layer shows intrinsic color dependent on thickness with first a blue coating being found, followed by a gold layer and finally a matte white coating indicative of thicker aluminum oxide. This more coherent barrier coating gives a greater degree of corrosion protection as well as forming an ideal surface for organic modification and paint adhesion. For paint adhesion specifically, the coherent blue coating was found to be optimal, as well as providing an excellent visual indicator of successful coating on both aluminum and steel parts.

In order to optimize the process on this scale chemical additives common to the electroplating industry were screened. These additives included surfactants to modify surface wettability and surface tension as well as to suppress side processes associated with gas evolution. After years of this development we have been able to apply a uniform thin aluminum oxide coating to mild steel (1010), stainless steels and various aluminum alloys successfully.

Performance Data

In order to characterize the coated aluminum oxide surface, electrochemical polarization testing was used. In this test, corrosion is induced on the steel surface by application of gradually increasing voltages. The current that results from the oxidative profile gives a comparison of corrosion voltage and corrosion rate that may be compared between coatings. In Figure 12, the black curve represents 1010 steel with an organic seal, all other colors represent different pulse conditions for the aluminum oxide coating with organic seal applied. For the most porous coatings (1 and 2) there is no improvement in corrosion rate over plain steel. Each of the other pulsed conditions show a significant reduction in corrosion rate and a high degree of anodic protection even for a very thin aluminum oxide coating.

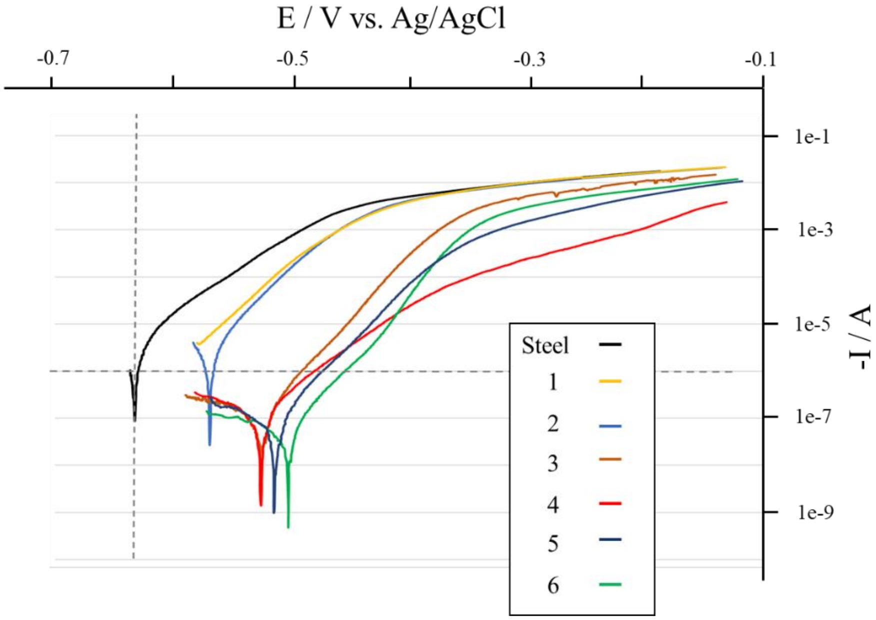


Figure 12. Potentiodynamic polarization testing for aluminum oxide coatings.

By using industry standard adhesion and corrosion resistance testing, these composite layers have been qualified against existing industry standard pretreatments such as grit-blasting and phosphating. Specifically, ASTM D1654 was used to quantify delamination of the polymer under corrosive attack. In this test the panel was scribed through the coating to the base steel to simulate damage. The sample was then subjected to an ASTM B117 standard salt spray treatment. After a given number of hours, the panel was removed, and a blade used against the scribe to forcibly remove the coating (Figure 13). A numerical value can be used to quantify the result based on the distance over which the paint delaminates. With the optimized aluminum oxide pretreatment, no scribe creep was detected (Figure 13B). Although the scribe itself showed corrosive damage, the corrosion was unable to undercut the coating and cause a loss of adhesion of the polymer. This shows that unlike traditional pretreatments, the aluminum oxide coating can protect a damage site from causing corrosion to spread across the part and cause widespread paint delamination. Ordinarily, damage this extensive would necessitate immediate repair or replacement of the part, leading to equipment non-availability and a loss of productivity. Without the concern of further damage, the site may instead be addressed at a regularly scheduled maintenance interval without loss of performance of the part.

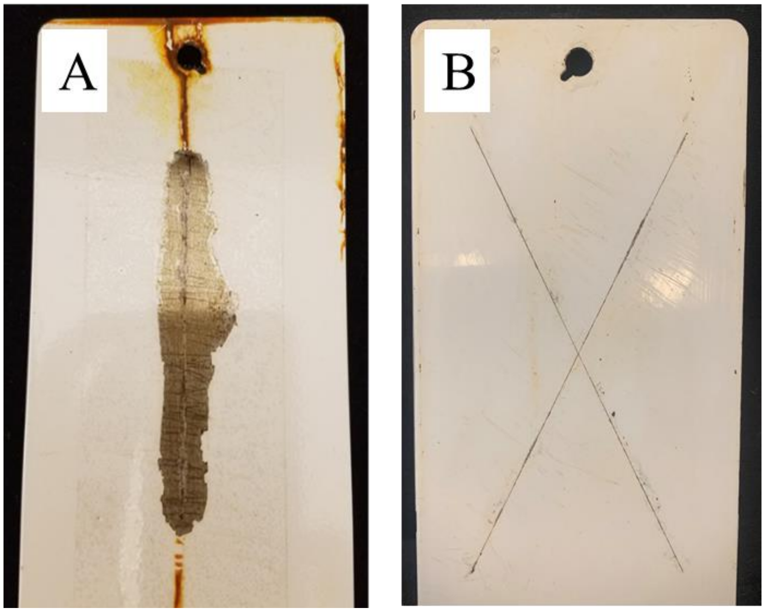


Figure 13. ASTM D1654 results for (A) industry standard phosphate pretreatment, epoxy primer and polyurethane top-coat, (B) aluminum oxide pretreatment with polyurethane top-coat and no primer.

Conclusions

Adherent aluminum oxide coatings have been electrochemically deposited from aqueous solutions onto various types of steel surfaces. A water stable aluminum salt was first characterized by voltammetric techniques, showing a shift in reduction potentials to facilitate aluminum deposition. By using a zirconium additive, adhesion of aluminum oxide coatings was improved. The EQCM testing showed that this was likely a result of a synergistic effect between Zr and Al in which a zirconium rich seed layer is initially deposited onto which an aluminum oxide matrix was grown. Pulse techniques were used to control and balance electrodeposition and precipitation events to build a structured aluminum oxide coating.

The coating was found to be adherent with variable surface morphologies based on pulse current process applied. Porous deposit morphologies can be dyed as anodized aluminum leading to custom colored steel surfaces. Plate like more compact coatings are more corrosion resistant and give a functional surface that can be used to promote adhesion of polymer coatings. The resultant surfaces require no primer to adhere polyurethane top-coats. Scribed salt spray exposure testing show no delamination of the top-coat after 1500 hours of exposure.

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