Current Density Anodizing and the 720 Rule

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Overview

- Anodizing basics
  - Process of oxide formation
  - Chemical Reactions
- Current Density Control in Anodizing
  - Ohm's Law
  - Behavior of system during anodize
  - Why current control
- 720 Rule and Application
  - How it works
  - Limitations

Overview
Goals

As metal finishers, scientists, manufacturers, we want predictable consistent performance – thickness, color, corrosion resistance.

- Need to understand what is happening in the anodizing tank.
- Why the voltage and current do what they do during the process
- Why your parts come out the way they do

Anodizing Basics

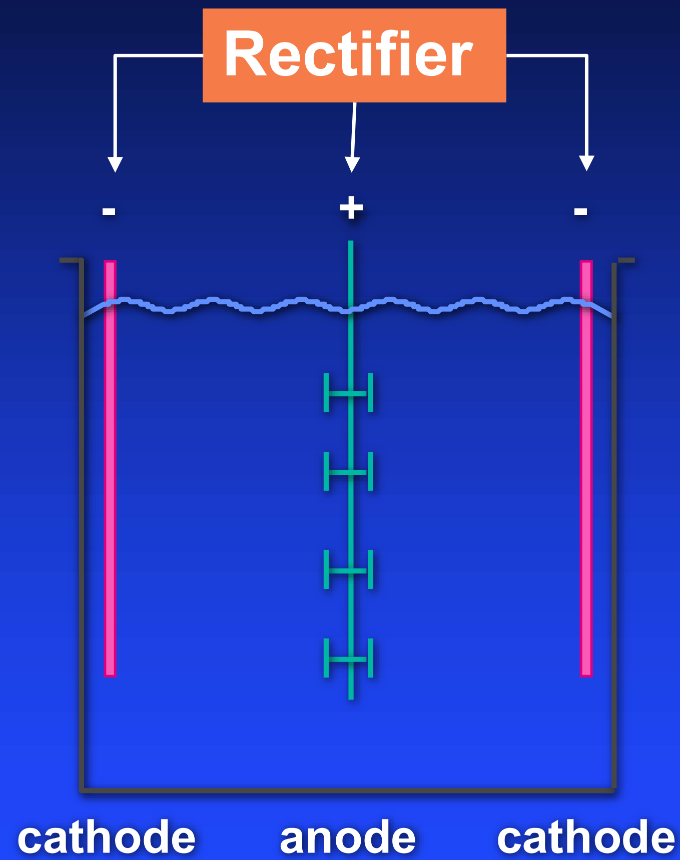
- Anodizing is the electrochemical oxidation of a metal to produce a stable oxide on the surface
- Essential ingredients:
  - Anode --- the part to be anodized – Al, Ti, etc.
  - Suitable cathode --- Al, Pb, C
  - Acid electrolyte ---H_2SO_4 H_3PO_4, H_2CrO_4
  - Direct current

Process of Oxide Formation

- Al ‘work’ is the anode (connected to the positive side of the DC power supply)
- Requires a cathode of suitable material (connected to the negative side of the DC power supply)

Process of Oxide Formation

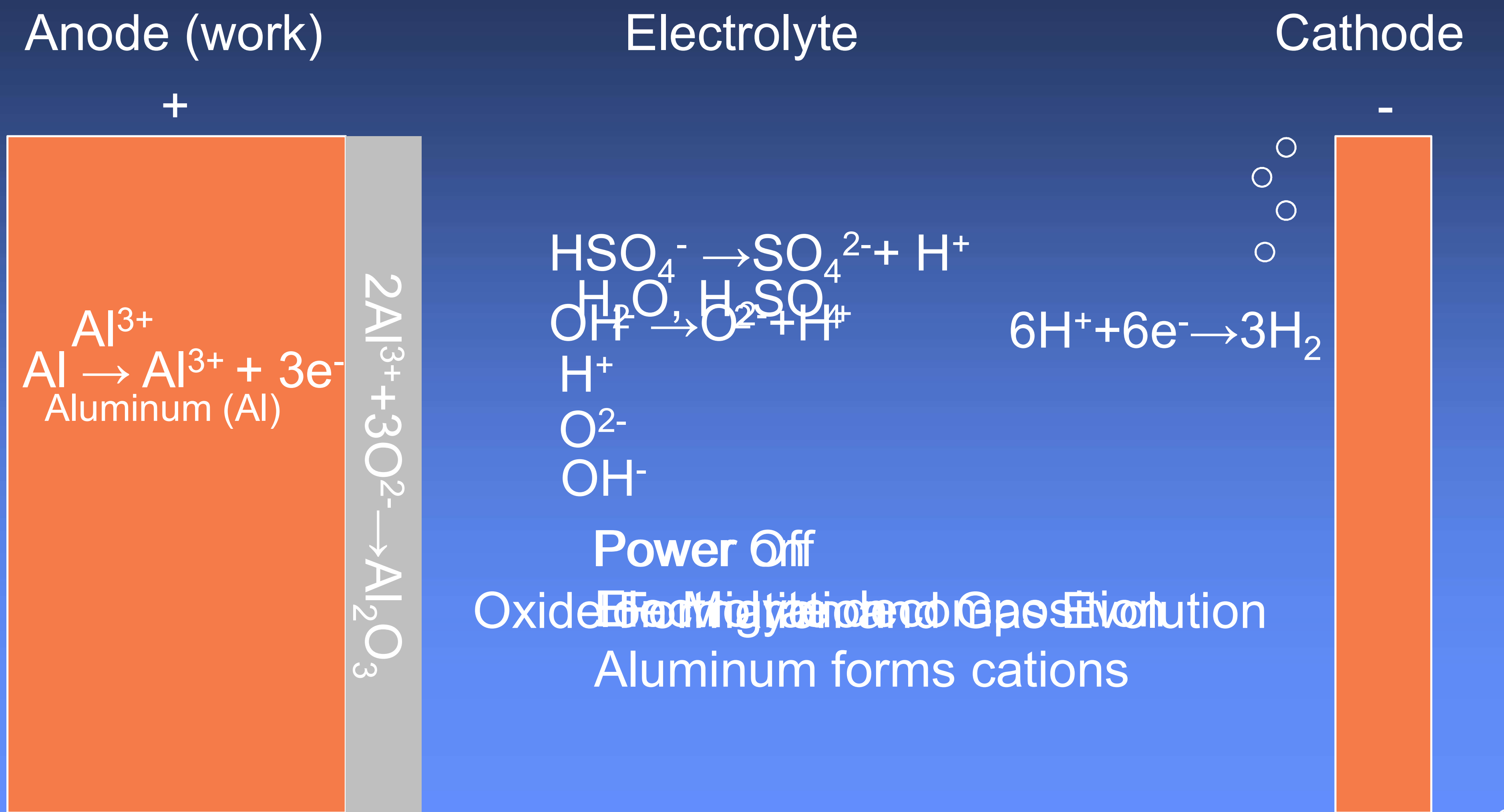
Typical Anodize Tank Setup



Process of Oxide Formation
Power Applied

- Electrolyte decomposes
  - Oxygen, hydroxide, and sulfate anions migrate to the anode
  - Hydrogen ions move to cathode
- Aluminum ions produced in anode
  - Al^{3+} cations migrate to aluminum/oxide interface
- Aluminum and oxygen ions combine to form aluminum oxide
- H_2 produced at the cathode

Process of Oxide Formation



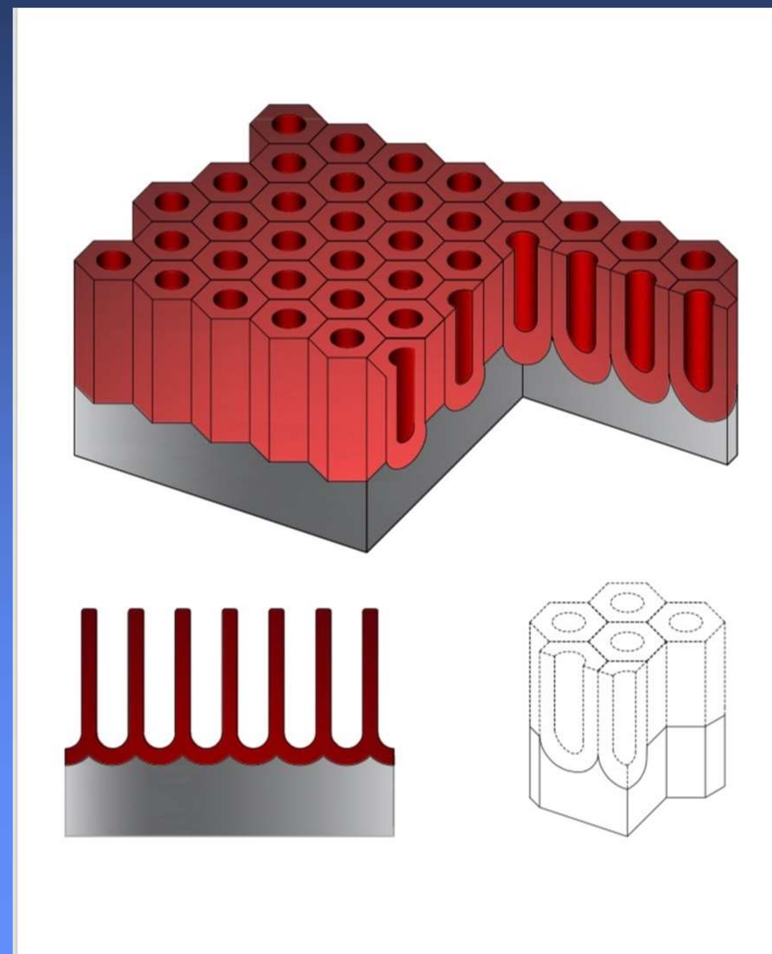
Process of Oxide Formation

- Cathode Reaction
  - $6H^{+} + 6e^{-} \rightarrow 3H_2(g)$
- Anode Reactions
  - $Al \rightarrow Al^{3+} + 3e^{-}$
  - $2Al^{3+} + 3O_2^{-} \rightarrow Al_2O_3$
  - $2Al^{3+} + 3OH^{-} \rightarrow Al_2O_3 + 3H^{+}$
- Overall
  - $2Al + 3H_2O \rightarrow Al_2O_3 + 6H^{+} + 6e^{-}$

Voltage appears nowhere
in the reactions, only electrons
Electron flow over time = current

Process of Oxide Formation

- Anodizing progresses
- Porous oxide formation initiated
- Reactions are the same
- Oxide formation still governed by current flow



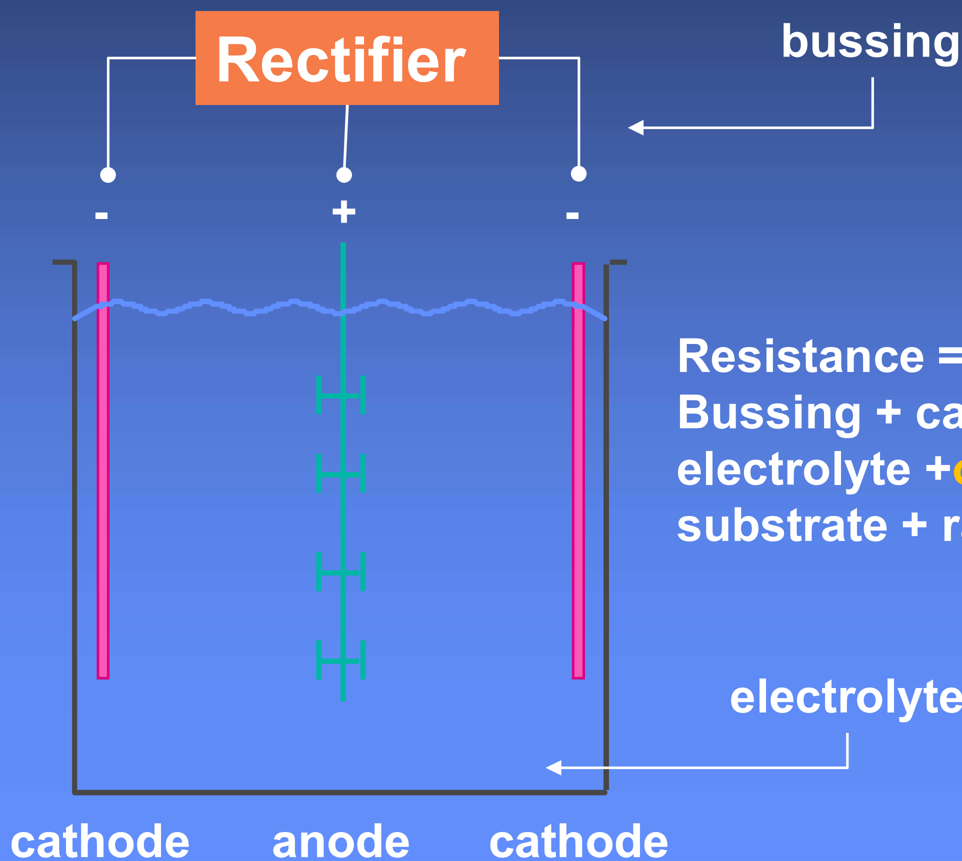
Process of Oxide Formation
Current Control

Overall Reaction

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$$

- Voltage does not appear in the reaction, only electrons
- Electron flow over time = current
- If we control the current, we control the reaction
- If we control the reaction, we control the rate of oxide formation and ultimately the oxide thickness and performance
- Therefore if we control the current, we control the oxide formation rate, the oxide thickness and performance

Behavior of System During Anodize



Resistance = Bussing + cathode+ electrolyte +oxide + substrate + rack

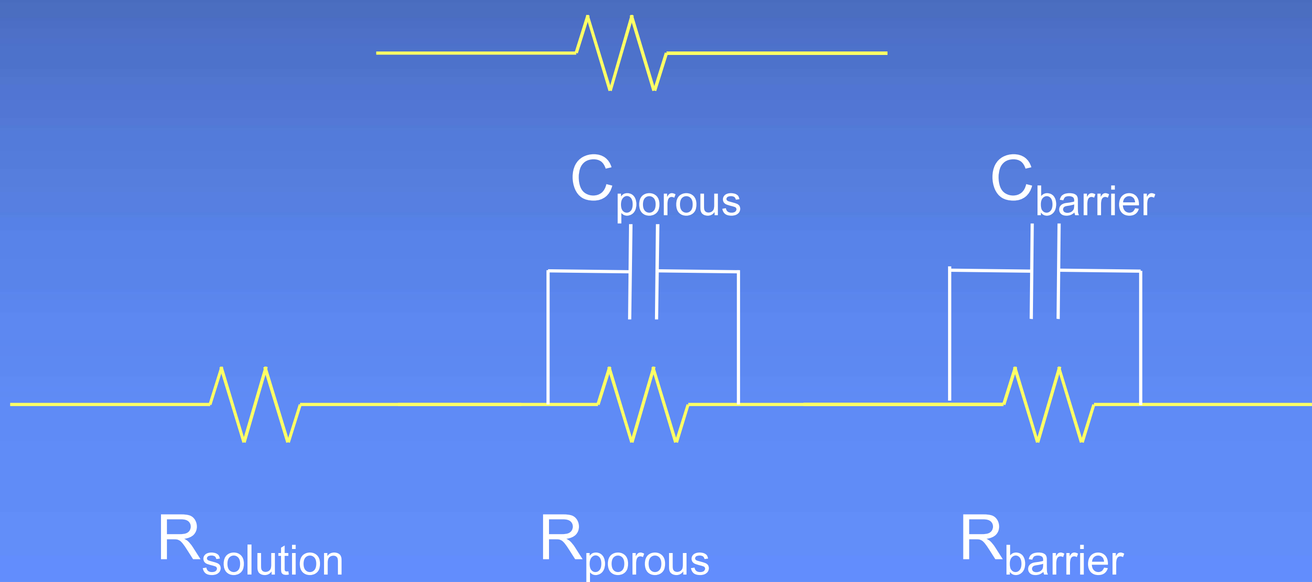
- Anodizing tank behaves as a DC circuit
- Consists of the rectifier and a resistance

Behavior of System During Anodize

- To a good approximation, the anodizing load behaves as a resistive DC circuit.
- Allows us to understand and predict the behavior of the process

Behavior of System During Anodize

- More in depth techniques such as AC electro-impedance spectroscopy
- Model behavior of the oxide and solution as a series of resistors with capacitors in parallel

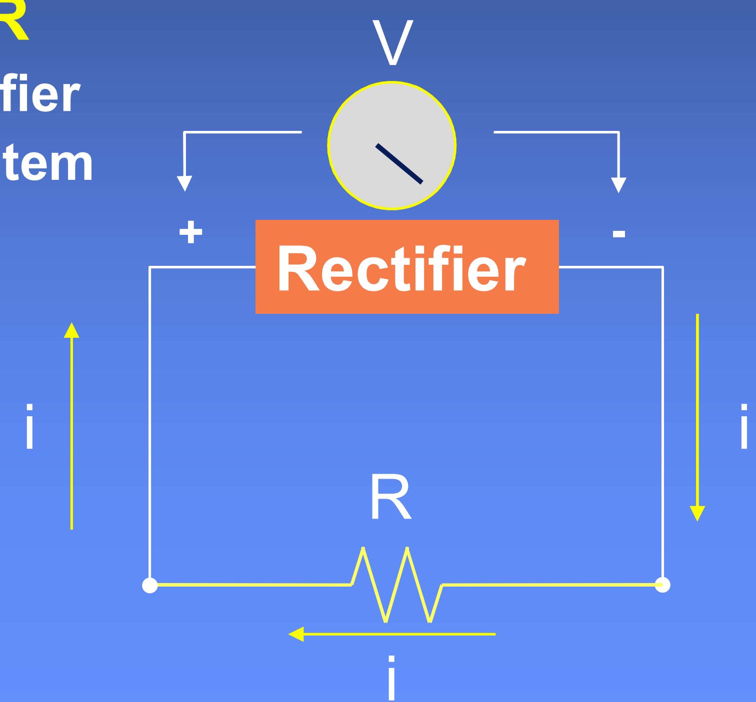


Behavior of System During Anodize DC Circuit

- Anodizing tank behaves as a DC circuit
- Consists of the rectifier and a resistance
- Resistance = Bussing + cathode+ electrolyte +oxide + alloy + rack + bussing

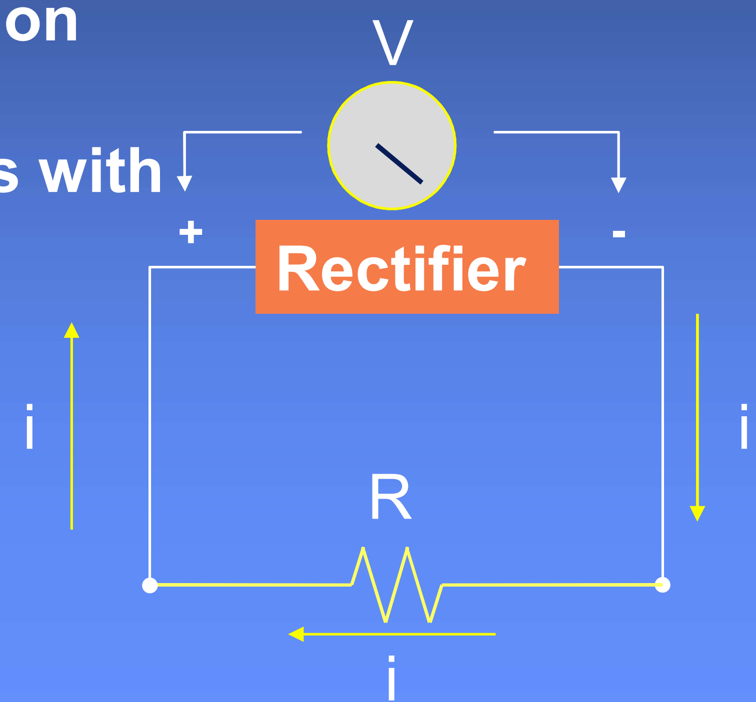
Behavior of the System During Anodize
Ohm's Law

- The DC electrical behavior of the anodizing system is described by Ohm's law
- **Voltage = current x resistance = i•R**
  - Voltage is the voltage across the rectifier
  - Current is the current through the system
  - Resistance is everything in the path



Behavior of the System During Anodize
Ohm's Law

- **Voltage = current x resistance**
- **If the voltage is fixed, current and resistance move in opposite direction**
  - **Resistance ↑, Voltage ↔ , Current ↓**
- **If current is fixed, voltage increases with increasing resistance**
  - **Resistance ↑, Voltage ↑, Current ↔**



Behavior of the System During Anodize

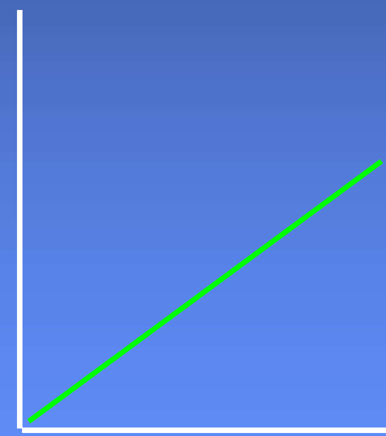
Ohm's Law

- **Voltage = current x resistance**
  - **Resistance is due to bussing, cathodes, electrolyte, oxide, substrate alloy, rack material, etc.**
  - **As oxide forms, the resistance of the 'circuit' increases**
  - **To maintain a constant (current) anodizing rate, the voltage must increase if the resistance increases**

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$$

Behavior of the System During Anodize
Current Control vs. Voltage Anodizing

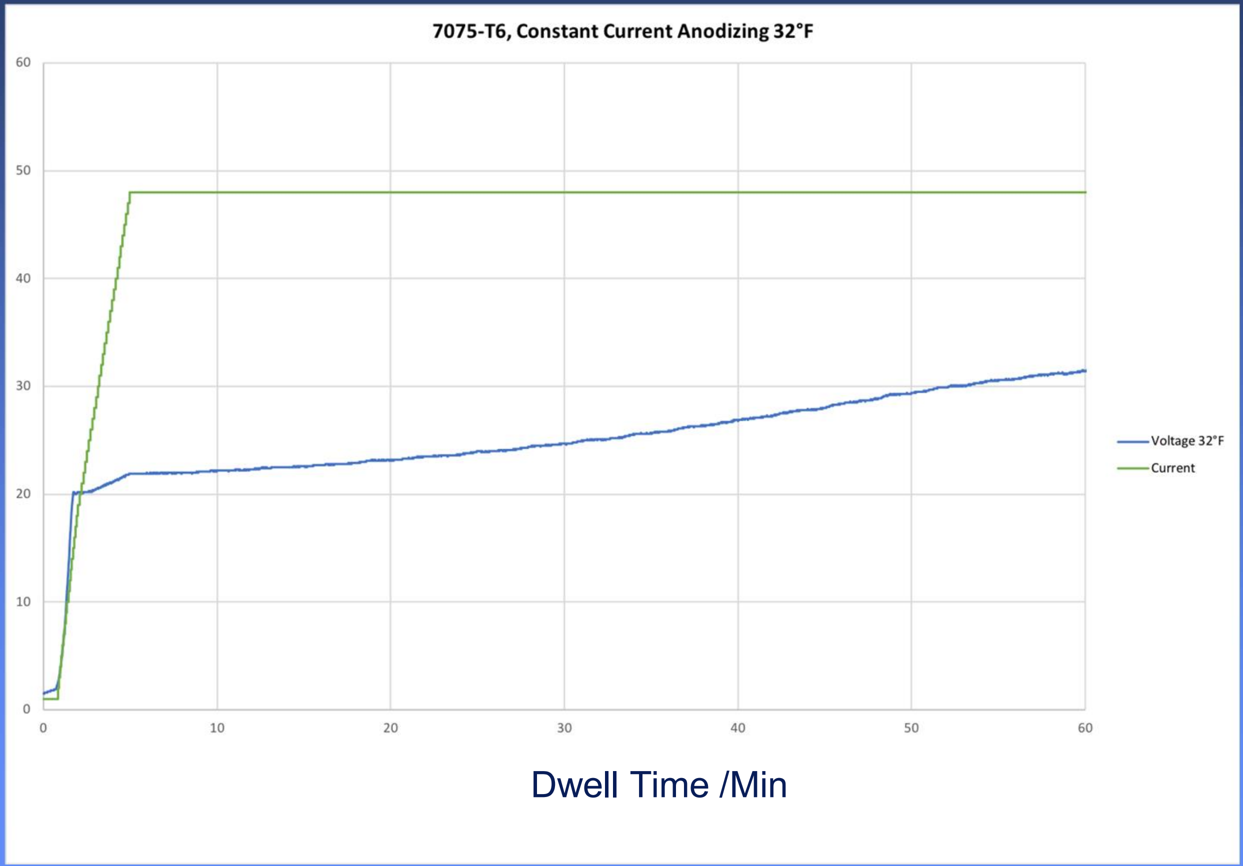
- Under constant current anodizing, the voltage of the rectifier must increase as the oxide grows
- By **controlling** the **current** we control the **oxide formation rate**.



Behavior of the System During Anodize
Current Density Anodize

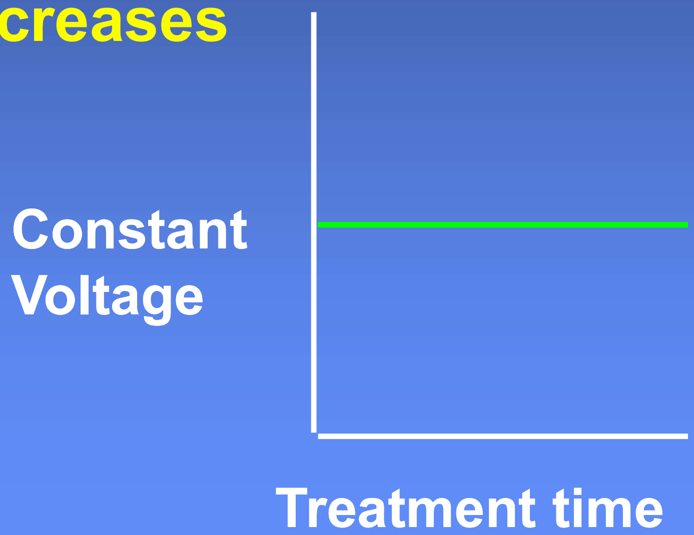
Voltage rises over time as oxide thickness increases and resistance increases

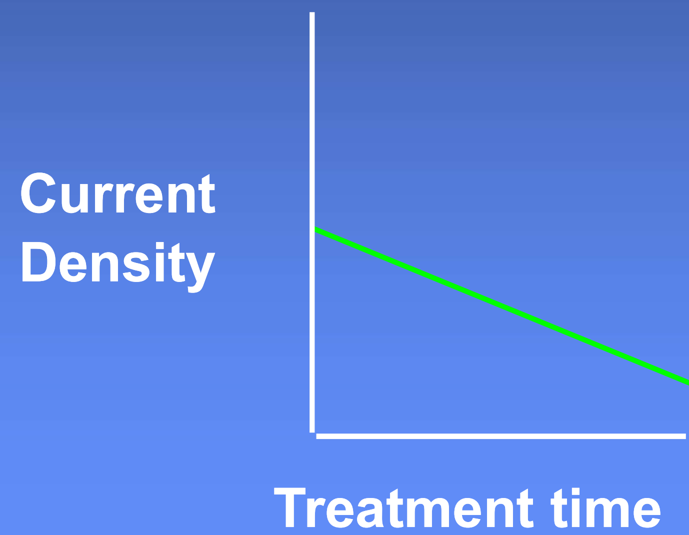
Final Thickness 2.0 mil



Behavior of the System During Anodize
Current Control vs. Voltage Anodizing

- Under constant voltage anodizing, the current of the rectifier must decrease as the oxide grows.
- If the voltage is not increased, the rate of oxide formation decreases

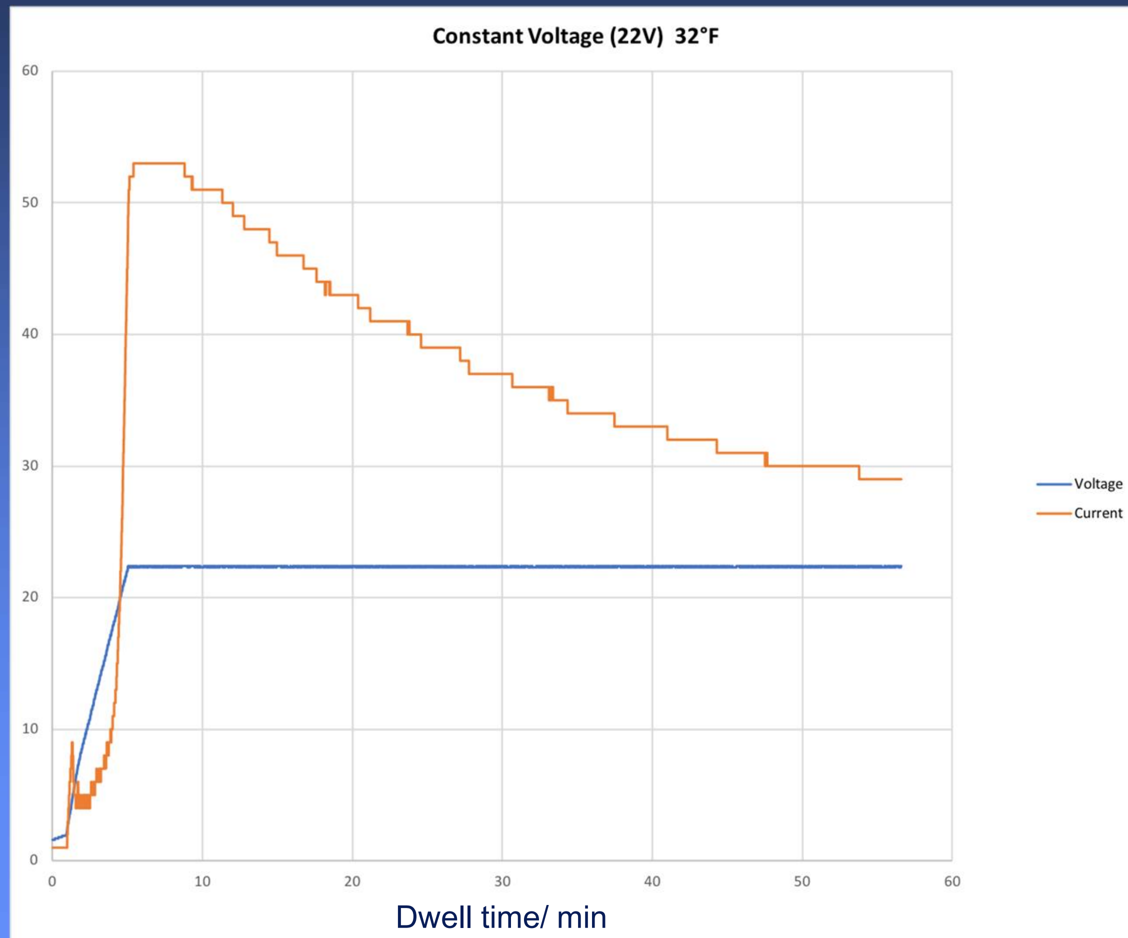




Behavior of the System During Anodize
Constant Voltage Anodize

Current drops as oxide thickness increases

Final Thickness 1.59 mil



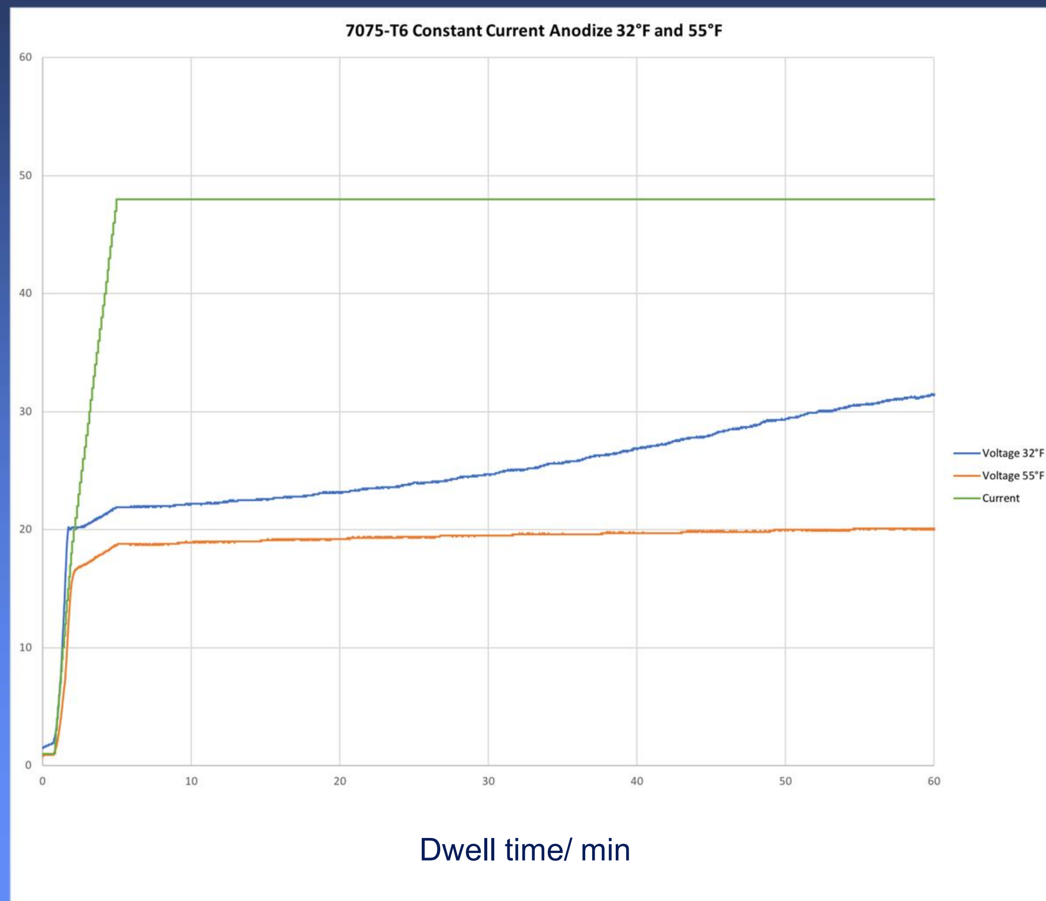
Anodize Control

Current Density vs. Voltage Anodizing

- Factors that affect current density
  - Rectifier current setting
- Factors that affect voltage
  - Rectifier voltage setting
  - Bath temperature
  - Oxide thickness
  - Racking
  - Acid Concentration
  - Alloy and Temper

Behavior of the System During Anodize
Temperature Variation

- At different temperatures 55°F and 32°F,
- Voltages different
- Current remains constant



Anodize Control
Current Density vs. Voltage Anodizing
Alloy and Temper

Alloy and Temper	Electrical Conductivity (percent IACS) (Minimum)	Electrical Conductivity (percent IACS) (Maximum)
1100 (all tempers)	57.0	62.0
2024-O	45.5	50.0
2024-T3	28.0	33.0
6061-O	47.0	51.0
6061-T6	40.0	45.0
7075-O	44.0	48.0
7075-T6	30.0	35.0

Anodize Control

Current Control vs. Voltage Anodizing

- Current controlled anodizing is immune from changes in
  - Bath temperature
  - Oxide thickness
  - Racking (Al vs Ti, size, etc)
  - Acid Concentration
  - Alloy and Temper (with some caveats)

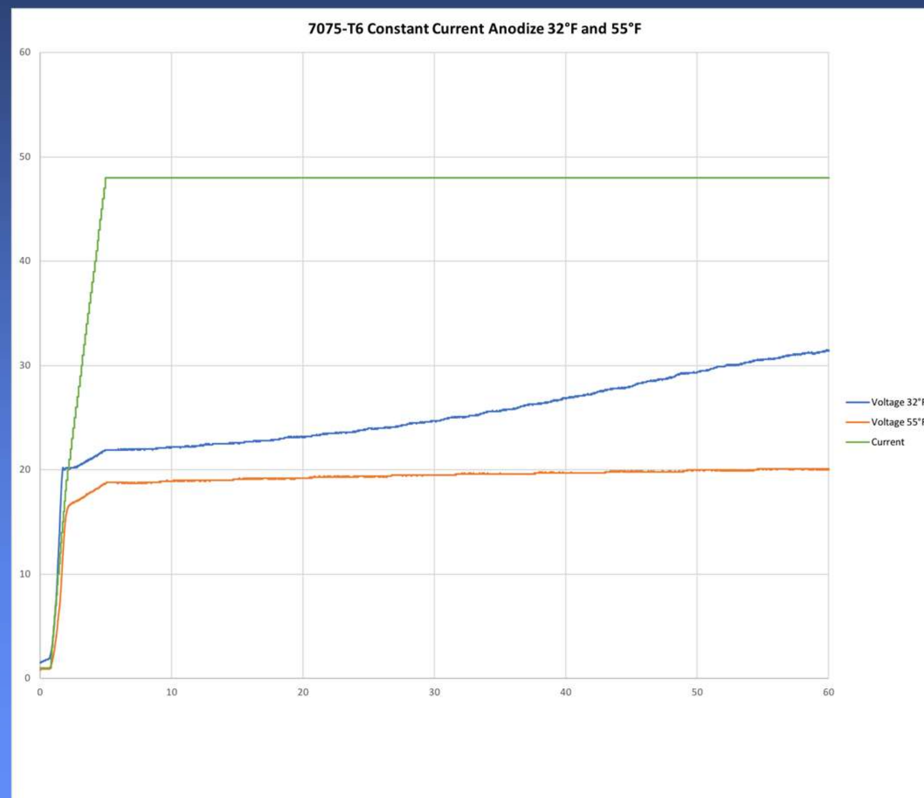
- As these factors change, the voltage simply rises or falls according to Ohm's law to keep current constant

Anodize Control
Example - Current Control Immunity to Temperature

- At different temperatures 55°F and 32°F,
- Voltages different
- Current remains constant
- What do we think the oxide thickness will be?

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$$

T = 32°F, 2.00 ±0.02 mil
T = 55°F, 1.95 ±0.02 mil



Anodize Control

Recap

- Understand the basic anodizing reactions.
- Understand the behavior of the anodizing system in terms of how the voltage and current behave during the process.
- Linked the formation of the oxide to the current flowing through the system
- Seen that current controlled anodize is largely immune to changes in the bath
- We can go one step further and predict the anodizing rate

Anodize Control - 720 Rule

Describes relationship between amount of current passed though an aluminum surface and the resultant oxide thickness

$$720\frac{A*min}{ft^2mil} = \frac{CD*t}{Thickness}$$

- CD is current density in amps per square foot
- T is exposure time in minutes
- Thickness in mils (0.001”, 25.4 micron)

Anodize Control

720 Rule Application – Process Time

Can rewrite to examine relationships of interest to us

$$t(minutes) = \frac{thickness}{CD} * 720\,\frac{A * min}{ft^2 mil}$$

At a current density of 24 ASF, 30 minutes to produce 1 mil oxide

$$t(minutes) = \frac{1\,mil}{24\,\frac{A}{ft^2}} * 720\,\frac{A * min}{ft^2 mil} = 30\,min$$

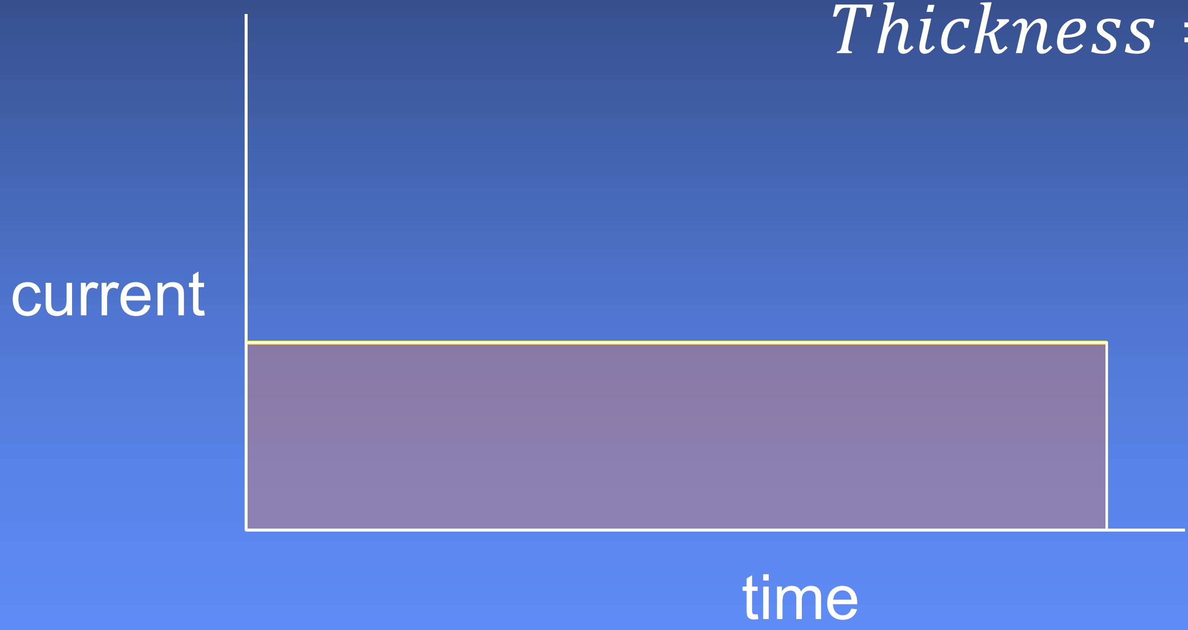
Anodize Control
720 Rule Application
Process time as function of current density

Current Density (amps per square foot)	Time to 1 mil (minutes)
12	60
18	40
24	30
30	24
40	18

Anodize Control - 720 Rule

Estimating Oxide Thickness–Steady State

$$Thickness = \frac{CD * t}{720\,\frac{A * min}{ft^2 mil}}$$

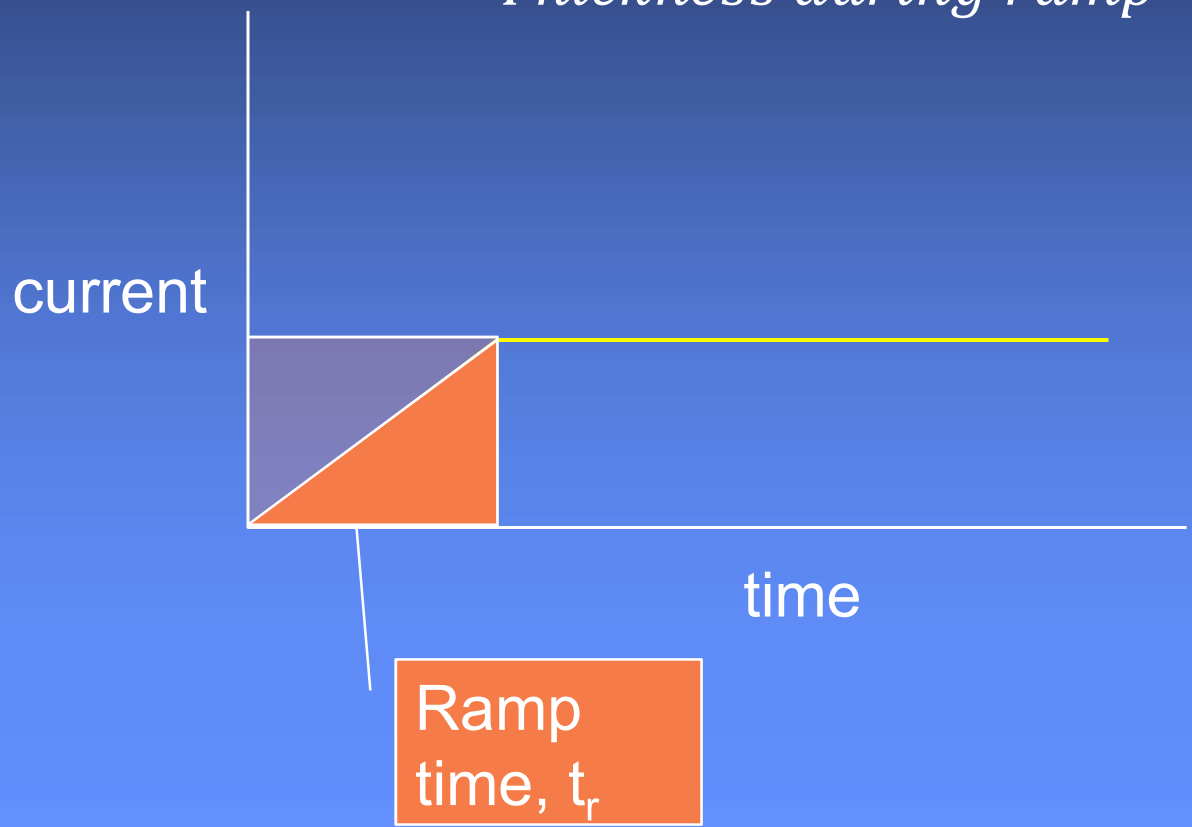


Area = L x W

Anodize Control - 720 Rule

Oxide Thickness Ramp Compensation

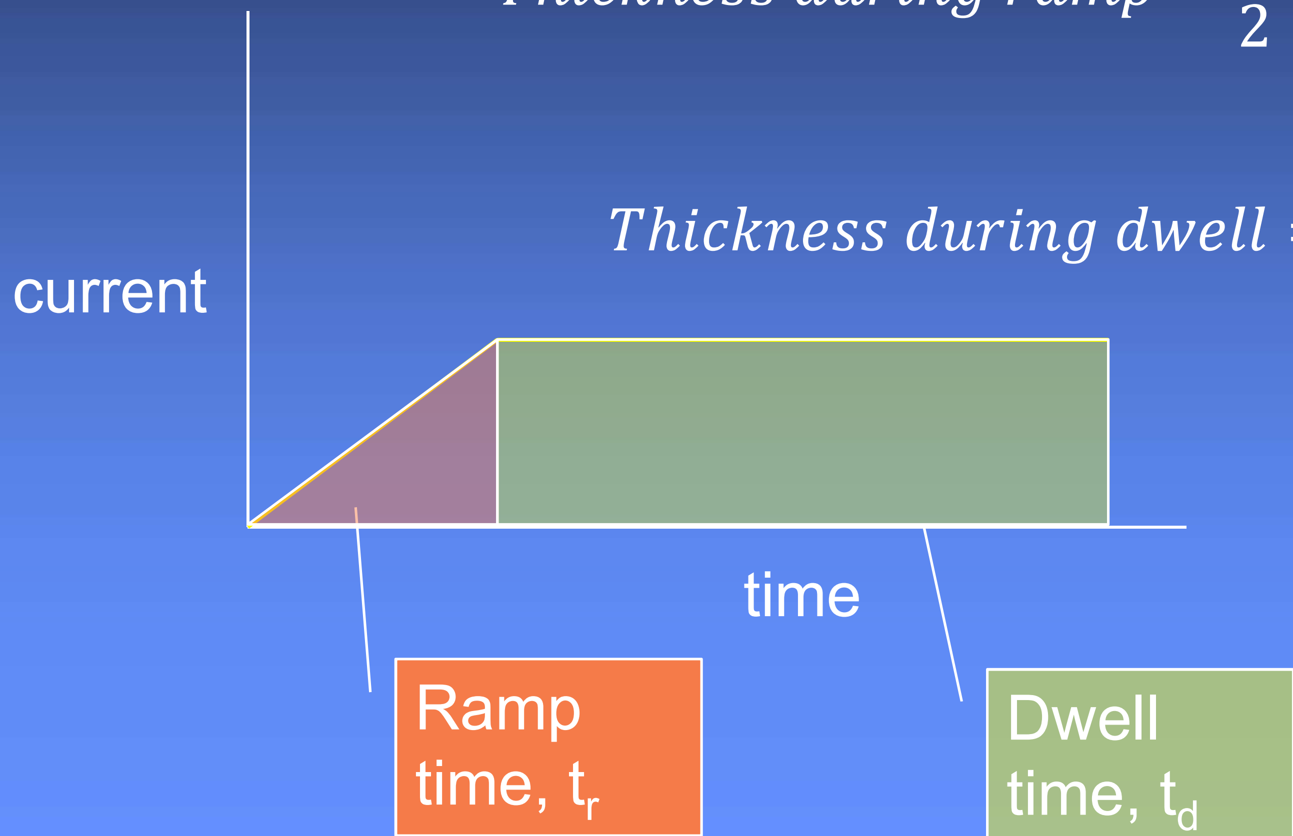
$$Thickness\ during\ ramp = \frac{1}{2} * \frac{CD * t_r}{720\,\frac{A * min}{ft^2 mil}}$$



Anodize Control - 720 Rule
Estimating Oxide Thickness

$$Thickness\ during\ ramp = \frac{1}{2} * \frac{CD * t_r}{720\,\frac{A * min}{ft^2 mil}}$$

$$Thickness\ during\ dwell = \frac{CD * t_d}{720\,\frac{A * min}{ft^2 mil}}$$



Anodize Control - 720 Rule
Worked example

5 minute ramp to 24 ASF, dwell for 55 minutes

$$Thickness\ during\ ramp = \frac{1}{2} * \frac{CD * t_r}{720\frac{A*min}{ft^2 mil}} = \frac{1}{2} * \frac{24*5}{720\frac{A*min}{ft^2 mil}}$$ = 0.083 mil

$$Thickness\ during\ dwell = \frac{CD * t_d}{720\frac{A*min}{ft^2 mil}} = \frac{24*55}{720\frac{A*min}{ft^2 mil}}$$ = 1.833 mil

Total thickness = 1.916 mil

Anodize Control - 720 Rule
Worked example #2

How long for 2 mils at 30 ASF, 10 minute ramp?

$$Thickness\ during\ ramp = \frac{1}{2} * \frac{CD*t_r}{720\frac{A*min}{ft^2 mil}} = \frac{1}{2} * \frac{30*10}{720\frac{A*min}{ft^2 mil}}$$ = 0.2083 mil

Need 2.00-0.2083 = 1.7917 mils during dwell

$$t(minutes) = \frac{thickness}{CD} * 720\frac{A*min}{ft^2 mil} = \frac{1.7917}{30} * 720\frac{A*min}{ft^2 mil} = 43\ \text{min}$$

A 10 minute ramp to 30 ASF followed by 43 minute dwell will produce a 2.0 mil oxide

Anodize Control - 720 Rule
Worked example #2 – the shortcut

How long for 2 mils at 30 ASF, 10 minute ramp?

Calculate the dwell time with no ramp

$$t(minutes) = \frac{2\,mil}{30\,\frac{A}{ft^2}} * 720\,\frac{A * min}{ft^2 mil} = 48\,min$$

Subtract half the ramp time = 48-5 = 43 minutes dwell time

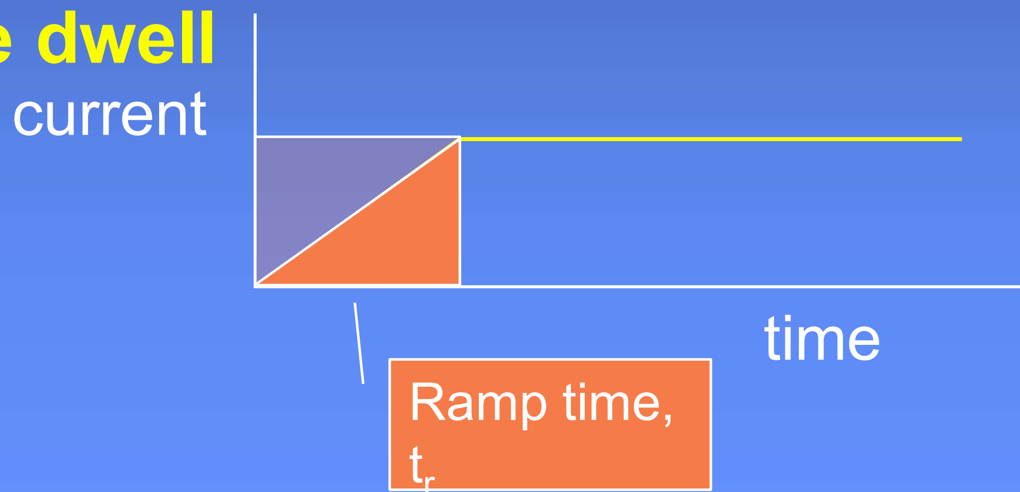
Anodize Control - 720 Rule
Worked example #2 – the shortcut

Why does this work?

Graphically we can see that the ramp produces half the oxide in a given amount of time that would be produced by full current.

A 10 minute ramp yields the same amount of oxide as a 5 minute dwell

48-5 = 43



Anodize Control - 720 Rule Limitations

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$$

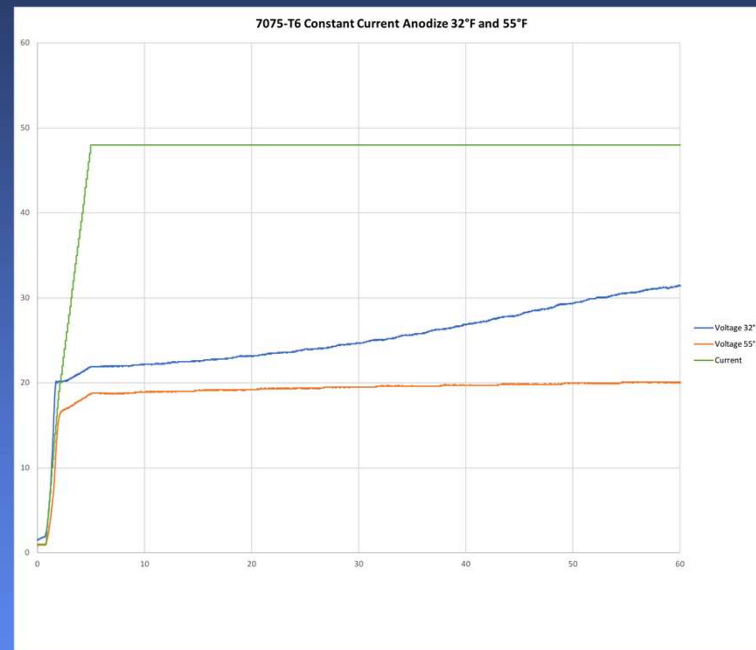
- 720 Rule provides a good estimate
  - Regardless of alloy, electrolyte composition, electrolyte temperature (Type II, Type III)
- When does 720 Rule break down?
- When other reactions and chemistries play a significant role in the process

Anodize Control

Divergence from 720 Rule – Increased Dissolution

- At different temperatures 55°F and 32°F,
- Voltages different
- Current remains constant

T = 32°F, 2.00 ±0.02 mil
T = 55°F, 1.95 ±0.02 mil



Difference in thickness due to increased dissolution by electrolyte at higher temperature

Anodize Control - 720 Rule Limitations

- 720 Rule breaks down when other reactions and chemistries play a significant role in the process
- Examples include
  - Intermetallics – some are oxidized, some dissolve, others remain as inclusions
  - Higher amounts of aluminum sulfate said to increase acidity ->more attack, lower formation rate

Anodize Control - 720 Rule Limitations

- Highly alloyed materials such as 2024 and 7075
- Some anodizers experience nonlinear or reduced oxide growth
  - Increased dissolution of oxide later in process (long times in tank, mossy coatings)
  - Pores open up -> increased surface area-> more dissolution
  - Higher anodizing voltages-> higher pore base temperature-> more dissolution
- Minimize with
  - Good agitation and cooling of tank
  - Good anodize control (properly chosen current density)

Recap

- Reviewed reactions for anodize process
- Examined behavior of the system as a DC circuit
- Learned about 720 for predicting anodize formation rates.

Conclusions

Advantages of anodizing by current density

- Control of the oxide formation
- Shorter process times – Type II and III
- Consistent finish properties
- Reproducibility from run to run – Six Sigma

Thank You

- Taylor Clarke – Process Chemist
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Florida Finishers Corporation