CATHODE OPTIMIZING SOLUTION
OPTIMIZE YOUR CHLOR - ALKALI MEMBRANE CELL

By Dino DiFranco

Electrode Solutions
About Me: (Continued)

- Joined ELTECH Systems / De Nora for 20 years (Anode Focused)
  - These companies commercialized Henri Beer’s historic 1968 Anode invention which is a thermally applied mixed metal oxide on titanium.

- Henri Beer’s invention of using metal oxides as an anode in an oxidizing environment delivers exceptional performance and can deliver 25+ years of service without appreciable voltage escalation.
  - While it can also function as a cathode, this technology is not optimum for cathodes which are in a reducing environment. Limitations include:
    - Voltage escalation
    - Poor adhesion
    - High wear rate
    - Limited lifetime
    - Require Polarization
    - Poor substrate protection
    - High cost

I believe there is room to improve chlor-alkali cathodes and this is one of the reasons I started Electrode Solutions.
IN-SITU CATHODE ACTIVATION

BENEFITS
• No Cathode Recoating
  ✓ No cell dis-assembly
  ✓ No shipping of cathodes
  ✓ No spare cathode requirements (Idle capital)
  ✓ No cathode distortion or thinning from recoating
  ✓ No cathode warranty constraints / concerns
  ✓ No large capital expense for recoating

• Operate at the LOWEST ENERGY CONSUMPTION
  ✓ Activate all areas capable of hydrogen evolution
  ✓ No voltage escalation (consistent cell room performance)
  ✓ Immediate recovery from upsets

• MUCH LESS expensive and BETTER than OEM supplied cathode coatings

• Possible improvement for the membrane
  ✓ Equilibrate the current density across the membrane surface
  ✓ Less heating at the membrane surface = Higher Efficiency
  ✓ Less hydrogen on the membrane = Lower H₂ in Cl₂
IN-SITU CATHODE ACTIVATION - History

- Some OEM’s have promoted in-situ activation in the past (CEC, ELTECH, etc).
- I promoted a product called VRS (Voltage Reduction Solution) for ELTECH in the early 2000’s.
- Many customers used it in their cell rooms
  - Voltage reduction was observed using VRS (Technical success)
  - Economics of using VRS were not satisfactory (Economic failure)

VRS was too expensive but it demonstrated the promise of a better cathode via in-situ activation.
**CATHODE OPTIMIZING SOLUTION (COS)** was developed to deliver optimized cathode performance at an economic price.

COS is added in-situ to the catholyte and immediately activates all surfaces capable of hydrogen evolution.

- Surfaces previously activated are renewed

COS is economical enough that it is continuously added to maintain the lowest energy consumption and achieve a stable cathode performance.

Unlike thermally applied coatings provided by OEM’s, COS will seal off the underlying nickel and protect the nickel substrate during power outages.
To avoid voltage escalation, the coating must protect the underlying nickel and be adherent. This is especially important during outages. **COS** is adherent to the nickel substrate and protects it.

Tape test result showing the adhesion of the Oxide Coating is compromised.
Porous OEM Cathode Coating allows corrosion and corrosion products (greenish color) to migrate to the surface.
Early chlor-alkali membrane cells were designed with a fixed gap between the cathode and the membrane to prevent membrane damage. These cells are referred to as “fixed gap” cells.
In a fixed gap cell, the hydrogen gas is evolved on the activated coarse mesh as shown here.
NEWER CELL DESIGNS AND/OR RETRO FITS OF OLDER CELLS INCORPORATE A ZERO GAP DESIGN WHEREIN A COMPRESSIBLE LAYER IS PLACED BETWEEN THE COARSE MESH AND A FINE SCREEN.
IN A ZERO GAP CELL, THE FINE MESH IS ACTIVATED AND THE HYDROGEN GAS IS EVOLVED ON THE FINE MESH ONLY.
MORE THAN 2/3 rds OF THE AVAILABLE CATHODE SURFACE AREA IS NOT ACTIVATED IN PRESENT DAY ZERO GAP CELLS.
ZERO GAP CHLOR-ALKALI MEMBRANE CELL
BY ELECTRODE SOLUTIONS

AFTER THE ADDITION OF Cathode Optimizing Solution
FROM ELECTRODE SOLUTIONS, ALL SURFACES IN THE CATHOLYTE ARE ACTIVATED AND EVOLVING HYDROGEN GAS, AND THE CELL VOLTAGE IS REDUCED!
ZERO GAP CHLOR-ALKALI MEMBRANE CELL
BY ELECTRODE SOLUTIONS

CATHODE OPTIMIZING SOLUTION
OPTIMIZES THE CATHODE OPERATION.
PREVIOUSLY UNACTIVATED SURFACES ARE
ACTIVATED AND PREVIOUSLY ACTIVATED
SURFACES ARE RENEWED. THE CATHODE
CURRENT DENSITY IS LOWERED.

Cathode Voltage vs Current Density

CATHODE VOLTAGE vs CURRENT DENSITY

CHLORINE GAS    HYDROGEN GAS

ANODE (ACTIVATED)  FINE MESH (ACTIVATED)  COMPRESSIBLE LAYER (ACTIVATED)  COARSE MESH (ACTIVATED)
Photos taken after adding COS to a zero gap cathode constructed with uncoated nickel components.

- Showing COS deposited on **ALL** cathode surfaces.
- Showing COS deposited on cushion layer and current collector.
- Bare nickel cushion layer
- Bare nickel current collector
- Showing COS deposited on current collector
Immediate results with COS.
OTHER BENEFITS OF A CATALYZED CUSHION LAYER

OEM supplied catalyzed fine mesh layers increase the temperature of the membrane by at least 5 °C according to AGC chemicals which lowers the Current Efficiency by 0.5-1%.

Catalyzing the cushion layer counters these negative effects and improves the operation.

AGC data presented at Clorosur Technical Seminar
OTHER BENEFITS OF A CATALYZED CUSHION LAYER

OEM supplied catalyzed fine mesh layers increase the hydrogen in chlorine.

Catalyzing the cushion layer with COS counters this negative effect and improves the operation.

AGC data presented at Clorosur Technical Seminar
HOW TO ADD COS

Addition Setup

To Electrolyzer

COS diluted 20:1 with 32 wt% Caustic

Caustic Recirculation Line

Metering Pump

Phase Finite Gap Zero Gap

<table>
<thead>
<tr>
<th>Phase</th>
<th>Finite Gap</th>
<th>Zero Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5-10 ml/m²</td>
<td>10-15 ml/m²</td>
</tr>
<tr>
<td>2</td>
<td>2-4 ml/m²</td>
<td>2-5 ml/m²</td>
</tr>
<tr>
<td>3</td>
<td>0.5-1.5 ml/m²</td>
<td>0.5-1.5 ml/m²-wk</td>
</tr>
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Electrode Solutions
COS lowered the voltage of each cell by ~90 mV.
COS lowered the voltage on three different recently installed OEM cathode coatings by 20-30 mV.
COS Savings retained after un-protected 6 hour power outage.
Minimum Voltage at ~10 ml/m² of COS
• COS corrected the voltage loss due to poor cathode polarization during power outages.
• Savings of ~20 mV on “good” cathodes and up to 115 mV on “bad” cathodes with an average savings of >70 mV.
• COS lowered the voltage on good condition UHDE cathodes.
• Savings of ~30-50 mV.
• COS lowered the voltage on OEM cathode coating and bare nickel cathodes.
• Long term stability.
TAKEN FROM THE DE NORA WEBSITE
### Electrode Solutions

#### COS Savings Analysis

**Electrolyzer Characteristics**
- Number of Electrolyzers: 1
- Cathodes per Electrolyzer: 183
- Total # of Cathodes: 183
- M2 per Cathode: 2.72
- Total Cathode M2: 497.8

**COS Requirements**
- Initial Addition: 15 ml/m2
- Continuous Additions: 1 ml/m2-week
- COS Price: $0.880 per ml
- Initial Addition Cost: $6,570
- Continuing Addition Cost: $63 per day

**Voltage Savings**
- Average Savings from COS: 0.070 Volts
- Current Density: 5.00 kA/m2
- Power Costs: $0.055 per kWh
- Rectifier efficiency: 95.0%

**Savings**
- Savings per day with COS: $242.07 per day

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**EVEN LARGER SAVINGS**

from ELIMINATION of OEM Recoating

Eliminate more than $500,000 in this example
AND
Achieve a lower voltage

**ROI is 37 Days**
OTHER POSSIBLE BENEFITS FROM COS

• Increase production or add additional cells if presently rectifier limited.

• Install longer life anodes
  ➢ Minimize anode recoating which can harm the anode elements
  ➢ A 2x life anode is only marginally more costly than a 1x life anode.

• Achieve longer membrane life by improving the current uniformity across the membrane and reducing membrane overheating.
  ➢ Lower nickel contamination of the membrane.

• Lower CO₂ footprint

• Easy, Inexpensive on-site conversion to Zero-Gap technology
CATHODE OPTIMIZING SOLUTION (COS):

- Eliminates Conventional Cathode Re-Coating
  - No Downtime
  - No Spare Cathodes required
  - No Crating and Shipping of Cathodes
- Recover lost Cathode Performance
- Delivers a lower voltage than OEM Cathode Coatings
  - ~30 mV savings on OEM coatings
- Protects the nickel substrate better than OEM Cathode Coatings
- Protects and activates all surfaces on the nickel cathode
- Easy and Safe to use
- Does not harm cell room components
- Does not contaminate the caustic product
- Corrects membrane over-heating observed in zero gap cells utilizing OEM zero gap cathodes.
  - Higher cell efficiency
  - Lower H₂ in Cl₂
- Very Economical to use
- Performance is mostly retained after power outages
- No warranty concerns
<table>
<thead>
<tr>
<th>Feature</th>
<th>OEM Coating</th>
<th>COS</th>
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<tbody>
<tr>
<td>Cost</td>
<td>~$1000/m²</td>
<td>~$10/m²</td>
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<tr>
<td>Stable Coating</td>
<td>No</td>
<td>Yes</td>
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<tr>
<td>Requires a Cell Room Outage/Downtime to Install</td>
<td>Yes</td>
<td>No</td>
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<tr>
<td>Requires Dis-assembly to install</td>
<td>Yes</td>
<td>No</td>
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<tr>
<td>Requires Shipping</td>
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<td>No</td>
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<tr>
<td>Requires Cathode Spares</td>
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<tr>
<td>Recover From Upsets</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Activate All Available Cathode Area</td>
<td>No</td>
<td>Yes</td>
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<tr>
<td>Require Polarization to Protect Coating</td>
<td>Yes</td>
<td>No</td>
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<tr>
<td>Adequately Protects the Nickel Substrate</td>
<td>No</td>
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<tr>
<td>Contaminates the Caustic Product</td>
<td>Yes</td>
<td>No</td>
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<tr>
<td>Removeable via Tape or a Water Hose</td>
<td>Yes</td>
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<tr>
<td>Delivers the Lowest Energy Consumption</td>
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<tr>
<td>Corrects Membrane Over-Heating in Zero Gap Cells</td>
<td>No</td>
<td>Yes</td>
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<tr>
<td>Warranty Requirements</td>
<td>Yes</td>
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Even if an OEM offers **FREE CATHODE COATING**, you are still better served with **COS** from Electrode Solutions.
OTHER OFFERINGS

• ON-SITE ANODE RECOATING
• ANODE RECOATING BY OLIN (USA)