Electrochemical Processes for Chemical Hazard Reduction

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Abstract

Electrochemistry is a growing area of study which may bring a fresh wave of chemical manufacturing to the world. With new methods available to create many of the most-used chemicals, introducing electrochemical methods should be considered, particularly in light of the scale of hazards this technology can reduce. This work details five incidents, extensively investigated by the Chemical Safety Board, where the event could have been prevented or mitigated if the process were done utilizing an electrochemical reaction instead of the standard reactions. Hydroxylamine and mononitrotoluene both experienced explosive decompositions, necessitating a search for more mild reaction conditions which can often be found in the world of electrochemistry. Acetylene and ammonia both were involved in incidents of leakage, prompting both better methods of production and refrigeration, respectfully, but also a reminder of the importance of plant layout. Polymerization is also discussed, allowing a discussion on modern electrochemical polymerization methods and also reinforcing strict safety standards in scaling up reactions. Each incident is reviewed in light of the uses, material properties, and current manufacturing methods of the chemical product being studied. These manufacturing methods will be followed by an electrochemical replacement that has been produced or theorized in publicly available literature, with additional comments on the feasibility of the required voltage, scalability potential, and linking this process with other incidents and processes.

Introduction

For more than 100 years, chemical processes have primarily been driven by energy derived from heat produced by coal, oil, and gas. Moving into a new age of energy production, improved technology has allowed the electricity from wind and solar farms to make up an increasing part of the grid, allowing a reimagined and more sustainable chemical industry. By leveraging cheaper and more abundant electrons, a wide range of chemical synthesis industries are able to consider replacing toxic oxidants, reducing operating temperatures, and even achieving more selective pathways that occur in fewer steps. Beyond these widely desired benefits of electrochemical reactions, there is a large opportunity to introduce inherently safer chemical production through these electrochemical methods. This less explored benefit is the motivation to demonstrate reaction pathways where electrochemical processes have a safety improvement that is valuable to consider.

In this work, we target chemical reactivity hazards in the chemical production industry that caused large-scale incidents to identify which might have been mitigated if an electrochemical production method was used. Five events were selected from a database of investigations by the Chemical Safety Board, who report critical errors that should be widely known in order to prevent repeated incidents at the cost of capital and lives, aiming to make public the errors that are of highest value to the wider chemical industry. A list of over one hundred such incidents were initially considered for this paper, and the criteria described below were ever-increasing level of scrutiny was utilized to narrow the list to five case studies which may be significantly impacted by alternate electrochemical routes.

A range of shortcomings, from faulty machinery to improper scale-up procedures, were discovered and noted for each. The incidents were then sorted to determine which issues were based solely on the chemical reaction involved in the process. Within this grouping of chemical reactions, research into electrochemical replacements for these chemical reactions began. A combination of quantity and quality of the research available was used to devise a ranking system, and the five highest-ranked incidents were selected as case studies for this review.

These five incidents will be analyzed based on the incident, material properties and uses, and a comparison of its traditional synthesis method with novel electrochemical methods found in literature. Each section will also conclude with an analysis of the state of knowledge for each electrochemical alternative, with brief comments on the identified gaps in existing knowledge and potential paths towards further innovation through a variety of research topics.

Case Study 1: Hydroxylamine

A. Incident Details

In February of 1999 in Allentown, PA, hundreds of pounds of hydroxylamine exploded after the process was improperly shut down. Concept Sciences Inc., the company operating the plant at the time, sustained serious losses and several deaths due to their improper handling of the material. The employees had shut down the process after distilling the first batch of hydroxylamine but delayed in starting the second phase of distillation; however, they failed to account for the decomposition that would occur in the material that was left in the tank and piping while they cleaned the still. This decomposition progressed explosively, most likely because of elevated temperature, concentration, and eventually pressure. While many homes and other buildings in plants nearby were damaged, the worst result of this accident was the five deaths and six injuries[1].

B. Material Properties and Uses

Hydroxylamine is typically a solid, colorless material that has thin and sharp crystal structure and is thermally unstable, so it is handled as a controlled aqueous solution or as salts. It can start to decompose at room temperature and in hot water and is soluble in liquid ammonia, water, and methanol as well as other acids. It melts at 34 °C, boils at 110 °C, and explodes at 265 °C, but it will ignite/explode at much lower temperatures if sufficient surface area is exposed to air. A concentrated, free base version, formed by treating HA salt with a strong base, may explosively decompose and Nissin Chemical Company Ltd. made a proprietary stabilizer that was generally successful in preventing decomposition[1].

Hydroxylamine is a key material for a wide range of industries, warranting the search for more efficient methods of high production volumes. The majority of its historical use has been for manufacturing nylons. Recently, it has become a component in several chemical syntheses as well as a solvent component for modern lithography processes. It is also a consideration in some biological processes due to its potential to produce methemoglobin, which prevents oxygen from reaching tissues[2].

C. Traditional Method

When the incident occurred at Concept Sciences, Inc., the method of hydroxylamine production was based on the use of hydroxylamine sulfate and potassium hydroxide. As shown in the chemical reaction below, this sulfate and hydroxide mixture produces the desired hydroxylamine with potassium sulfate and water as biproducts.

$$(NH_2OH)_2 * H_2SO_4 + 2\ KOH_2 \rightarrow NH_2OH + \ K_2SO_4 + 2H_2O$$

This was typically scaled to ensure the product was about a 30 wt.% hydroxylamine solution before filtering the aqueous potassium sulfate slurry. The remaining mixture underwent vacuum distillation to separate the hydroxylamine from dissolved potassium sulfate to reach a purity of

50 wt.%, and this step is where the incident arose from. The last step was to purify the distillate through an ion exchange system[1].

During the accident, a secondary reaction, the explosive decomposition of hydroxylamine, took place. Fueled by high temperatures and pressures, along with an increasing concentration of hydroxylamine, this decomposition is typically of similar strength to an identical weight of TNT. A study on the decomposition of hydroxylamine noted that crystals will form when the hydroxylamine concentration is over 80 wt.% and that the crystals may explosively decompose above 85 wt.%[3]. These crystals were watched for and observed by Concept Sciences, Inc. personnel, which is why solution of 30 wt.% hydroxylamine was used to wash away crystals that had formed. Despite this procedure, the additional hold-up time in the process allowed water to evaporate and caused the purity to go much higher than was expected[1].

The next year, 2000, Nissin Chemical Company also had an explosion in their process to make 50 wt.% hydroxylamine. This process was similar to what CSI used, and the explosion caused four fatalities.

In response to the issues that caused this incident, we sought to understand the ways that it can be avoided in the future. Hydroxylamine became hazardous when allowed to build up to high concentrations and become exposed to high temperatures. Can hydroxylamine be synthesized without high temperatures and with automatically controlled concentrations? A system is needed that can produce the necessary concentration without the heat that risks decomposition.

D. Electrochemical Method

Over the past 30 years, various research articles on producing hydroxylamine via electrochemical synthesis have been published, each with specific strengths and weaknesses, but overall showing that high concentrations can be produced while maintaining sufficiently low temperatures to introduce safety improvements. High temperatures are a primary culprit of the Concept Sciences, Inc. accident, and not only can electrochemistry mitigate this danger by driving reactions with potential instead of heat, but a selective process may also even be able to produce desired concentrations at low or ambient temperatures.

i. Basic Method

A study of the viability of electrochemically synthesizing hydroxylamine was published in 1996 by Otsuka, Sawada, and Yamanaka at the Tokyo Institute of Technology. Their setup included a gas-fed Hydrogen-Nitric Oxide fuel cell to synthesize hydroxylamine. The NO reactant flows through a gas diffusion electrode to react at a graphite cathode with iron-phthalocyanine electrocatalysts in contact with liquid 3 M H_2SO_4, forming liquid phase hydroxylamine. The first figure from their publication, which shows this fuel cell, is shown below in Figure 1.

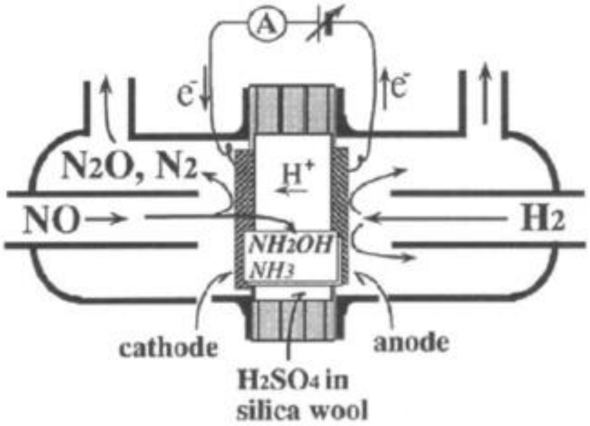

Figure 1: Hydrogen-Nitric Oxide fuel cell for electrochemical hydroxylamine synthesis[4]

The reactions at each electrode are also shown below.

Anode:

$$H_2 \rightarrow 2H^+ + 2e^- \quad ; E^o = 0V$$

Cathode:

$$2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O \quad ; E^o = 1.59\ V$$

$$2NO + 4H^+ + 4e^- \rightarrow N_2 + H_2O \quad ; E^o = 1.68\ V$$

$$NO + 3H^+ + 3e^- \rightarrow NH_2OH \quad ; E^o = 0.38\ V$$

$$NO + 5H^+ + 5e^- \rightarrow NH_3 + H_2O \quad ; E^o = 0.73\ V$$

$$2H^+ + 2e^- \rightarrow H_2 \quad ; E^o = 0\ V$$

The standard potentials indicate that the overall reaction is electrogenerative when hydrogen oxidation occurs at the anode. Alternatively, the cell could be operated electrolytically by oxidizing water at the anode.

The study was conducted in order to understand the best catalyst for this electrochemical reaction. Platinum and ruthenium were the most active catalysts for reducing nitric oxide into hydroxylamine, ammonia, and nitrous oxide. Selectivity is still low, even for this most active catalyst – stated to be around 63%. Selectivity is much higher for Fe-Pc (Iron-Phthalocyanine, 90%) and its activity was the third highest (just over half of what platinum produced) despite requiring under a third of the current passed as platinum did (84 Coulombs for 255 μmol using Fe-Pc versus 232 Coulombs for 448 μmol using Pt). A full table of results from this paper is shown below[4].

A variety of carbon materials were explored for the cathode as well. The values above utilized graphite (Gr) but the researchers also experimented with active carbon (Ac), carbon whisker (CW), and carbon black (CB) with Fe-Pc to see which provides the best selectivity and conversion. Active carbon gave the highest selectivity (99%) and second highest conversion (15.2%) while carbon whisker showed the second highest selectivity (93%) and the highest conversion (17.6%)[4].

ii. Expansion of Electrochemical Method:

An update, written in 2006, was mostly based upon the 1996 paper and provides some parameters that could improve the logistical outlook of electrochemical hydroxylamine production. This paper follows the same nitric oxide – hydrogen fuel cell configuration and specifies sulfuric acid as the optimal electrolyte. An interesting observation from the authors of this article is the relationship between current efficiency (electrons consumed versus charge passed) of hydroxylamine versus fuel cell voltage. The current efficiency increases as the fuel cell voltage decreases until it peaks at 80% when the fuel cell voltage is very close to 0 Volts and then the efficiency begins to decrease at negative fuel cell voltages. It is theorized that the decrease in efficiency when voltage drops below 0 Volts is due to reduction of hydroxylamine to ammonia at the cathode, but analysis of non-hydroxylamine species was not done to confirm this hypothesis[5].

E. Analysis

The electrochemical replacement for hydroxylamine production is clearly viable and with enough data to warrant further research and development for modern improvement on the proof of concept shown here. Even several decades ago, very high selectivity was found alongside up to 80% current efficiency. This high selectivity came at the price of activity, however, and the systems shown to work noted issues with larger scales because of a lack of optimal catalyst options. An opportunity for further research into this electrochemical replacement would be to understand how catalyst options have developed over the past 25 years. This research would also require replicable results of high concentrations of hydroxylamine being produced and theoretically being able to maintain an upper limit on its conversion through controlling temperature, pressure, electrolyte conditions, etc. Such catalyst exploration should be paired with new findings in reactor design and other engineering progress that could further the capabilities of this system.

In the theoretical expansion of hydroxylamine published in 2006, the authors note that other methods of hydroxylamine production will likely form nitrous oxide and ammonium sulfate as undesired byproducts. Future work will hopefully mitigate these byproducts and lead to a new method that will produce a much purer hydroxylamine solution that is more scalable than previous synthesis methods as there is more control over hydroxylamine concentration, heating, contamination, and other factors that can accelerate decomposition[5]. There are still potential hazards in pumps, pipe friction, and other heat producers that will need to be assessed, and there are still inherent dangers to hydroxylamine as a chemical. While it is significantly slower, hydroxylamine shows minor decomposition at lower temperatures but it does not typically go beyond control until the system reaches an onset temperature slightly above 100 °C (dependent on the salt that may also be present)[6]. Hydroxylamine remains corrosive and toxic regardless of temperature and safety measures must always be taken seriously. It is difficult to estimate what equipment would be necessary for this electrochemical system as research showed relatively low conversions; however, the traditional reactors would certainly be replaced by electrochemical cells before entering a product purification process.

Controlled parameters that work in a more continuous manner would have saved property and lives in the incident noted. A process that shows safety improvements in addition to economic viability is one that strongly reinforces the idea that electrochemical reactions deserve more consideration and implementation.

Case Study 2: Mononitrotoluene (MNT)

A. Incident Details

On October 13, 2002, a leakage of steam through a series of manual valves began heating 1,200 gallons of mononitrotoluene inside a distillation column. The column was shut down when the incident started, allowing several days of decomposition without being checked by the operators. This decomposition of such a large volume resulted in an eventual explosion and fire that impacted the surrounding area. The initial explosion shot debris into a mononitrotoluene storage tank, which began burning for almost 3 hours alongside several other smaller fires. Massive remnants up to 6 tons in weight, were scattered beyond plant boundaries and landed dangerously close to crude oil storage tanks adjacent to the plant. As a result of these circumstances, a shelter-in-place order was enacted while both plant and local emergency responders fought the series of fires.

The Chemical Safety Board noted that a key cause of this incident was that the First Chemical Corporation failed to evaluate the hazards of processing mononitrotoluene. The plant also did not equip their process with the proper protection through alarms, interlocks, and automatic pressure releases. Even the protection in place, an alarm for a tray in the isolated column, was silenced and ignored by the operator, highlighting a key failure in operating procedures in the plant as well[7].

B. Material Properties and Uses

Mononitrotoluene is formed by nitric and sulfuric acids reacting with toluene. MNT is an aromatic nitro compound that is purified through separation, washing, stripping of toluene, and finally distilled into its three isomers, all of which will be explained in further detail below[7]. This chemical melts from a yellow crystal at 15.5 °C to a yellow liquid that boils at 232.6 °C, so it remains liquid under most mild conditions; however, it is not stable over the same range as its flash point is 106.1 °C. Even at ambient temperatures, it must still be handled with care, as any inhalation and ingestion can result in a number of toxicity symptoms[8].

Mononitrotoluene plays a vital role in a variety of industrial and agricultural chemical processes. Pigments, antioxidants, and photographic chemicals are all primary uses, and a range of herbicides and pesticides also find their basis involving Mononitrotoluene. Certain positional variants, namely the ortho- and para-mononitrotoluene, are also useful for explosive detection[9].

C. Traditional Method

Mononitrotoluene is formed by reacting toluene with a mixture of nitric and sulfuric acids. This mixture of acids, toluene, water, and the mononitrotoluene product is sent to a separator to concentrate and recycle the acid. The remaining product stream is washed before going through a toluene stripper that leaves a purified mononitrotoluene liquid. This purified product is taken through a series of three distillation columns and separated into the ortho-, meta-, and para-mononitrotoluene isomers[7].

The chemical reactions are shown below, where the nitric acid and sulfuric acid react to form the nitronium ion and other ions that are used to regenerate sulfuric acid and produce water.

$$HNO_3 + 2H_2SO_4 \leftrightarrow NO_2^+ + H_3O^+ + 2HSO_4^+$$

$$C_6H_5CH_3 + NO_2^+ \rightarrow C_7H_7NO_2 + H^+$$

$$H^+ + H_3O^+ + 2HSO_4^+ \rightarrow H_2O + 2H_2SO_4$$

Where the produced mononitrotoluene ($C_7H_7NO_2$) includes the ortho-, meta-, and para-mononitrotoluene isomers[10].

In the incident described above, it was the first of the set of three separation columns that exploded. This column had a height of around 44.2 meters, a diameter of 2.1 meters, and utilized stainless steel packing. The separation process within this column required it to be run under vacuum and contained a range of ambient (top of column) to 176.7 °C (bottom of column), with the reboiler heat being produced by 2.07 MPa gauge steam. This bottoms product was mostly cleaned of the ortho-mononitrotoluene isomer and was pumped into the second distillation column or to be recycled. The top product, mostly clean ortho-mononitrotoluene, was pumped through a cooler and either refluxed or sent to storage [7].

Between the inadequate safety precautions and the inherent concerns with the process, an alternative must be considered for future facilities to be protected from similar issues that could be equally impactful. Such an alternative should look to moderate the temperatures required for separation in order to avoid vaporization and decomposition of the product.

D. Electrochemical Method

An electrochemical method of mononitrotoluene production answers some of these concerns, particularly that of temperature. Electrochemical technology for the nitration of toluene has proven viable at or near atmospheric temperature (25 °C) since the early 1980s, and further expansion on electrochemical nitration has reinforced the greater control of synthesis conditions.

i. Basic Method

A study in the Journal of Electrochemistry authored by Achord and Hussey in 1981 outlines nitrating aromatic hydrocarbons through an electrochemical pathway. This publication looks at electrochemically nitrating anthracene, naphthalene, 1-nitronaphthalene, and mononitrotoluene, the focus of this section.

The overall mechanism includes oxidizing hydrocarbons in solutions with NO_2^- and N_2O_4 to react the hydrocarbon radical with the NO_2 radical with other acid reactions simultaneously. In the study referenced, this nitration was done in acetonitrile and nitromethane solutions with one of NO_2^-, $NO_2(N_2O_4)$, or NO_3^-. For toluene, the electrolysis was done with N_2O_4 in a solution of $MeCN$ and $MeNO_2$. Varying currents between 1.75 and 2.5 volts were passed and tested for the yields of each toluene product, with the highest total yield found by passing 2.5 V through a medium of 0.2 M NO_2 in $MeCN$ to get a 36% yield of 2-nitrotoluene, 25% yield of 4-

nitrotoluene, and trace amounts of 3-nitrotoluene. In producing a graph of the percentage yield of mononitrotoluenes as a function of the percentage of the total charge that is passed, the authors do note that this method does appear to be inefficient. The data shows increasing yield percentages as the charge increases from 0 to 100 percent; however, the maximum percent yield recorded was just over 30%[11].

Beyond this baseline experiment, the authors continued testing the electrochemical nitration of toluene for various purposes. The next major experiment was done under the same solution conditions ($MeCN$ and $MeNO_2$) but now under constant 2.00 V potential and at 25 °C. This was done, in part, to understand the interaction of NO_3^- with the solutions. Measurable amounts of nitrotoluenes were produced once the $MeNO_2$ solution was saturated with $LiNO_3$, but this experiment was much less successful overall for the production of nitrotoluene compounds. Despite this drawback, the authors conclude with their belief that the yields of the nitrated compounds they studied by electrochemical methods do appear comparable to yields by conventional chemical nitration, but it is dependent on getting the correct reactant ions based on the desired reaction[11].

ii. Expansion of Electrochemical Method

Moving more broadly to electrochemical nitration of aromatics, this area of research has experienced considerable growth that makes an excellent case for electrochemistry as a means to make processes simpler and safer. The main article on this topic, published by Blum et al in 2021, shows that progress in this field represents a selective, mild, and scalable method of nitration. The key to their research is utilizing nitrite as a safe source of the required NO_2 that does not require acidic conditions.

The electrodes used in the update are simply made from graphite, which is considerably cheaper than many alternatives, and are in a solution of acetonitrile. To begin this reaction, the nitrite must react with 1,1,1-3,3,3-hexafluoroisopropan-2-ol (HFIP) to produce the NO_2 and N_2O_4 that will dissociate into the needed ions for the nitration. A range of conditions were tested, with the optimal current density of 15 $\frac{mA}{cm^2}$ and a charge of 2.5 farads producing a 96% yield in 50 minutes of electrolysis at room temperature in the test reaction using 1,4-dimethoxybenzene. It's noted that reaction as a whole is able to be scaled and powered cleanly and easily, both very important characteristics of a system looking to protect chemical plants from the dangers of traditional aromatic nitration[12].

E. Analysis

This replacement for the production of mononitrotoluene is a niche case that may provide utility to the select companies that make this product on a large scale. These specific systems do not appear very well developed yet, with the authors of the basic study reminding readers of the lack of efficiency of electrochemically producing mononitrotoluene. Advancements could still be made in this field that bring new vitality; however, as the use cases may be limited, there does not appear to be a driving factor for mononitrotoluene specifically.

Where electrochemistry becomes more widely applicable is when the scope is broadened to electrochemical nitration of all aromatics. Aromatic nitration is a well understood and developed field that has had applications to many industries, driving the desire to research a better and safer pathway. Moderate temperatures appear to be the biggest desire of such a new process, a desire which was realized as the studies discussed proved that electrochemical nitration can occur very close to room temperature (25 °C). On the smaller scale that these experiments have been done over, it is difficult to understand the scale of equipment that would be needed to fully replace conventional technology, but it appears that more rigorous testing equipment would need to accompany electrochemical production methods to ensure greater control over the system. Also within the laboratory scale, these moderate temperatures did not prevent effective conversion, so properly chosen solvents and current density can still support similar yields as traditional methods of aromatic nitration, and this greater level of control can have huge implications for the improved safety of future chemical facilities.

Case Study 3: Acrylic Polymerization

A. Incident Details

On January 31, 2006, Synthron's Morganton, North Carolina facility received an order marginally larger than their typical batch size. The managers on site scaled reactants to match this order to save time by not having to make two separate batches. Despite only a minor increase in desired output and a seemingly reasonable required increase in the reactant monomer, the reaction produced over double the energy than typically expected in the reactor, far exceeding the cooling capacity and enacting a runaway reaction. The pressure within the reactor quickly increased even with solvent vapors venting, and these vapors added another hazard in the flammable cloud formed indoors. An ignition source was soon found, and the subsequent explosion destroyed the facility, damaged off-site structures, injured 14 workers, and killed one.

The Chemical Safety Board simplified the root causes down to the fact that the reactor lacked safeguards against such runaway reactions and, perhaps more importantly, the failure of plant managers to consider process safety impacts of scaling a reaction without proper knowledge[13].

B. Material Properties and Uses

Acrylic polymers are typically very transparent even when heated, unless they are dyed. The properties are not typically impacted by moisture either in air or even submersion, which is a result of UV stabilization that many facilities conduct. These polymers are also easy to form through both cutting and bending to a variety of shapes based on consumer need.

These polymers are very resistant to a range of temperatures and chemicals and can withstand many cleaning solutions and weaker inorganic acid solutions. Despite their durability, acrylic polymers are noted to be kept separate from hydrocarbons that are aromatic or chlorinated, and esters and ketones should also not be used in acrylic polymer reactions. Acrylic polymers are denser than water, very resistant to absorption, and have a very low dielectric constant, all reasons which reinforce why this material is so widespread.

Acrylic polymers are an important set of materials because of their widespread and versatile uses. They are commonly seen in decorative and lighting fixtures, able to be easily dyed to a chosen color, and certain windows and skylights are also made from these polymer chains. Outdoor signs and furniture are additional uses of acrylic polymers that further show the range of uses that are possible because of the material's durability[14].

C. Traditional Method

Semibatch polymerization reactors are those which have a batch of reactants added at the start and others added throughout the process. This is a typical way to conduct polymerization, where the monomers, initiators, and solvents are added early on and then additional reactants are added throughout the process to control the reaction rate and eventually terminate the polymerization[15].

The acrylic polymers produced by Synthron were the result of free-radical polymerization of monomers in flammable solvents. The specific liquid polymer being formed was Synthron's

Modarez MFP-BH. This polymerization was done in a 5.68 m^3 reactor where operators would add a specific mixture of solvents and monomers before heating the reactor with steam to the expected boiling point. Once the desired temperature was achieved, the steam was shut off and an initiator solution was added while the temperature was kept high through the heat produced. To control the vapors released, a water-cooled heat exchanger completely condensed them into a liquid that flowed back into the reactor. A small outlet pipe led to a scrubber and vent in order to maintain atmospheric pressure in the tank. From the reactor vessel, the product flows out of the bottom as a liquid, which can be dried into powders by silica adsorption at a later stage[13].

Progress in polymerization would be a system that can maintain similar levels of production and simplicity while also being able to have better control over specific batch size. Safety progress should also be made in terms of controlling the reaction's temperature and escaping flammable vapors.

D. Electrochemical Method

Electrochemistry certainly has an answer to concerns over controlling reaction parameters. As shown in the research below, electrochemical reactions include a wide variety of inputs that can be adjusted endlessly until a more appropriate outcome is found. This precise control appears to allow for very specific product specifications, batch sizes, and improved safety outcomes.

i. Basic Method

A specialized type of polymer, those that are conductive, was an early area of study for electrochemical synthesis. Specifically, this work looked at polypyrrole and polythiophene and are useful for LEDs, sensors, and many other applications. Polymerization through electrochemical means is an excellent choice for these conducting polymers because the film thickness is more easily controlled when it's directly in contact with a conducting surface. The drawback, mitigated by pre-treating the electrodes with analogs of the polymers, is the lack of ability of the polymer to stick to the electrode[16].

Prior to the electrochemical step in the process, monomers were created through more traditional synthesis methods and obtained a purity of 95%. The electropolymerization then occurs in two primary steps, cathodic electrografting and polymerization from anodic polarization. The cathodic electrografting utilized glassy carbon and required the monomer to strongly adsorb to the cathode. This step is crucial, and a solvent must be carefully chosen to not compete with the monomer making a connection with the cathode. For this research, N,N-Dimethylformamide was used after testing it several times to ensure it did not wash off the "prepolymer" film that deposited at -1.9 V. Part (a) of the figure below helps visualize this first step[16].

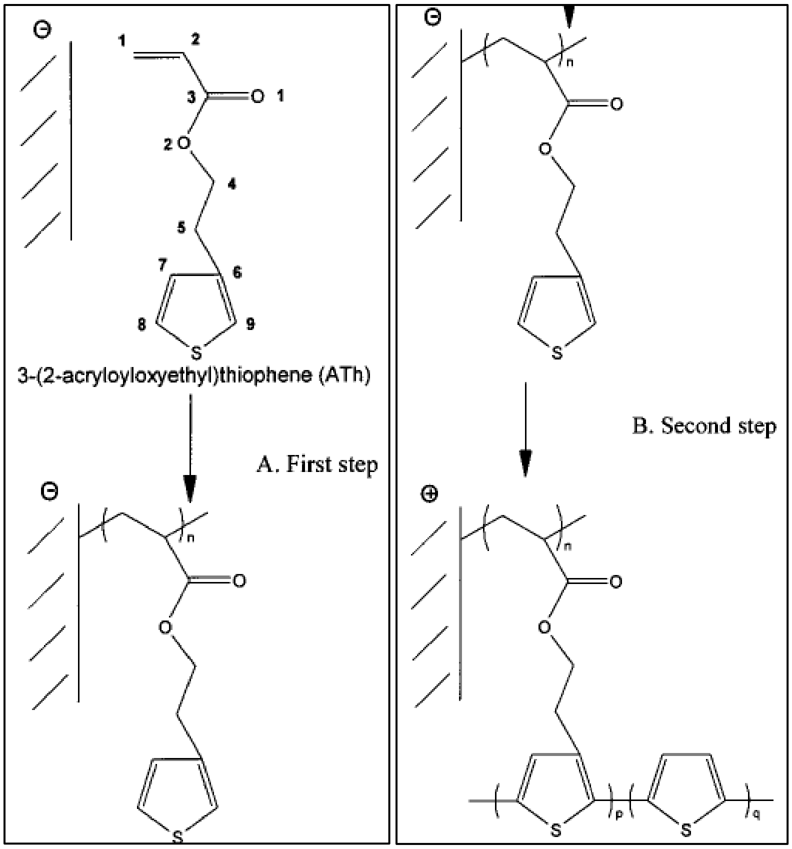

Figure XX (a)____(b)____[16]

Once adsorbed, this monomer can undergo an electroreduction step which maintains connection to the surface while forming a polymer chain that does not require additional current to progress until it is terminated by the limiting film thickness, which was able to be increased up to 100 nm by increasing the monomer concentration[17].

The next step, anodic polymerization of the grafted material, is more directed to the transition to becoming conducting. The electrodes, already with a grafted film, are anodically polarized, which triggers polymerization of the aromatic rings on the molecule, shown in part (b) of the figure above.

A wealth of details are available in the original articles, which discuss film electroactivity, redox potentials, and many more fine details of how this system function that are beyond the scope of this review. The important takeaway from such research is that polymerization can readily be done through grafting monomer films to an electrode and building out from there. This shows that not only has electropolymerization been theorized or even proved as a concept, but it was also being refined and introduced for niche cases over 20 years ago[16].

ii. Expansion of Electrochemical Method

A broader use for electrochemical polymerization has been found in making more uniform chains in photoinitiated polymerization reactors, allowing for a more complete and balanced curing process on metallic objects with complex shapes.

In this work by Decker et al in 2004, the authors reference over a dozen past studies on the use of electropolymerization for conducting polymers but instead wanted to apply this to a step in the production of automotive varnishes that would allow them to cure more consistently. They used a range of copper, aluminum, and silicon cathodes and either platinum or glassy carbon anodes. Electrolytes solutions of ammonia and ammonium chloride or potassium chloride were used[18].

The electro-initiated polymerization was successful in still developing the three-dimensional network of polymers needed from the reaction. The reaction progressed for about half an hour, which was the time that allowed for the maximum 40% conversion, which was about the same for photon- and electron-induced polymerizations After 30 additional minutes of treatment, this polymer block was resistant to water and inorganic solvents, and other properties were satisfactory. These properties were surprisingly homogenous throughout the film, with the surface reaching a similar conversion to the polymers in the bulk[18].

One drawback to this experiment, and perhaps to electrochemical polymerization as a whole, was the roughness of the submerged surface potentially owing to the formation of gas bubbles from side reactions. While difficult to understand and prevent, it is possible to achieve a smoother coating using monomer variations with different ion groups that do not lead to gas-producing side reactions. In finding ways to reduce and eliminate this roughness, the researchers also noted that it appears sufficient to simply connect the cathode to the electrolyte solution by a small conductor that minimizes surface area contact[18]. This is reasonable based on the previously understood fact that polymerization can continue without additional charge added to it once the monomer is attached.

E. Analysis

While the above research indicated feasibility and understanding of electrochemical polymerization, it does not appear to be widely applicable as of the date of these papers. Much of the utility of said electropolymerization lies within the field of conducting polymer films, where the desired thickness control is very useful, but will require significantly more space to produce the same production amount as traditional polymerization batch reactors. This control over the reaction conditions answers the concerns over traditional polymerization reactions, but much broader understanding and testing is needed before electrochemistry can be seen as the answer to industrial polymerization.

The key takeaways from this section are still valuable. There are several control mechanisms over electrochemical polymerization such as solvent choice, electrode materials, and voltage to go alongside the possibilities of these reactions happening at more moderate, even ambient, temperatures. These represent a more diverse arrangement of adjustments that can be made to precisely control a reaction. As demonstrated across several electropolymerization papers, even minor adjustments in any of these categories yield noticeably different results, keeping the door open to further research to understand the exact bounds of what is possible in terms of purity, reaction selectivity, and much more.

Case Study 4: Acetylene

A. Incident Details

On January 25, 2005, highly flammable acetylene was inadvertently released into a shed at Acetylene Services Company's Perth Amboy facility. A valve on the decanted water line was typically left open during winter months to prevent freezing in the water line, but this also appeared to give the produced acetylene a path into the shed and mix with a potential propane leak from the propane heater or supply tubing. The shed lacked ventilation and allowed for acetylene buildup to find an ignition source and explode.

The Chemical Safety Board notes a range of causes that led to this incident, with the clearest lapses in process safety being the lack of standard operating procedures to check the entire process, as well as relocating these drains and vents to safer locations, most likely outdoors. Meeting National Fire Protection Association codes as well as other training and testing at the facility are additional causes that should be considered for facilities that could experience similar flammable buildups[19].

B. Material Properties and Uses

Not long after its discovery in 1836, acetylene was the basis for most organic synthesis processes as the simplest derivative of alkyne hydrocarbons. Much of its use also stemmed from the fact it was the only significant petrochemical product with a triple bond[20]. It is significantly less dense than water and will rise in open air. As a colorless gas with a boiling point of -83.89 °C and a flash point of -17.78 °C, it is very prone to combustion, so it is often handled as a liquid; however, this liquid is highly explosive and requires extensive precautions. When used in a process, piping must be separated from any heat source that could accidentally raise the temperature above 185 °C, as this temperature has been recorded as the starting point for a self-sustaining decomposition that can cause a sudden explosion[21].

Acetylene has a wide range of uses beyond its typical use as welding fuel. The most common use of acetylene is actually as a reactant for a set of organic chemicals, particularly those used for preparing plastics. Certain batteries and even vitamins have components stemming from chemicals formed partly from acetylene. Other chemicals created from acetylene are used for food flavoring, perfumes, plexiglass, urethane and other resins, and a range of polymers[20].

C. Traditional Method

The Acetylene Services Company (ASCO) made acetylene in the gaseous form through a reaction of calcium carbide and water. In addition to acetylene gas, this process also produced water, lime, and excess heat, as shown in the reaction below.

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2 + heat$$

The reactants were combined at a fixed rate in a vessel that was already partially filled with water. A series of compressors moved the acetylene gas from the generator to have impurities removed before being packaged into cylinders for shipping. In order to maintain a nearly continuous process, the byproducts, a slurry that is mostly lime, were drained to a nearby pit to await pumping to a series of decanting tanks.

These open-top tanks were connected in a series of decreasing lime amounts, with each tank draining settled lime to be removed as waste. The water in this slurry is eventually (after passing through 5 of the 6 tanks) recycled to maintain the water level in the acetylene generator. The shed noted in the incident above held the pumps for both components of this decanting process and was heated via propane without intentional ventilation[19].

A new method of acetylene synthesis is important to explore, especially if it can be done with alternative methods of byproduct handling that would reduce safety concerns that were unfortunately realized at ASCO's facility.

D. Electrochemical Method

The formation of acetylene via electrochemical pathways is reasonably simple and appears to be well-controlled in all laboratory experiments. As will be shown below, acetylene can be made without significant gas byproducts, allowing for a cleaner and safer method of production and handling.

Environmental considerations are also a factor in favor of electrochemical methods of acetylene production, as those discussed below are made with carbon dioxide and methane. Both of these are greenhouse gases that currently have less demand than supply in the chemical industry, requiring alternative methods of use or sequestration to reduce global impact.

i. Basic Method

In this exploration of electrochemical production of acetylene, McEnaney et al. created a cycle that was brough to feasibility by the use of lithium. Lithium hydroxide is broken down into elemental lithium that can then react to form a carbon intermediate that is then hydrolyzed to form acetylene and reproduce lithium hydroxide. The reaction progression is shown below[22].

$$2\ LiOH \rightarrow 2\ Li + H_2O + \frac{1}{2}\ O_2(g)$$

$$2\ Li^+ + 2\ e^- \rightarrow 2\ Li$$

$$2\ OH^- \rightarrow H_2O + \frac{1}{2}\ O_2(g) + 2\ e^-$$

$$2\ Li + 2\ CO_2 \rightarrow Li_2C_2(s) + X$$

$$Li_2C_2(s) \rightarrow 2\ LiOH + C_2H_2(g)$$

Where X is a variety of byproducts that could be formed if lithium and carbon dioxide react in different ratios than 2:2.

Following the production of lithium metal (produced by a molten salt solution around 450 °C under a constant current), the product was allowed to be cooled before being cut into a pellet to be exposed to carbon dioxide between temperatures of 22 °C and 450 °C and then being added to water. The highest percentage yield (a little over 15%) of acetylene was found at 350 °C for 8-20 hours. This current efficiency of 15% is clarified to be over 80% of the maximum that could be have been achieved based on the oxygenated lithium byproducts that would also begin forming. While this may seem disappointing, the authors also note that alternative precursors were used, and graphitic carbon resulted in a 55% current efficiency to acetylene, hopefully prompting research into further optimization[22].

Each alternative feedstock option, methane, carbon monoxide, or graphitic carbon, each had different byproducts that could be made, and these should be taken into account based on the sensitivity of the system being tested. Certain byproducts may not be easily decomposed back into useful components and present additional costs in raw materials. Additional costs are also estimated to be an issue when trying to optimize the feedstocks, where graphitic carbon may have a better conversion, but it is balanced out by being a significantly more expensive component to use[22].

ii. Expansion of Electrochemical Method

The following method of acetylene production is an even more recent take on the electrochemical approach to this synthesis but relies on more intense conditions and uses components that cannot be as easily recycled compared to the basic method described above.

The first step in this process is utilizing a form of electrochemical reduction with carbon dioxide and oxygen to form solid carbon. This may either be direct reduction of carbon dioxide or a 2-step process of combining carbon dioxide and oxygen to a carbonate ion which is then reduced into solid carbon and oxygen. The goal is still to be able to combine metallic carbide (calcium or lithium are the easiest for acetylene) with water to form acetylene and a hydroxide product. While the process of carbon dioxide gas being directly used to form metal carbides and then acetylene is still addressed, the uniqueness of this paper is in looking at an intermediate step for the carbon dioxide to be electrochemically reduced. This reduction of carbon dioxide also happens at high temperatures in a molten salt and the solid carbon that is formed becomes the electrode for the formation of the metal carbide[23].

The rest of this work discusses how various types of electrodes perform in terms of Faradic efficiency as well as at what voltages they produce substantial amounts of the desired product (typically a carbide intermediate or acetylene). Based on this data and results from other preliminary tests, calcium was their metal of choice as it was much less prone to form other compounds with carbon, unlike lithium producing several variations with different carbon amounts. Their tests also concluded that the Faradic efficiency for acetylene was doubled by utilizing calcium carbide instead of calcium oxide in the melt, and the mechanisms for this can be reviewed in the paper but is beyond the scope of this review[23].

E. Analysis

Developments in the electrochemical production of acetylene are very recent, with the expansion of this method coming in early 2024. With such research still on the forefront of some academic research labs, it is expected to see significant growth and improvement across the next iterations and discoveries in this field. The primary drawback of this is that no method has been pronounced as the best way to produce acetylene on a large scale, as each pathway has issues that would become exacerbated at large scales. One such concern is the oxygenated byproducts that lithium and calcium can form, as some are not easily broken back down in the process and can cause complications when they build up. On the positive side of this, cyclic electrochemical processes have the capabilities to avoid hydrogen, carbon monoxide, and carbon dioxide production, which could lead to more severe issues on a plant scale.

Despite the reduction in gaseous products that have led to many safety concerns in traditional acetylene production, there may not be a consequential reduction in the risk of the acetylene itself until these processes can happen at more moderate temperatures. The containment of electrochemical cells is a layer of protection that gives more process control, but such control systems will need to develop alongside other progress in order to ensure that electrochemical acetylene production becomes safe enough to warrant changing from the traditional method.

Additionally, as these new synthesis methods have only been tested at laboratory scale, it is difficult to know exactly what equipment would be needed and which traditional parts of an acetylene production plant would be replaced. At the very least, this electrochemical method of acetylene production requires cells that can withstand temperatures needed for molten salt electrolysis as well as additional reaction vessels that will not leak the produced acetylene.

Case Study 5: Electrochemical Refrigeration

A. Incident Details

On August 23, 2010, Millard Refrigerated Services had a severe process issue at their Theodore, Alabama plant during the restarting of the ammonia refrigeration system. Hydraulic shock resulted in a pipe that failed and released over 32,000 pounds of anhydrous ammonia while also causing a failure of the facility's evaporator coil. This ammonia release traveled a quarter of a mile to a downwind river dock with hundreds of workers. Over 150 crew members and contractors reported exposure, with one losing consciousness and 32 requiring hospitalizations.

While deflagration was not the outcome of the 2010 incident, a similar ammonia release in 2007 resulted in an explosion after a water fountain provided an ignition source for an ammonia cloud that reached the concentration that could be exploded.

The Chemical Safety Board has listed several lessons that should come from this incident. Avoiding the grouping of evaporators to one set of control valves as well as automatic pressure controls were the first on this list. Operating procedure changes, such as not manually changing the evaporator operating procedure and ensuring enough time for pumps to remove liquid refrigerant from the evaporators, are also included[24].

B. Material Properties and Uses

Anhydrous ammonia is a strong-smelling, colorless gas under atmospheric conditions. It rises in air and can react with water to form cloudy gas mixtures which can return to the ground. This makes ammonia particularly dangerous in the case of a leak, as it remains at the same level as people while not always being easily visible[24]. Ammonia is also corrosive with its alkaline properties and must typically be shipped in steel containers that are kept away from any sources of heat. Anhydrous ammonia also absorbs water which can lead to the formation of ammonium hydroxide. This type of ammonia can react with the moisture in various parts of the body and the ammonium hydroxide's caustic properties become very threatening through necrosis and cellular destruction[25].

The majority of ammonia is used as fertilizer, but its use as a refrigerant is a notable secondary use. Ammonia can also be used in manufacturing a range of materials and can be used to purify water and clean via various cleaning solutions[25].

C. Traditional Method

The refrigeration system in use at the time of the incident was dominantly used to freeze meat before marine transport. The requirements for this system were almost 65000 kg of ammonia between the minimum temperature of -40 °C and maximum temperature of 43 °C. The pressures also had a wide range, with some points under vacuum and others as high as 1.45 MPa gauge. Such a range of pressures leaves the system always threatened by risks of hydraulic shock, the cause of the incident discussed above. The process worked by having ammonia liquid evaporated into vapor by removing heat from the freezers, involving a high pressure liquid in becoming a low pressure vapor leaving this system. A condenser then assisted this stream to becoming a high pressure vapor entering a condenser that rejected the fluids heat and returned the ammonia back to its storage as a high pressure liquid, ready to start the cycle over again[24].

D. Electrochemical Method

In seeking methods of refrigeration that stray from the use of dangerous chemicals, learning about the modern capabilities of electrochemical refrigeration is necessary. Since 2020, a range of new technologies has become viable while also being more environmentally friendly and safer than their ammonia-driven predecessors.

i. Basic Method

The concept of electrochemical refrigeration is based on the thermally regenerative electrochemical cycle (TREC). Their benefits include high efficiency (therefore low weight and volumes can be used), low noise levels, and general environmental friendliness for their sustainable power generation and not using dangerous refrigerants. This system can thrive on the prevalent but difficult to use low-grade heat, held in solar and geothermal heat as well as waste heat from fuel cells[26].

Electrochemical systems have an inherent temperature dependence in their electrode potentials, simply referred to as a temperature coefficient. Such coefficient is defined as the change in voltage over the change in temperature and can be solved in the following equation, where S_B is the molar entropy of the product, S_A is the molar entropy of the reactant, *n* is the number of exchanged electrons, and *F* is the Faraday constant[27].

$$\alpha = \frac{S_B - S_A}{nF}$$

A temperature coefficient for a given cell is the difference between the temperature coefficients for both positive and negative electrodes. This value can be positive or negative depending on the electrodes and leads directly to an understanding of power generation with the TREC. If a cell has a negative temperature coefficient, this means that the cells voltage will decrease as temperature increases, and this becomes one of four processes in the TREC. Shown in *Figure XX* below, this power generation cycle has heating (1), charging (2), cooling (3), and discharging steps (4)[28].

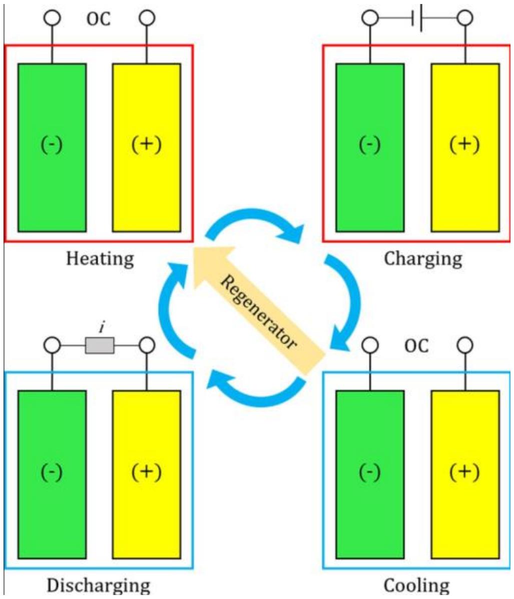

Figure XX: Basic Thermally Regenerative Electrochemical Cycle (TREC)[28]

If the cell has a negative temperature coefficient, then taking the process to a higher temperature will decrease the voltage. At this higher temperature, the cell is charged so the voltage increases gradually. During the electrochemical reaction here, heat is drawn in from its surroundings and the cell entropy increasing according to this absorption. Entering stage 3, the cell is cooled and therefore increases its open-circuit voltage (because of the negative temperature coefficient). This increasing voltage is eventually discharged once at the lower temperature and the cycle repeats. The figure below is useful for visualizing the charge capacity through the 4 processes, where the left side is for a negative temperature coefficient and the right side for a positive value (source).

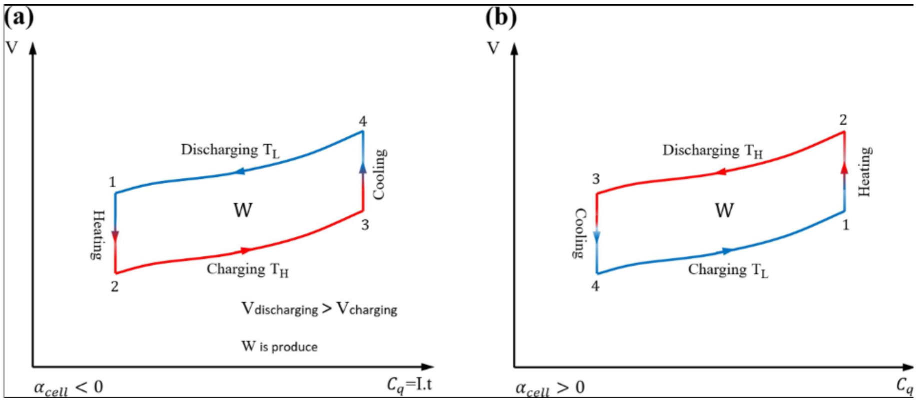

Figure XX:TREC Voltage Versus Charge Capacity Diagrams[28]

Net work (W) is produced in this cycle, as shown by the fact that discharge voltage is higher than that when charging. This is the cycle that, when operated in reverse, becomes a refrigerator. Shown below is the refrigeration version of figures *XX* and *XX*, where work is now needed but heat can be removed from the system instead of added.

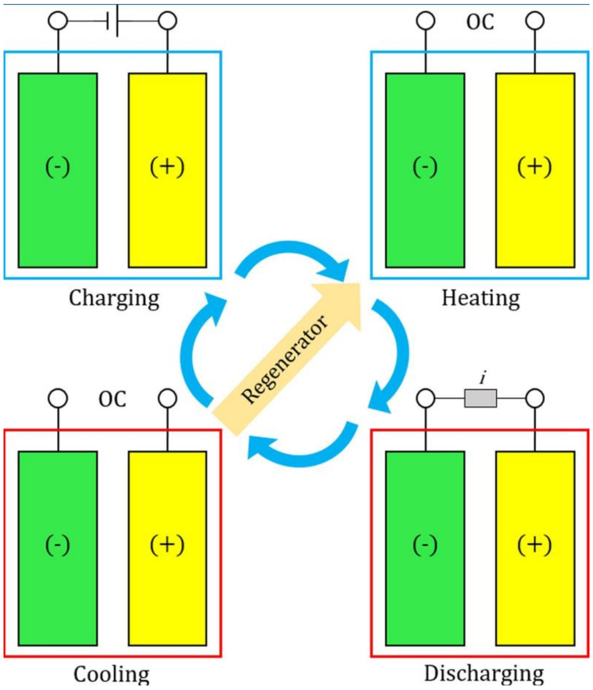

Figure XX: Basic Thermally Regenerative Electrochemical Refrigerator (TRER)[28]

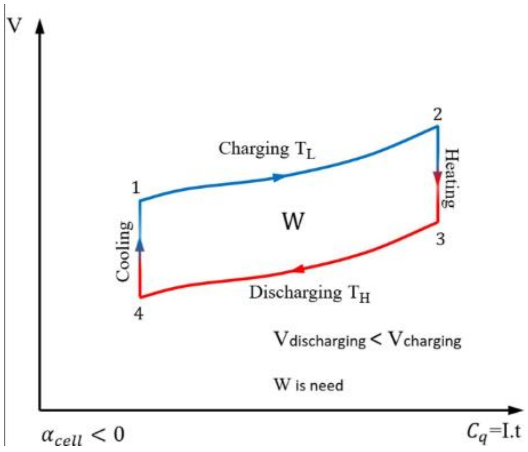

Figure XX: TRER Voltage Verus Charge Capacity Diagram[28]

To clarify, this reverse cycle, now known as a thermally regenerative electrochemical refrigerator (TRER), is charged at a low temperature, voltage is decreased from heat absorption (because the temperature coefficient is negative), heated to its high temperature, and then discharged at that higher temperature before being cooled. Again, power must be added because this system discharges at a lower voltage that it is initially charged at. Utilizing both TRER and traditional TREC cells, a continuous model of refrigeration can be developed.

In the system's governing equations, this system is treated more like an engine than a typical reaction, and many features such as efficiency are defined the same as for a typical heat engine. Very few equations will be presented here as it goes beyond the desire to simply bring attention to the feasibility of electrochemical replacements. The equations in this literature review utilize several unique features compared to typical engines, such as internal cell resistances to calculate work loss across the cycle. Other examples include utilizing the temperature coefficient to calculate overall efficiency and finding charge capacities for each electrode. Dozens of additional articles have been written concerning the analysis of these systems and their improving efficiencies that have brought them to relevance for future refrigeration systems[28].

ii. Expansion of Electrochemical Method

Getting into more detail about a specific application of electrochemical refrigeration systems, a 2021 study by Duan et al. has analyzed a continuous cycle using iron and vanadium. They used $Fe^{2+}/Fe^{3+}$and VO^{2+}/VO_2^+ as redox couples that would not undergo side reactions and also had high solubility and large entropy change and the electrolyte solution used included sulfuric acid. In the charging and heat absorbing (endothermic) cell, the following reactions took place.

Cathodic half-cell: $Fe^{3+} + e^- \rightarrow Fe^{2+}$

Anodic half-cell: $VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e^-$

In the other side of the cycle, the discharging and heat releasing (exothermic) cell, the following reactions took place.

Cathodic half-cell: $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$

Anodic half-cell: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

These reversible chemical reactions occur at approximately the same rate in either cell, sustained by external energy added to the system. As briefly mentioned in the basics of this case study, this additional energy is needed because heat being transferred from the exothermic cell cannot fully satisfy the endothermic cell's consumption as there is some level of imperfection in the heat transfer and the system must follow the second law of thermodynamics.

When running, the authors also looked to understand the role that temperature played in the efficiency of the system. By varying from a difference of 10 K to 50 K (endothermic cell ranging from 293 K to 273 K and the exothermic cell ranging from 303 K to 323 K), the data shows a decrease in refrigeration capacity as the endothermic cell got colder (the system's temperature difference increased). The system's coefficient of performance also decreased from around 12.5 at a temperature difference of 10 K down to around 4 at a temperature difference of 50 K.

As a whole, the experiment was very successful, both in understanding the range of operating conditions that electrochemical refrigeration could take place under and in measuring several key parameters. What they eventually found was that, when running with a current density of 60 A m^{-2} this system had the same or better coefficient of performance compared to standard vapor compression cycles. Polarization loss, alongside other more detailed parameters of the system that impact the performance such as the electrolyte's state of charge and flow velocity, are beyond the scope of this review but contribute to the authors' thorough comparison of electrochemical versus traditional refrigeration systems[29].

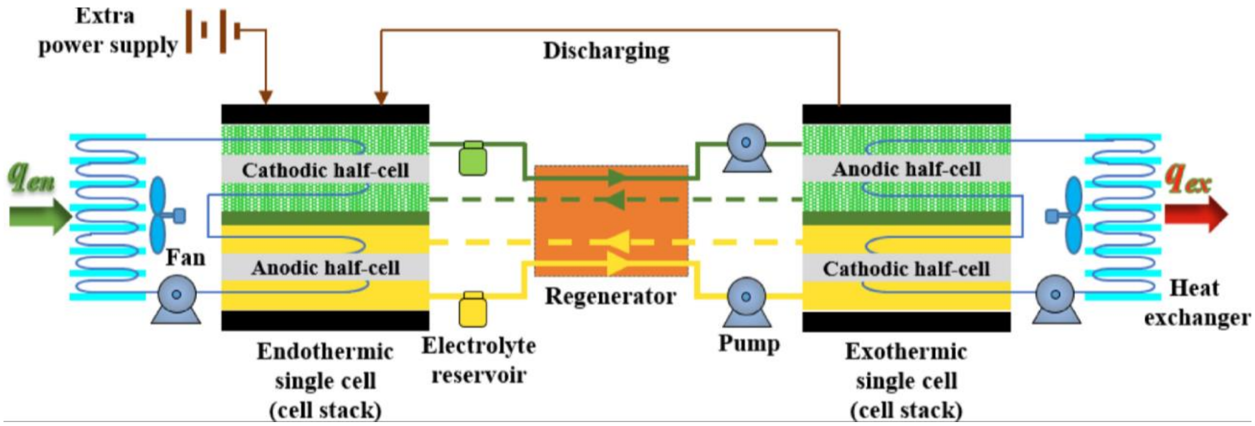

Figure XX: Complete

E. Analysis

Electrochemical refrigeration is perhaps the most unique application in this review and its case must be dominantly built on its safety when scaled up, as large quantities of cooling fluids are what have typically caused problems and led to this case study. While the small-scale viability of this alternative appears promising and gives additional control of a traditional system, it is difficult to estimate the ease of which this could be scaled up to industrial levels. Theoretically, all electrochemical systems are simply a group of cells that could be replicated and stacked as many times as needed. In reality, the costs may greatly exceed what any company is willing to do, especially if it adds additional layers of complexity in needing pumps and exchangers that divide incoming fluid into dozens of cells. Research into a slightly larger system could be a good use of time, especially if economic estimates are run and provide favorable results that show that electrochemical cells and the instrumentation needed can efficiently replace the storage tanks and massive condensers and evaporators which traditional refrigeration sites use.

While this understanding of electrochemical refrigerators will be useful to reinforce that the bounds of electrochemistry are beyond what many people believed to be possible, it would be unreasonable to claim it is the optimal future for every chemical process. This is especially true for refrigeration, where a wealth of innovation has taken place in the past 10 years. Thermoelectric cooling is one such system, where a semiconductor joins with a heat sink and DC power to draw heat from one metal to another. This is already in practice in some microprocessor cooling systems and is incredibly efficient and mechanically inert. Magnetic refrigeration is another cooling alternative that uses an effect known as the magnetocaloric effect where electromagnetic coils can remove heat around an object. Its low power requirement gives it a broader range of utilities even beyond industrial uses and uses water instead of other harmful chemicals. A final example is simply using carbon dioxide as a coolant as technology has progressed enough to allow its safe and effective use[30].

Overall Summary and Recommendations:

Throughout this work, it's clear that electrochemical systems are not only catching up with traditional synthesis techniques, but they are also surpassing specifications in many situations. Electrochemical systems are being researched, tested, and implemented around the world, thriving with modern technology and ability to efficiently run with typically lower energy costs than other methods. For regions with limited access to traditional energy sources, such as coal and natural gas plants, the electrochemical technology being developed for recycling PVC and treating wastewater are huge advantages to modernizing and sustaining even the most remote places in the world.

Among the new systems being developed to advance chemical production, electrochemistry remains valuable because of its theoretical and proven successes alongside the safety improvements that should drive change in an industry with such history of fatal accidents. The electrochemical replacements introduced in this review show ways that process requirements can still be met but with more control over the parameters that have proven dangerous when unmonitored.

The discussion and sources here are almost entirely laboratory-scale and have not been evaluated at the scale and demand of a full chemical process. While exciting and reasonable for a smaller company to attempt to implement, many of these processes are too risky to take on at a large scale. Such full-scale analysis is an obvious requirement for novel technology to be introduced, especially if it holds the promise of safer processing. Several large companies appear to be taking this challenge on in some form, as goals for net zero carbon emissions by 2050 are becoming more real as that year gets closer. For example, BASF is working alongside Linde and SABIC to create the first demonstration plant for electric steam cracker furnaces[31]. In another application of electrochemistry, Evonik is scaling up the use of electrodialysis, which will allow salt byproducts to be more easily separated into the process's raw matierals[32]. Former processes, including Olin's electrolysis of salts yielding hydrogen and other useful chemicals as well as Liquid Light Corp's multi-million dollar CO_2-to-chemical technologies from a decade ago, are also examples that should be studied[33,34].

As electrochemical processes continue to progress, we also recommend keen observation of these large-scale electric and electrochemical processes being completed by industry giants to learn from their successes and shortcomings.

As a whole, the evidence in this report and all research that went into choosing these five events leads to a very clear, but broad, recommendation. All chemical plants, but particularly those that are not operating at a massive scale, should conduct a review of the current state of electrochemical production of all materials manufactured at the site, including intermediate chemicals. Millions of articles are available online and large, research-driven universities with electrochemical research capabilities are also available for consultation in many regions. This baseline analysis should be considered due diligence for the employees, neighboring citizens, and even shareholders of the facility as electrochemical techniques can mitigate the chances and consequences of safety incidents at the plant.

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